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### Physicochemical Controls on Alteration and Copper Mineralization in the Sungun Porphyry Copper Deposit, Iran

by

Ardeshir Hezarkhani

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

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### ABSTRACT

The Sungun porphyry copper deposit is associated with an Andean-type, calcalkaline diorite/granodiorite to monzonite/quartz-monzonite stock of Miocene age which intruded Eocene volcanosedimentary and Cretaceous carbonate rocks. The intrusive phases are related by fractional crystallization, although surprisingly, the diorite/granodiorite which hosts the mineralization postdates the more evolved quartz monzonite. Copper mineralization was accompanied by both potassic and phyllic alteration. The hydrothermal system involved both magmatic and meteoric waters, and boiled extensively. Molybdenum was concentrated at a very early stage in the evolution of the hydrothermal system and copper later. Early hydrothermal alteration, which was caused by high temperature (340 to >500 °C), high salinity (~60 wt % NaCl equiv.) orthomagmatic fluid, produced a potassic assemblage characterized by addition of K and Cu and depletions in Na, Ca, Mg and Fe in the central part of the stock. Propylitic alteration, which is attributed to a liquid-rich, lower temperature (240-330 °C), Ca-rich, evolved meteoric fluid occurred contemporaneously with potassic alteration, but in the peripheral parts of the stock. Phyllic alteration occurred later, at temperatures in the range from 300 to 360 °C, overprinting these earlier alterations, and was accompanied by additions of Si (silicification) at the expense of Na, K and Fe and remobilization of Cu from the potassic zone. It resulted from the inflow of oxidized and acidic meteoric waters with decreasing temperature of the system. During potassic alteration, copper solubility is calculated to have been >100,000 ppm, whereas the copper content of the initial fluid responsible for ore deposition was 1200-3800 ppm. This indicates that the fluid was initially undersaturated with respect to chalcopyrite, which agrees with the observation that veins which formed at T>400 °C contain molybdenite but rarely chalcopyrite. Copper solubility drops rapidly with decreasing temperature, and at 400 °C is 1000 ppm. At temperatures <300 °C, the solubility drops to <1 ppm. These calculations are consistent with observations that the bulk of the chalcopyrite deposited at temperatures between approximately 300 and 360 °C. We propose that the Sungun deposit formed partly in response to the sharp temperature decrease and pH increase that accompanied boiling, and partly as a result of the additional

heat loss, increase in pH and decrease in aCI which occurred as a result of mixing of acidic Cu-bearing magmatic waters with cooler meteoric waters of lower salinity and near-neutral pH.

### RÉSUMÉ

Le gisement de type porphyre cuprifère de Sungun est associé à un stock Andéen d'âge Miocène composé de roches dont la composition varie de dioritiquegranodioritique à quartz-monzonitique qui ont fait intrusion dans des séries volcanosédimentaires ainsi que des carbonates d'âge Crétacé. Les phases intrusives successives sont apparentées par un processus de cristallization fractionnée malgré le fait que, de façon surprenante, ce soit les unités dioritiques-granodioritiques hôtes de la minéralization en cuivre qui aient fait intrusion au travers des monzonites quartzifères plus évoluées. La minéralisation en cuivre s'est accompagnée d'une altération potassique et d'une altération phyllique. Des fluides d'origine magmatique et météorique furent impliqués dans le système hydrothermal responsable de la minéralisation et ont été soumis à une ébullition prononcée. Le molybdène a été concentré très tôt dans l'évolution du système hydrothermal tandis que le dépôt du cuivre a suivi plus tard. L'altération hydrothermale précoce, qui s'est effectuée à partir de fluides orthomagmatiques de haute temérature (340 à > 500 °C) et de forte salinité (~ 60 wt.% NaCl equiv.), a été responsable de la formation d'un assemblage potassique, charactérisée par l'ajout de K et Cu et par l'extraction partielle de Na, Ca, Mg et Fe, dans la partie centrale du stock. L'altération propylitique, qui a impliqué un fluide météorique évolué majoritairement liquide, de plus basse température (240-330 °C) et riche en calcium, s'est produite concurremment à l'altération potassique mais dans les parties périphériques du stock. L'altération phyllique, plus tardive, s'est superposée aux altérations précédentes à des températures oscillant entre 300 et 360 °C, et fut accompagnée par une addition de Si (silicification) contre une diminution de Na, K et Fe, et par une mobilization du Cu hors de la zone d'altération potassique. L'altération phyllique et le lessivage du cuivre ont résulté d'un influx de fluides météoriques oxydés et acides suite au déclin de température du système hydrothermal. Au cours de l'altération potassique, la solubilité du cuivre a été évaluée à > 10,000 ppm, tandis que le contenu initial en cuivre du fluide reponsable de la minéralization a été calculé à 1,200-3,800 ppm. Ceci indique que le fluide était

initialement sous-saturé relativement à la chalcopyrite, en accord avec le fait que les veines formées à une température supérieure à 400 °C contiennent de la mplybdénite mais rarement de la chalcopyrite. La solubilité du cuivre décroît rapidement avec une baisse de la température, et, à 400 °C, celle-ci est de 1,000 ppm. À des températures inférieures à 300 °C, la solubilité du cuivre s'abaisse au dessous de 1 ppm. Ces calculs sont en accord avec les observations qui indiquent que le dépôt de la majeure partie de la chalcopyrite s'est effectué approximativement entre 300 et 360 °C. Nous proposons que le gisement de Sungun se soit formé en partie en réponse à baisse abrupte de la température et à une augmentation du pH accompagnant l'ébullition, et en partie suite à une perte additionnelle de chaleur, une augmentation de pH et une diminution de l'activité de CI-due au mélange du fluide magmatique acide porteur de cuivre avec des eaux météoriques plus froides, diluées et neutres.

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This study is dedicated to Arezou, my dear wife for her patience and moral support all through my research work.

### PREFACE

This research was initiated as a collaboration between the author and his supervisor, Professor A. E. Williams-Jones. The thesis comprises six Chapters, two of which are in manuscript format. Chapters III and V have been submitted to Economic geology, (Chapter III has been accepted for publication). Prof. A. E. Williams-Jones (who provided advice on research methodology, helped evaluating and interpreting the data and critically reviewed the text) is a co-author of the manuscripts. Professor. C. H. Gammons (Montana Technical University, U.S.A) is third author on Chapter V. He reviewed the manuscript with helpful comments and valuable interpretations on the data. Field work and core logging were carried out by Prof. Williams-Jones and the author in the summer of 1993, and by the author in the summer of 1994. Petrographic studies, fluid inclusion microthermometry, SEM analyses of fluid inclusion decrepitates were carried out by the author. Electron microprobe analyses were conducted by the author with the assistance of G. Poirier. Major and trace element compositions of whole rocks were analysed using X-ray fluorescence spectrometry by T. Ahmedali at the Department of Earth and Planetary Sciences, McGill University. Rare Earth Elements were analysed using the neutron activation method by Dr. E. Hoffman at Activation Laboratories, Ancaster, Ontario. Sulphur isotope compositions were determined by N. Morisset using a quadropole mass spectrometer at the stable isotope laboratory, Ottawa University. Oxygen isotope compositions were determined by D. Pezderic at the University of Saskatchewan.

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# CHAPTER I

## **CHAPTER I**

### **GENERAL INTRODUCTION**

#### **INTRODUCTION**

Ore deposits are concentrations of metallic minerals that have economic potential. They are different in their compositions, modes of occurrence, types and, above all, in their origins. One of the most important challenges in economic geology is to understand the factors that are responsible for producing exploitable concentrations of these minerals. The close spatial and temporal association of mineral deposits with granitic rocks suggests that there is a genetic relationship between them. This suggestion is strengthened by the observation that deposits of Cu-Mo, Sn-W, Nb-Zr-REE-U are associated with granites having distinctly different petrochemical signatures i.e., metaluminous (calc-alkaline) peraluminous, and peralkaline, respectively (Barnes, 1979; Stemprok, 1987; Strong, 1983; Bernard et al., 1990). The composition of the granitic rocks and the country rocks into which they intruded, the evolution of the granites, the depth of granite emplacement, the evolution of the orthomagmatic fluids, the involvement of non-magmatic waters, and fluidrock interaction are key factors controlling the genesis of metallic mineral deposits. My interest is the metallogeny of copper in porphyry-style deposits.

Porphyry copper deposits are closely associated with intrusive calc-alkaline granitic bodies which were emplaced at shallow crustal levels (Gustafson and Hunt, 1975). The relationship between granitic plutons and the copper deposits hosted by them has long been an issue of debate. Three basic models have been proposed for this type of ore deposit: 1) the orthomagmatic model in which ore fluids and metals are derived directly from the crystallizing pluton (e.g. Gustafson and Hunt, 1975; Burnham, 1979; Cline, and Bodnar, 1991; Cline, and Bodnar, 1994); 2) the remobilization (meteoric water) model in which the plutons merely serve as heat engines to drive hydrothermal convective cells that leach metals from the surrounding wall rocks (e.g. Norton, 1984); and 3) the mixed magmatic meteoric model (Brimhall, 1980; Bowman et al., 1987; Norman et al., 1991). Although many authors accept that meteoric waters play an important role in mineralization, there is much less agreement over whether or not they introduce metals. In some cases, it is clear that meteoric fluids improve grades; in others there is evidence that the role is destructive. However, even in the former cases, it is not clear whether the metals were added or simply remobilized. The above notwithstanding, a majority of researchers today support the third hypothesis, i.e., initial transport of copper by orthomagmatic fluids, and its subsequent deposition as a result of cooling either in response to mixing with meteoric waters, boiling or a combination of the two. In this thesis I evaluate the geology and geochemistry of the Sungun porphyry copper deposit in northwestern Iran. The results of the study support the third hypothesis in which both magmatic and meteoric fluids played important roles in concentrating the Cu mineralization to economic levels.

### A SUMMARY OF THE GEOLOGY OF IRAN

In order to characterize the different geological units in Iran, it is convenient to visualize the country as comprising two marginal active belts (Berberian, 1983), one in the north-eastern part (Kopeh Dagh) and the other in the south-western part (Zagros), resting on the Turanian "Hercynian" and Arabian Precambrian plates, respectively. The other major units, which are referred to as Central Iran, Alborz, and Makran (Stöcklin, 1972), are situated between those two main plates. The Iranian plateau is a highly elevated (average

about 2 Km) region located in the convergence zone between the Arabian and the Eurasian plates, and is considered to be a part of the Alpine-Himalayan orogenic belt (Fig. 1). It has undergone intense compressional movements, crustal shortening and active faulting, and is considered one of the most tectonically and seismically active continental collision zones in the world (Berberian 1976).

### Zagros fold belt

The Zagros fold belt is located on the northeastern margin of the Arabian plate and comprises a sedimentary succession consisting of limestones, sandstones, and shales from a Paleozoic platform, miogeosynclinal limestones and shales of Middle Triassic to Miocene age, and synorogenic Plio-Pleistocene conglomerates (Berberian, 1976; Berberian, 1983). The Zagros region was folded during a Plio-Pleistocene orogenic episode. There has been no igneous or metamorphic activity in the fold belt since the late Precambrian.

#### Zagros thrust zone

The northwestern margin of the Zagros folded belt terminates in the Zagros thrust, which has a strike of roughly N45W, and extends from eastern Turkey in the northwest to the Straits of Hormoz in southern Iran. The rocks in this zone represent the deepest part of the Zagros trough, and include Upper Cretaceous ophiolites and Radiolarites. They are considerably compressed and were emplaced as klippen which were thrust southeastward over the Mesozoic and Tertiary rocks of the Zagros fold belt. The Zagros thrust is

Figure 1. Mesozoic porphyry provinces of the world and related mountain belts. (modified after Sutherland, and Cathro, 1976). The Sungun porphyry copper deposit, Iran, is located in the Alpine-Himalayan orogenic belt.



considered to be the suture line that separates the Arabian platform from the Iranian platform.

#### Sanandaj-Sirjan Zone

This zone is located in the northeastern part of the Zagros thrust zone, and is distinguished from the Central Iran Zone by the consistency of the Zagros trend, a near lack of Tertiary volcanism, and the generally poor development of Tertiary formations (Shahabpour, 1983). Some authors believe that this zone is actually a part of the Central Iran Zone (Ricou, 1976). The Sanandaj-Sirjan zone has undergone several phases of metamorphism and magmatism. The most important characteristics of this zone are greenschist facies metamorphism of Paleozoic and lower Mesozoic rocks during the late Mesozoic, and magmatism during the early Tertiary, consisting of intrusion of granodiorite batholiths like that at Hamedan and numerous laccoliths and stocks.

#### **Central Iran Zone**

The Central Iran Zone acted as a stable platform during the Paleozoic. It is separated from the Sanandaj-Sirjan Zone by a linear trend of depressions (back arc basins), notably Rezaiyeh lake, Gavkhoni, and Jaz Murian. Although this zone was stable during the Paleozoic, numerous "horsts" and "graben" were created by late Triassic tectonic activity. During creation of the horsts and graben, most of the Precambrian crystalline basement and the Infra-Cambrian to Triassic platform cover rocks were preserved. The graben consist of faulted and folded Jurassic-Cretaceous strata. The Sahand-Bazman igneous (Tertiary volcanic, volcanoclastic and plutonic rocks) and metallogenic belt, which contains two large porphyry copper deposits (Sar-Cheshmeh and Sungun), is considered to be part of this zone (discussed later).

#### The Lut Block

The Lut block (Lower Triassic) is considered to be an old stable platform (Stöcklin, 1977; Stöcklin and Setudenia, 1972). This block is elongated north-southward. It is overlain by a thick sequence of Mesozoic sedimentary rocks (thickness more than 5000 m), dominantly sandstones and shale, and Tertiary volcanic rocks consisting of rhyolite, dacite, andesite, and tuff (with an average thickness of 3000 m). The units do not show any evidence of folding and faulting.

#### Alborz and Kopeh Dagh Zones

The Alborz and Kopeh Dagh zones are considered to mark the site of crustal compression of central Iran against Eurasia (Berberian, 1982). The Alborz mountains form an arcuate mountain range bordered by the southern coast of the Caspian sea. Deformation in the Alborz mountains is characterized by thrust faulting. In the northern part of the range, faults dip southward, possibly indicating underthrusting of the southern Caspian block (Berberian, 1983). In the southern part, reverse faults dip northward as a result of compression against the northern boundary of Iran. To the east of the Alborz Zone, fault

plane solutions indicate some left lateral strike-slip movement (Jackson, and McKenzie 1984). There are insufficient data to draw meaningful conclusions about the structural regime in the western part of the Alborz range. Most of the range is composed of Eocene volcanoclastic rocks (the Karaj formation consists of 4000 metres of Eocene pyroclastics and tuffs), and the volume of these rocks increases towards the east.

The Kopeh Dagh region has a gradational contact with the Alborz Zone, in the west. The most important rocks in this region are Oligo-Miocene limestones with intercalated shales and marls. Triassic carbonates and Jurassic shales are also exposed. Except for minor volcanism, which occurred at the end of the Pleistocene, igneous activity during the Mesozoic and Cenozoic eras was rare.

#### The Eastern Iran and Makran Zones

The Eastern Iran and Makran Zones are post-Cretaceous flysch-mollasse belts which join each other in southeast Iran and continue into the Pakistan-Baluchistan ranges (Berberian, 1983). Huber (1978) proposed that the flysch sediments were deposited on an Upper Cretaceous ophiolite-melange basement together with a basal conglomerate.

#### THE SUNGUN PORPHYRY

The Sungun porphyry copper deposit is hosted by a diorite/granodiorite to monzonite/quartz-monzonite stock (Mehrpartou, 1993), located 75 km northwest of Ahar in the Azarbaijan province of northwestern Iran (Figs. 2 and 3). The stock is part of the

Sahand-Bazman igneous and metallogenic belt (northern Iran), a deeply eroded Tertiary volcanic field, roughly 100 by 1700 km in extent (from Turkey to Baluchistan in southern Iran), consisting mainly of rhyolite and andesite, with numerous felsic intrusions. The volcanics were laid down unconformably over folded and eroded Upper Cretaceous andesitic volcanic and sedimentary rocks (~500 meter thick). Subduction and subsequent continental collision during the Paleocene to Oligocene caused extensive alkaline and calc-alkaline volcanic and plutonic igneous activity (Etminan, 1978; Shahabpour, 1983; Berberian, 1983), including intrusion of a porphyritic calc-alkaline stock at Sungun during the Miocene (Emami, 1992). Bordering the belt to the southwest are the complexly folded, faulted, and metamorphosed Tertiary and Paleozoic sedimentary rocks which form the Zagros Mountains (Waterman and Hamilton, 1975).

#### A REVIEW OF PORPHYRY COPPER DEPOSITS

Definitions proposed for porphyry copper deposits include both economic and geologic characteristics (e.g. Parson, 1956; Skinner, 1969; Lowell and Guilbert, 1970). Porphyry copper deposits contain more than five million tons of low-grade copper ore, averaging less than 2 percent copper. Copper mineralization is usually in the form of fine-grained chalcopyrite, and is so uniformly dispersed over the mineralized volume that inexpensive, bulk mining methods can generally be used for exploitation. Porphyry copper deposits account for more than half of the world's annual copper production, and contain about two-thirds of the world's copper resources (Cox et al., 1973b).

The association of porphyry copper mineralization with calc-alkaline rocks in

Figure 2. Geological map of Iran.





**Alborz Mountains** 



Makran



Sanandaj-Sirjan zone



**Central Iran** 



Zagros fold belt



Kopet Dagh



Eastern Iran

Lut block



Sahand-Bazman belt

### SYMBOLS

Study area Fault Thrust Fault



Figure 3. Location of the Sungun porphyry copper deposit.


convergent plate boundaries has led to a conclusion that porphyry copper magmas could be produced by partial melting of metalliferous oceanic sediments and basalts in subduction zones (Lowell and Gilbert, 1970; Sillitoe, 1972; Page et al., 1972; Sillitoe, 1973; Whitney, 1975; Gustafson and Hunt, 1978; Watmuff, 1978; Beane and Titley, 1981; Titley and Beane, 1981; Chivas, 1981; Whitney, 1985). Burnham (1979) suggested that mafic rocks, whether they are oceanic basalts or lower crustal amphibolites, normally contain sufficient copper to ultimately yield a porphyry copper deposit, provided there is extensive hydrothermal activity in the porphyry system at shallow crustal levels to concentrate the metal. These mafic magmas apparently are not the immediate parents of the copper porphyry magmas because they are generally too poor in potassium to yield the porphyries by differentiation alone, despite evidence (Chappell, 1974) that the porphyry magmas appear to have been derived from igneous type source rocks. Therefore, it is postulated that the porphyry magmas were produced mainly by the interaction of mantle-derived magmas with the lowermost crustal rocks. The principal role of the mantle-derived magmas is thus to provide large quantities of heat for partial melting and assimilation of lower crustal rocks.

The mineralization in porphyry copper deposits is usually disseminated in and adjacent to the igneous body (e.g. Fountain, 1972; Sillitoe, 1972; Beane and Titley, 1981). Porphyry copper deposits have several common features: 1) they are all associated with calc-alkaline plutons (e.g. Sillitoe, 1972; Eastoe, 1982; Whitney, 1985; Dilles, 1987; Whitney, 1988; Dilles et al., 1992), 2) they have extensive systems of deep fractures concentrated on the apical parts of the pluton as well as in the adjacent wall rock (Roedder, 1971; Nash, 1976; Eastoe, 1978; Ford, 1978; Ahmad et al., 1980; Brimhall, 1980; Chivas, 1981; Reynolds and Bean 1985; Bowman et al., 1987), 3) the hydrothermal alteration

assemblage in their fracture systems is distributed centro-symmetrically (Nash, 1976; Eastoe, 1978; Ford, 1978; Chivas, 1981; Beane and Titley, 1981; Reynolds and Bean, 1985), 4) the alteration halos are commonly zoned from potassic to phyllic, argillic and then to propylitic, from the core to the margins, respectively (Nash, 1976; Eastoe, 1978; Ford, 1978; Chivas, 1981; Beane and Titley, 1981), 5) the primary ore minerals are also centro-symmetrically distributed in the fracture system, roughly coinciding with the alteration halo (Eastoe, 1978; Chivas, 1981; Dilles, 1987; Dilles et al., 1992), 6) the stable isotope characteristics provide evidence of the mixing of two diverse source fluids (magmatic and meteoric fluids), (Sheppard et al., 1971; Taylor, 1974; Shelton 1983; Williams-Jones and Samson, 1989; Dilles et al., 1992).

# MAGMA SOURCE ROCK COMPOSITION

It is well accepted that the composition of the magmatic source rocks, the environment of magmatic emplacement, and the depth of emplacement are the critical factors that determine the nature and intensity of mineralization in a porphyry system (e.g. Brimhall, 1980; Whitney, 1988), but there are few articles that examine this quantitatively. It has been proposed that the so-called "I-type magmas," which are thought to be derived by the partial melting of pre-existing igneous rocks or arkoses (e.g. Chappell, 1984; Chappell, and Stephens, 1988), produce the granodioritic and quartz monzonitic plutons, which are associated with Cu-Mo deposits, but again few articles have been written to show the relation between the petrochemistry of these "source rocks" and the Cu-Mo mineralization. There are several major characteristics which determine the degree of mineralization within a porphyry copper system. The most important constraint is the water content of the magma. The T-H<sub>2</sub>O relations of magmas associated with porphyry systems govern such variables as the depth of emplacement, extent of fracturing, concentration of metals of interest in the melt, mineralogy, texture, water saturation in different parts of the pluton, the occurrence of boiling, etc., and are unique for the different types of melted source rocks (e.g. Whitney, 1975; Whitney, 1988; Candela, 1989).

### THE EFFECT OF WATER CONTENT

The water content of the magma must be high enough to produce extensive fracturing at a depth of 1-6 km and also enough to keep the magma temperature at levels sufficient for emplacement at <4 km (e.g. Whitney, 1988; Dilles et al., 1992). The metal content of the magma is inversely proportional to the degree of source rock melting and is therefore related to the T-P<sub>H2O</sub>-depth relations. At the onset of partial melting, the concentration ratio of metals in the melt to the source rocks is high but decreases as melting progresses (e.g. Dilles, 1987; Whitney, 1988; Candela, 1989; Candela and Boulton, 1990). Experimental work has shown that melting only 20% of an average mafic-basaltic amphibolite containing 80 ppm copper would produce a melt with approximately 400 ppm copper (Barnes, 1979; Burnham, 1979). This is why some experimentalists maintain that there is no difficulty in obtaining a copper rich magma from an average mafic-basaltic amphibolite (e.g. Brimhall, and Crerar, 1987).

The metal content of the aqueous phase that separates from the magma in the watersaturated carapace is strongly dependent upon the partition coefficient between the fluid and the melt (Candela, 1984; Candela, 1989; Candela and Boulton, 1990). According to experimental studies, the copper sulphide mineralization in a porphyry copper deposit requires concentration of magmatic copper during fractional crystallization, and partitioning of Cu into the exsolved magmatic fluid (e.g. Candela et al., 1984; Candela and Boulton, 1990; Keppler and Wyllie, 1991; Hemley et al., 1992). The solubility of copper in the hydrothermal fluids is dependent on the availability of chloride ions and perhaps other ligands, which can form stable complexes with this metal (e.g., Ryabchikov et al., 1980; Var'yash, and Rekharskiy, 1981b; Eastoe, 1982; Wood et al., 1985; Crerar et al., 1985; Candela, 1989; Bartos, 1989; Hemley, et al., 1992). The stability of these complexes is a function of  $fO_2$ , pH, T, and P, and ligand concentration in the fluid (e.g. Ford, 1978; Eastoe, 1982; Crerar et al., 1985). However, the relative importance of changes of these parameters is not well understood.

### THE EFFECT OF SULPHUR CONTENT

The sulphur partition coefficient must be high enough to form sulphides, and is strongly dependent upon the oxidation state ( $fO_2$ ) of the magma. When the  $fO_2$  is low, the dominant sulphur species is H<sub>2</sub>S, which is soluble in the melt (e.g., Crerar et al., 1985; Brimhall, and Crerar, 1987) and tends to precipitate sulphides upon crystallization of the magma. But at higher  $fO_2$  values, SO<sub>2</sub>, which is insoluble in the melt, becomes the dominant sulphur species, making it possible for hydrothermal fluids to transport large quantities of metals and sulphur. Precipitation of sulphides from these fluids is promoted by hydrolysis of the SO<sub>2</sub> at lower temperatures (e.g. Burnham, 1979; Urab, 1985; Keppler, and Wyllie, 1991). Higher  $fO_2$  magmatic conditions are thought to be responsible for generating high-sulphur copper porphyries.

# PORPHYRY COPPER DEPOSITS IN IRAN

In Iran, all known porphyry copper mineralization occurs in the Cenozoic Sahand-Bazman orogenic belt (Fig. 2). This belt was formed by subduction of the Arabian plate beneath central Iran during the Alpine orogeny (Takin, 1972; Berberian et al., 1981; Berberian, 1982) and hosts two major porphyry Cu deposits. The Sar-Cheshmeh deposit is the only one of these currently being mined, and contains 450 million tonnes of sulphide ore with an average grade of 1.13 % Cu and ~0.03 % Mo (Waterman and Hamilton, 1975). The Sungun deposit, which contains 650 million tonnes of sulphide reserves grading 0.76 % Cu and ~0.01 % Mo (unpublished data of the Iranian Copper Company), is scheduled for development in 1997. Sar-Cheshmeh, Sungun and a number of other subeconomic porphyry copper deposits are all associated with mid- to late-Miocene granodiorite to quartz-monzonite stocks (Shahabpour 1982; Emami 1992). At the Sungun porphyry copper deposit, the volcanics were laid down unconformably over folded and eroded Upper Cretaceous andesitic volcanic and sedimentary rocks (~500 meter thick). Subduction and subsequent continental collision during the Paleocene to Oligocene caused extensive alkaline and calc-alkaline volcanic and plutonic igneous activity (Etminan, 1978; Shahabpour, 1982; Berberian, 1983), including intrusion of a porphyritic calc-alkaline stock at Sungun during the Miocene (Emami, 1992).

The porphyry copper deposits in the Sahand-Bazman igneous and metallogenic belt are poorly understood. There are no publications on the Sungun deposit, and very few papers published about the Sar-Cheshmeh deposit (Waterman and Hamilton, 1975; Shahabpour, 1994, 1996). Apart from an unpublished reconnaissance fluid inclusion and petrologic study by Mehrpartou (1993), this is the first comprehensive study of the Sungun deposit. Fluid inclusion studies of the Sar-Cheshmeh porphyry copper deposit are described in an abstract by Etminan (1978). There have been no stable isotope studies on either the Sungun or Sar-Cheshmeh deposits.

### METHODS OF INVESTIGATION

This research involved the following steps:

1) mapping and sampling in order to establish field relations among the various rock types in the Sungun deposit.

2) logging and sampling of 10,000 m of drill core to evaluate the subsurface geology of the Sungun deposit.

3) mineralogical and geochemical studies of representative rocks for the purpose of understanding the petrogenetic relationships among the various types of intrusives. 4) geochemical (including sulphur and oxygen isotopic) and mineralogical investigations to determine the relationships between three main alteration episodes and the mineralization.

5) Studies of fluid inclusions in quartz from mineralized quartz veins, in order to determine the timing and pressure-temperature conditions of ore-forming fluids in the granodioritic stock, and the subsequent P-T-X evolution of the fluid.

6) Evaluation of the physicochemical controls of alteration and mineralization using thermodynamic data.

### THESIS ORGANIZATION

Chapters II, III and IV discuss the petrology, hydrothermal evolution and magmatic processes involved in the formation of the Sungun porphyry copper deposit. Chapter II presents the detailed rock chemistry, petrography and petrology of the various rock suites in the Sungun stock. Chapter III presents detailed fluid inclusion and stable isotope studies, that are used to estimate the pressure, temperature, composition and origin of the hydrothermal fluids. These data provide the basis for proposing a model for the hydrothermal evolution of the Sungun stock and an opportunity to evaluate the importance of this evolution to copper mineralization. A complete list of the microthermometric analyses is provided in Appendix II and the mineral microprobe analyses in Appendix III. In Chapter IV, we approach the problem of element mobility and the path of mass change reactions. Representative rocks from the main alteration zones (potassic, transition, phyllic and argillic alteration zones) were chosen for this study to characterize the hydrothermal evolution and related element mobility during each alteration episode (Appendix I). A description of lithology and alteration patterns has been made to provide details of the mineralogical and chemical changes. The results have been used to postulate a reaction path for the alteration in the Sungun deposit. Chapter V reports the results of a chemical investigation of silicate, oxide and sulphide minerals. Textural relationships indicate that these minerals formed mainly in response to hydrothermal processes. In this chapter, the relationship between the crystallization of these minerals and that of copper mineralization is investigated in terms of timing and chemical evolution. These data have been integrated with those from Chapter III to support a genetic model that explains the copper mineralization in the Sungun deposit (Chapter VI). All mineral chemistry data presented in this Chapter are listed in Appendix III.

In Chapter VI, a genetic model for the Sungun porphyry copper deposit is proposed, based on geological mapping, fluid inclusion, mineral chemistry, thermodynamic calculations, trace element analyses and stable isotope data. It considers the evolution of the Sungun hydrothermal system, and evaluates the magmatic and meteoric fluid controls of mineralization.

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# **CHAPTER II**

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**Igneous Petrology of the Intrusive** 

**Rocks Hosting the Deposit,** 

# INTRODUCTION

The Sungun porphyry copper deposit is one of two major copper deposits associated with calc-alkaline intrusive rocks (stocks) in the Cenozoic Sahand-Bazman volcanic belt, which extends north-westward from Sahand volcano in Azarbaijan province, to the Bazman volcano in south-east Iran, a distance of approximately 1700 km (Fig. 1). This belt, which was first identified by Stöklin (1977), consists of alkaline and calc-alkaline volcanic rocks and related intrusives (I-type) and was formed by subduction of the Arabian plate beneath central Iran during the Alpine orogeny (Berberian et al., 1981; Berberian, 1982; Pourhosseini, 1982).

The oldest rocks in the Sungun area are Upper Cretaceous carbonate rocks and are overlain disconformably by Eocene basic volcanics and sandstones. In the Early to Middle Tertiary (Eocene to Miocene), a major episode of volcanism, plutonism, and deformation occurred in the Sahand-Bazman belt. In the Sungun area, magmatism was initiated by eruption of Eocene volcanic rocks, which continued to Upper Miocene time. The composition of these rocks varies from andesite to rhyolite. Associated intrusive rocks comprise mainly diorite/granodiorite, granite and monzonite. This episode was an expression of Andean-type magmatism that developed along the continental margin in response to subduction tectonics to the north (Berberian, 1982).

This Chapter addresses some unresolved questions on the petrology, petrochemistry and petrogenesis of the Sungun stock. The emphasis is on the evolution of the magma, which is modelled using the composition of the rocks that comprise the stock, and a variety of other geological data including the results of mapping, drill core logging, petrography,

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Figure 1. Simplified geological map of the Sungun area. (after Lescuyer et. al., 1978).



and mineral chemical analyses. Petrographic studies were carried out on 60 thin and polished thin sections of the freshest rocks; 14 of them were selected for electron microprobe analyses, and the results are presented in Appendix I. Twenty whole rock samples were analyzed for major and trace elements using X-ray fluorescence (XRF), and the results are in Appendix II. These whole-rock geochemical data were supplemented by analyses from Mehrpartou (1993).

# **GEOLOGICAL SETTING**

The Sungun intrusive complex is located about 75 km north-west of Ahar (northwestern Iran), in Azarbaijan province in north-western Iran (Fig. 1), and intruded along the Sungun anticline into Cretaceous limestone and Eocene tuff (equivalent to the Karaj formation) and agglomerate of andesitic to trachytic composition. To the north and east, the stock is bounded by hydrothermally altered Cretaceous limestone (skarn), which contains economic copper mineralization.

The oldest rocks exposed in the study area (Fig. 2) are a ~500 m sequence of Cretaceous limestone with intercalations of shale, and a ~1500 m thick sequence of Middle to early Late Tertiary, intermediate composition, calc-alkaline volcanic, and tuffaceous rocks intruded by numerous calc-alkaline dykes. The entire stock and volcanic "cover rocks" are located within a caldera (Fig. 1). Geological relations in the Sungun area have been interpreted from more than 10,000 m of drill core made available by the Ahar Copper Company. The stock has a plan area of approximately 3.45 km<sup>2</sup> (1.5 x 2.3 km), (elongated NW-SE), and consists of three different intrusive phases. All intrusive units contain the

**Figure 2.** A geological map of the Sungun deposit, showing the field relationships among the various phases of the Sungun intrusion, and the country rocks. The major intrusive bodies are monzonite/quartz-monzonite in the west and later diorite/granodiorite in the east. Both these units are bounded to the north and east by Cretaceous limestone. Andesitic to dacitic dykes are distributed mostly in the north and western parts of the Sungun deposit (outside the main stock). Mineralized trachyandesitic dykes occur mainly within the diorite/granodiorite and less commonly in the quartz-monzonite. Skarn-type alteration (and associated mineralization) occur as a narrow rim along the eastern and northern margin of the stock in the Sungun valley, (modified after Mehrpartou, 1993).



same assemblage of minerals: plagioclase, K-feldspar, quartz, biotite, hornblende (which is typically altered to biotite and/or chlorite), titanite, rutile, scheelite, apatite, minor magnetite, and zircon. The intrusives at Sungun are 1) monzonite/quartz-monzonite; 2) diorite/granodiorite; and 3) andesitic and related dykes, in order of emplacement (Fig. 2). Monzonite/quartz-monzonite intrusions are mainly porphyritic, and exposed to the west of the diorite/granodiorite intrusion, and in a small body in the southeast (Fig. 2). Diorite/granodiorite forms the central part of the Sungun stock and intrudes monzonite/quartz-monzonite (Fig. 2). All the intrusives are generally unfoliated and commonly porphyritic, suggesting a shallow level of emplacement (Carten, 1986). The latter interpretation is supported by a stratigraphic reconstruction, which shows that the maximum depth of intrusion was 2000 m.

Rocks in the study area were subjected to intense hydrothermal alteration, especially within and adjacent to the diorite/granodiorite intrusive (Chapters III, IV and V). Petrographically fresh rocks were only available for sampling at depths >500 m below the present erosional surface. Even in the outermost part of the area, it is not possible to find completely fresh igneous rocks in outcrop. Several stages of hydrothermal alteration and associated mineralization have produced new minerals, created new textural relationships and in many cases obliterated the primary character of the rock.

#### PETROGRAPHY

### Monzonite and quartz-monzonite

Monzonite and quartz-monzonite are light grey in colour and contain megacrysts of K-feldspar, plagioclase, biotite and hornblende in a fine-grained matrix. The contact between monzonite and the adjacent quartz-monzonite is gradual, and chemical analyses show that these two rock types are chemically the same, but different in terms of texture (discussed later).

The monzonite/quartz-monzonite intrusives can be distinguished from the other units by the presence of up to 30 volume percent of K-feldspar and up to 25 volume percent of euhedral to subhedral tabular plagioclase phenocrysts. The other important phenocryst phases are quartz (up to 20 vol. %) and euhedral to subhedral biotite phenocrysts (up to 10 vol. %), hornblende phenocrysts, ( $\leq 2$  vol. %), and anhedral to highly corroded quartz phenocrysts (up to ~20 vol. %). The groundmass consists mainly of quartz, K-feldspar and plagioclase (An<sub>1-25</sub>). Quartz in the groundmass is mostly interstitial and commonly contains biotite and muscovite inclusions, which show that it formed late. The groundmass coarsens and the phenocrysts increase in size with increasing depth and distance from wall rock contacts.

In shallow exposures, plagioclase phenocrysts (up to 5 mm in diameter) are, euhedral and normally zoned (An<sub>40-15</sub>), partially resorbed tabular crystals, which have strongly sericitized, calcite-bearing cores (An<sub>40-25</sub>). According to Wall et al., (1987), this type of alteration in plagioclase is consistent with the early crystallization of an anorthitic core which becomes unstable on cooling and preferentially alters to sericite and calcite in the presence of aqueous fluids. There are two types of K-feldspar; phenocrysts, up to 20 mm in diameter, containing euhedral to subhedral inclusions of plagioclase (An<sub>40-15</sub>) and biotite, and K-feldspar pseudomorphs (up to 10 mm in diameter) which replaced plagioclase phenocrysts. Biotite phenocrysts are up to 3 mm in diameter and have been altered to chlorite and sericite at shallow depths in the pluton. Hornblende (up to 9 mm in diameter) displays blue to pale green pleochroism of variable intensity, and twinning, and has a composition intermediate between magnesio-hornblende and edenitic hornblende (based on the Papike classification, 1988). Augite has been reported to occur at depth by Mehrpartou (1993) but was not observed during the present study. Based on textural relationships the sequence of crystallization of phenocryst phases was plagioclase and hornblende followed by quartz, K-feldspar and biotite.

Accessory minerals include titanite, apatite, zircon, rutile, magnetite, ilmenite, monazite, scheelite, and uraninite which occur randomly, both in the silicate phases and interstitial to them. Titanite is more abundant than the other accessories, and forms anhedral grains intergrown with magnetite and rutile. Ilmenite forms sparse isolated grains locally rimmed by titanite. The sulphide minerals are rare and consist of pyrite and traces of chalcopyrite, galena and sphalerite. Together with chlorite, they replace biotite or occur interstitially to quartz and feldspar in the groundmass.

### Diorite/granodiorite

Diorite/granodiorite is porphyritic, and ranges from fine-grained in the northern part to coarse-grained in the west and northwest, where it intrudes monzonite to quartzmonzonite (Fig. 2). Dark green xenoliths (up to 12 cm in diameter) consisting of hornblende, biotite (which impart the colour), and plagioclase phenocrysts set in a finegrained groundmass of quartz and feldspar are common in the outer parts of the diorite/granodiorite intrusion (discussed later). The contact with the monzonite/quartzmonzonite is not well exposed, and, where seen, is commonly brecciated. A feature of the porphyritic diorite/granodiorite is that it contains numerous mineralized dykes. The contact between diorite/granodioritic rocks and Cretaceous limestone is well exposed in the northern and eastern parts of the study area. In the east the latter has been altered to skarn which locally contains abundant copper mineralization.

Phenocrysts comprise about 50 percent by volume of the rock and are represented mainly by plagioclase up to 4 mm in diameter (~30 vol. %), K-feldspar up to 20 mm in diameter (~10 vol. %), amphibole up to 5 mm in diameter (~10 vol. %) quartz up to 2 mm in diameter (~7 vol. %) and biotite up to 4 mm in diameter (<3 vol. %). The amphibole has a composition intermediate between magnesio-hornblende and edenitic hornblende (based on the classification of Papike, 1988). Except at depth, it has been completely replaced by biotite and is only recognizable from the characteristic amphibole morphology of pseudomorphs and in some cases rutile needles aligned in the direction of the principal cleavages (Fig. 3). Textural relationships show that quartz, plagioclase and K-feldspar phenocrysts formed shortly after amphibole phenocrysts, and that biotite phenocrysts formed during the last stage of magmatic crystallization. Quartz phenocrysts are anhedral and rarely contain biotite and muscovite inclusions.

Most of the plagioclase phenocrysts have been altered to sericite, quartz, calcite, and gypsum. Based on petrography and electron microprobe analyses, two generations of plagioclase are distinguishable in terms of size, inclusions, and composition; large crystals (phenocrysts) with highly altered cores and relatively small crystals with clear carlsbad twinning (An<sub>1-5</sub>), that are interpreted to have formed during a sodic alteration episode,

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**Figure 3.** Photomicrograph of brown biotite which replaced amphibole in the diorite/granodiorite suite. The rim consists of opaque oxide minerals like magnetite and hematite. The rutile needles which have grown along the cleavages are a common feature of the Sungun biotite. The biotite is replaced locally by chlorite. To the right of the large crystal, are numerous small hydrothermal biotite crystals which are mainly greenish-brown colour in plain polarized light.



because of the compositional similarity to the albitic rims around K-feldspar which were clearly developed during sodic alteration (see Chapter III and IV). Plagioclase phenocrysts range in composition from oligoclase-andesine in the core  $(An_{15-32})$  to albite  $(An_{1-5})$  at the rim.

Petrographic observations and microprobe analyses also indicate the presence of two compositionally distinguishable types of K-feldspar within this rock unit, I) phenocryst, and II) hydrothermal K-feldspar. K-feldspar phenocrysts are mainly anhedral, medium to small in size (up to 20 mm) and perthitic ( $Or_{97}Ab_2An_1$  to  $Or_{99}Ab_1$  and  $Ab_{76}Or_1An_{23}$  to  $Ab_{81}Or_3An_{16}$ ) and contain up to 1.7 wt % BaO. They commonly contain small inclusions of primary biotite, plagioclase, and the accessory minerals, apatite, titanite, and zircon. Hydrothermal K-feldspar may be distinguished from magmatic K-feldspar by the absence of perthitic intergrowths.

The biotite phenocrysts are brown, up to 3 mm in diameter, Fe-enriched and subhedral. Pale-brown to greenish-brown, Mg-enriched biotite forms small ragged crystals interpreted to be of hydrothermal origin.

Quartz phenocrysts in this suite are commonly rounded, suggesting that pressures fluctuated during crystallization (Whitney, 1989). The presence of hornblende as phenocrysts, in the freshest samples in deep part of the stock (i.e., as an early liquidus phase) indicates that the diorite/granodioritic magma contained >3 wt percent H<sub>2</sub>O, which led to water saturation during early crystallization (Whitney, 1989; Burnham, 1979). The latter could be the reason that this intrusion was potentially able to alter the Cretaceous carbonate rocks to skarn at the contact.

Accessory minerals are apatite, zircon, rutile, titanite, ilmenite, monazite, scheelite

and uraninite in order of abundance. These minerals occur both in the silicate phases (i.e., biotite, plagioclase and K-feldspar) and interstitial to them (in the groundmass). The sulphide minerals consist of pyrite, chalcopyrite, molybdenite, argento-pentlandite, a silver telluride (hessite ?), galena, and sphalerite and occur as inclusions in altered biotite or interstitially in the matrix of the rock.

As mentioned before, diorite/granodiorite contains mafic rounded xenoliths. They are fine- to medium-grained, and contain green hornblende (1 mm long, and 5 vol. %), biotite (>1 mm in diarneter, and ~8 vol. %), and plagioclase ( $An_{10-28}$ , and 30 vol. %) phenocrysts. Accessory minerals are apatite (euhedral), zircon (euhedral to anhedral), magnetite (euhedral to subhedral) and titanite (subhedral to anhedral). The groundmass is microcrystalline, and is formed mainly from quartz and feldspar. The hornblende occurs as ragged laths, or as irregularly distributed subhedral to euhedral phenocrysts. Crystal rims have been altered to biotite, magnetite, and plagioclase. Along the margins of the xenoliths, there are concentrations of ragged grains of biotite, suggesting the reaction of hornblende to biotite.

Based on the mineralogical and petrographic similarity of the xenoliths to diorite, the xenoliths are interpreted to have formed by stoping of earlier crystallized material during ascent of later pulses of magma. A small proportion of xenoliths consists of green to greenish brown pyroclastic rocks and tuffs. They contain plagioclase (An<sub>35-20</sub>), broken quartz and opaque minerals, in a fine-grained matrix of quartz, chlorite and feldspar (mainly plagioclase).

**Dykes**
Two types of dyke crosscut the granodiorite, I) light-brown, highly altered and mineralized andesitic dykes, up to 2 m thick (called mineralized dykes in Figure 2), II) dark-brown almost fresh and unmineralized andesitic dykes, up to 4 m thick. The phenocryst phases in the mineralized dykes are plagioclase, K-feldspar, quartz, biotite and hornblende. The phenocryst/groundmass ratio is approximately one. The groundmass consists mainly of quartz and feldspar. Biotite and hornblende phenocrysts are altered to chlorite, and feldspars are altered to sericite. Accessory minerals consist of titanite and lesser magnetite. Sulphide minerals in mineralized dykes consist mainly of pyrite (up to 10 vol. %) and chalcopyrite (<1 vol. %). A conspicuous feature of these dykes is the presence of spherically-shaped secondary magnetite. These spheres are thought to represent replacement of precursor pyrite. Unmineralized dykes contain biotite, amphibole (magnesio-hornblende), and zoned euhedral plagioclase (from  $An_{10-15}$  to  $An_{15-35}$ ) phenocrysts. The proportion of phenocrysts to groundmass is 1:3. One of the characteristics of unmineralized dykes is the absence of K-feldspar. These dykes belong to the youngest phase of granodioritic-related igneous activity, and cut both monzonite/quartzmonzonite in the north and diorite/granodiorite in the centre of the stock (Fig. 2).

### MAJOR AND TRACE ELEMENT GEOCHEMISTRY

Representative samples of least altered diorite/granodiorite, monzonite/quartzmonzonite, andesite and mineralized dykes were analyzed for major and trace element compositions. All samples were analyzed by XRF techniques in the Geochemistry Laboratory, McGill University, except for six samples, which were analysed for REE using the neutron activation method at ACTLABS Ontario. Thirty whole rock analyses of the igneous rock, reported by Mehrpartou (1993) were incorporated in the data base. Hydrothermal alteration affected all the rock units, and caused re-distribution/mobilization of the alkali elements (e.g., K, Na and Sr) and silica (added as silicification) in almost all rock types (see alteration section in Chapter III for detailed information).

The classifications of Winchester and Floyd (1977) and Cox et al., (1979) show that the Sungun igneous rocks are mainly in the range of trachyandesite to andesite (Fig. 4a and b). They are also classified as syncollisional medium to high K, calc-alkaline rocks, which are generated from partial melting of basalt in continental arc settings (Figs. 5 and 6). There is a clear petrochemical similarity between the Sungun igneous rocks and calc-alkaline rocks elsewhere in the Sahand-Bazman belt (Pourhosseini, 1982; Hezarkhani, 1988; Hassanzadeh, 1993).

The different intrusives making up the Sungun stock have compositions which define a single linear trend on Harker diagrams for several major element oxides, suggesting a common source for and evolution of their magmas. Figures 7 and 8c show that MgO, CaO, MnO, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents decrease with increasing SiO<sub>2</sub>. These negative trends are consistent with fractional crystallization of ferromagnesian minerals like hornblende (discussed later). Trends of increasing alkalis (Na and K) with increasing SiO<sub>2</sub> are also consistent with such fractionation (crystallization of progressively more sodic plagioclase and of K-feldspar), although the possibility that they also partly represent the effects of potassic and sodic alteration and silicification can not be excluded (Fig. 8). Similar trends have been reported for porphyry copper deposits elsewhere (e.g., Dilles, 1987; Gill, 1981; Eastoe, 1978; Mason, 1978). Aluminum is highly immobile in porphyry copper deposits

**Figure 4.** Log ( $Zr/TiO_2$ ) vs. Log (Nb/Y), and SiO<sub>2</sub> vs. Na<sub>2</sub>O + K<sub>2</sub>O plots for the different igneous suites in the Sungun stock. These diagrams classify the rock suites as having compositions ranging from andesite and dacite to trachyandesite. Diagrams after Winchester and Floyd (1977), and Cox et al., (1979),



Figure 5. a. AFM plot of analyses of the Sungun stock. Skaergaard (tholeiitic) and Cascade (calc-alkaline) trends are from Carmichael et al., (1974) the Sungun intrusive rocks delineate a calc-alkaline trend. Trends of low K arc and shoshonitic volcanic suites are from Ewart (1982). b.  $K_2O$  (wt %) vs.  $SiO_2$  (wt %) diagram showing the classification of Gill (1981). The Sungun intrusive rocks are classified as medium to high K andesite.



Figure 6. a. Nb \* 2, Zr/4, Y diagram showing the tectonic setting (within plate arc) of different rock suites in the Sungun deposit, diagram after Pearce et al. (1984). b. LogNb vs. logY, which shows that all the rock types in the Sungun stock fall in the volcanic arc felsic field diagram after Meschede (1986). Abbreviations; WPA = within plate arcs, WPT = within plate tholeiites, P MORB = primitive mid-ocean ridge basalts, N MORB = normal mid-ocean ridge basalts, VAB = volcanic arc basalts, WPG = within plate granites, VAG = volcanic arc granites, ORG = ocean ridge granites.



Figure 7. Harker diagrams for the different suites of intrusive rocks at Sungun. a. MgO vs.  $SiO_2$ , b. CaO vs.  $SiO_2$ , c. MnO vs  $SiO_2$  and d.  $TiO_2$  vs.  $SiO_2$ . All diagrams have negative trends, which is consistent with the evolution of the corresponding magma(s) by fractional crystallization of minerals like hornblende and Ca-plagioclase. Possible fractionation curves are indicated by least square polynomial fits to the data (solid lines). The dark and light shaded fields correspond to the monzonite/quartz-monzonite and diorite/granodiorite fields, respectively.



**Figure 8.** Harker diagrams for the different suites of intrusive rocks at Sungun, showing trends of increasing  $K_2O$  (a) and  $Na_2O$  (b), negative trend for  $Fe_2O_3$  (c) and scattered distribution of  $Al_2O_3$  (d) with increasing SiO<sub>2</sub>. Possible fractionation curves are indicated by least square polynomial fits to the data (solid lines). The dark and light shaded fields correspond to the monzonite/quartz-monzonite and diorite/granodiorite fields, respectively.





(Grant, 1986), and displays the same behaviour at Sungun, i.e., it shows a systematic variation with  $SiO_2$  (Fig. 8d).

The behaviour of a number of trace elements with increasing SiO<sub>2</sub> leads to the same conclusion as with many of the major elements, i.e., that variations in the primary compositions of the Sungun intrusives were the result of fractional crystallization (Fig. 9). The decreasing trends for Ni (which substitutes for Fe or Mg in hornblende) and Sr (which substitutes for Ca in hornblende and plagioclase) are consistent with their compatibility in early crystallizing minerals. Similarly the increasing trend of Rb, which substitutes for K, is consistent with the late crystallization of K-feldspar and biotite. The compatible trace elements Sc and Y and incompatible trace elements La, Zr, Nb and Th, as expected, also display negative and positive trends with SiO<sub>2</sub>, respectively. The above notwithstanding, not all elements exhibit behaviour that can be explained by fractional crystallization. Chromium, shows a positive trend with increasing SiO<sub>2</sub>. This is very unexpected as chromite is generally a very early liquidus phase and Cr is typically concentrated in mafic and ultramafic rocks. A possible explanation for the behaviour of Cr is that it did not saturate in the magma and because of its high charge/radius ratio behaved incompatibly (Fig. 9h).

An interesting feature of Figures 7 and 8 is that, although the two main intrusive suites define the same trends on these Harker-type diagrams, they forms separate fields. Somewhat surprisingly, however, the more evolved monzonite/quartz-monzonite suite was intruded before the less evolved diorite/granodiorite suite, which hosts the bulk of the mineralization. In most cases the fields for these suites overlap. This and their colinearity suggest that the two suites crystallized from the same magma. However, in several cases,

notably for Co vs.  $SiO_2$  and Sc vs.  $SiO_2$ , the fields are quite separate which may indicate separate magmas. This could, in turn, help explain why the more evolved phase of the pluton was introduced earlier. The late unmineralized andesite dykes generally plot in the same field as the main diorite/granodiorite intrusion, which is consistent with both units having crystallized from the same magma. By contrast the mineralized dykes plot in both fields and more commonly in the monzonite/quartz-monzonite field. This may indicate that the mineralized dykes have a different affinity to the unmineralized dykes. More probably, however, the data distribution is an artifact of alteration.

All the Sungun intrusive rock types have similar distributions on chondritenormalized spider diagrams, characterized by strong enrichment in most incompatible elements and depletion in compatible elements (Fig. 10). These distributions are important feature of calc-alkaline arc magmatism (Cox, et al., 1979). Generally diorite/granodiorite is more enriched in compatible elements than monzonite/quartz-monzonite, and vice versa in respect to incompatible elements.

Chondrite-normalized rare earth element diagrams for the monzonite/quartzmonzonite and diorite/granodiorite show that these rocks are enriched in both compatible and incompatible REE's relative to Chondrite (Fig. 11 and Table 1). The rocks are characterized by LREE enrichment (La/Yb<sub>(N)</sub> > 30) and lack a Eu anomaly. Monzonite/quartz-monzonite is more enriched in LREE and depleted in HREE than diorite/granodiorite or andesite, whereas diorite/granodiorite andesite, and mineralized dykes have similar profiles which is consistent with their crystallization from the same magma. The profiles for the various units fall within the range of typical calc-alkaline magmas (low SiO<sub>2</sub> and high SiO<sub>2</sub> andesites) generated in

Sample No. Dril-core No. Type <sup>1</sup>	25-522 25 Granodiorite (K)	34-163 34 Mineralized dykes (K)	33-281 33 Granodiorite (Frs)	44-409 44 Andesitic dykes (Phc)	30-168 30 Mineralized dykes (Phe)	21-32 21 Monzonite/ quartz-monzonite (Frs)
La (pom)	46.7	64.5	51.0	27.4	40.2	139.0
Ce	76.6	106.0	81.0	50.0	67.2	228.0
Nd	24.9	34.0	25.4	23.0	23.8	72.0
Sin	3,6	4.4	3.5	3.1	3.8	9.3
Eu	0.9	1.2	0.9	1.0	1.0	2.2
Gd	2.4	1.9	2.5	1.7	2.8	4.4
Tb	0.3	0.3	0.3	0.3	0.4	0.6
Dy	1.6	1.6	1.7	1.6	2.1	3.1
Yb	0.9	0.9	0.9	1.3	1.2	1.0
Lu	0.1	0.1	0.2	0.2	0.3	0.1

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TARLE	Neutron Activation	Analyses of REE'S (	(now) from the Sung	un Denosit
IADLE I,	Incution Activation	Analyses of REE 5 (	(քրու) ուսու ուշ օսոչ	gun Deposit

<sup>1</sup> Frs = fresh rock, K = potassic alteration zone, Phc = phyllic alteration zone

**Figure 9.** Harker diagrams for the different suites of intrusive rocks at Sungun, **a**. Ni, **b**. Sr, **c**. Rb, **d**. Sc, **e**. (high Sc content in diorite/granodiorite, and much lower in andesite and monzonite rocks ), Y, **f**. Th, **g**. Co, (Co is higher in diorite/granodiorite, than the andesite and monzonite), **h**. Cr, **I**. Nb and **j**. Zr. Possible fractionation curves are indicated by least square polynomial fits to the data (solid lines). The dark and light shaded fields correspond to the monzonite/quartz-monzonite and diorite/granodiorite fields, respectively.







subduction zones (Hickey-Vargas, et al., 1989).

# P-T CONDITIONS OF CRYSTALLIZATION

As discussed in Chapter III, we have estimated the pressure of emplacement of the stock to be ~500 bars from stratigraphic reconstruction. This pressure corresponds to the lower-pressure limit of stability of the assemblage plagioclase and K-feldspar in a granodiorite pluton (Whitney, 1985; Whitney, 1975). Magmatic temperatures were estimated from geothermometry based on the solubility of zircon and monazite in the magma (e.g., Rapp et al., 1987; Watson and Harrison, 1983). Application of these geothermometers yielded temperatures of 680 to ~780 °C, respectively, for the monzonite, and ~675 to 760 °C, respectively for the granodiorite (cf. Mulja et al., 1995). The higher temperatures from the zircon geothermometer can be attributed to the fact that zircon is one of the earliest minerals to crystallize, i.e., these temperatures are close to that of the liquidus. Thus in summary, the above data suggest that the monzonitic and dioritic magmas in the Sungun stock crystallized over a temperature interval of 675 to 780 °C and at a pressure of 500 bars.

#### **GEOCHEMICAL EVOLUTION**

Depletion of Fe, Ca, Mg, Sr, Y, Mn and Ni (Figs. 7, 8 and 9) and enrichment of K, Na and Rb from diorite/granodiorite to monzonite/quartz-monzonite (Figs. 8 and 9c) are consistent with early fractionation of pyroxene(?), hornblende, and calcic plagioclase, and

Figure 10. A Chondrite-normalized trace element spider diagram showing the compositions of the different intrusive suites in the Sungun stock. All suites display strong enrichment in most incompatible elements (low field strength elements, e.g. Ba, Sr, Ce, U, and Th) relative to chondrite, and depletion in compatible elements which is an important characteristic of calc-alkaline arc magmatism. They are also depleted in some high field strength elements e.g. P, V and Y. Chondrite normalization factors are from McDonough and Frey (1989).



Figure 11. Chondrite-normalized REE plots of selected samples from different rock suites in the Sungun porphyry copper deposit. The rocks display a strong LREE enrichment (La/Yb<sub>(N)</sub> > 30) and lack a Eu anomaly (see the text for discussion). Also shown on the diagram are fields for Andean calc-alkaline rocks (Hickey-Vargas et al., 1989).



later crystallization of biotite, albite, muscovite and K-feldspar. This evolution is also supported by the REE profiles in which diorite/granodiorite is HREE-enriched relative to monzonite/quartz-monzonite, but LREE-depleted. An unusual feature of the REE profiles, however, is the lack of a Eu anomaly. Normally, a negative Eu anomaly develops with magmatic evolution due to fractional crystallization of early, more calcic plagioclase (Henderson, 1984). However, at high  $fO_2$  conditions, Eu will be present mainly as Eu<sup>+3</sup> and therefore very little Eu<sup>+2</sup> may be available for incorporation in plagioclase. This may be the explanation for the lack of a Eu anomaly in the Sungun stock

Based on the previous arguments, and the field relationships between the monzonite and granodiorite, we propose, as a working hypothesis, that diorite/granodiorite and monzonite/quartz-monzonite represent less and more evolved batches of a calc-alkaline magma. It is possible to determine the extent of fractionation of a magma from the changing concentration of incompatible trace elements relative to compatible trace elements. In the case of rocks that have been subjected to alteration, it is important that the trace elements are also immobile, i.e., that except for overall mass gain or loss, any changes in trace element concentration will be due to fractionation. The latter will be evident as distributions with negative trends, and the overall mass gains and losses as deviations from the fractionation trends along lines that pass through the origin (MacLean and Barrett, 1993; MacLean, 1990).

We have used Y to represent the compatible trace element and Zr and Nb as alternative incompatible trace elements. Other potentially compatible elements yielded appreciable scatter and were therefore not considered further. The plots of Nb vs Y and Zr vs Y are presented in Figure 12. Also shown on this diagram are fractionation curves

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representing polynomial least squares fits through the data and dashed lines towards and away from the origin to show the directions of mass gains and losses, respectively. These diagrams confirm the earlier conclusion that diorite/granodiorite is less evolved than monzonite/quartz-monzonite. They also suggest that even the least altered rocks have undergone some mass change. In order to quantitatively evaluate the degree of fractionation, it is necessary to first project the composition of each sample to the fractionation curve along lines of mass change (through the origin) and then select the least evolved sample (highest Y and lowest Zr content) to represent the parent magma. We took the latter to be sample 58-71 which has a projected initial concentration of 22 ppm Y, and 97 ppm Zr or 23 ppm Y and 8 ppm Nb (Figs. 12a and b). With fractionation, the projected Zr content of the diorite/granodiorite ranged up to 110 ppm and the Nb content up to 12 ppm. Projected ranges for these elements in the more evolved monzonite/quartz-monzonite were 113 to 140 ppm and 13 to 21 ppm, respectively. The degree of fractional crystallization was calculated using the following Raleigh fractionation equation of Shaw (1979):

$$C_i^{P} = (1-X) C_i^{D} + X.(KD_i).C_i^{Crystal} * 100$$
 (1)

where  $C_i$  is the concentration of element i (e.g., Zr) in the parental rock P, D is the daughter rock, X is the degree of fractional crystallization, and KD<sub>i</sub> is the partition coefficient for the  $i_{th}$  element between rock (crystal) and magma. The calculated degree of fractional crystallization, is between 15 and 22 % using the data for Zr (KD from Nash and Crecraft, 1985) and 17 to 24 % using the data for Nb (KD from Sweeney et al., 1992).

### CONCLUSIONS

The Sungun deposit is a composite stock, emplaced at a paleo-depth of ~2000 m, at temperatures ranging between 670 and 780 °C, and comprising early monzonite/quartzmonzonite and a later diorite/granodiorite phase. The parental magma was a medium to high K andesite or diorite similar in composition to syncollisional calc-alkaline magmas generated in continental arc settings (e.g., Figs. 5 and 6). The presence of hydrous minerals like hornblende in the freshest diorite/granodiorite indicates that the corresponding magma initially contained >3 wt percent H<sub>2</sub>O (wet magma). The high level emplacement of this magma, led to its saturation with water and the exsolution of fluids at an early stage of crystallization (which is reflected by the replacement of early hornblende with biotite), and subsequently Mo and then Cu mineralization in the stock (see Chapters III, IV and V).

The Harker diagrams drawn for the major igneous suites display trends for compatible and incompatible major and trace elements which are consistent with fractional crystallization. Negative trends for Ca, Mg and Mn and positive trends of K, Na and Rb with increasing SiO<sub>2</sub>, and the mineralogy of the intrusive suggest that a parental magma of diorite/granodiorite composition evolved by fractional crystallization of hornblende and Caplagioclase. The conclusion that the major intrusive suites evolved by fractional crystallization is supported by the behaviour of the immobile trace elements, Y, Zr and Nb. The degree of fractionation was estimated using a Rayleigh fractionation equation which related the concentration of Zr, Nb and Y in the least altered sample to their concentrations in progressively more evolved samples. The results of these calculations indicate that the compositions of the various rock types can be explained by up to 24 % fractionation of a

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Figure 12. Diagrams showing the concentration of a. Y vs. Zr, and b. Y vs. Nb. Fractional crystallization trends are indicated by curves representing least square fits to the data. Samples off the curve are projected onto the curve by straight lines (dashed arrow) projected through the origin. Their deviations indicate the extent of mass gain or mass loss (negative or positive deviations from the fractional crystallization curve). The degree of fractional crystallization required to produce quartz-monzonite/monzonite from granodioritic magma, ranges from ~15 to ~24 % and has been calculated using the concentration of Y, Zr and Nb based on the KD's of Zr and Nb between crystal and liquid in felsic magmas. See text for more information.



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diorite magma to produce the more evolved monzonite/quartz-monzonite suite.

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# **CHAPTER III**

#### **INTRODUCTION TO CHAPTER III**

In Chapter II, the petrology, geochemistry and petrogenesis of the calc-alkaline intrusives were described for the Sungun igneous rocks. The evolution of the stock is potentially important as a control on copper mineralization at Sungun. In this Chapter the petrological conclusions of Chapter II are used to understand the ore fluid chemistry. Fluid inclusion microthermometry, decrepitate analyses, and sulphur and oxygen stable isotope techniques provide a database which permit evaluation of the origin of mineralizing fluid(s), and the physicochemical changes which lead to wallrock alteration and copper mineralization.

# **CHAPTER III**

# **Controls of Alteration and Mineralization**

## in the Sungun Porphyry Copper Deposit, Iran:

## **Evidence from Fluid Inclusions and Stable Isotopes.**

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#### ABSTRACT

The Sungun porphyry copper deposit is located in northwestern Iran (Azarbaijan province), and is associated with diorite/granodiorite to quartz-monzonite of Miocene age which intruded Eocene volcanosedimentary and Cretaceous carbonate rocks. Copper mineralization was accompanied by both potassic and phyllic alteration. Field observations and petrographic studies demonstrate that emplacement of the Sungun stock took place in several intrusive pulses, each with associated hydrothermal activity. Molybdenum was concentrated at a very early stage in the evolution of the hydrothermal system and copper somewhat later. Four main vein Groups have been identified: I) quartz + molybdenite + anhydrite  $\pm$  K-feldspar with minor pyrite, chalcopyrite and bornite; II) quartz + chalcopyrite + pyrite  $\pm$  molybdenite; III) quartz + pyrite + calcite  $\pm$  chalcopyrite  $\pm$  anhydrite (gypsum)  $\pm$ molybdenite; IV) quartz  $\pm$  calcite  $\pm$  gypsum  $\pm$  pyrite. Early hydrothermal alteration produced a potassic assemblage (orthoclase-biotite) in the central part of the stock, propylitic alteration occurred contemporaneously with potassic alteration, but in the peripheral parts of the stock, and phyllic alteration occurred later, overprinting the earlier alteration. The early hydrothermal fluids are represented by high temperature (340 °C to 500 °C), high salinity (up to 60 wt % NaCl equiv.) liquid-rich fluid inclusions, and high temperature (320 °C to 550 °C), low-salinity, vapour-rich inclusions. These fluids are interpreted to represent an orthomagmatic fluid which boiled episodically; the brines are interpreted to have caused potassic alteration, and deposition of Group I and II quartz veins containing molybdenite and chalcopyrite. Propylitic alteration is attributed to a liquid-rich, lower temperature (240 °C to 330 °C), Ca-rich, evolved meteoric fluid. Influx of meteoric

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water into the central part of the system, and mixing with magmatic fluid produced salinities ranging from 1 to 19 wt % NaCl equivalent in Group II and III veins. Phyllic alteration and copper leaching resulted from the inflow of oxidized and acidic meteoric waters with decreasing temperature of the system. A late episode of boiling occurred in the upper part of the phyllic alteration zone, and was associated with significant chalcopyrite deposition.

#### INTRODUCTION

Although porphyry copper deposits have been intensively studied in the Mesozoic-Cenozoic orogenic belts of the American Cordillera and East Pacific Rim (e.g., Sillitoe, 1973; Ahmad et al., 1980; Bean and Titley, 1981; Cline, and Bodnar, 1991; Dilles, and Einaudi, 1992) and their genesis is relatively well understood, there have been few investigations of this style of mineralization in Iran and southern Asia. In Iran, all known porphyry copper mineralization occurs in the Cenozoic Sahand-Bazman orogenic belt (Fig. 1). This belt was formed by subduction of the Arabian plate beneath central Iran during the Alpine orogeny (Berberian, and King, 1981; Pourhosseini, 1981; Niazi, and Asoudeh, 1978) and hosts two major porphyry Cu deposits. The Sar-Cheshmeh deposit is the only one of these being mined, and contains 450 million tonnes of sulphide ore with an average grade of 1.13 % Cu and ~0.03 % Mo (Waterman and Hamilton, 1975). The Sungun deposit, which contains 500 million tonnes of sulphide reserves grading 0.76 % Cu and ~0.01 % Mo (unpublished data of the Iranian Copper Company), is currently being developed. Sar-Cheshmeh, Sungun and a number of other subeconomic porphyry copper deposits are all associated with mid- to late-Miocene granodiorite to quartz-monzonite stocks (Shahabpour 1982; Emami 1992).

The Sungun deposit area was first described by Bazin and Hübner (1969), who reported skarn-type mineralization at the contact between Cretaceous limestone and the granodioritic stock. On the basis of the overall geological setting and alteration patterns, Etminan (1977) proposed that the Sungun Cu deposit is porphyry-related. Mehrpartou (1993) subsequently made a preliminary study of the igneous petrology and fluid inclusions, Figure 1. Geological map of Iran showing major lithotectonic units as follows: 1) Zagros fold belt: Paleozoic platform sediments overlain by miogeosynclinal Mid-Triassic to Miocene sediments, and syn-orogenic Pliocene-Pleistocene conglomerates; 2) Sanandaj-Sirjan zone: Mesozoic granodioritic intrusions and metamorphosed Mesozoic sediments; 3) Central Iran zone: Paleozoic platform sediments disrupted by late Triassic tectonic activity, and including horsts of Precambrian crystalline basement and Cambrian to Triassic cover rocks; 4) Sahand-Bazman belt: Calc-alkaline volcanic and Quartz monzonite and quartz diorite intrusions of dominantly Miocene age, hosting Cu-Mo porphyry style mineralization; 5) Lut Block: The Lut block is considered to be an old stable platform (Stöcklin, and Setudenia, 1972; Stöcklin 1972), covered by thick Mesozoic sediments and Eocene volcanics; 6) Alborz and Kopeh Dagh zones: Eocene volcanic and volcanoclastic rocks in the Alborz segment, and in the Kopeh-Dagh segment; 7) The Eastern Iran and Makran zones: Post-Cretaceous flysch-mollasse sediments;





**Alborz Mountains** 



Makran



Sanandaj-Sirjan zone



Lut block



**Eastern Iran** 



Sahand-Bazman belt

### SYMBOLS

Study area Fault Thrust Fault



**Central Iran** 



Zagros fold belt



Kopet Dagh

and concluded that the overall characteristics of the deposit are very similar to those predicted by the generalized porphyry deposit model of Lowell and Guilbert (1970). However, these studies have not provided sufficient data to evaluate the evolution of the mineralizing system and establish a genetic model.

The purpose of this paper is to elucidate the hydrothermal history of the Sungun porphyry deposit and identify the factors controlling  $Cu \pm Mo$  mineralization. To aid us in this task we have documented alteration and vein mineral paragenesis petrographically, conducted a fluid inclusion study, analyzed oxygen and sulphur isotopic compositions of selected minerals, investigated mineral chemistry and calculated mineral stabilities and solubilities. This information has enabled us to determine the conditions under which the deposit formed, reconstruct the fluid evolution, and develop a model which satisfactorily explains the concentration of Cu mineralization to economic levels. By comparing the results from this study with data available from Sar-Cheshmeh and porphyry copper deposits in other parts of the world, we have been able to contribute a better understanding of the nature of Sahand-Bazman porphyry copper province.

#### **GEOLOGICAL SETTING OF THE SUNGUN DEPOSIT**

The Sungun porphyry copper deposit is hosted by a diorite/granodiorite to quartzmonzonite stock (Mehrpartou, 1993), located 75 km northwest of Ahar in the Azarbaijan province of northwestern Iran (Fig. 1). The stock is part of the Sahand-Bazman igneous and metallogenic belt (northern Iran), a deeply eroded Tertiary volcanic field, roughly 100 by 1700 km in extent (from Turkey to Baluchistan in southern Iran), consisting mainly of rhyolite and andesite, with numerous felsic intrusions. The volcanics were laid down unconformably over folded and eroded Upper Cretaceous andesitic volcanic and sedimentary rocks (~500 m thick). Subduction and subsequent continental collision during the Paleocene to Oligocene caused extensive alkaline and calc-alkaline volcanic and plutonic igneous activity (Berberian, 1983; Shahabpour, 1982; Etrninan, 1978), including intrusion of a porphyritic calc-alkaline stock at Sungun during the Miocene (Emami, 1992). Bordering the belt to the southwest is a major zone of complexly folded, faulted, and metamorphosed Tertiary and Paleozoic sedimentary rocks which form the Zagros Mountains (Waterman & Hamilton, 1975).

#### SUNGUN STOCK AND PERIPHERAL INTRUSIVE ROCKS

The Sungun stock is a complex intrusive body which outcrops over an area of about 1.5 by 2.3 km (Fig. 2). The stock consists of three different intrusive phases 1) monzonite/quartz monzonite; 2) diorite/granodiorite; and 3) andesite and related dykes, listed in order of emplacement. The monzonite/quartz-monzonite is volumetrically the most important and includes most of the western part of the intrusive complex at the current erosional surface. The diorite/granodiorite is volumetrically the next most important and hosts most of the mineralization. These two intrusive phases are cut by monzonitic and andesitic dykes, which in the northern and eastern parts of the Sungun stock are also locally mineralized. Petrographic studies have shown that mineralized dykes are mainly andesitic and are related to the diorite/granodiorite intrusive phase. The diorite/granodiorite and

monzonite/quartz-monzonite contain some mafic xenoliths, whereas xenoliths are rare in the mineralized dykes.

The Sungun diorite/granodiorite intrudes Cretaceous limestones (~500 m thickness) and lower Tertiary volcanic, volcanoclastic, and related sedimentary rocks (~1000 to ~1500 m thickness). The latter consist of andesitic to trachytic tuff and agglomerates, with intercalated marly tuff. This rock unit is inferred to be coeval with intrusion of the younger mineralized dykes. Andesite porphyry dykes intrude both the stock and surrounding rocks (Fig. 2). Some of the andesite dykes are highly altered and mineralized. Quaternary trachytic to andesitic lavas are exposed locally to the west and south of the deposit. They are unaltered and contain no known mineralization.

The Sungun stock is highly altered, and even in the outermost part of the intrusion it is not possible to find completely fresh rock. Metasomatic effects are also evident in the country rocks, particularly in the eastern part, where limestone has been altered to garnetpyroxene and amphibole-epidote skarns containing disseminated pyrite, chalcopyrite, sphalerite and galena, together with calcite, quartz and magnetite.

#### PETROGRAPHIC OBSERVATIONS OF THE STOCK

Petrographic observations of polished thin sections from different parts of the complex indicate that the mineralized diorite/granodiorite contains ~50 % by volume of phenocrysts consisting mainly of zoned plagioclase (An<sub>15-32</sub>) highly altered hornblende, K-feldspar, quartz and biotite. Apatite, zircon, scheelite, titanite, uraninite and rutile are present in minor to trace amounts. Hornblende was the earliest major mineral to crystallize

Figure 2. Detailed geological map of the Sungun area showing the distribution of different igneous suites (modified from Mehrpartou 1993).





and forms euhedral to subhedral phenocrysts. Quartz phenocrysts crystallized next and are ubiquitously rounded or embayed, which is a predicted consequence of isothermal decompression of a water vapour-undersaturated magma (Whitney 1989). Plagioclase phenocrysts (mainly subhedral) formed shortly after the quartz phenocrysts (mainly euhedral), and biotite phenocrysts (subhedral to anhedral) formed late. The diorite/granodiorite groundmass is microcrystalline and consists mainly of quartz, plagioclase, and K-feldspar, with lesser biotite and amphibole.

Monzonitic and quartz-monzonitic rocks contain 60 to 70 volume percent phenocrysts and are distinguished petrographically from the diorite/granodiorite by the presence of up to 30 volume percent of K-feldspar phenocrysts. The other important phenocryst phases are quartz (up to 20 %) and plagioclase (up to 25 %). Plagioclase ( $An_{17}$ . <sub>35</sub>) appears to have been the first of these phenocryst minerals to crystallize, as indicated by the common occurrence of euhedral to subhedral inclusions of plagioclase in K-feldspar. Accessory minerals include magnetite, apatite, zircon, monazite, scheelite, titanite, uraninite and rutile, which occur as inclusions in the silicate phases and interstitial to them. The sulphide minerals consist of pyrite, chalcopyrite, traces of molybdenite, galena and sphalerite, and form inclusions in secondary biotite or are disseminated throughout the matrix of the rock.

Andesite dykes consist mainly of plagioclase  $(An_{22-27})$ , K-feldspar, biotite, quartz and highly altered amphibole. Plagioclase occurs both as microcrystals in the groundmass and phenocrysts (up to 10 mm in diameter), and comprises more than 40 % of the total volume of the rock unit. K-feldspar crystals comprise around 30 volume percent of the total volume of the rock and occur both as phenocrysts and in the groundmass. Amphibole occurs only as phenocrysts (up to 5 mm in length), and comprises less than 7 % of the rock. Apatite, quartz, and magnetite occur as inclusions in the plagioclase and K-feldspar.

Mineralized porphyry dykes that cut the Sungun stock are pervasively altered, and contain abundant argillized feldspar and biotitized amphibole phenocrysts in an aphanitic groundmass. A small proportion of primary biotite is also present. The pre-alteration modal mineralogy of these mineralized dykes is estimated to have been 32 % plagioclase, 30 % orthoclase, 25 % quartz, and 14 % mafic and accessory minerals.

#### ALTERATION AND MINERALIZATION

Alteration and related mineralization in the Sungun porphyry copper deposit have been investigated by geological mapping, and detailed studies of the mineralogy, petrography and chemistry of a large number of drill cores and outcrop samples from various parts of the stock (Fig. 3). Hydrothermal alteration and mineralization at Sungun are centered on the stock and were broadly synchronous with its emplacement (Figs. 4 and 5). Early hydrothermal alteration was dominantly potassic and propylitic, and was followed by later phyllic, silicic and argillic alteration.

#### **POTASSIC ALTERATION**

The earliest alteration is represented by potassic mineral assemblages developed pervasively and as halos around veins in the deep and central parts of the Sungun stock (Figs. 4 and 5). Potassic alteration is characterized by K-feldspar, irregularly shaped

Figure 3. Detailed alteration map of the Sungun deposit.



Outlines of Cu mineralization

crystals of Mg-enriched biotite, and anhydrite. This alteration displays a close spatial association with mineralization; perhaps as much as 80 percent of the copper, and all the molybdenum were emplaced during this alteration episode. On average, potassically altered rocks contain 28 % plagioclase, 35 % orthoclase (2 mm to 2 cm in diameter), 20 % quartz, 15 % mafic minerals (mainly biotite, and sericite and chlorite after biotite), and 2 % chalcopyrite, pyrite, titanite, zircon, scheelite, uraninite, bismuthinite and rutile. Petrographic observations and microprobe analyses indicate the presence of two compositionally distinguishable types of biotite within this alteration zone; 1) primary biotite, which is Fe-enriched, brown in color, and generally euhedral; 2) hydrothermal biotite, which is mainly pale-brown to greenish-brown in color, very ragged, and Mgenriched (Table 1). The hydrothermal biotite is generally interstitial to feldspar and quartz, and locally replaced hornblende and primary biotite phenocrysts. Electron microprobe data indicate that some grains of potassium feldspar are rimmed by albite  $(An_{1-4})$  suggesting a later transition alteration event. Magnetite is rarely present, except in skarns. Relict crystals of secondary biotite are observed almost everywhere in the stock, suggesting that potassic alteration was initially very extensive but has been subsequently overprinted and obliterated by later stages of alteration.

#### **PROPYLITIC ALTERATION**

There is a relatively sharp boundary between the propylitic and potassic alteration zones in the deep part of the deposit, but at shallow levels this contact is obscured by later phyllic alteration (Figs. 4 and 5). Propylitic alteration is pervasive and represented mainly

	Hydrothermal Biotite (greenish-brown Colour)						Magmatic Biotite (dark-brown Colour)				
Sample no.	25-431	25-431	25-431	25-431	34-477	25-514	34-477	34-163	34-164	34-163	
Dril-core no.	25	25	25	25	34	25	34	34	34	34	
Туре	К	К	К	К	Phe	Frs	Phc	Trn	К	Trn	
SiO <sub>2</sub> (wt %)	41.29	39.25	39.03	38.74	41.29	38.58	37.27	37.60	38.58	37 27	
TiO <sub>2</sub>	2.02	2.17	2.11	3.91	2.02	3.82	4.27	4.95	3.82	4.27	
Al <sub>2</sub> O <sub>1</sub>	15.05	15.50	15.54	15.53	15.05	14.55	13.53	22.86	14.55	13.53	
FeO <sup>2</sup>	2.53	4.17	4.18	4.79	2.53	15.69	16.38	13.51	15.69	16.38	
MnO	0.00	0.04	0.01	0,02	0.00	0.17	0.18	0.06	0.17	0.18	
MgO	23.18	21.50	21.58	21.39	23.18	14.34	14,40	14.39	14.34	14.40	
CaO	0.00	0.00	0.04	0,04	0.00	0.03	0.01	0.13	0.03	0,01	
Na <sub>2</sub> O	0.14	0.18	0.17	0.20	0.14	0.30	0,30	0.09	0.30	0.30	
K <sub>2</sub> O	10.51	10.43	10.25	10.34	10.51	9.35	9.41	2.26	9.35	9.41	
F	2.60	1.96	2.10	1.87	2.60	0.38	0.33	0.38	0.38	0.33	
CI	0.04	0.09	0.08	0.07	0.04	0,20	0,17	0.05	0.20	0.17	
Total	97.35	95.29	95.09	96.91	97.35	97.41	96.24	96.29	97,41	96.24	
No, of atoms											
based on 11 O											
Si	2.77	2,75	2.72	2.68	2.77	2.81	2.77	2.72	2.81	2.77	
Ti	0.10	0.11	0.11	0.20	0.10	0.21	0.24	0.05	0.21	0.24	
Al	1.20	1.28	1.29	1.27	1.20	1.26	1.20	2.02	1.26	1.20	
Fe	0.14	0.24	0.24	0.28	0.14	0,96	1.02	0.84	0.96	1.02	
Mn	0,00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	
Mg	2.32	2.23	2.24	2.20	2.32	1.56	1.60	1.37	1.56	1.60	
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	
Na	0.02	0.02	0.02	0.03	0.02	0.04	0.04	0.01	0.04	0.04	
К	0.90	0.93	0.91	0.91	0.90	0.90	0.89	0.21	0.87	0.89	
F	0.55	0.43	0.46	0.41	0.55	0.09	0.08	0.09	0.09	0.08	
Cl	0.00	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.02	
F/(F+Cl)	1.00	0.98	0.98	0.98	1.00	0.82	0.80	0.90	0.82	0.80	
Fe/(Fe+Mg)	0.06	0.10	0.10	0.11	0.06	0.38	0.39	0.38	0.38	0.39	

TABLE 1. Composition of Magmatic and Hydrothermal Biotite in the Sungun Porphyry Copper Deposit

Frs = fresh rock, Trn = transition zone, K = potassic zone, Phc = phyllic FeO = total Fe

**Figure 4.** Profiles showing the distribution of Cu grades and alteration assemblages along cross-section A-A. Numbers on surface indicate drill holes. The thick lines represent dykes.



A-A Section



**Figure 5.** Profiles showing the distribution of Cu grades and alteration assemblages along cross-section B-B. Numbers on the surface indicate drill holes. The thick lines represent dykes.



**B-B Section** 



by chloritization of primary and secondary biotite and groundmass material in rocks peripheral to the central potassic zone. Epidote replaced plagioclase, but this alteration is less pervasive and intense than chloritization. Microprobe analyses indicate that the chlorite composition corresponds mostly to that of clinochlore and pycnochlorite. Minor minerals associated with propylitic alteration are albite, calcite, sericite, anhydrite (gypsum), and pyrite.

#### TRANSITION ALTERATION

Potassic alteration is overprinted by a large zone of pervasive transition alteration in the central part of the stock, which grades upwards into phyllic alteration. Transition alteration is characterized by albite replacement of more An-rich plagioclase, and albite rims on orthoclase. Minor sericite and pyrite also partially replaced plagioclase, biotite and hornblende. A distinguishing characteristic of this type of alteration is the white color of the affected rocks. This change of color from the original gray to white reflects a strong depletion of ferromagnesian minerals like hornblende and biotite.

#### PHYLLIC ALTERATION

The transition from transition alteration to phyllic alteration is gradual and is marked by an increase in the proportion of muscovite. It is difficult to separate transition and phyllic alteration because of intense silicification during the latter alteration. Phyllic alteration is characterized by the replacement of almost all rock-forming silicates by sericite and quartz, and overprints the earlier-formed potassic and transition zones. Pyrite forms up to 5 volume percent of the rock, and occurs in veins and disseminations. Quartz veins are also surrounded by weak sericitic halos. Vein-hosted pyrite is partially replaced by chalcopyrite. The highest copper grades at Sungun are associated with potassic and phyllic alteration (Figs. 4 and 5). Silicification was synchronous with phyllic alteration and variably affected much of the stock and most dykes.

#### **ARGILLIC ALTERATION**

Feldspar is locally altered to clay down to a depth of 400 m, and within 80 m of the erosional surface the entire rock has been altered to an assemblage of clay minerals, hematite and quartz. The affected rocks are soft and white colored. XRD analyses indicate that kaolinite is the dominant phyllosilicate, and that it is accompanied by illite. The shallow alteration is interpreted to represent a supergene blanket over the deposit and the deeper clay alteration of feldspar may have had the same origin. However, the possibility can not be excluded that the latter represents an advanced argillic stage of the hypogene alteration.

#### MINERALIZATION

Hypogene copper mineralization was introduced during potassic alteration, and to a lesser extent during phyllic alteration, and exists as disseminations and in veinlet form. During potassic alteration, the copper mineralization consisted of chalcopyrite and minor bornite; later hypogene copper mineralization consisted mainly of chalcopyrite. Hypogene molybdenum mineralization (molybdenite) was concentrated mainly in the deep part of the stock and is associated exclusively with potassic alteration, where it is found in quartz veins accompanied by K-feldspar, anhydrite, sericite, and lesser chalcopyrite (see section on vein classification). Alteration of feldspars and biotite (from potassically altered rocks) was accompanied by an increase in sulphide content outward from the central part of the stock. Copper mineralization increases toward the margins of the central potassic zone, from less than 0.20 wt % to 0.85 wt % (Figs. 4 and 5). There is also a positive correlation between silicification and copper mineralization. The maximum Cu grade is associated with biotite, orthoclase, and sericite (potassic zone; Figs. 4 and 5) while the pyrite content is highest (3-10 vol % of the rock) in the marginal quartz-sericite (phyllic) zone. The ratio of pyrite to chalcopyrite in the zone of richest hypogene copper mineralization in the potassic alteration zone is as low as 4:1, but toward the margins of the stock the ratio increases to 15:1.

At the exposed surface of the deposit, rocks are highly altered and the only mineral which has survived supergene argillization is quartz. Most of the sulphide minerals have been leached, and copper was concentrated in an underlying supergene zone by downward percolating ground waters. This zone is very limited and consists of a thin (up to 20 m) blanket containing covellite, chalcocite, and digenite located below a thin, intensely oxidized cap.

#### VEIN AND VEINLET CLASSIFICATION

The Sungun deposit contains well-developed stockwork mineralization that is concentrated in the potassic and transition zones (the transition zone is actually the outermost part of the potassic zone and is characterized by a low content of biotite and abundant sericitization) (Fig. 6). Based on mineralogy and cross-cutting relationships, it is possible to distinguish four main Groups of veins representing four episodes of vein formation (Fig. 6): *I*) quartz + molybdenite + anhydrite  $\pm$  K-feldspar with sporadic pyrite, chalcopyrite and bornite, *II*) quartz + chalcopyrite + pyrite  $\pm$  molybdenite, *III*) quartz + pyrite + calcite  $\pm$  chalcopyrite  $\pm$  anhydrite (gypsum)  $\pm$  molybdenite, *IV*) quartz, and/or calcite, and/or gypsum  $\pm$  pyrite.

In order to determine the volume percent of each vein type in the different alteration zones, we have used the two-dimensional method of Haynes (1984). First, we split the core (drill core No. 25) along its diameter to expose a rectangular surface of dimension 2R by T, where R is the radius of the core, and T is the total length of split core. The density of all veins in a given core was measured by the sum of the lengths of veins which had been exposed in the cut area divided by the area. The length of the fracture is a function of the radius of the core and the angle with which the fracture intersects the core; the area of the rectangle is 2RT (Haynes 1984).

The stockwork system is dominated volumetrically by Group IV and Group I veins (up to 21 and 24 % by volume of the rock, respectively). Group II and Group III veins occupy up to 15 volume percent and 13 volume percent of the rock, respectively. The integrated vein volumes vary between 0 and 22 percent, and average about 16 percent.

#### **GROUP I VEINS**

Group I veins are discontinuous, vary in thickness between 0.5 and 3 mm, and formed during the early fracturing of the porphyry stock. Molybdenite is the most important sulphide mineral, and occurs mainly along vein margins; K-feldspar, anhydrite, chalcopyrite, bornite and pyrite occur in the central part of the vein, and less commonly at the margins. There are also some traces of bismuthinite (Bi<sub>2</sub>S<sub>3</sub>) in the molybdenite grains (Fig. 7a). Pyrite and chalcopyrite partially replace the molybdenite. Quartz comprises from 60 to 95 percent of the volume of the veins. The veins are surrounded by potassic, and less commonly phyllic and propylitic alteration haloes.

#### **GROUP II VEINS**

Group II veins generally crosscut and in places offset the Group I veins. The most important characteristics of Group II veins are well-developed sericitic alteration haloes and the lack of K-feldspar. The volume ratio of chalcopyrite to pyrite is 2:1. Molybdenite contents vary from traces to less than 5 volume percent of the vein. The alteration haloes are most obvious in the potassic alteration zone, where hydrothermal biotite in the halo was destroyed. The sericitic alteration haloes have thicknesses varying between 1 and 5 mm. Vein quartz is relatively coarse-grained and tends to be oriented perpendicular to the walls of the vein. Sulphide minerals are located mainly in a narrow discontinuous layer in the vein centers, but in some cases the sulphides are disseminated through the quartz. Group II veins occur in all alteration zones, but are concentrated mainly in the potassic alteration zone. Their thickness varies from 3 to 30 mm, and they are generally more continuous than Group I veins.

#### **GROUP III VEINS**

Group III veins cross-cut both Group I and II veins, and in some cases offset the earlier-formed veins. Group III veins are most abundant in the phyllic alteration zone, and are relatively continuous, commonly layered, and vary in thickness from 3 to 50 mm. Quartz occurs mainly near the vein margins with anhydrite, calcite, and sulphide minerals intergrown in the vein centres. Quartz is relatively coarse grained, and locally shows optical zoning (overgrowths). The only copper mineral is chalcopyrite, which is observed mainly as small blebs and inclusions in pyrite. Early-formed anhedral to subhedral grains of pyrite are replaced by anhedral grains of chalcopyrite (Figs. 7b & 7c).

Group II and III veins appear to have a common origin with Group III veins probably having formed by re-opening of Group II veins. As will be discussed in the section on fluid inclusions, primary saline fluid inclusions similar to those in Group II veins, are present in the centres of zoned quartz crystals in Group III veins. The paucity of chalcopyrite and other copper minerals in Group III veins suggests that they have been leached by later fluid circulating in these veins.

#### **GROUP IV VEINS**

Group IV veins crosscut all the other vein Groups, and represent the youngest veinforming event in the Sungun stock. They are very thick (up to 17 cm), and filled by quartz,

**Figure 6.** Diagram showing the volume proportions of the different vein Groups in each of the alteration zones.


and/or calcite, and/or gypsum. Group IV veins are found mainly in the propylitic zone, but also occur locally in the phyllic and potassic alteration zones. The only sulphide mineral is pyrite, which occupies ~10 vol % of these veins. Group IV veins are usually surrounded by zones of silicification up to 3 cm wide.

## FLUID INCLUSION STUDIES

Fluid inclusions are abundant in quartz of all vein types, and range in diameter from 1  $\mu$ m up to 15  $\mu$ m. The majority of inclusions examined during this study had diameters of 4-12  $\mu$ m. They are also common in quartz phenocrysts, but are too small (<3  $\mu$ m) to be analyzed microthermometrically. Most of our measurements were conducted on fluid inclusions in Group I and II veins, with a few from Group III veins. Group IV veins do not contain any workable fluid inclusions.

## FLUID INCLUSION CLASSIFICATION

Fluid inclusions were classified into three main types based on the number, nature, and proportion of phases at room temperature. The following types of fluid inclusions have been identified:

LV inclusions consist of liquid + vapour  $\pm$  solid phases with the liquid phase volumetrically dominant. These fluid inclusions are common in all mineralized quartz veins, and are abundant in Group II and III veins. The diameter of these fluid inclusions ranges from 3 to 12  $\mu$ m.

**Figure 7.** Scanning electron photomicrographs of: a) molybdenite with associated anhedral bismuthinite and pyrite. b) pyrite altered to chalcopyrite. c) chalcopyrite filling fractures in pyrite. Abbreviations: Bi = bismuthinite, Mo = molybdenite, Cp = chalcopyrite, Py = pyrite, Qtz = quartz.









Vapour bubbles are variable in size, but constitute less than 35 % of inclusion volumes. The inclusions homogenize to liquid. In a small number of fluid inclusions, small cubes of halite (< 1  $\mu$ m in diameter), and unidentified transparent or opaque minerals (mainly hematite) were observed. The distribution and volume of solid phases are irregular, (< 5 % to > 10 %) suggesting that they represent trapped solids rather than daughter minerals.

VL inclusions also contain vapour + liquid  $\pm$  solid phases. Vapour bubbles are variable in size, but in all cases consist of > 60 % of the inclusion volume. These inclusions mainly homogenize to vapour, and rarely to liquid, or by critical behavior. Most VL inclusions contain only vapour + liquid. However, some inclusions contain a single solid phase which is either halite or an unidentified mineral which is also thought to have been trapped.

LVHS inclusions are multiphase, and consist of liquid + vapour + halite + other solids. Based on the number and type of the solids, we have further classified LVHS fluid inclusions into three subtypes. Subtype S<sub>1</sub> inclusions are characterized by the presence of halite + chalcopyrite  $\pm$  anhydrite  $\pm$  K-Fe-Cl phase (identification of this mineral is discussed below). Halite (up to 25 %), anhydrite (up to 10 %) and chalcopyrite (up to 6 %) have consistent phase ratios and are interpreted to be daughter minerals. Vapour bubbles occupy < 25 % of the inclusion by volume. Subtype S<sub>2</sub> inclusions contain sylvite in addition to the phases in S<sub>1</sub> inclusions. The solid phases occupy ~60 % of inclusion volumes, and the vapour bubbles ~20 %. Subtype S<sub>3</sub> inclusions contain halite, which is commonly accompanied by hematite, but do not contain chalcopyrite, sylvite and the K-Fe-Cl phase. The volume of the solid phases is typically <40 % of the inclusions, and bubble volumes range between 20 and 60 %.

#### SOLID PHASES IN FLUID INCLUSIONS

Halite and sylvite in the inclusions were identified by their cubic and sub-cubic The identification was confirmed by SEM-EDAX analyses which shapes and isotropy. yielded peaks for Na/Cl and K/Cl respectively. Sylvite was distinguished from halite by its rounded edges and lower relief; it also dissolves at lower temperatures. Halite crystals were generally larger and more common than those of sylvite, and have a well defined habit. Chalcopyrite was identified on the basis of its optical characteristics (opacity and triangular cross section) and composition in opened inclusions (SEM-EDAX analyses yielded peaks for Cu, Fe and S). Anhydrite forms transparent anisotropic prisms (Fig. 8a) and was shown by SEM-EDAX analyses to consist only of Ca and S (elements lighter than F could not be analyzed). Hematite was easily identified from its red color, hexagonal shape, extremely high index of refraction and high birefringence (this identification was confirmed by SEM-EDAX analyses on opened inclusions, which only produced a peak for Fe). A solid with a rounded shape, transparent to pale green color, and strong birefringence, which dissolves at ~200 °C, was shown by SEM-EDAX analyses to consist of K, Fe, and Cl. This solid could be the K-Fe chloride, erythrosiderite (K<sub>2</sub>FeCl<sub>5</sub> . XH<sub>2</sub>O).

## DISTRIBUTION OF FLUID INCLUSIONS TYPES

**Figure 8.** Scanning electron photomicrographs of daughter minerals from decrepitated quartz-hosted fluid inclusions. a = Group II quartz veins, An = anhydrite and Ha = halite. b = Group I quartz veins; accumulations of both halite and sylvite crystals.





# Figure 8

The Sungun intrusions have undergone repeated episodes of fracturing and healing, with multiple generations of fluid inclusions representing the evolution of hydrothermal fluids and corresponding alteration and mineralization.

LV inclusions are found in all vein Groups, but occur in variable proportions. They are most abundant in the Group II and III veins, and rare in Group I veins. Most LV inclusions are distributed along healed fractures, and are of secondary origin.

VL inclusions are found in quartz phenocrysts from fresh rocks and in Group I, II and III quartz veins. Some of these inclusions occur in growth zones in Group I and II quartz veins, where they are accompanied by LVHS fluid inclusions, indicating that at least some of them are primary. VL inclusions are generally elongated and have rounded ends, but some have negative crystal shapes. Some of the VL inclusions have variable liquidvapour ratios, and may have formed from the necking down of LVHS inclusions or heterogeneous entrapment of liquid and vapour.

LVHS inclusions are found in all veins, from the deepest, potassically altered part of the stock (Group I and II veins) through to the shallow level veins. The fluids occupy cavities ranging from 1  $\mu$ m to 10  $\mu$ m in diameter. At shallow levels (Group III veins), most of the LVHS inclusions are of subtype S<sub>3</sub>, but at deeper levels (mainly Group I and II veins), subtypes S<sub>1</sub> and S<sub>2</sub> predominate. Up to seven solid phases have been observed in a single LVHS inclusion. The co-existence of LVHS inclusions (mainly LVHS<sub>1</sub> and LVHS<sub>3</sub>) and vapour-rich inclusions with consistent phase ratios in the growth zones of quartz grains from potassic and phyllic alteration zones suggests a primary origin, and co-existence of two immiscible aqueous fluids.

#### Fluid inclusion population I

LVHS<sub>1</sub>, LVHS<sub>2</sub> and VL fluid inclusions occur in Group I and II quartz veins from the potassically altered zone (350 to 500 meters below the present erosional surface), but are rare at shallow levels in the phyllic alteration zone. In Group I veins, LVHS<sub>1</sub> and LVHS<sub>2</sub> fluid inclusions commonly form isolated clusters in the cores of quartz grains. VL inclusions commonly occur along microfractures, but they are also present in clusters with LVHS<sub>1</sub> fluid inclusions. LVHS<sub>1</sub>, LVHS<sub>2</sub> and VL fluid inclusions, that have been identified in quartz from Group II and III veins in phyllic alteration zones at shallow levels may be relics of earlier potassic alteration. These three fluid inclusion types are interpreted to represent the earliest episode of fluid entrapment in the deposit.

## Fluid inclusion population II

At shallower levels, in the phyllic alteration zone, there is a close association of solid-rich LVHS<sub>3</sub> and VL fluid inclusions. They are found together in growth zones but occur mainly along healed fractures. This population of inclusions is spatially associated with LV inclusions, especially in Group III veins, but the chronological relationship between the two inclusion populations is unclear.

Fluid inclusion population III

LV fluid inclusions occur in all vein Groups, but are most common in Group II and III veins from phyllic and propylitic alteration zones. They are clearly located along fracture planes, and are secondary in origin. LV inclusions appear to represent a later stage fluid that circulated in the intrusion.

## FLUID INCLUSION MICROTHERMOMETRY

Microthermometric studies were carried out on 25 samples of quartz from Group I, II and III veins. Temperatures of phase changes in fluid inclusions were measured with a Fluid Inc. U.S.G.S.-type gas-flow stage which operates by passing preheated or precooled N<sub>2</sub> gas around the sample (Werre et al., 1979). Stage calibration was performed using synthetic fluid inclusions. Accuracy at the standard reference temperatures was  $\pm 0.2$  °C at -56.6 °C (melting point for CO<sub>2</sub>),  $\pm 0.1$  °C at 0 °C (melting point of ice),  $\pm 2$  °C at 374.1 °C (critical homogenization of H<sub>2</sub>O), and  $\pm 9$  °C at 573 °C (alpha to beta quartz transition). The heating rate was approximately 1 °C/min near the temperatures of phase transitions.

#### LOW TEMPERATURES PHASE CHANGES

The temperatures of initial (Te) and final melting of ice ( $Tm_{ice}$ ) were measured on types LV, VL and LVHS fluid inclusions. In the case of type VL inclusions,  $T_e$  was difficult to determine, because of the high vapour/liquid ratios. Clathrate formation was not observed in any of the inclusions, which rules out the possibility of there being significant  $CO_2$  in the system. The crushing of quartz under anhydrous glycerine confirms this conclusion; the vapour bubble collapsed during crushing in all but a few inclusions, and in the latter inclusions the bubble size was unchanged or increased slightly, indicating that the maximum pressure of incondensible gases was ~1 bar.

The temperature of initial ice melting (T<sub>e</sub>) of most LV fluid inclusions was between -34 ° and -14 °C (Fig. 9), suggesting that NaCl  $\pm$  KCl are the principal salts in solution. The Tm<sub>ice</sub> values for these inclusions range from -1 ° to -10 °C (Fig. 10), corresponding to salinities of 1.7 to 14 wt. % NaCl equiv., respectively (Sterner et al., 1988). A small proportion of LV inclusions in quartz phenocrysts in shallow dykes have T<sub>e</sub> between -25 ° and -39 °C, suggesting the presence of CaCl<sub>2</sub>, FeCl<sub>2</sub>, or MgCl<sub>2</sub> in addition to NaCl and KCl. The Tm<sub>ice</sub> values for LV fluid inclusions in Group I quartz veins range from -1.3 ° to -8.1 °C, corresponding of a salinity of 2.3 to 9.6 wt percent NaCl equiv. (Sterner et al., 1988); in Group II quartz veins they range from -1.2 ° to -10.5 °C, corresponding to a salinity from 2.1 to 14.5 wt percent NaCl equiv.; and in Group III quartz veins they range from -2.1 to -12.3 °C corresponding to a salinity from 3.5 to 16.3 wt percent NaCl equivalent.

The T<sub>e</sub> value of VL fluid inclusions ranges from -48 ° to -18 °C with a mode of ~-26 °C suggesting that Na and K are the dominant cations in the solution. The Tm<sub>ice</sub> value for these inclusions varies from -0.5 ° to -14.9 °C, which corresponds to a salinity between 0.8 and 18.5 wt % NaCl equivalent. The low T<sub>e</sub> (-31 °C to -46 °C) for some of the VL inclusions in Group I and II veins could indicate that these inclusions are the product of necking down of LVHS inclusions (see below).

Owing to the small volume of liquid in LVHS fluid inclusions, it is difficult to measure  $T_e$  and Td hydrohalite. The eutectic temperatures that could be measured in Group I and II veins (LVHS<sub>1</sub> and LVHS<sub>2</sub>) range from -30 ° to -64.4 °C, suggesting important

Figure 9. Histograms of eutectic temperatures for LV, VL and LVHS fluid inclusions from mineralized quartz veins.



Figure 10. Histograms of final ice melting and hydrohalite dissolution temperatures for fluid inclusions from mineralized quartz veins.





concentrations of Fe, Mg, Ca, and/or other components in addition to Na and K in this type of inclusion (Fig. 9). Eutectic temperatures for the CaCl<sub>2</sub>-H<sub>2</sub>O, NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O, and FeCl<sub>3</sub>-H<sub>2</sub>O systems are -49.8 °, -52 ° and -55 °C, respectively (Linke, 1965), and could explain the low first melting temperatures observed for some of the LVHS inclusions. Hydrohalite dissolution temperatures vary between -5 ° and -32 °C in LVHS inclusions (Fig. 10). SEM-EDAX analyses of the residues of decrepitated fluid inclusions showed that Fe and Ca are more abundant than Mg (discussed later).

LVHS fluid inclusions (subtype LVHS<sub>3</sub>) in Group III vein quartz yield distinctly different microthermometric data from those of LVHS<sub>1</sub> and LVHS<sub>2</sub> inclusions in Group I and II veins. The eutectic temperatures vary from -29 ° to -43 °C and the hydrohalite dissolution temperature (Tm<sub>HH</sub>) varies between -2 °C and -13 °C (Fig. 10).

## HIGH TEMPERATURE PHASE CHANGES

LV fluid inclusions homogenize to liquid (Th<sub>L</sub>) at temperatures between 240 ° and 330 °C, with a well defined mode at Th<sub>L</sub> of ~270 °C for Groups I and II, and 300 °C for Group III mineralized quartz veins (Fig. 11). Almost all VL inclusions homogenize to vapour (Th<sub>v</sub>) between 320 ° and 500 °C. VL inclusions from Group III veins homogenize at temperatures between 375 ° and 535 °C (Fig. 11), but some of the VL inclusions from Group II veins exhibit no changes until the temperature is within ~30 °C of the homogenization temperature; the vapour then rapidly expands to fill the inclusion, indicating a near-critical density fluid (cf. Roedder, 1984).

The liquid and vapour phases in LVHS<sub>1</sub> and LVHS<sub>2</sub> inclusions from Group I veins

Figure 11. Histograms of homogenization temperatures for LV, VL and LVHS fluid inclusions from mineralized quartz veins.



homogenize to liquid at temperatures between ~280 ° and ~500 °C (Fig. 11) and between ~260 ° and ~460 °C in Group II veins. The liquid-vapour homogenization temperature for LVHS<sub>3</sub> inclusions is from ~220 ° to ~420 °C in Group I and II veins and ~220 ° to ~390 °C in Group III veins (Fig. 11). The first mineral to dissolve in LVHS<sub>2</sub> inclusions is sylvite, at temperatures between 55 ° and 119 °C (Group I and II veins). The K-Fe chloride phase (LVHS<sub>1</sub> and LVHS<sub>2</sub>) dissolves between 200 ° and 256 °C, and halite in these inclusions dissolves between 280 °C and 498 °C (Group I and II veins). Salinities based on the halite dissolution temperature range from 36 to 60 wt % NaCl equivalent (Sterner et al., 1988) (Fig. 12). The halite dissolution temperatures for LVHS<sub>3</sub> inclusions are 230 ° to 450 °C in Group I and II quartz veins. The halite dissolution temperatures (Td<sub>Halite</sub>) in LVHS<sub>3</sub> inclusions in Group III quartz veins are 198 ° to 351 °C (Td<sub>Halite</sub><Th<sub>L-V</sub>) which correspond to salinities of 31 to 42 wt % NaCl equiv. with an average of 34 wt. % NaCl equivalent.

Most LVHS<sub>1</sub> inclusions (Group I and II veins) and LVHS<sub>3</sub> inclusions in Group I and II veins homogenized by vapour disappearance (Fig. 13). By contrast LVHS<sub>2</sub> inclusions (Group I and II veins) homogenized mainly by halite dissolution. LVHS<sub>3</sub> inclusions in Group III veins commonly homogenized by both vapour disappearance and halite dissolution (Fig. 13). Anhydrite and chalcopyrite did not dissolve on heating to temperatures in excess of >600 °C.

## COMPOSITIONAL TRENDS IN THE SYSTEM NaCl-KCl-H<sub>2</sub>O

The data for LVHS<sub>2</sub> fluid inclusions from Group I and II veins define a trend in the system NaCl-KCl-H<sub>2</sub>O similar to the halite trend of Cloke and Kesler (1979) but directed

Figure 12. Histograms of salinities (wt % NaCl equivalent) from microthermometric data for LV, VL and LVHS fluid inclusions, in mineralized quartz veins.



Figure 13. Liquid-vapour homogenization temperature vs. halite dissolution temperature for halite-bearing fluid inclusions (all LVHS inclusions) in mineralized quartz veins.



Liquid-Vapour homogenization temperature (°C)

more strongly towards the H<sub>2</sub>O apex than in other porphyry systems (e.g. Cloke and Kesler, 1979; Eastoe 1978; Ahmad, and Rose, 1980; Wilson et al., 1980). The trend at Sungun may reflect the combined effects of halite saturation and boiling (Fig. 14). *K/Na* ratios of LVHS<sub>2</sub> inclusions defining the trend vary between ~0.19 and ~0.35. The absence of sylvite in LVHS<sub>1</sub> and LVHS<sub>3</sub> inclusions is evidence for a *K/Na* atomic ratio of < 0.2 (Roedder, 1984), which is supported by SEM-EDAX analyses on decrepitates from these inclusions.

## DECREPITATE COMPOSITIONS

Residues from decrepitated fluid inclusions were analyzed using the procedures of Haynes et al. (1988). Ten cleaned, doubly polished thin sections were heated rapidly to a temperature of 450 °C which was sufficient to cause most inclusions to decrepitate (Figs. 8a & 8b). The sections were analyzed using a JEOL JSM-840A scanning electron microscope equipped with a Tracor Northern energy dispersive X-ray spectrometer in raster mode.

The following elements were present in appreciable concentrations in the residues: Na, Ca, K, Fe, Mg, Cl and S. Only Cl, however, was consistent in its concentrations among the various residues analyzed. Other elements varied by at least a factor of two (e.g., Na) and in some cases (e.g., Ca), ranged from 0 to >20 wt %. Copper is present only in residues from LVHS<sub>2</sub> inclusions. In general Na<sup>+</sup> is the dominant cation in residues from all three solid-bearing inclusion types. However, in LVHS<sub>3</sub> inclusions, the atomic proportion of  $Ca^{2+}$  approaches and in some cases exceeds that of Na<sup>+</sup>. Next to Na<sup>+</sup>,  $Ca^{2+}$  is the most important cation in LVHS<sub>1</sub> inclusions and has high but variable concentrations in LVHS<sub>2</sub> inclusions. The concentration of K<sup>+</sup>, as expected, is highest in LVHS<sub>2</sub> inclusions and

Figure 14. A NaCl-KCl-H<sub>2</sub>O phase diagram showing the compositions of  $LVHS_2$  fluid inclusions determined from the dissolution of halite and sylvite (phase diagram after Roedder, 1984).



among the other cations is exceeded only by that of Na<sup>+</sup>. In these inclusions the *K/Na* ratio ranges from 0.18 to 0.73 and has a mean of 0.36. The *K/Na* ratios of LVHS<sub>1</sub> and LVHS<sub>3</sub> inclusions are 0.03 to 0.15 and 0.07 to 0.24, respectively.

The molalities of the above elements were calculated with the aid of microthermometrically estimated salinities and are presented in the Table 2. Of particular interest is the unusually high molality of S, which varied from 0.35 to 0.44 in LVHS<sub>1</sub>, 0.15 to 2.18 in LVHS<sub>2</sub>, and 1.25 to 2.41 in LVHS<sub>3</sub> inclusions. Some of the high S molalities may reflect contamination with anhydrite. However even inclusions with little or no Ca contain up to 0.6m S. The molality of Cu varied from 0.02 to 0.06, and compares favorably with estimates of 0.02 to 0.04m obtained by relating the volume of the daughter mineral to the volume of fluid in eight LVHS<sub>2</sub> inclusions.

#### STABLE ISOTOPE GEOCHEMISTRY

#### **OXYGEN ISOTOPES**

Oxygen isotope analyses were conducted on five samples of quartz from Group I, II and III veins in the potassic, transition and phyllic alteration zones (Table 3). Quartz grains were separated using both heavy liquid and hand picking methods. The <sup>18</sup>O/<sup>16</sup>O ratios were determined by D. Pezderic at the Department of Geological Sciences, University of Saskatchewan, employing methods similar to those described by Sheppard and Taylor (1974). The  $\delta^{18}$ O values of quartz are the same (9.5 ‰) in all samples (3) from the potassic alteration zone (Group I veins), and are slightly higher for the transition (Group II veins)

				-	-										
No.	Types	Ca wt%	Na w1%	K wt%	Fe wt%	Mg wt%	Al wi%	Cl wt%	S wt%	Mn wt%	Cu wt%	ation charg	Anion charg Balance	Fotal charge Balance	K / Na Ratio
1	LVHS <sub>1</sub>	0.54	12.89	0.40	20,85	0.00	0.31	62.19	1.41	1.40	0.00	18.03	-18.42	-0.39	0.03
2	LVHS	8.25	18.95	0.92	0.98	1.82	1.79	65.69	1.39	0.21	0.00	16.69	-19.40	-2.71	0.05
3	LVHS	8,25	20.95	3.11	0.98	1.82	1.60	61.69	1.39	0.21	0.00	17.91	-18.27	-0.36	0.15
4	LVHS <sub>2</sub>	2.83	21.26	9.34	3.15	1.80	0.00	60.37	1.25	0.00	0.00	16.22	-17.81	-1.59	0.44
5	LVHS <sub>2</sub>	1.24	16.46	11.99	3.70	2.21	1.58	60.62	1.11	1.09	0.00	16.81	-17.79	-0.99	0.73
6	LVHS <sub>2</sub>	0.83	25.36	6.59	2.83	1.80	1.50	59.11	1.98	0.00	0.00	17.80	-17.91	-0.11	0.26
7	LVHS,	0.00	24.11	4.43	5.08	3.62	0.00	60.51	2.11	0,00	0.14	17.35	-18,38	-1.03	0.18
8	LVHS,	13.39	13.62	3.07	1.81	5.44	0.17	55.51	6.99	0.00	0.23	19.07	-20,02	-0.95	0.23
9	LVHS	7.05	21.47	6.14	3.40	0.00	0.00	60.33	1.22	0.00	0.39	16.32	-17.78	-1.46	0.29
10	LVHS	9.39	18.63	7.36	3.39	0.84	0.00	56,09	3.44	0.75	0.11	17.47	-17.97	-0.49	0.40
11	LVHS,	0.00	25.78	8.58	3.11	0.00	0.00	61.63	0.47	0.12	0.31	15.17	-17.68	-2.51	0.33
12	LVHS <sub>2</sub>	0.00	24.80	8.58	0.57	1.48	0.98	. 62.85	0.47	0.27	0.00	15.69	-18.02	-2.33	0.35
13	LVHS,	18.44	12.67	0.92	3.73	2.61	1.10	55.29	5.24	0.00	0.00	20.32	-18.86	1.46	0.07
14	LVHS <sub>3</sub>	20.06	15.89	2.56	4.81	0.91	0.14	47.89	7.74	0.00	0,00	21.07	-18.34	2,73	0.16
15	LVHS	9.13	9.52	2.31	6.14	3.87	2.93	60.02	4.01	0.00	0,00	19.56	-19.43	0.13	0.24
16	LVHS,	20.14	10.92	1.16	4.39	0.54	0.36	57.79	4.70	0.00	0.00	18.30	-19.23	-0.93	0.11
17	LVHS,	21.95	10.69	2.11	2.96	0.21	1.14	54.52	5.28	1.03	0.00	19.57	-18.67	0.90	0,20

 TABLE 2. Composition of Decrepitate Residues from Different types of Fluid Inclusions (SEM-EDAX)

No.	Types	Mol. Ca	Mol. Na	Mol. K	Mol. Fe	Mol. Mg	Mol. Al	Mol. <u>Cl</u>	Mol. S	Mol. Mn	Mol. Cu		
1	LVHS	0.14	5.61	0.10	3.73	0.00	0.12	17.54	0.44	0.26	0.00		
2 3	LVHS <sub>1</sub> LVHS <sub>1</sub>	2.06 2.06	8.24 9.11	0.24 0.80	0.18 0.18	0.75 0.75	0.66 0.59	18.53 17.40	0.43 0,43	0.04 0.04	0.00 0.00		
4	LVHS₂	0.71	9.25	2.39	0,56	0.74	0.00	17.03	0.39	0.00	0.00		
5	LVHS <sub>2</sub>	0.31	7.16	3.07	0.66	0.91	0.59	17.10	0.35	0.20	0.00		
6	LVHS <sub>2</sub>	0.21	11.03	1.69	0.51	0.74	0,59	16.67	0.62	0.00	0.00		
7	LVHS <sub>2</sub>	0.00	10,49	1.13	0.91	1.49	0,00	17.07	0.66	0.00	0.02		
8	LVHS <sub>2</sub>	3.34	5.93	0.79	0.32	2.24	0.06	15.66	2.18	0.00	0.04		
9	LVHS <sub>2</sub>	1.76	9.34	1.57	0.61	0.00	0.00	17.02	0,38	0.00	0.06		
10	LVHS <sub>2</sub>	2.34	8,10	1.88	0.61	0.35	0,00	15.82	1.07	0.14	0.02		
11	LVHS <sub>2</sub>	0.00	11.21	2.19	0,56	0.00	0.00	17.38	0.15	0.02	0.05		
12	LVHS <sub>2</sub>	0.00	10,79	2.19	0.10	0.61	0,36	17.73	0.15	0.05	0.00		
13	LVHS3	4.60	5.51	0.24	0.67	1,07	0.41	15.60	1.63	0.00	0.00		
14	LVHS3	5.01	6.91	0.66	0.86	0.37	0.05	13.51	2.41	0,00	0.00		
15	LVHS,	2.28	4.14	0.59	1,10	1.59	1.09	16.93	1.25	0.00	0.00		
16	LVHS3	5.03	4.75	0.30	0.79	0.22	0.13	16.30	1.47	0,00	0.00		
17	LVHS,	5.48	4.65	0.54	0.53	0.09	0.42	15.38	1.65	0.19	0.00		

TABLE 2. (cont')

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Sample					δ <sup>18</sup> Ο
no.	Mineral	Vein type	Alteration Type	Yield Values	%0
25-437	Quartz	I	Potassic	16.5	9.5
25-466	Quartz	I	Potassic	16.9	9.5
25-487	Quartz	I	Potassic	15.9	9.5
34-498	Quartz	II	Transition	16.2	10.1
36-213	Quartz	III	Phyllic	16.0	10.3

TABLE	3.	0xygen	Isotope	Results	of	the	Mineralized	group	Quartz	Veins.
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Chapter III

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and phyllic (Group III veins) zone samples at 10.1 and 10.3 % respectively. The corresponding  $\delta^{18}$ O values for the fluids in Group I and II quartz veins are +6.5 to +7.1 %, assuming an average temperature of vein formation of 450 °C, and 5.2 in Group III quartz veins assuming an average temperature of 360 °C (discussed later). These values are consistent with a dominantly magmatic source for the vein forming fluids. It should however, be noted that the Group III veins are interpreted to represent re-opened Group II veins, and it is thus possible that the  $\delta^{18}$ O values for the Group III vein samples are related to their earlier history.

#### **SULPHUR ISOTOPES**

Sulphur isotopic analyses were performed on 15 pyrite, anhydrite, chalcopyrite and molybdenite samples separated from Group I, II and III veins. Mineral separation was performed by heavy liquids and by hand picking. The purity of the separated minerals was confirmed by examination with a binocular microscope. The analyses were performed at the Stable Isotope Laboratory at the University of Ottawa.

Sulphur isotopic data are reported in Table 4. Although the data are limited, there is no evidence that any of the minerals vary systematically in isotopic composition with respect to mineral paragenesis or alteration. The four molybdenite samples analyzed have  $\delta^{34}$ S values between -0.3 and -2.0 per mil, the three chalcopyrite samples have  $\delta^{34}$ S values of -1.4 to -1.6 per mil, the five pyrite samples have  $\delta^{34}$ S values ranging from -0.5 to -3 per mil and the two anhydrite samples have nearly identical  $\delta^{34}$ S values of 11.6 and 11.8 per mil. In the Group I and II veins, the textural relationships between the sulphide (i.e., pyrite,

chalcopyrite and molybdenite) and anhydrite show that they have been co-precipitated. For Group I veins the only mineral pairs for which data are available from which to calculate temperature are pyrite-molybdenite, anhydrite-pyrite and anhydrite-molybdenite. The temperatures calculated from  $\Delta^{34}S$  for anhydrite-pyrite, anhydrite-molybdenite and anhydrite-chalcopyrite pairs from the Group I veins range from 450 ° to 485 °C. The  $\Delta^{34}$ S value for molybdenite-pyrite is too small to permit reliable calculation of temperature. Trapping temperatures of primary fluid inclusions in Group I quartz veins vary between 330±20° and 500±20°C. The isotopic temperatures from S-isotope geothermometry are therefore in good agreement with the fluid inclusion data and suggest attainment of sulphur isotopic equilibrium (Fig. 15). Unfortunately  $\delta^{34}$ S data for Group II veins were restricted to values for chalcopyrite and pyrite from separate samples, and a temperature for these veins could not be calculated. However, the  $\delta^{34}$ S values are very similar to those for the corresponding minerals in Group I veins suggesting that temperature was also similar. Anhydrite-pyrite, anhydrite-chalcopyrite and pyrite-chalcopyrite pairs for Group III veins yielded temperatures of 450±20 °C, 470±20 °C and 360±20 °C, respectively. We interpret this disagreement to reflect earlier deposition of anhydrite as a higher temperature Group II vein mineral in a vein that was subsequently re-opened to allow entry of Group III veinforming fluids. This interpretation is supported by textural relationships which suggest that the sulphide minerals were precipitated later than the anhydrite.

The  $\delta^{34}$ S of the fluid responsible for forming Group I and II veins was estimated from trends of  $\delta^{34}$ S for co-existing anhydrite and sulphide (Fig. 16). The two sets of data display good linear correlations and regress to a common  $\delta^{34}$ S value of ~2.7 per mil which

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		<u>.</u>		δ <sup>H</sup> S%,		_									
Sample	Vein Stage	сср	ру	mo	anh	۵ <sup>4</sup> 5%-۲۷ са	r T'C	∆ <sup>24</sup> S‰ <sub>242</sub> m.	<u>. т°с</u>	AHS% antipy	ಗೆಂ	<b>А<sup>H</sup>S%•альто</b>	۳°C	<b>А<sup>34</sup>S%•ыл-ха</b> р	<u> </u>
25-437	I		-1.5	-0.8	11.8				•	13.3	465 °C ± 20°C	12.6	470 °C ± 20 °C		
25-461	1			-1.1	11.8							12.9	460 °C ± 20 °C		
25-466	I		-1.7	-0,3	11.8					13.5	480 °C ± 20°C	12.1	485 °C ± 20 °C		
106-529	I I	-1.4		-2	11.8			0,6	475 °C ± 20 °C			13.8	455 °C ± 20 °C	13.2	470 °C ± 20 °C
33-125	11	-1.6													
25-397	li –		-1.5												
36-213	111	-1.6	-0,5		11.6	1.1	360 °C ± 20 °C			12.1	470 °C ± 20 °C			13.2	470 °C ± 20 °C
21-127	Ш		-3		11.6					14.6	450 °C ± 20 °C				

## TABLE 4. Sulfur Isotope Data from Sulfate and Sulfide Minerals in Different Stage Veins from Sungun Deposit

is interpreted to represent the  $\delta^{34}S$  of the early ore fluid, and is consistent with an orthomagmatic source for the sulphur.

#### DISCUSSION

#### **PRESSURE- TEMPERATURE CONDITIONS**

The maximum pressure of fluid entrapment can be calculated from the estimated thickness of the overlying rock column at the time of intrusion, which at Sungun is estimated to have been between 1.5 and 2.0 km. The latter represents ~500 m of Cretaceous limestone, plus 1000 to 1500 m lower Tertiary volcanic, volcanoclastic, and related sedimentary rocks. This corresponds to a lithostatic pressure of 400 to 500 bars (assuming an average rock density of 2.7 g/cm<sup>3</sup>) and a hydrostatic pressure of 150 to 200 bars (assuming a fluid density near 1 g/cm<sup>3</sup>).

LVHS<sub>1</sub> fluid inclusions occur with VL inclusions in Group I quartz veins associated with potassic alteration, and together with LVHS<sub>2</sub> fluid inclusions define fluid population *I*. The homogenization temperatures for type LVHS<sub>1</sub> inclusions (generally Th<sub>L-V</sub> > Td<sub>Halite</sub>) vary between 330 ° and ~500 °C, and for co-existing VL inclusions vary between 400 ° and 500 °C (Fig. 17); LVHS<sub>2</sub> inclusions homogenize at temperatures from 280 ° to 500 °C (generally Th<sub>L-V</sub> < Td<sub>Halite</sub>). Similar temperatures are predicted by the sulphur isotopic data (Fig. 15). At these temperatures the maximum pressure for the co-existence of these two fluid inclusion types (bubble point curve) is approximately 300 to 400 bars. On
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**Figure 15.** Comparison of vein formation temperatures calculated from fluid inclusion microthermometry, and sulphur isotopic fractionation. The temperatures estimated by the two different methods are similar except for Group III veins where temperatures based on S isotopic fractionation between anhydrite and pyrite are anomalously high.



Figure 16. A  $\delta^{34}$ S mineral versus  $\Delta^{34}$ S sulphate- sulphide diagram for coexisting anhydrite and sulphides. The inclined sold lines represent linear regressions through the data for sulphides and anhydrite, respectively. These intersect at a value of  $\delta^{34}$ S = ~2.7 per mil and suggest a similar reservoir composition for early and late sulphide mineralization.



**Figure 17.** Liquid-vapour homogenization temperature vs. salinity plotted on a section from the NaCl-H<sub>2</sub>O system (halite saturation and critical curves from Chou, 1987).



the other hand, the existence of LVHS fluid inclusions with  $Td_{Halite} > Th_{L-V}$  (mainly LVHS<sub>2</sub>) implies that pressure was locally or temporarily much higher. In fact, pressures estimated for those inclusions range as high as 1200 bars. However, as already discussed, the lithostatic pressure was 400 to 500 bars. We therefore propose that fluid pressure exceeded lithostatic pressure and that pressure generally oscillated between 150 bars (hydrostatic) and >500 bars in response to repeated cracking and sealing of the rock. In summary pressure during the

trapping of fluid population I varied from 150 to >500 bars and temperature was ~450 °C.

Fluid *II* is defined by the co-existence of LVHS<sub>3</sub> and VL inclusions. There is a clear similarity of the liquid-vapour homogenization temperatures for fluid inclusions in this population (Fig. 17). In Group I and II veins, LVHS<sub>3</sub> inclusions homogenize by vapour disappearance after halite dissolution at a modal temperature of 350 °C. Based on data from Sourirajan and Kennedy (1962) and Chou (1987) for the NaCl-H<sub>2</sub>O system, the corresponding fluid pressure was ~200 bars. VL inclusions (vapour rich) homogenize to a vapour at between 380 ° and 520 °C, i.e., at significantly higher temperatures than LVHS<sub>3</sub> inclusions. We attribute this to heterogeneous entrapment of liquid and vapour during boiling. In Group III veins, the LVHS<sub>3</sub> inclusions homogenize at temperatures <300 °C by both vapour disappearance and halite dissolution. Fluid *II* was thus trapped at considerably lower temperatures than fluid  $I (\leq 350 ° \text{ vs. } 350 - 500 °C)$  and underwent cooling with the development of a progressively more open fracture system represented by Group III veins. The pressure was dominantly hydrostatic (150 - 200 bars).

The LV fluid inclusions of Fluid *III* represent a later fluid that circulated in the intrusion. These inclusions homogenize to liquid at temperatures between 240 ° and 330

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<sup>o</sup>C. Using the data of Chou (1987), the minimum corresponding pressure is below ~150 bars. We propose that the majority of the LV fluid inclusions were trapped when the stock was fractured and conditions were dominantly hydrostatic.

### **FLUID EVOLUTION**

The high trapping temperatures (350 to >500 °C) and high salinity of LVHS<sub>1</sub> and LVHS<sub>2</sub> fluid inclusions suggest that Fluid population *I* probably represents an orthomagmatic fluid. We propose that this fluid exsolved as a high density phase from a diorite/granodiorite magma (the solidus temperature of this magma and emplacement pressure are above the critical point curve for high salinity fluids in the system NaCl-KCl-H<sub>2</sub>O), and subsequently saturated with halite and boiled. Furthermore, we propose that the LVHS<sub>2</sub> fluid inclusions generally represent the pre-boiled fluid, and the LVHS<sub>1</sub> and VL inclusions, the high and low density products of boiling.

The conclusion that  $LVHS_2$  fluid inclusions represent the pre-boiled fluid is based on the fact that their compositions, as discussed previously, delineate a so-called halite trend on a NaCl-KCl-H<sub>2</sub>O diagram (Fig. 14), similar to those reported for other porphyry copper deposits (e.g., Quan et al., 1987; Wilson et al., 1980; Ahmad and Rose, 1980; Eastoe, 1978; Ford, 1978). These trends have been interpreted by Cloke and Kesler (1979) as being due to early saturation of the fluid with halite and subsequent trapping of the fluid over an interval of cooling. We propose that this was also the case for the LVHS<sub>2</sub> fluid inclusions, i.e., that they were largely trapped before the onset of widespread boiling. However, the displacement of the trend towards the H<sub>2</sub>O apex and the existence of LVHS<sub>2</sub> fluid inclusions which homogenize by vapour disappearance, suggest that there must have been some boiling even at this early stage of fluid evolution. The halite trend, represented by fluid inclusions that homogenize by halite dissolution, is described by the path M-N-O on Figure 18. Liquids trapped between points N and O would be on the halite trend because they are in equilibrium with halite. By contrast, LVHS<sub>2</sub> fluid inclusions, which homogenize by vapour disappearance (Th<sub>L-V</sub> > Td<sub>Halite</sub>), probably record sudden lowering of pressure from M-N-O along N-P or N-Q (isothermal) and boiling. This decompression likely occurred episodically due to fluid overpressuring (recorded by LVHS<sub>2</sub> fluid inclusions which appear to have been trapped at pressures greater than lithostatic; see previous section), hydrofracturing and resultant sharp changes from supra-lithostatic to hydrostatic conditions.

Our interpretation that  $LVHS_1$  fluid inclusions are the products of boiling is supported by the facts: 1) that they almost invariably homogenized by vapour disappearance; and 2) that they are commonly associated spatially with VL inclusions. We conclude that  $LVHS_1$  and VL fluid inclusions record a later stage in the evolution of the Sungun hydrothermal system than the  $LVHS_2$  fluid inclusions, i.e., a stage when conditions were closer to hydrostatic and Fluid *I* boiled extensively.

We propose that the source of Fluid *II* (LVHS<sub>3</sub> and VL fluid inclusions) was also mainly orthomagmatic (high salinity), but that this fluid circulated at lower temperature than Fluid *I* (~350 °C vs. 350 ° - 500 °C) and mixed with an external fluid. Mixing is suggested by the high concentrations of Ca measured in residues of decrepitated inclusions; these could have been introduced from the surrounding limestones. It is also suggested by a trend from higher temperature and higher salinity to lower temperature and lower salinity for

LVHS<sub>3</sub> and LV fluid inclusions (Fig. 17). Coexistence of LVHS<sub>3</sub> fluid inclusions (which homogenize largely by vapour disappearance) with VL fluid inclusions indicate that Fluid *II* boiled extensively.

Fluid *III* (L-V inclusions) circulated mainly in Group II and Group III veins at temperatures from 330 ° to 240 °C. We propose that the source of Fluid *III* was mainly meteoric water, and that it mixed to variable degrees with magmatic fluids. This conclusion is based on the decrease in salinity from 18 wt % down to 1 wt % NaCl equiv. (Fig. 17) in LV fluid inclusions and the corresponding decrease in homogenization temperature.

Fluids *II* and *III* commonly coexist in Group II and Group III veins. We interpret this to record the downward movement of Fluid *III* (dominantly meteoric), which initially was at conditions indicated by point X on Figure 18, and its subsequent evolution along a path of increasing temperature due to mixing with orthomagmatic fluids, which originated at point M. At point Y the fluid reached its maximum depth and subsequently ascended along an adiabatic cooling curve (Y-Z).

The fluid inclusion data discussed above indicate that there was a general decrease in temperature and salinity with time in the fluid responsible for ore deposition. Homogenization temperatures of fluid inclusions decrease from around 500 °C in Group I veins to about 240 °C in Group III veins, and the salinity of LVHS fluid inclusions decreases from 55 wt % NaCl equiv. in Group I veins to 33 wt % equiv. in Group III veins; the salinity of LV inclusions decreases from 18 wt % to 1 wt % NaCl equiv. These changes in fluid temperature and salinity reflect the cooling of a saline aqueous fluid exsolved from a diorite/granodiorite magma, and its subsequent boiling and mixing with meteoric waters as conditions evolved from being dominantly lithostatic to dominantly hydrostatic.

Figure 18. Pressure-temperature diagram for the system NaCl-H<sub>2</sub>O showing the proposed mechanisms for the formation of the LVHS fluid inclusions VL and lower salinity LV inclusions. The LVHS inclusions are envisaged to represent part of a boiling fluid of orthomagmatic origin first trapped at a temperature of approximately 540 °C and pressure of 500 bars (M). M-N-O is the path that explains the LVHS<sub>1</sub> and LVHS<sub>2</sub> inclusions which homogenize by the halite disappearance. Liquids trapped between points N and O are in equilibrium with halite. To form the  $LVHS_3$  fluid inclusions which homogenize by vapour disappearance, it is necessary to invoke sudden lowering of pressure along N-P or N-Q (isothermal) until the fluid is in equilibrium with vapour (see text for more information). Point X represents the assumed initial P-T conditions for the evolved meteoric fluid. This fluid moved downwards into the system and mixed with orthomagmatic fluids, thereby evolving along a path of increasing temperature and pressure. At point Y the fluid reached its maximum depth and subsequently ascended along an adiabatic cooling curve (Y-Z). Trapping of this fluid lead to the formation of LV inclusions. Abbreviations:  $C.P.H_2O =$ critical point of water, L = Liquid, V = vapour, NaCl = halite. Diagram modified after Chou (1987), with liquidus curves from Bodnar (1992).



### ALTERATION AND MINERALIZATION

The presence of molybdenite and anhydrite in Group I veins, chalcopyrite and anhydrite in Group II veins and chalcopyrite and anhydrite in LVHS<sub>1</sub> and LVHS<sub>2</sub> inclusions from vein Groups I and II suggests that Fluid *I* was responsible for the transport and eventual deposition of Mo, Cu, Fe and S. Molybdenite was deposited at the margins of the Group I veins, where deposition was controlled by decreasing temperature from ~520 ° to ~450 °C. This cooling also stabilized K-feldspar (potassic alteration) at the expense of plagioclase and biotite at the expense of hornblende; the *K/Na* ratio was approximately 0.3. The rarity of chalcopyrite in Group I veins and abundance in Group II veins indicates that physico-chemical conditions only became appropriate for bulk Cu deposition during formation of Group II veins, i.e. after some evolution of the hydrothermal system. The occurrence of anhydrite in the hypogene mineral assemblage can be explained by the hydrolysis of SO<sub>2</sub> upon cooling:

### $4SO_2 + 4H_2O = 3H_2SO_4 + H_2S$

Thus, the breakdown of  $SO_2$ , which is believed to occur around 400 °C (Burnham, 1981; Burnham, and Ohmoto, 1980), is a possible source for both sulphate (to form anhydrite) and sulphide (to form molybdenite, pyrite, and chalcopyrite).

A fluid of mainly mixed meteoric and magmatic origin circulated later in the central part of the stock, at temperatures between 240 ° and 420 °C. Late fractures, or reopened veins, provided the pathways for this fluid to circulate in the system. It is proposed that at a

temperatures around 350 °C, partial boiling and subsequent mixing with meteoric fluids was responsible for the variation in salinity in the Group III vein-hosted fluid inclusions (Fig. 18). This fluid (Fluid *II*), when circulated in the central part of the intrusion, progressively increased in temperature to a maximum of 420 °C causing destabilization of the previously formed K-feldspar from the potassic alteration zone. With increasing temperature, the *K/Na* ratio of the related fluid decreased progressively (0.2), thereby favoring the neo-formation of albite which rimmed the previously formed K-feldspar. In the upper levels of the intrusion this fluid produced widespread lower temperature sericitization, and as a result of having a lower pH and higher  $fO_2$ , remobilized early formed copper sulphide minerals into highly fractured zones where they were reprecipitated.

During the formation of potassic alteration at the main stage of mineralization, (380 ° to 520 °C), the peripheral part of the stock was altered propylitically at lower temperatures (240 ° to 420 °C). The circulation of Fluid *III*, which did not penetrate into the hotter and most central part of the intrusion, caused this alteration zone. This fluid also may have caused some of the argillic alteration later, in which almost all the feldspars were altered to kaolinite and other clay minerals.

### CONCLUSIONS

The multiple intrusions of dioritic and granodioritic to quartz-monzonitic rocks at Sungun indicate a long-lived intrusive episode associated with repeated fracturing and hydrothermal activity. Mineralogical, fluid inclusion and isotopic analyses from the deposit indicate three distinct hydrothermal fluids. The first hydrothermal fluid caused potassic alteration and Cu

 $\pm$  Mo mineralization. This fluid was characterized by high temperatures and moderate to high salinities, and was probably magmatically derived. It was responsible for the wide distribution of Group I and II mineralized quartz veins, at temperatures ranging from 380 ° to 520 °C, and boiled episodically. The data from oxygen and sulphur isotope analyses suggest a magmatic source for the corresponding hydrothermal mineralization in those veins. The second hydrothermal fluid (Fluid *II*) was formed mainly by the mixing of magmatic fluid, at moderate to low temperatures (up to 420 °C), with a predominantly, meteoric fluid (Fluid *III*) and also boiled. This fluid was responsible for the transition and sericitic alteration zones in the upper portion of the stock. The third hydrothermal fluid (Fluid *III*) consisted of low temperature, low to moderate salinity (1 to 18 wt % NaCl equiv.) and oxidized meteoric water, which was responsible for peripheral propylitic alteration in a zone outside the core of potassically altered rock, and possibly argillic alteration when it was allowed to penetrate into the system.

The three interpreted hydrothermal fluids correspond to three different populations of fluid inclusions in Sungun veins. Phase equilibria and stratigraphic reconstruction indicate that the majority of the fluid inclusions in Group I and II quartz veins were trapped at temperatures from 350 ° to 520 °C (with a mode of 360 ° to 380 °C) under pressure conditions that ranged from > lithostatic to hydrostatic (i.e. the fluid boiled episodically). Fluid *II* inclusions have variable homogenization temperatures and are interpreted to represent heterogeneous entrapment, which suggests a second boiling episode. The two boiling episodes correspond to: 1) potassic alteration in the deep and central part of the stock followed by Cu  $\pm$  Mo mineralization; and 2) phyllic alteration in the upper part of the stock. Fluid *III* formed by progressive dilution of magmatic fluid with meteoric waters. The majority of the Fluid *III* inclusions were trapped at 240 ° to 420 °C under a hydrostatic pressure of 150 bars.

The later hydrothermal evolution was controlled by the incursion of dilute meteoric fluids into the permeable stockwork system (source of Fluid II). This addition of external fluids increased *Na/K* ratios in the progressively heated fluids, and caused the remobilization of previously precipitated copper sulphide s through acidification and oxidation, and redeposition in highly fractured zones. This is evident from the occurrence of chalcopyrite as overgrowths on earlier grains of chalcopyrite.

Molybdenite deposition was controlled by decreasing temperatures due to cooling. Final supergene enrichment of copper minerals was very limited, and consists of a thin blanket containing covellite, chalcocite and digenite, located below an intensely altered cap.

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## **CHAPTER IV**

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### Mass Transfer and Element Mobility Associated with

**Hydrothermal Alteration** 

### INTRODUCTION

In Chapter II, it was shown that the Sungun deposit is hosted by a composite intrusive, comprising early diorite/granodiorite and later monzonite/quartz-monzonite, which was emplaced at a paleo-depth of ~2000 m, and at temperatures of 670-780 °C. The parental magma was a medium to high-K andesite and trachyandesite similar in composition to syn-collisional calc-alkaline magmas generated in continental arc settings (Chapter II). Copper mineralization occurs within the diorite/granodiorite, which is the most strongly altered intrusive phase.

Chapter III documented hydrothermal evolution during alteration and mineralization. Three distinct hydrothermal fluids were identified. The first hydrothermal fluid caused potassic alteration and Cu±Mo mineralization, was characterized by high temperatures and moderate to high salinities, and was derived magmatically. The second hydrothermal fluid formed mainly by mixing magmatic fluid with a predominantly meteoric fluid, resulting in lower temperature and salinities. This fluid was responsible for transition alteration at depth and sericitization at higher levels. The third hydrothermal fluid consisted of relatively oxidized meteoric water, which produced a peripheral propylitic alteration zone outside the core of potassically altered rock. Therefore, the alteration in dioritic/granodioritic rocks at Sungun can be classified into three different types: I) potassic, II) propylitic and, III) phyllic.

Many studies of porphyry copper deposits have provided descriptions of minerals present in different alteration zones, and chemical characteristics of fluids associated with alteration episodes (e.g., Carten, 1986; Brimhall, 1980). However, there have been only a

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few attempts to determine the complete evolutionary path of alteration, with corresponding quantification of mass changes in different alteration zones during reaction with hydrothermal fluids (i.e. Brimhall, and Ghiorso, 1983; Brimhall, 1979).

In this chapter, the mass changes of major and minor elements that accompanied alteration in dioritic/granodioritic rocks of the Sungun porphyry copper deposit are evaluated quantitatively. The method of Gresens (1967), as modified by Grant (1986) is employed to calculate mass changes, and is based on elements that were immobile during alteration. These elements are used to establish the bulk mass/volume changes during the different alteration episodes, and correct the analyses of the altered rocks. The masses of components added to or removed from the rock as a result of its interaction with hydrothermal fluids are determined by comparing the corrected analyses for the altered rocks with those of least altered equivalents.

### METHODOLOGY

Representative samples were examined from the different alteration zones in the deposit. Detailed petrographic studies of wallrocks, veins and alteration envelopes were performed on more than 100 hand samples and 60 polished thin sections (see Chapter III). Mineral identification and qualitative estimation of mineral abundances were conducted using optical microscopy, electron microprobe analyses, and scanning electron microscopy. Lithogeochemical analyses were performed by X-ray fluorescence spectrometry, with a detection limit of 0.01 wt. % for major elements (as oxides), and 2 ppm for trace elements, (except TiO<sub>2</sub> 10 ppm, and Cu and Mo 1 ppm). The major alteration and ore minerals in

fourteen samples were analyzed using a JEOL-8900L electron microprobe, with 15 kV acceleration voltage, 8 nA beam current, 2 µm beam diameter, and 25 second peak counting times. The mineral standards used were orthoclase (Al, K, Si), albite (Na), diopside (Ca, Mg), andradite and magnetite (Fe), spessartine (Mn, Si, Al), fluorite (F), and synthetic MnTi (Mn, Ti).

### ALTERATION

Hydrothermal alteration and mineralization at Sungun are centered on the diorite/granodiorite intrusion and were broadly synchronous with its emplacement (Fig. 1). Early hydrothermal alteration was dominantly potassic and propylitic, and was followed by later transition and phyllic alteration.

### **POTASSIC ALTERATION**

The earliest alteration in diorite/granodiorite, which was produced by fluxes of magmatic fluids away from the pluton center, is represented by potassic mineral assemblages developed pervasively and as halos around veins in the deep and central parts of the Sungun stock (Figs. 2 and 3). Potassic alteration is characterized by K-feldspar, irregularly shaped crystals of Mg-rich biotite, and anhydrite. On average, potassically altered rocks contain 28 % plagioclase, 35 % orthoclase, 20 % quartz, 15 % mafic minerals (mainly biotite, and sericite and chlorite after biotite), 2 % chalcopyrite, pyrite, titanite, and zircon, and traces of scheelite, uraninite, bismuthinite and rutile. Biotite occurs primarily as

Figure 1. Detailed alteration map of the Sungun deposit. It emphasizes the effect of supergene argillic alteration at the current erosional surface.



a replacement of hornblende, and as anhedral grains discerninated through the groundmass, and is inferred to be mainly of hydrothermal origin (Table 1). It is greenishbrown, shows ragged, anhedral shapes, and occurs generally interstitial to feldspar and quartz. Relict crystals of secondary biotite are observed almost everywhere in the stock, suggesting that potassic alteration was initially very extensive but has been subsequently overprinted by later alteration. Biotite that replaced amphibole commonly contains inclusions of chalcopyrite and/or pyrite. Primary biotite is present only as rare phenocrysts.

Potassium feldspar can be either magmatic, occurring mainly as perthitic phenocrysts, or is hydrothermal, having formed during potassic alteration. K-feldspar domains in perthite have a compositional range of  $Or_{97}Ab_2An_1$  to  $Or_{99}Ab_1$ , and albite domains compositions ranging from  $Ab_{76}Or_1An_{23}$  to  $Ab_{81}Or_3An_{16}$ . The compositions of the perthitic feldspars require subsolidus exsolution at ~500 °C (Tuttle and Bowen, 1958). Magmatic K-feldspar has a composition ranging from  $Or_{88}Ab_{10}-An_2$  to  $Or_{99}Ab_1$ , and variable but relatively high barium contents (BaO up to 1.74 wt %). Hydrothermal Kfeldspar is distinguished from its magmatic equivalent by the absence of perthitic intergrowths. Hydrothermal K-feldspar is also much more albitic having a composition of  $Or_{72}Ab_{27}An_1$  to  $Or_{78}Ab_{10}An_{12}$ .

Rutile occurs as small grains and needles associated with titanite and biotite. Textural relationships suggest that titanium was not mobilized during alteration and mineralization, as rutile is closely associated with parent minerals (hornblende, biotite or titanite).

**Figure 2.** Profiles showing the distribution of Cu grades and alteration zones along crosssection C-C. Numbers on surface identify drill holes.





**Figure 3.** Profiles showing the distribution of Cu grades and alteration zones along crosssection D-D. Numbers on surface indicate drill holes.





### **PROPYLITIC ALTERATION**

Propylitic alteration is characterized by chloritization of primary and secondary biotite, amphibole and groundmass material in rocks peripheral to the central potassic zone. Epidote replaces plagioclase, but this replacement, is less pervasive and intense than chloritization. Microprobe analyses indicate that the chlorite composition corresponds mostly to that of clinochlore and pycnochlorite. The variation in chlorite composition is minor, and is mainly reflected in Fe/(Fe + Mg) values (Table 2). Minor minerals associated with propylitic alteration are albite, calcite, sericite, anhydrite (gypsum), and pyrite. Mass transfer calculations were not done for this type of alteration due to a lack of reliable analyses.

### TRANSITION ALTERATION

The outermost part of the potassic alteration zone, which contains lesser biotite and K-feldspar, and a greater proportion of sericite, has been termed the transition zone. Mineralogically, this alteration is represented by chloritization and sericitization of both primary and secondary biotite, and sericitization in the groundmass. This alteration is also characterized by albite replacement of more An-rich plagioclase, and albite rims on orthoclase. A distinguishing characteristic of this type of alteration is the white color of the affected rocks. This change of color from the original gray to white reflects a strong depletion of ferromagnesian minerals like hornblende and biotite, which is obvious in isocon diagrams (discussed later).

	Magmatic Biotite (dark-brown Colour)							Hydrothermal Biotite (greenish-brown Colour)						
Sample no.	25-514	34-163	33-437	33-437	33-437	33-437	•	34-477	25-431	34-477	34-477	34-477	34-477	
Dril-core no.	25	34	33	33	33	33		34	25	34	34	34	34	
Type <sup>1</sup>	Frs	Trn	К	К	К	КК		<u>K</u>	K	Phc	Phc	Phc	Phc	
Si(). (wt (%)	28.58	37 77	38 54	37 70	38 34	37 70		43 72	30 03	41.20	30.25	30.03	28 74	
$\operatorname{TiO}_2$ (we b)	3.87	4 27	3.24	4 00	3 98	4 03		2 65	211	2 (12)	217	211	3 72	
	14 55	13 53	15.45	14 10	14 17	14.85		17 17	15 54	15.05	15 50	15.54	15.81	
FnO <sup>4</sup>	15.60	16.38	13.73	15 30	15.42	14.05		3 87	4 18	2.5.05	4 17	4.18	7 54	
MnO	017	018	0.06	0.05	0.06	0.04		0.01	0.01	0.00	0.04	0.01	0.00	
MgO	14.34	14.40	15.00	14.94	15.07	14.78		17.41	21.58	23.18	21.50	21.58	18.38	
CaO	0.03	0.01	0.00	0.00	0.00	0.00		0.05	0.04	0.00	0.00	0.04	0.02	
Na <sub>2</sub> O	0.30	0.30	0.10	0.10	0.13	0.11		0.15	0.17	0.14	0.18	0.17	0.24	
K <sub>2</sub> O	9.35	9.41	10.25	10.16	10.05	10.21		9.94	10.25	10.51	10.43	10.25	10.52	
F	0.38	0.33	1.03	0.75	0.73	0.82		1.92	2.10	2,60	1.96	2.10	1.58	
Cl	0.20	0.17	0.19	0.22	0.23	0.23		0,08	0.08	0.04	0.09	0.08	0.15	
Total	97.41	96.24	97.11	97.31	98.18	97.02		96.97	95.09	97.35	95.29	95.09	96.71	
No. of atoms														
based on 11 O														
Si	2.81	2.77	2.77	2.75	2.77	2.75		2.94	2.72	2.77	2.73	2.72	2.72	
Ti	0.21	0.24	0.18	0.22	0.22	0.22		0,13	0.11	0.10	0.11	0.11	0.20	
Al	1.26	1.20	1.32	1.22	1.22	1.28		1.37	1.29	1.20	1.28	1.29	1.32	
Fe	0.96	1.02	().8()	0.93	0.93	0.86		0.22	0.24	0.14	0.24	0.24	0.44	
Mn	0.01	0.01	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	
Mg	1.56	1.60	1.61	1.63	1.62	1.60		1.74	2.24	2.32	2.23	2.24	1.94	
Ca	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	
Na	0.04	0.04	0.01	0.01	0.02	0.02		0.04	0,02	0.02	0.04	0.02	0.03	
К	0.90	0.89	0.94	0.95	0.93	0.95		0.95	0.91	0.90	0.93	0.91	0.94	
F	0.09	0.08	0.23	0.17	0.17	0.19		0.41	0.46	0.55	0.43	0.46	0,39	
Cl	0.02	0.02	0.02	0.03	0.03	0.03		0.01	0.01	0.00	0.01	0.01	0.02	
F/(F+Cl)	0.82	0.80	0.92	0.85	0.85	0.86		0.98	0.98	1.00	0.98	0.98	0.95	
Fe/(Fe+Mg)	0.38	0.39	0.33	0,36	0,36	0.35		0.11	0.10	0.06	0,10	0.10	0.18	

TABLE 1. Representative Electron Microprobe Analyses of Magmatic and Hydrothermal Biotite In the Sungun Porphyry Copper Deposit

Fis = fresh rock, Trn = transition zone, K = polassic zone, Phc = phynic FeO = total Fe
Sample No.	-34-164	34-161	34-163	34-163	34-162	33-163	34-163	34-163	34-163	25-514	25-514	25-514	25-514	25-514	34-477	34-477
Dril-core No.	34	34	34	34	34	33	34	34	34	25	25	25	25	25	34	34
Туре'	Pro	Pro	Pro	Рто	Phe	Phe	Phc	Phc	Phc	<u>K</u>	<u>K</u>	<u> </u>	<u> </u>	<u>K</u>	Pro	Pro
SiO <sub>2</sub> (wt %)	30.09	29.94	30.39	30.45	29.89	29.18	31.11	29.91	30.06	30.75	27.90	27.64	29.63	28.70	29,91	29.89
TiO,	0.05	0.02	0.03	0.02	0,02	0.03	0.02	0.03	0,00	0.06	0.05	0.07	0.04	0.01	0.03	0.02
$Al_2O_3$	18.28	18,18	18,11	18.09	18.06	17.59	18.61	18.64	18.32	21.40	20.39	20,18	21.39	20.88	18.64	18,06
FeO <sup>2</sup>	14.32	13.70	14.47	13.57	14.74	14.07	13.10	15.18	13,85	16.44	17.02	16.72	11.22	12.06	15,18	14.74
MnO	0.20	0.24	0.15	0.17	0.21	0.24	0.17	0.16	0.21	0.05	0.08	0.08	0,11	0.15	0.16	0.21
MgO	24.50	24.40	24.16	24.15	24.18	24.04	22.87	23.76	24.60	18.42	21.48	21.04	23.85	25,24	23,76	24.18
CaO	0.05	0.05	0.07	0.07	0.04	0.06	0,09	0.08	0.06	0.08	0.07	0.06	0.03	0.04	0.08	0.04
Na <sub>2</sub> O	0.03	0.09	0.04	0.06	0.07	0.05	0.10	0.09	0,03	0.01	0.01	0.03	0.02	0.04	0,09	0.07
K <sub>2</sub> O	0.09	0.07	0.15	0,35	0.19	0,10	0.26	0.07	0.09	1.32	0.04	0.03	0.66	0.14	0.07	0,19
F	0.28	0.27	0.35	0.37	0.31	0.27	0.35	0.30	0.19	0.16	0.36	0.20	0.39	0.17	0.30	0,31
Cl	0.02	0.06	0.02	0.05	0.01	0.03	0.04	• 0.06	0.02	0.01	0.00	0.01	0.01	0.01	0.06	0.01
Total	87.91	87,01	87.94	87.34	87.71	85.65	86.72	88,28	87.42	88.69	87.40	86.06	87.35	87,42	88,28	87.71
No. of atoms																
based on 11 O																
				_												
Si	2.96	2.97	2.99	3.00	2.96	2.95	3.07	2.94	2.97	3.10	2.80	2.82	2.88	2.81	2.94	2.96
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0,00	0.00	0.01	0,00	0.00	0.00	0.00
Al	2.13	2,14	2.11	2.12	2.12	2.11	2,18	2.18	2.15	2.50	2,43	2.44	2.47	2.43	2.18	2,12
Fe	1.18	1,14	1.19	1.12	1.22	1,19	1.08	1.25	1,14	1.35	1,43	1,43	0.91	0.99	1.25	1.22
Mn	0,02	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.00	0,01	0.01	0.01	0.01	0.01	0.02
Mg	3.59	3,61	3.54	3.55	3.57	3,63	3.36	3.48	3,62	2.70	3.20	3.20	3.46	3.68	3.48	3.55
Ca	0.01	0,00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00
Na	0.01	0.02	0.01	0.01	0.01	0.01	0,02	0.02	0.01	0.00	0.00	0.01	0.00	0.01	0.02	0.01
K	0.01	0.01	0.02	0,04	0.02	0.01	0,03	0.01	0.01	0.17	0.01	0.00	0.08	0.02	0.01	0.02
F	0.09	0.08	0.11	0,12	0.10	0.09	0,11	0.09	0.06	0.05	0.11	0.06	0.12	0.05	0.09	0,10
Cl	0.00	0.01	0.00	0.01	0.00	0.01	0,01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0,00
Total	10.00	10.00	9.99	9.99	10.02	10.03	9.88	10.00	9,99	9.88	10.00	9.99	9.93	10.00	10.00	10.00
F/(F+Cl)	1.00	0.89	1.00	0.92	1.00	0.90	0.92	0.90	1.00	0.00				<b>.</b> • <i>(</i>	0.90	
re/(fe+Mg)	0.25	0.24	_0.25	0.24	0.25	0.25	0.24	0.26	0.24	0,33	0.31	0.31	0.21	0.21	0.26	0.26

TABLE 2. Representative Electron Microprobe Analyses of Chlorite In the Sungun Porphyry Copper Deposit

K = potassic zone, Phc = phyllic alteration zone, Pro = propylitic zone FeO = total Fe

#### **PHYLLIC ALTERATION**

Phyllic alteration is characterized by replacement of almost all primary silicates by muscovite (sericite) and quartz, and overprints the earlier-formed potassic assemblage. Sericite is generally the most abundant alteration mineral in the Sungun deposit, and occurs mainly in the phyllic and potassic alteration zones. Thirty microprobe analyses were performed on sericite (Table 3). Sericite commonly forms as irregular, oriented grains containing relicts of biotite and amphibole, and inclusions of zircon. Some of these crystals are phengite (Table 3). The concentration of fluorine in sericite ranges from 0.22 to 0.05 atom per molecule formula (apmf), whereas chlorine contents are lower, (0.01. apfu). Silicification was synchronous with phyllic alteration and variably affected much of the stock and most dykes.

#### **ARGILLIC ALTERATION**

Feldspar is locally altered to clay minerals to a depth of 400 m, and within 80 m of the present-day surface, all rocks have been altered to an assemblage of clays, hematite and quartz. XRD analyses indicate that kaolinite is the dominant phyllosilicate, and that it is generally accompanied by illite. This shallow alteration is interpreted to represent a supergene blanket over the deposit, and the deeper clay alteration of feldspar may have had the same origin. However, the possibility can not be excluded that parts of the latter may locally represent an advanced argillic stage of hypogene alteration. Mass transfer

	Pr	nengite	Muscovite									
Sample No.	33-236	33-237	33-237	25-325	34-477	34-477	34-477	34-477	34-477	25-198		
Dril-core No.	33	33	33	25	34	34	34	34	34	25		
Туре '	Phc	Phc	Phc	K	Phc	Phc	Phc	Phc	Phc	Phc		
			_							<u> </u>		
SiO <sub>2</sub> (wt %)	42.70	43.29	47.24	50.96	47.34	46.95	46.19	51.31	50.54	44.58		
TiO <sub>2</sub>	0.98	0.74	0.69	0.10	0.22	0.33	0.15	0.11	0.12	0.21		
Al <sub>2</sub> O <sub>3</sub>	21.35	23.59	29.51	28.45	28.30	31.36	33.75	28.13	27.34	27.17		
FeO <sup>2</sup>	8.80	7.80	3.43	0.92	2.76	1.72	0.81	1.14	1.22	5.61		
MnO	0.02	0.03	0.00	0.01	0.03	0.01	0.00	0.00	0.01	0.03		
MgO	11.65	10.45	3.52	2.74	3.92	2.87	1.02	3.55	3.77	7.84		
CaO	0.00	0.03	0.02	0.18	0.02	0.01	0.01	0.13	0.11	0.05		
Na <sub>2</sub> O	0.12	0.07	0.16	0.09	0.31	0.38	0.37	0.16	0.13	0.07		
K <sub>2</sub> O	10.18	10.10	9.55	8.84	11.40	11.17	11.03	9.52	9.52	7.75		
F	0.98	1.01	0.22	0.73	0.40	0.40	0.22	0.83	0.90	0.35		
Cl	0.08	0.05	0.03	0.13	0.05	0.08	0.05	0.12	0.10	0.01		
Total	96.85	97.16	94.36	93.15	94.74	95.28	93.59	94.99	93.76	93.64		
No. of atoms												
based on 11 O												
			•									
Si	2.95	2.95	3.19	3.38	3.21	3.14	3.12	3.36	3.36	3.06		
Ti	0.05	0.04	0.04	0.00	0.01	0.02	0.01	0.01	0.01	0.01		
Al	1.75	1.91	2.37	2.25	2.28	2.49	2.72	2.19	2.16	2.22		
Fe	0.51	0.44	0.19	0.05	0.16	0.10	0.05	0.06	0.07	0.32		
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Mg	1.20	1.06	0.35	0.27	0.40	0.29	0.10	0.35	0.37	0.80		
Ca	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.00		
Na	0.02	0.01	0.02	0.01	0.04	0.05	0.05	0.02	0.02	0.01		
К	0.90	0.88	0.82	0.75	0.99	0.95	0.95	0.80	0.81	0.70		
F	0.21	0.22	0.05	0.15	0.09	0.09	0.05	0.17	0.19	0.08		
Cl	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00		
F/(F+Cl)	0.95	0.96	1.00	0.94	0.90	0.90	0.83	0.94	0.95	1.00		
Fe/(Fe+Mg)	0.30	0.29	0.35	0.16	0.29	0.26	0.33	0.15	0.16	0.29		

TABLE 3. Representative Electron Microprobe Analyses of Muscovite in the Sungun Porphyry Copper Deposit

<sup>1</sup> Phc = phyllic alteration zone, K = potassic alteration zone,<sup>2</sup> FeO = total Fe

calculations were not done for this type of alteration due to its uncertain origin and the lack of reliable analyses.

### NORMATIVE MINERALOGY

The normative composition of representative samples from each alteration zone has been calculated using whole rock chemistry and compositions of the constituent minerals (see Appendices I and III). An inexact matrix was used to calculate mineral abundance by the linear least squares regression method (Spear et al., 1982; Böhlke, 1989).

$$\mathbf{A} \cdot \mathbf{X} = \mathbf{B} \tag{1}$$

In this equation, the matrix A represents the stoichiometric coefficients of the elements in each mineral, B is the matrix of the molar abundance of the elements obtained from the whole rock analysis, and X is a vector containing the molar abundance of each mineral, i.e., the unknown parameter. The solution for X represents a least squared fit of mineral abundance to whole rock composition. Weight percent abundance of minerals and rock density were calculated by using mineral molecular weights and densities (Fig. 4; Table 4). Potassic alteration is characterised by 23 % K-feldspar, 22 % quartz, 19 % muscovite, 16 % biotite, 13 % albite, 2 % anhydrite, <0.1 % chlorite, 1.9 % epidote, 1.5 % pyrite, 0.8 % chalcopyrite, and 0.2 % magnetite. The transition zone is characterized by 19 % K-feldspar, 23 % quartz, 19 % muscovite, 15 % biotite, 10 % albite, 4 % anhydrite, 4 % chlorite, <0.1 % chalcopyrite, 10 % albite, 4 % anhydrite, 4 % chlorite, <0.1 % chalcopyrite, 1 % kaolinite, and <0.1 %

Table 4	Calculated	Normative	Mineral	Ahundancee
Tame 4,	Calculated	normanye	winiciai	Abunuances

Sample #	Alteration	Density	Quartz	K-feldspar	Biotite	Muscovite	Albite	Chlorite	Epidote	Pyrite	<u>Chalcopyrite</u>	Kaolinite	Anhydrite	Magnetite	Total
30-168	Potassic	2.74	21,82	26.53	19.33	12.00	13.98	0.00	3.10	2.10	1.14	0.00	0.00	0.00	100,00
21-32	Potassic	2.77	23.12	23,85	15.21	20.10	10.96	0.00	2.41	1.81	0.12	0.00	2.12	0.30	100.00
26-277	Potassic	2.74	21.33	24.20	13.17	22.45	12.34	0.30	1.81	0.54	0.65	0.00	3.11	0.10	100.00
44-345	Potassic	2.75	21.75	14.98	18.09	21.00	16.81	0.00	2.10	1.98	0.19	0.00	3.10	0.00	100.00
44-371	Potassic	2.81	22.08	26.30	12.76	20.97	11.96	0.00	0.00	1.10	1.70	0.00	2.73	0.40	100.00
Average o	of Potassic Alteration	2.76	22.02	23.17	15.71	19.30	13.21	0.06	1.88	1.51	0.76	0.00	2.21	0.16	100.00
30-200	Transition	2.73	24.32	17.11	17.21	21.81	10.78	2.32	0.07	2.90	1.18	0.20	2.10	0.00	100.00
25-522	Transition	2.72	22.76	23.65	14.32	11.45	8.83	7.65	0.27	1.85	1.70	2.10	5.32	0.10	100.00
25-122	Transition	2.76	22.31	15.30	13.00	24.74	11.70	4.32	0.00	1.60	0.90	1.90	4.23	0.00	100.00
Average (	of Transition Alteration	2.74	23.13	18.69	14.84	19.33	10.44	4.76	0.11	2.12	1.26	1.40	3.88	0.03	100.00
7-150.6	Phyllic	2.67	34.71	4.32	13.10	20.56	6.78	5.30	0.00	1.89	1.90	10.21	1.23	0.00	100.00
25-275	Phyllic	2.54	28.67	1.60	4.65	23.11	12.20	4.56	0.00	2.10	0.90	20.71	1.50	0.00	100.00
33-281	Phyllic	2.69	29.23	8.10	10.72	20.10	10.21	1.67	0.00	1.90	1.01	14.08	2.98	0.00	100.00
26-237	Phyllic	2.71	28.54	8.21	15.20	27.41	4.37	0.00	0.00	4.11	0.64	7,52	4.00	0.00	100.00
25-371	Phyllic	2.61	27.95	3.76	10.11	24.30	3.83	6.10	4.21	3.39	0.19	14.65	1.51	0.00	100.00
Average a	of Phyllic Alteration	2.64	29.82	5.20	10.76	23.10	7.48	3.53	0.84	2.68	0.93	13.43	2.24	0.00	100.00

**Figure 4.** Variations in normative mineralogy in alteration zones in the Sungun porphyry copper deposit. Kaolinite occurs in the phyllic alteration zone, and to a lesser extent in the propylitic zone. This may reflect supergene alteration, which is widespread in the deposit. In the propylitic alteration zone, albite, oligoclase and orthoclase react to form muscovite and quartz. Muscovite is present in all alteration zones. Sulphide abundance is significant in the potassic, transition and phyllic alteration zones. The density profile was obtained by summing the multiples of weight proportion and the density of the different minerals in each alteration zone. The calculated average densities of all altered rocks are lower than that of the least-altered rock, and are particularly low in the strongly altered phyllic zone.



magnetite. Phyllic alteration contains 5 % K- feldspar, 30 % quartz, 23 % muscovite, 11 % biotite, 8 % albite, 2% anhydrite, 4 % chlorite, 1 % epidote, 3 % pyrite, 1 % chalcopyrite, 13% kaolinite (Fig. 4; Table 4).

# MASS CHANGES DURING ALTERATION

#### MASS BALANCE CALCULATIONS

Several methods have been used to calculate mass losses or gains in ore deposits: the volume factor method of Gresens (1967); the isocon method of Grant (1986); and the immobile element method of MacLean and Kranidiotis (1987). In this study, mass gains and losses during alteration were calculated using the method of Grant (1986). In order to avoid errors due to variations inherent in the density of the least altered rock, a sample from the deepest part of the diorite/granodiorite intrusion was selected and tested by comparing it with the other "fresh" rocks from the deposit. This sample, a diorite/granodiorite # 30-138, is very similar compositionally to the other "fresh" rock and was used to represent the least altered rock (see below). Petrographic examination indicates that even in this sample there was limited alteration of feldspars, hornblende and biotite to muscovite, quartz and oxides. However, this will not greatly affect interpretations of the alteration reactions, which are based on comparisons between different alteration zones.

The isocon approach of Grant (1986) is mathematically similar to that of Gresens (1967), but differs in the graphical representation of the data. In Gresens' method, the components that are likely to have been immobile during alteration can be used to identify

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any volume change, which may have taken place. If it is assumed that volume change is a factor common to the behaviour of all components, it is possible to calculate gains or losses of the other components. Mass gains and losses are calculated using the following relationship:

$$X_{n} = [F_{v} (S^{b} / S^{a})C_{n}^{b} - C_{n}^{a}] * 100$$
(2)

where  $X_n$  is the mass gain or loss for component n,  $F_v$  is the volume factor,  $S^b$  is the specific gravity of the altered sample,  $S^a$  is the specific gravity of the unaltered (original) sample,  $C_n^{\ b}$  is the concentration of component n in the altered sample, and  $C_n^{\ a}$  is the concentration of component n in the unaltered (original) sample. In the isocon method of Grant (1986), equation 2 is reformulated as:

$$DX_{n} = 100 (M^{b} / M^{a}) X_{n}^{b} - X_{n}^{a}$$
(3)

where  $\mathbf{M}^{\mathbf{b}} / \mathbf{M}^{\mathbf{a}}$  is the mass ratio between the altered sample and the unaltered sample. This ratio is calculated by plotting the concentration of components in the altered rock (e.g., X axis) versus those in the unaltered sample (e.g., Y axis). The components that are immobile will fall on a line of slope  $\mathbf{M}^{\mathbf{b}} / \mathbf{M}^{\mathbf{a}}$ , referred to as the isocon. Components that lie above the isocon have been added while those which are below the line have been lost during the alteration. The slope of the isocon (mass factor) can be determined graphically, and is used to calculate the mass gains and losses of the remaining components by applying equation 3.

# MASS FACTORS

Estimation of the mass factor (i.e., identification of the isocon) may be complicated by the fact that, in addition to mass changes during alteration, the diorite/granodiorite rock suite may also have undergone compositional change due to fractional crystallization. Fortunately, as shown in Chapter II by the behaviour of compatible immobile trace elements, e.g., Y, fractional crystallization in the diorite/granodiorite intrusion was comparatively limited, <10 %. Consequently, it is reasonable to assume that mass changes due to magmatic processes were unimportant.

The least altered diorite/granodiorite samples are typically found in the deepest part of the deposit. Four of these rocks were selected and compared in terms of element concentrations. Pair-wise comparisons of these samples yield isocons having mass factors of approximately one; most elements plot close to or on these isocons, which indicates that potential precursor samples have very similar compositions (Fig. 5; Table 5). Based on these results, sample 30-138 was selected to represent the precursor (least altered) rock for comparison with alteration zone rocks.

# MASS CHANGES

# Potassic alteration

type	Granodiorite		Fresh Rock							
no.	1	2	3	4		Mulecular	Proportions			
sample	30-138	30-149	34-282	58-71	1	2	3	4	Range	Average
					30-138	30-149	34-282	58-71		
		g/100 g								
SiO <sub>2</sub>	60.54	60,53	61,68	56.04	69,73	69,57	70,34	65.03	5,30	68,31
TiO <sub>2</sub>	0.58	0,57	0.57	0.73	0,50	0.49	0.49	0.64	0.14	0,54
Al <sub>2</sub> O <sub>3</sub>	15.96	15.88	16.02	16.41	10.83	10.76	10.77	11.22	0.47	10,92
Fe <sub>2</sub> O <sub>3</sub>	4.91	4.94	4,94	6.34	2.13	2.14	2.12	2.77	0,65	2,34
MnO	0.10	0.1	0.09	0.12	0,10	0.10	0.09	0.12	0.03	0,10
MgO	2.61	2.56	2,52	3.73	4.48	4,39	4,28	6.45	2.17	5.04
CaO	4.66	4.98	4.64	6,39	5.75	6.13	5.67	7.94	2.28	6,58
Na₂O	3,96	4.04	3,85	3.55	4.42	4,50	4.26	3.99	0.51	4.25
K₂O	2.63	2,48	2,58	2.32	1.93	1.82	1.88	1.72	0.16	1.80
P <sub>2</sub> O <sub>5</sub>	0.24	0.24	0.24	0.23	0.12	0,12	0.12	0.11	0.00	0,12
		a/1000 ka								
BaO	833,0	835	944.0	684.0	833,0	787.0	944.0	684.0	260,0	-28.0
Сө	53.0	80	58.0	61.0	· 53.0	59.0	58.0	61,0	3.0	6,3
Со	12.0	21	19.0	24.0	12.0	15.0	19.0	24.0	9.0	7.3
Cr <sub>2</sub> O <sub>3</sub>	56.0	49	64.0	57.0	56.0	47.0	64.0	57.0	17.0	0,0
Cu	64.0	98	224.0	81.0	64.0	201.0	224.0	81.0	143,0	104.7
Ni	27.0	22	25.0	42.0	27.0	29,0	25.0	42.0	17.0	5,0
Pb	7.0	18	7.0	9.0	19.0	6.0	7.0	9.0	3,0	0.3
Sc	19.0	85	16.0	26,0	95.0	19.0	16.0	26.0	10.0	1.3
V	95.0	53	99.0	141.0	50.0	98.0	99.0	141.0	43.0	17.7
Zn	50.0	17	52.0	58.0	17.0	55.0	52.0	58.0	6.0	5.0
Ga	17.0	10	17.0	18.0	9.0	17.0	17.0	18.0	1.0	0.3
Nb	9.0	16	10.0	5.0	14.0	13.0	10.0	5.0	8.0	0.3
Rb	64.0	58	56.0	50.0	64.0	56.0	56.0	50.0	6.0	-10.0
Sr	664.0	699	715.0	1334.0	664.0	210.0	715.0	1334.0	1124.0	89.0
Th	90	9	10.0	10.0	9.0	7.0	10.0	10.0	3.0	0.0
U.	0.0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ŷ	18.0	18	17.0	20.0	18.0	19.0	17.0	20.0	3.0	0.7
71	99.0	104	105.0	96.0	99.0	115.0	105.0	96.0	19.0	6.3

TABLE 5. Variations in Major and Trace Element Mass Changes in the Fresh Rocks

Mass transfers are calculated, adjusting for total mass change, using the method explained in the text. I otal He as  $He_2U_3$ .

M.D<sup>(1)</sup> = measures of dispersion

 $\delta^{(2)}$  = standard deviation

Figure 5. Isocon diagram comparing two "least altered" rocks. Almost all major oxides fall on or near a line with a slope or mass factor (M.F.) of one.



Comparison of sample 25-453 (representative of the potassic alteration zone) with least altered sample 30-138, shows that the immobile elements, Ti, Al and Ga plot close to or on a line of constant mass with a slope of 1.0 (Fig. 6). However, the elements Zr and Nb which are generally considered to be geochemically immobile, plot off the line, possibly due to a nugget effect.

As expected from the mineral assemblage in the potassic alteration zone, K and Ba are enriched in sample 25-453 and copper, predictably, is strongly enriched. By contrast Na is depleted, as are Fe, Ca and Mn. Mass changes associated with potassic alteration are presented graphically in Fig. 9 and numerically in Table 6. Most calculated volume factors (V.F) lie between 0.99 and 1.04, (Table 7, Fig. 6) indicating that there was essentially no volume change.

#### Transition alteration

The transition alteration zone is transitional between the potassic alteration zone and the phyllic alteration zone, but is clearly superimposed on the potassic alteration zone. In order to determine mass changes associated with this alteration, the reference for comparison was therefore a potassically altered rock (25-453). Comparison of a representative sample of rock that has undergone transition alteration (25-122) with potassically altered rock (25-453) shows that TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Zr and Ga plot close to or on a line of constant mass with a slope of approximate 1.0 (Table 6, Fig 7). Most calculated volume factors also lie between 0.99 and 1.02, indicating that there was essentially no

**Figure 6.** An isocon diagram comparing a representative sample of the potassic alteration zone (25-453), with a representative sample of least altered rock (30-168). The dashed line (isocon) is drawn for the largest number of potentially immobile elements (solid squares). The best constraints on mass changes during potassic alteration are given by  $TiO_2$ ,  $Al_2O_3$  and Ga. Only those elements on the isocon, and those present in appreciable concentrations have been labelled. The inset histogram shows the distribution of mass factors calculated for each element.



type	Po	tassic Altera	tion	_									
no.	<u> </u>	2	3	Mule	cular Propo	rtions	Mass Changes	in the Potassic	Alteration Zon	θ			
sample	25-453	29-195	7-150,6	1	2	3	1	2	3	Range	Average	<u>M.D'''</u>	δ <sup>(1)</sup>
				25-453	29-195	7-150.6	25-453	29-195	7-150.6				_
		g/100 g											
SiO <sub>2</sub>	61.51	64.47	58.88	71.84	72.66	73.00	2,19	3.22	2.77	1.03	2,73	0,36	0,24
TiO <sub>2</sub>	0.48	0.49	0.49	0.42	0.42	0.61	-0.08	-0,08	0,13	0.21	-0.01	0.09	0,06
Al <sub>2</sub> O <sub>3</sub>	15,86	16.00	15.98	10.58	10.63	11.10	-0.26	-0,13	0.35	0.61	-0.02	0,24	0,15
Fe₂O₃	4.02	3.36	4.51	1.77	1.43	2.10	-0,38	-0,74	-0.02	0.72	-0.38	0.24	0.17
MnO	0.04	0.05	0.02	0.04	0.05	0.02	-0.06	-0,05	-0.07	0.02	-0,06	0.01	0.00
MgO	2.36	1.87	1.35	4.11	3.14	2,50	-0,39	-1.29	-1.86	1.47	-1.18	0,53	0.35
CaO	2.72	3,12	2.65	3,40	3.77	3,52	-2.44	-2.46	-2.23	0.22	-2,38	0.10	0,06
Na₂O	3.87	4.49	2.46	4.38	4.91	2,96	-0.04	0.42	-1.35	1.77	-0.32	0.68	0.43
K₂O	4.03	4.02	4.60	3,00	2.89	3.64	1.11	1.11	1.83	0.72	1.35	0.32	0.20
P205	0.25	0.25	0.25	0.12	0.12	0.13	. 0.01	0.00	0.02	0.01	0,01	0.00	0.00
		a/1000 ka											
BaO	1497 0	1219.0	1288.0	1497.0	1219.0	1288.0	690.6	401.4	473.2	289.1	521.7	112.6	71.0
Ce	123.0	111.0	79.0	123.0	111.0	79.0	72.8	60.3	27.0	45.8	53.4	17.6	11.2
Co	9.0	1.0	3.0	9.0	1.0	3.0	-3.1	-11.4	-9.4	8.3	-8.0	3.2	2.0
Cr <sub>2</sub> O <sub>3</sub>	132.0	83.0	63.0	132.0	83.0	63,0	79.0	28.1	7.3	71.8	38,1	27,3	17.4
Cu	619.0	140.0	1826.0	619.0	140.0	1826.0	577.2	79.0	1832,5	1753.4	829,6	668.6	425,9
Ni	91.0	36,0	33.0	91.0	36.0	33.0	66.6	9.4	6.2	60,3	27.4	26,1	16.0
Pb	30.0	13.0	21.0	30,0	13.0	21.0	23.9	6.2	14.6	17.7	14.9	6.0	4.2
Sc	15.0	9.0	10.0	15.0	9.0	10.0	-4.2	-10.4	-9.4	6.2	-8.0	2.5	1.6
V	71.0	65,0	61.0	71.0	65,0	61.0	-25,0	-31.2	-35,4	10.4	-30.5	3.7	2.5
Zn	60.0	25.0	29.0	60,0	25.0	29.0	10.4	-26.0	-21.8	36,4	-12.5	15.3	9.4
Ga	18.0	17.0	19.0	18,0	17.0	19.0	1.0	0.0	2.1	2.1	1.0	0.7	0,5
Nb	15.0	15.0	17.0	15.0	15.0	17.0	6.2	6.2	8.3	2.1	6,9	0,9	0.6
Rb	74.0	76.0	102.0	74.0	76.0	102.0	10.4	12.5	39.5	29.1	20.8	12.5	7.7
Sr	867.0	900,0	365,0	867.0	900,0	365.0	211.1	245.4	-311.0	556,4	48.5	239.7	147.0
Th	27.0	23,0	26,0	27.0	23,0	26.0	18.7	14.6	17.7	4.2	17.0	1,6	1.0
U	5.0	2.0	10.0	5.0	2.0	10,0	5.2	2.1	10.4	8,3	5.9	3.0	2.0
Y	12.0	11.0	13.0	12.0	11.0	13.0	-6,2	-7.3	-5,2	2.1	-6.2	0,7	0,5
Zr	109.0	112.0	112.0	109.0	112.0	112.0	10.4	13.5	13.5	3.1	12.5	1.4	0.8

TABLE 6. Major and Trace Element Mass Changes at the Sungun Deposit (the Previously Altered Rock is the Original Rock for the Next Alteration Stage Except for Phyllic Alteration which is Superimposed on Potassic Alteration)

Mass transfers are calculated, adjusting for total mass change, using the method explained in the text. Total He as He<sub>2</sub>O<sub>3</sub>. M.D<sup>W</sup> = measures of dispersion

 $\delta^{(2)}$  = standard deviation

						TABLE 6	i. (cont'd)						
type	<u></u>	ansition Alterat	ion 3	- Mule	cular Propor	tions	Mass Changes I	n the Transitio	n Alteration Zo	ne			
sample	25-122	25-522	30-200		2	3	1	2	3	Range	Average	M.D**	δ <sup>(4)</sup>
eattiple				25-122	25-522	30-200	25-122	25-522	30-200				
		g/100 g											
SiO2	61.66	61.98	61.66	71.72	71.93	72.64	-0.12	-0.76	-0.38	0,63	-0.42	0.22	0.15
TiO <sub>2</sub>	0.51	0.49	0.47	0.58	0.43	0.42	0.16	0.01	-0.20	0,37	-0.01	0,13	0.09
Al <sub>2</sub> O <sub>3</sub>	15.92	15.88	15.98	10,33	10.86	11.09	-0.26	0.24	-0.01	0.50	-0.01	0.17	0.12
Fe <sub>2</sub> O <sub>3</sub>	3.88	3.44	3.91	1.70	1.50	1.73	-0.07	0.08	-0.39	0.47	•0.13	0.17	0.11
MnO	0.14	0.13	0.13	0,14	0.13	0,13	0.10	0,08	0.11	0.03	0,10	0.01	0.01
MgO	2.04	1.76	1.85	3.54	3.04	3,25	-0.59	-0.10	0.78	1.38	0.03	0,50	0.33
CaO	4.14	4.19	3.25	5,16	5.21	4.10	1.83	1.50	0.61	1.22	1.31	0.47	0.30
Na <sub>2</sub> O	3,54	3.48	3.11	3,99	3.92	3,55	-0,41	-1.03	0.62	1.65	-0.27	0.59	0.39
K₂O	3.07	3.85	3.96	2.28	2.85	2,98	-0.75	-0.04	-0,69	0.71	-0.49	0.30	0.19
P₂O₅	0.25	0.26	0.22	0.12	0.13	0.11	0.00	0.01	-0,02	0.03	0,00	0,01	0.01
		g/1000 kg											
BaO	981.0	1203.0	863.0	981.0	1203,0	863.0	-536.6	-16.6	-442.0	520.0	-331.8	210.1	130.6
Сө	81.0	93.0	75.0	81.0	93.0	75.0	-43.7	-18.7	-4.2	39.5	-22.2	14.3	9.4
Co	10.0	12.0	10.0	10.0	12.0	10.0	1.0	11.4	7,3	10.4	6.6	3.7	2.5
Cr <sub>2</sub> O <sub>3</sub>	40.0	46.0	83,0	40.0	46.0	83.0	•95,7	-38.5	20.8	116,5	-37.8	39.1	27.5
Cu	36.0	43.0	87,0	36.0	43.0	87.0	-29.1	-21.8	23.9	-45.8	-9,0	22.0	13.6
NI	44.0	25,0	43.0	44.0	25.0	43.0	-48.9	-11.4	10,4	59,3	-16,6	21.5	14.1
Pb	36.0	7.0	58.0	36.0	7.0	58.0	6.2	-6.2	38.5	44.7	12.8	17.1	10,9
Sc	13.0	15.0	13.0	13.0	15.0	13.0	-2.1	6.2	3.1	8.3	2.4	3,0	2,0
v	74.0	70.0	66,0	74.0	70,0	66.0	3.1	5.2	5.2	2.1	4.5	0.9	0,6
Zn	115.0	61.0	62.0	115.0	61.0	62.0	57,2	37.4	34.3	22.9	43.0	9.5	5.8
Ga	17.0	17.0	18,0	17.0	17.0	18.0	-1.0	0.0	-1.0	1.0	-0.7	0,5	0.3
Nb	15.0	14.0	16.0	15.0	14.0	16.0	0.0	-1.0	-1.0	1.0	-0.7	0.5	0,3
Rb	77.0	98.0	112.0	77.0	98.0	112.0	3,1	22.9	10.4	19.8	12.1	7.2	4.7
Sr	352,0	732.0	430.0	352.0	732.0	430.0	-535.6	-174.7	67.6	603.2	-214.2	214.2	143.1
Th	13.0	17.0	18.0	13.0	17.0	18.0	-14.6	•6.2	-8,3	8,3	-9.7	3.2	2.0
U	2,0	5,0	5.0	2.0	5.0	5,0	-3.1	3.1	-5.2	6.2	-1.7	3,2	2.0
Y	14.0	13.0	13.0	14.0	13.0	13.0	2.1	2.1	0.0	2.1	1.4	0,9	0,6
Zr	114.0	117.0	110.0	114.0	117.0	110.0	5,2	5.2	-2.1	7,3	2.8	3,2	2.0

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						TABLE 6	(cont'd)						
type no.	Phy 1	ulic Alteration 2	Zone 3	- Mule	cular Propo	rtions	Mass Changes	in the Phyllic	Alteration Zone				
sample	25-371	25-275	25-239	1	2	3	1	2	3	Range	Average	M.D'''	δ(4)
· · · · · · · · · · · · · · · · · · ·				25-371	25-275	25-239	25-371	25-275	25-239	<u>E</u>			
SiO <sub>2</sub>	68,01	g/100 g 69,09	71.09	74.23	81.87	79.73	2.49	9.57	7,00	7.08	6.03	2.68	1.70
TiO <sub>2</sub>	0.51	0,58	0.64	0.42	0.52	0.54	0.00	0.11	-0.07	0.18	0.01	0.06	0.04
Al <sub>2</sub> O <sub>3</sub>	15.88	15.69	15.98	10.74	10.96	10.56	0.17	0,34	-0.56	0.90	-0.02	0.36	0.23
Fe <sub>2</sub> O <sub>3</sub>	2.68	2.26	2,40	1.10	0.12	1.01	-0.69	-1.36	-1.13	0.23	-1.06	0.25	0.16
MnO	0.05	0.01	0.02	0.05	0.01	0.02	0.01	-0,04	0.00	0.05	-0.01	0.02	0.01
MgO	3.41	1.03	1,59	5.55	1.82	2.66	1.50	-1.38	0.17	2.87	0.10	0.98	0.68
CaO Na₂O	4.23 0.91	1.55 0.23	1.69 0.08	4.95 0.96	0.70 0.26	2.03 0.09	1.60 -3,56	-3.19 -4.83	-1.55 -2.98	4,80 1.84	-1.05 -3.79	1.77 0.69	1.15 0.44
K₂O	3.56	4.78	4.48	2.48	3.61	3.21	-0.54	0.75	-0.45	1.30	-0.08	0.56	0.34
P <sub>2</sub> O <sub>5</sub>	0.12	0.28	0.33	0.06	0.14	0,16	-0.07	0.02	0.03	0.10	-0.01	0.04	0.03
		q/1000 kg											
BaO	657.0	739,0	485.0	657.0	739.0	485.0	-873,6	-499,2	-835,1	374.4	-736.0	157,8	97.1
Сө	74.0	68.0	81.0	74.0	68.0	81,0	-51.0	-44.7	2.1	53,0	-31,2	22.2	13,7
Co Cr <sub>2</sub> O <sub>3</sub>	12.0 279.0	0.0 40.0	20.0 111.0	12.0 279.0	0.0 40.0	20.0 111.0	3.1 152.9	-1.0 -44.7	17.7 49.9	18.7 197.6	6.6 52.7	7.4 66.8	4.6 46.6
Cu	715.0	872.0	691.0	715.0	761.3	-1180,4	677.0	840.3	652.1	163.3	723.1	78,1	48.2
Ni	93.0	14.0	67.0	93.0	14.0	67.0	2.1	-22.9	35.4	58.2	4,9	20.3	13,8
Pb	12.0	14.0	13.0	12.0	14.0	12.5	-18.7	1.0	-8.8	19.8	-8.8	6.6	4.7
Sc	18.0	11.0	11.0	18.0	11.0	11.0	3.1	2.1	1.0	2.1	2.1	0.7	0.5
V	95.0	62.0	106.0	95.0	62.0	106.0	25.0	-3.1	46.8	49.9	22.9	17.3	11.8
Zn	39.0	6,0	17.0	39.0	6,0	16.5	-21.8	-19,8	-13.0	8.8	-18.2	3.5	2.2
Ga	21.0	17.0	17.0	21.0	17.0	17.0	3.1	0,0	-2.1	5.2	0.3	1,8	1.2
Nb	22.0	13.0	21.0	22.0	13.0	20.7	7.3	-2.1	3.8	9.4	3,0	3.4	2.2
Rb	61.0	90.0	103.0	61.0	90,0	103,3	-13.5	14.6	1.4	28.1	0,8	9.5	6.6
Sr	271.0	69.0	66.0	271.0	69.0	66.3	-619.8	-864.2	-310.6	553.6	-598,2	191.7	130.8
Th	13.0	20.0	8.0	13.0	20.0	8.3	-14.6	-3.1	-18.4	15.3	-12.0	5.9	3.7
U	4,0	0.0	1.0	4.0	0.0	1.0	-1.0	-2.1	-9.4	8.3	-4.2	3.5	2.1
Y Zr	14.0 151.0	4.0	12.0	14.0 151.0	4,0	12.1	2.1	•7,3 21 8	-0.9	9.4 21.8	+2.0 30 3	3.5	2.3
<u>~1</u>	101.0	100.0	137.0	101.0	100.0	130.3		<u> </u>		21.0	30,3	0.9	9,9

Sample #	Alteration	Relatively Immobile Elements	M.F.	V.F	Average M.F.	Average V.F.
30-168	1	Ti, Al, Ga, Si, Zn, P	1.01	1.06		
21-32		Ti, Zn, Al, Ga, Si, Mn, Ca	1,00	0.99		
26-277		Cr, P, Ti, Al, Ga	1.00	1.08		
44-345		Y, Sc, Ti, Al, Ga, Si	1.00	1.02		
44-371	Potassic	Mn, Th, Ti, Al, Ga, Si, Co	1.03	0.99	1.01	1.01
44-409		Fe, Ti, Al, Ga	1.02	0.99		
44-429		Y, Ti, Zn, Al, Ga, Si	1.02	1.00		
29-195		Nb, Ti, Al, Ga, Si, Co, Ca	1.00	1.01		
25-517		Y, Zr, Th, Ti, Al, Ga	1,00	1.01		
25-122	1	Ti, Al, Ga, V, Rb, Nb, Zr, P	1,02	0.99		
25-522	Transition	Ti, Rb, Ga, P	1.02	0.99	1.01	0.99
30-200		Y, Ti, Źn, Ál, Ga, Si, P	1.00	1.01		
7-150,6	1	Ti, Th, Zr, Si, Al, Ga	1.00	0.99		
25-275		Mn, Mg, Al, Ga, P	1.00	1.01		
33-281		Ti, Th, Si, Al, Ga, Ca	1.04	1.01		
26-237	Phyllic	V, Fe, P, Th, Zr, Si, Al, Ga	1.04	1.08		
25-371	•	Al, Ni, Ti, Y	1.02	0.99	1.02	1.01
25-239		Ti, Y, Th, Zr, Si, Al, Ga. Pb	1.01	0.99	•••	•••= •

Table 7. Element Immobility,	Mass Factor (MF)	) and Volume Factor	(VF) Calculations Based on
the Isocon Method (Gra	ant, 1986). Samp	le 30-138 Has Been	Chosen as Precursor.

**Figure 7.** Isocon diagram comparing the composition of a representative sample of a altered rock from the transition zone with that of a representative potassically altered rock. See text and caption of Figure 6 for details.



volume change. The mass changes of major and trace elements are plotted in Figure 9 (also see Table 6).

Relative to potassically altered rocks, Cu, Na, Mg, Ba, and Fe were depleted and Ca and Mn were added in the transition zone. Absolute mass gains and losses are evaluated quantitatively in Figure 9 and Tables 7.

#### Phyllic alteration

The phyllic alteration zone is characterized by the presence of large proportions of sericite and pyrite and near absence of biotite and K-feldspar. Phyllic alteration has strongly overprinted earlier potassic alteration. Comparison of potassically altered sample 25-453 and representative sample of 25-371 for phyllic alteration shows that the immobile elements Al and Ti plot close to or on a line (Fig. 8) of constant mass with a slope of 1.0. However, Zr and Nb, which are typically immobile, plot off the line, due possibly, as discussed earlier, to a nugget effect. Most calculated volume factors lie between 0.99 and 1.04, indicating that there was only minor volume change. The most important mass changes in the phyllic alteration zone relative to potassically altered rock are strong depletion of Na and Ba, moderate depletion of K, Fe and Rb, and addition of Ca, Mg, Mn, and SiO<sub>2</sub> and Cu (Figure 9 and Table 6).

# DISCUSSION

**Figure 8.** Isocon diagram comparing the composition of a representative sample of a representative phyllically altered rock with that of a potassically altered rock. See text and caption of Figure 6 for details.



Based on studies of fluid evolution in the Sungun deposit (Chapter III), potassic alteration (biotite and K-feldspar) and associated  $Cu \pm Mo$  mineralization were caused by a high temperature, high salinity fluid of dominantly magmatic origin. Subsequent transition and phyllic alteration in the deeper and shallower parts of the stock, respectively, were produced by the incursion of dilute meteoric fluids and mixing of these fluids with residual orthomagmatic fluids. This addition of external fluids increased Na/K ratios in the progressively heated fluids, and caused the remobilization of previously precipitated copper sulphides through acidification and oxidation, and redeposition in highly fractured zones (Chapter III). At all stages in the evolution of the Sungun hydrothermal system, alteration appears to have taken place with no appreciable change in volume as shown by the fact that the volume factors (V.F.) calculated earlier are close to unity.

In the potassic alteration zone, the principal chemical changes were an enrichment of K and Ba, and depletions of Na, Ca, Mg, Mn and Fe. Mineralogically, these changes were accommodated by crystallization of K-feldspar and biotite at the expense of plagioclase and amphibole (Chapters II and III). The replacement of plagioclase and amphibole by K-feldspar and biotite respectively, served to add K and remove Ca and Na. The changes in K and Na are consistent with fluid inclusion data (Chapter III) which suggest a comparatively high K/Na ratio and low concentrations of cations of other major elements. Barite was not found in the Sungun deposit, and the only minerals that could accommodate Ba are K-feldspar and mica, which formed in potassically altered rocks (Appendix III). Copper was added to potassically altered rocks in significant amounts as might be expected from the dissemination of chalcopyrite and bornite in this zone.

Based on the chemical analyses, bulk densities calculated from the inexact matrix,

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**Figure 9.** Mass change profiles for major element oxides and trace elements during alteration based on a sample of least altered rock as a reference for potassic alteration, and potassically altered rock as a reference for transition zone and phyllically altered rock (mass gain and loss corrected using the isocon method). Units are weight percent for major oxides and ppm for trace elements. Percentage changes are relative to concentrations in the least altered or potassically altered reference samples.

grams added or removed per 100 g of rock



changes in percent





grams added or removed per 100 g of rock











gram added or removed per tonne of rock





changes in percent

gram added or removed per tonne of rock



changes in percent

microprobe analyses of the minerals which characterize the potassic alteration zone, and the mass changes discussed above (Tables 5 and 6), the overall reaction for the conversion of  $1,000 \text{ cm}^3$  of fresh diorite/granodiorite to  $1,000 \text{ cm}^3$  of average potassically altered rock (calculated from the average mass changes in Table 6) is:

Fresh (Hornblende, Plagioclase, K-feldspar) + 2.73 Si<sup>+4</sup> + 1.35 K<sup>+</sup> + 0.45 Cu<sup>+</sup> + 0.01  $P^{+5}$ =Potassically altered rocks (Hydrothermal biotite, K-feldspar, quartz, anhydrite, pyrite, chalcopyrite) + 0.02 Al<sup>+3</sup> + 0.38 Fe<sup>+3</sup> + 0.06 Mn<sup>+2</sup> + 2.38 Ca<sup>+2</sup> + 0.32 Na<sup>+</sup> + 0.01 Ti<sup>+4</sup> + 1.18 Mg<sup>+2</sup> + 3.97 H<sup>+</sup>

In the transition alteration zone, Ca was added, Na, Fe and Mg were relatively unchanged, and K, Ba and Cu were depleted. The losses of K and Ba relative to Na are consistent with the replacement of K-feldspar by albite. However the substantial addition of Ca is surprising and may reflect the presence of anhydrite (or gypsum) which is more typical of potassic alteration (Table 6 and Appendix III). The mass changes discussed above reflect the following reaction (calculated from the average mass changes in Table 6) between hydrothermal fluid and potassically altered rock:

Potassically altered rock (Hydrothermal biotite, K-feldspar, quartz, anhydrite, pyrite, chalcopyrite) + 0.10 Mn<sup>+2</sup> + 1.31 Ca<sup>+2</sup> + 0.04 H<sup>+</sup> + 0.03 Mg<sup>+2</sup> = Transition zone rock (muscovite, quartz, albite, epidote, gypsum, pyrite) + 0.13 Fe<sup>+3</sup> + 0.01 Ti<sup>+4</sup> + 0.49 K<sup>+</sup> + 0.27 Na<sup>+</sup> + 0.42 Si<sup>+4</sup> + 0.01 Al<sup>+3</sup> + 0.02Cu<sup>+</sup> Phyllic alteration like transition alteration, is superimposed on the potassic alteration zone and is characterized by sericitization of feldspars (see Chapter III). Compared to the potassic alteration zone, the phyllic alteration zone is depleted in Na, K, Fe and Ba and enriched in Si and Cu (Fig. 8). The losses of Na, K and Fe reflect the sericitization of alkali feldspar and ferromagnesian minerals (e.g., hydrothermal biotite which had been formed during potassic alteration), respectively. The addition of Si is consistent with the widspread silicification which is a major feature of phyllic alteration. The addition of Cu and its depletion in the transition alteration zone is consistent with mobilization of this element and its concentration in the upper parts of the pluton during phyllic alteration. The mass changes associated with phyllic alteration are shown in Figure 9 and in Table 7.

The overall reaction based on the major oxides for the conversion of  $1,000 \text{ cm}^3$  of potassically altered rock to  $1,000 \text{ cm}^3$  of the phyllically altered rock, calculated from the average mass changes in Table 6, is:

Potassically altered rocks (Hydrothermal biotite, K-feldspar, quartz, anhydrite, pyrite, chalcopyrite) + 6.03 Si<sup>+4</sup> + 0.10 Mg<sup>+2</sup> + 0.01 Ti<sup>+4</sup> + 0.35 Cu<sup>+</sup> = Phyllically altered rocks (quartz, muscovite, epidote, pyrite, kaolinite) + 1.06 Fe<sup>+3</sup> + 0.01 Mn<sup>+2</sup> + 1.05 Ca<sup>+2</sup> + 3.79 Na<sup>+</sup> + 0.02 Al<sup>+3</sup> + 0.01 P<sup>+5</sup> + 15.43 H<sup>+</sup> + 0.08 K<sup>+</sup>

### CONCLUSIONS

1) Isocon plots illustrate that Al, Ti and Ga were relatively immobile during alteration, and that mass was essentially conserved.

2) At all stages in the evolution of the hydrothermal system (potassic, transition and phyllic), alteration appears to have taken place with no appreciable change in volume as shown by the fact that the volume factors (V.F.) calculated earlier are close to unity.

3) In the potassic alteration zone, the changes in major elements were an enrichment of K and depletions of Na, Ca, Mn, Mg and Fe. These changes were due to replacement of plagioclase and amphibole by K-feldspar and biotite, respectively. Potassic alteration was associated with a large addition of Cu as might be expected from the occurrence of disseminated chalcopyrite and bornite in this zone.

4) In the transition alteration zone, Ca was added, Na, Fe and Mg were relatively unchanged, and K, Ba and Cu were depleted. The loss of K and Ba relatively to Na reflects replacement of K-feldspar by albite (which is evident from microscopic observations). Addition of Ca is surprising and may reflect the presence of, anhydrite (or gypsum) which is more typical of potassic alteration.

5) Phyllic alteration was accompanied by the depletion of Na, K, Fe and Ba and enrichment of Si and Cu. The losses of Na, K and Fe reflect the sericitization of alkali feldspar and destruction of ferromagnesian minerals. The addition of Si is consistent with widspread silicification, which is a major feature of phyllic alteration, and the addition of Cu, with mobilization from the transition zone which is depleted in this element.

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# **CHAPTER V**

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#### **INTRODUCTION TO CHAPTER V**

Some parameters essential for the understanding and modeling of the Sungun porphyry copper deposit (e.g., pH,  $fO_2$ ,  $fS_2$ ,  $aK^+$  and  $aNa^+$ ) could not be accurately quantified in the investigation of natural samples in Chapters III and IV. However, the temperature and pressure conditions determined in the previous Chapters, and the data derived for fluid and rock compositions allow estimation of the alteration and mineralization based on thermodynamic data. This modeling is presented in Chapter V, and the results provide additional insights into the chemical processes involved in alteration, and copper dissolution and deposition in the Sungun porphyry copper deposit.

# **CHAPTER V**

## **Condition of Alteration/Mineralization and Controls**

### of Chalcopyrite Dissolution/Deposition in the

# Sungun Porphyry Copper Deposit, Iran

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#### ABSTRACT

The Sungun porphyry copper deposit is hosted in a dioritic to quartz-monzonitic stock that intruded Eocene volcanosedimentary and Cretaceous carbonate rocks. Copper mineralization is associated with both potassic and phyllic alteration. Temperatures of early potassic and late phyllic stages of alteration/mineralization are estimated from fluid inclusion and isotopic data (see Chapter III) to have been 360-450 °C and 300-360 °C, respectively. These data also indicate that the hydrothermal system involved both magmatic and meteoric waters, and boiled extensively.

In this paper, thermodynamic data are used to delineate the stability fields of alteration and ore mineral assemblages as a function of  $fS_2$ ,  $fO_2$  and pH for the two alteration/mineralization stages. These calculations show that at 450 °C, the  $fO_2$  was between -20 and -23, and the pH between 5.5 and 6.5, and that at 360 °C the corresponding values were -31 to -27, and 4 to 8, respectively. The solubility of chalcopyrite was evaluated in this range of conditions using the recent experimental data of Zotov et al. (1995), and Gammons et al., (1996). During potassic alteration (450 °C), copper solubility is calculated to have been >100,000 ppm, whereas the copper content of the initial fluid responsible for ore deposition is estimated from fluid inclusion data to have been 1200-3800 ppm. This indicates that the fluid was initially undersaturated with respect to chalcopyrite, which agrees with the observation that veins formed at T >400 °C and contain molybdenite but rarely chalcopyrite. Copper solubility drops rapidly with decreasing temperature, and at 400 °C is approximately 1000 ppm, i.e., within the range estimated from fluid inclusion data. At temperatures <300 °C, the solubility drops to <1

ppm. These calculations are consistent with observations that the bulk of the chalcopyrite deposited at Sungun is hosted by veins formed at temperatures between approximately 300 and 360 °C. Other factors that may reduce chalcopyrite solubility are increases in pH, and decreases in  $fO_2$  and  $aCI^-$ . We propose that the Sungun deposit formed partly in response to the sharp temperature decrease and pH increase that accompanied boiling, and partly as a result of the additional heat loss, increase in pH and decrease in  $aCI^-$  which occurred as a result of mixing of acidic Cu-bearing magmatic waters with cooler meteoric waters of lower salinity and near-neutral pH.

#### INTRODUCTION

The Sungun porphyry deposit is one of two major copper deposits associated with calc-alkaline intrusive rocks in the Cenozoic Sahand-Bazman volcanic belt of northwestern Iran. Proven reserves are 500 million tons of disseminated sulphide ore grading 0.76 % Cu and ~0.01 % Mo. Recently, Hezarkhani and Williams-Jones (see Chapter III) reconstructed the evolution of the hydrothermal fluid responsible for alteration and mineralization at the Sungun deposit. Early hydrothermal alteration produced a potassic assemblage (orthoclase-biotite) in the central part of the stock, propylitic alteration occurred contemporaneously with potassic alteration, but in the peripheral parts of the stock, and phyllic alteration occurred later, overprinting these earlier alterations. The early hydrothermal fluids are represented by high temperature (340 °C to 500 °C), high salinity (up to 60 wt % NaCl equiv.) liquid-rich fluid inclusions, and high temperature (320 °C to 550 °C), low-salinity, vapour-rich inclusions. These fluids are interpreted to represent an orthomagmatic fluid which boiled episodically; the brines are interpreted to have caused potassic alteration. Influx of meteoric water into the central part of the system and mixing with magmatic fluid produced salinities ranging from 1 to 19 wt % NaCl equivalent. Phyllic alteration and copper leaching resulted from the inflow of oxidized and acidic meteoric waters with decreasing temperature (range from 300-380 °C, with a mode of 360 °C) of the system. A late episode of boiling occurred in the upper part of the phyllic alteration zone, and was associated with significant copper deposition.

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The purpose of this paper is to review the present state of our knowledge of the geology and geochemistry of the Sungun deposit, and to attempt to put some constraints on the physical and chemical environment at the time of its formation. We also provide a quantitative evaluation of the processes potentially responsible for the transport and deposition of copper. For this purpose, we have updated the early works of Crerar and Barnes (1976) and Brimhall (1980) by incorporating recent experimental data on the solubility of copper in hydrothermal brines (Var'yash and Rekharskiy, 1981; Var'yash, 1991; Zotov et al., 1995; Xiao et al., in prep.).

### **GEOLOGICAL SETTING**

The Sungun porphyry copper deposit is located 75 km northwest of Ahar in the Azarbaijan province of northwestern Iran (Fig. 1), and is hosted by a diorite/granodiorite to monzonite/quartz-monzonite stock of Miocene age (Emami, 1992). The deposit is situated in the Sahand-Bazman igneous and metallogenic belt, a deeply eroded Tertiary volcanic field, roughly 100 by 1700 km in extent, consisting mainly of rhyolite and andesite with numerous felsic intrusions. The volcanics were laid down unconformably over folded and eroded Upper Cretaceous andesitic volcanic and sedimentary rocks (~500 m thick). The Sahand-Bazman belt was presumably formed during subduction of the Arabian plate beneath central Iran during the Alpine orogeny, and subsequent continental collision during the Paleocene to Oligocene (Berberian, 1983; Shahabpour, 1982; Etminan, 1978). Bordering the belt to the southwest is a major zone of complexly folded, faulted, and metamorphosed Tertiary and Paleozoic sedimentary rocks which form the

Figure 1. Simplified geologic map of the Sungun area. (after Lescuyer et al., 1978).



Zagros Mountains (Waterman & Hamilton, 1975).

The Sungun stock is a composite intrusion, with a plan area of around 3.45  $\text{km}^2$ (1.5 x 2.3 km). The stock contains three different intrusive bodies: 1) monzonite/quartz monzonite; 2) diorite/granodiorite; 3) andesite and related dykes, in order of emplacement (Fig. 2). Intrusive activity in the region terminated with the emplacement of granodioritic to dioritic dykes. Based on stratigraphic reconstruction, Hezarkhani and Williams-Jones estimate that the maximum depth of intrusion was 2000 m (see Chapter III). All intrusive units represent a high K andesitic parental magma (see Chapter II) and contain the same assemblage of minerals: plagioclase, K-feldspar, quartz, hornblende, biotite, titanite, apatite, and zircon. The entire stock and volcanic "cover rocks" (especially in the western part of the stock) are located within a caldera (Fig. 2). Previous work has shown that the Sungun stock intruded along an anticline of folded Cretaceous limestone and Eocene tuff (equivalent to the Karaj formation) and agglomerate of andesitic to trachytic composition (Chapter II). To the north, the Sungun stock is bounded by hydrothermally altered Cretaceous limestone (skarn), which extends to the east, and contains subeconomic copper mineralization.

#### MINERAL COMPOSITIONS

The compositions of silicate and oxide minerals were determined with an automated JEOL-8900L electron microprobe. Operating conditions were 15 Kv, 8 nA, a 2 mm beam, and 25 second peak (35 seconds for F and Cl) and background counting times. Standards were orthoclase (Al, K, Si), albite (Na), diopside (Ca, Mg), magnetite

**Figure 2.** Geological map of the Sungun deposit area, showing field relationships among the various subtypes of Sungun intrusive rocks, and the outline of the mineralized zone. The porphyritic monzonite/quartz-monzonite rims a central, later diorite/granodiorite pluton, and Cretaceous limestone and associated skarn border the north and east. Andesite and andesitic dykes are distributed through the north and western parts of the deposit (mainly outside the stock). Mineralized dykes intrude the diorite/granodiorite stock in the central part of the deposit. Skarn-type alteration (and associated mineralization) occurs predominantly adjacent to the eastern margin of the stock. (modified from Mehrpartou, 1993).



(Fe), spessartite (Mn, Si, Al), fluorite (F), and synthetic MnTi (Mn, Ti). Except where otherwise mentioned, the minerals analyzed were from the diorite/granodiorite which hosts the bulk of the mineralization.

#### MINERALOGY OF THE VEIN SYSTEMS

The Sungun deposit consists of a stockwork system of veins. The stockwork is best developed in the potassic and phyllic alteration zones, and comprises four main styles of veining (Table 1). Group I veins consist of quartz + molybdenite + anhydrite  $\pm$ K-feldspar with sporadic pyrite, chalcopyrite, bornite, magnetite, pyrrhotite and bismuthinite. They are discontinuous, vary in thickness between 0.5 and 3 mm, and formed during early fracturing of the porphyry. Molybdenite occurs mainly along vein margins, whereas K-feldspar, anhydrite, chalcopyrite, bornite and pyrite are concentrated in the central part of the veins. Group II veins consist of quartz + chalcopyrite + pyrite  $\pm$ molybdenite  $\pm$  pyrrhotite  $\pm$  titanite  $\pm$  magnetite  $\pm$  hematite, and generally cross-cut and in places off set Group I veins. Group II veins have well-developed sericitic alteration haloes and lack K-feldspar or hydrothermal biotite. These veins occur in all alteration zones, but are mainly concentrated in the phyllic, and to a lesser extent the potassic alteration zones. Group III veins consist of quartz + pyrite + calcite  $\pm$  chalcopyrite  $\pm$ anhydrite  $\pm$  molybdenite  $\pm$  rutile  $\pm$  hematite, and are most abundant in the phyllic alteration zone. They are relatively continuous, commonly polyphase layered, and vary in thickness from 3 to 50 mm. The only copper mineral is chalcopyrite, which is observed mainly as small blebs and inclusions in pyrite. Early-formed anhedral to subhedral grains

of pyrite are replaced by anhedral grains of chalcopyrite. Group IV veins consist of quartz, and/or calcite, and/or gypsum  $\pm$  pyrite. These veins are very thick (up to 17 cm), and are filled by quartz  $\pm$  calcite  $\pm$  gypsum. Group IV veins are found mainly in the propylitic zone, but also occur locally in the phyllic and potassic alteration zones. The only sulphide mineral is pyrite, which occupies ~10 vol % of these veins. Group IV veins are usually surrounded by narrow (<3 cm) envelopes of silicification. Figures 3 and 4 illustrate the vein parageneses as a function of alteration and vein type.

#### ALTERATION AND MINERALIZATION

Alteration and related mineralization in the Sungun porphyry copper deposit has been investigated by detailed studies of the mineralogy, petrography and chemistry of a large number of drill cores and outcrop samples. Early potassic and propylitic alteration, and later sodic, phyllic, and argillic alteration stages have been recognized, and are described in in Chapters III and IV. The distribution of various alteration types is very irregular, but is centered broadly on the diorite/granodiorite. The overall alteration pattern consists of a large peripheral propylitic alteration zone, and a core of potassic alteration crosscut by an irregular phyllic alteration zone (see Chapters III and IV).

The bulk of the copper mineralization at Sungun is hosted by diorite/granodiorite. Copper grades are unequally distributed and do not correlate with molybdenum grades. The hypogene copper and molybdenum mineralization was introduced during potassic alteration by high-temperature, high-salinity magmatic fluids (see Chapter III for details). Three principal types of mineralization have been identified. Type I is characterized by molybdenite and pyrite, with traces of magnetite, hematite, quartz, K-feldspar, biotite, anhydrite and pyrrhotite (represented by Group I veins); Type II contains chalcopyrite (as the main copper mineralization in the Sungun deposit), pyrite and quartz, with traces of molybdenite, hematite, magnetite, pyrrhotite and titanite (Group II veins); and Type III consists of chalcopyrite and pyrite, with minor molybdenite, hematite, calcite and rutile (Group III veins).

### Type I Mineralization

The first Type of mineralization is temporally and spatially related to the earliest, pervasive potassic alteration, in the deep and central parts of the deposit, and is dominated by the molybdenite. Grains of molybdenite extend into subhedral and euhedral quartz crystals in Group I veins, and are also disseminated in the matrix of potassically altered rocks. Minor chalcopyrite is present in some veins but not in the altered rocks.

Potassic alteration is characterized by K-feldspar and irregularly shaped crystals of Mg-rich biotite, as well as an abundance of anhydrite. On average, potassically altered rocks contain 28 % plagioclase, 35 % orthoclase (2 to 20 mm in diameter), 20 % quartz, 15 % biotite (commonly altered to sericite and chlorite), and 2 % chalcopyrite, pyrite, titanite, zircon, scheelite, uraninite, bismuthinite and rutile.

Petrographic observations and microprobe analyses indicate the presence of two compositionally distinct types of biotite within this alteration zone: primary biotite, which is Fe-rich, brown in color, and generally euhedral; and hydrothermal biotite, which is

		Magn	natic Biotit	e		Hydrothermal Biotite						
Sample no.	25-514	34-163	33-437	33-437	33-437	33-437	34-477	25-431	34-477	34-477	34-477	34-477
Dril-core no.	25	34	33	.33	33	33	34	25	34	34	34	34
Туре 1	Frs	Tm	К	К	K	К	<u> </u>	К	Phe	Phc	Phc	Phc
$SiO_2$ (wt %)	38.58	37.27	38,54	37.70	38.34	37.79	43.72	39.03	41.29	39.25	39.03	38,74
TiO <sub>2</sub>	3.82	4,27	3,26	4.00	3,98	4.03	2.65	2.11	2.02	2.17	2.11	3.72
Al <sub>2</sub> O <sub>3</sub>	14.55	13.53	15.45	14.10	14.17	14.85	17.17	15.54	15.05	15.50	15.54	15.81
FeO <sup>2</sup>	15.69	16.38	13.23	15.30	15.42	14.17	3.87	4,18	2.53	4.17	4.18	7.54
MnO	0.17	0.18	0.06	0.05	0,06	0.04	0.01	0.01	0.00	0.04	0.01	0.00
MgO	14.34	14.40	15.00	14.94	15.07	14,78	17.41	21.58	23.18	21.50	21.58	18.38
CaO	0.03	0.01	0.00	0.00	0.00	0.00	0.05	0.04	0.00	0.00	0.04	0,02
Na <sub>2</sub> O	0.30	0,30	0.10	0.10	0.13	0.14	0.15	0.17	0,14	0.18	0.17	0.24
K20	9.35	9.41	10.25	10.16	10,05	10.21	9.94	10.25	10.51	10,43	10.25	10.52
F	0.38	0.33	1.03	0.75	0.73	0.82	1.92	2.10	2.60	1.96	2.10	1.58
CI	0.20	0.17	0.19	0.22	0.23	0.23	0.08	0.08	0.04	0.09	0.08	0.15
Total	97.41	96.24	97.11	97.31	98.18	97.02	96.97	95.09	97.35	95.29	95.09	96.71
No. of atoms						•						
based on 11 O												
Si	2.81	2.77	2.77	2.75	2.77	2.75	2.94	2.72	2.77	2.73	2,72	2.72
Ti	0.21	0.24	0.18	0.22	0.22	0.22	0.13	0.11	0.10	0.11	0.11	0.20
Al	1.26	1.20	1.32	1.22	1.22	1.28	1.37	1.29	1.20	1.28	1.29	1,32
Fe	0.96	1.02	0.80	0.93	0.93	0.86	0.22	0.24	0.14	0.24	0.24	0.44
Mn	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.56	1.60	1.61	1.63	1.62	1.60	1.74	2.24	2.32	2.23	2.24	1.94
Са	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.04	0.04	0.01	0.01	0.02	0.02	0.04	0.02	0.02	0.04	0.02	0.03
К	0.90	0.89	0.94	0.95	0.93	0.95	0.95	0.91	0.90	0.93	0.91	0.94
F	0.09	0.08	0.23	0.17	0.17	0.19	0.41	0.46	0.55	0.43	0.46	0.39
- Cl	0.02	0.02	0.02	0.03	0.03	0.03	0.01	0.01	0.00	0.01	0.01	0.02
				2.2.4					2,00		2,01	
F/(F+Cl)	0.82	0.80	0.92	0.85	0.85	0.86	0.98	0.98	1.00	0.98	0.98	0.95
Fe/(Fe+Mg)	0,38	0.39	0.33	0.36	0.36	0.35	0.11	0.10	0.06	0.10	0,10	0.18

TABLE 1. Representative Electron Microprobe Analyses of Magmatic and Hydrothermal Biotite In the Sungun Porphyry Copper Deposit

<sup>1</sup> Frs = fresh rock, Trn = transition zone, K = potassic zone, Phc = phyllic <sup>2</sup> FeO = total Fe

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Figure 3. Relative mineral abundances in various alteration zones in the Sungun deposit. Widths of bars denote qualitative abundances.

Minerals	Fresh Rock, Granodiorite	Potassic Zone	Transition Zone	Phyllic Zone	Propylitic Zone
Biotite					
K-feldspar					
Albite					
Amphibole					
Quartz					
Chlorite	:				
Apatite					
Magnetite					
Titanite					
Bornite					
Chalcopyrite					
Pyrite	•				
Molybdenite					
Sphalerite					
Galena					
Pyrrhotite					
Calcite					
Rutile					
Epidote			_		
Sericite					
limenite					

Figure 4. Relative mineral abundances in different vein types in the Sungun deposit. Widths of the bars denote qualitative abundances.

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Group IV veins Group I Veins Group II veins Group III veins Minerals K-feldspar Quartz Chlorite Apatite Magnetite Titanite Bornite Chalcopyrite Pyrite Molybdenite Sphalerite Galena Pyrrhotite Calcite Rutile Epidote Sericite Anhydrite

pale-brown to greenish-brown in color, very ragged, and Mg-rich (Table 2).

Primary biotite occurs as phenocrysts in all rock types, forming books up to 3 mm in diameter. These grains have dark brown pleochroism, and often contain inclusions of apatite and zircon. Inclusions of primary biotite (up to 0.2 mm in diameter) are relatively common in plagioclase and K-feldspar phenocrysts. The hydrothermal biotite is generally interstitial to feldspar and quartz, and locally replaces hornblende and primary biotite phenocrysts. It can be distinguished from primary biotite by lower Fe/(Fe+Mg) ratios (up to 0.41), and higher fluorine contents (up to 0.55 wt % F; Fig. 5 and Table 2). Lower Fe contents in hydrothermal biotite are most likely related to precipitation of pyrite and chalcopyrite, or an increase in  $fO_2$  (Chivas, 1981). Relict crystals of hydrothermal biotite are observed almost everywhere in the stock, suggesting that potassic alteration was initially extensive but was subsequently overprinted by later alteration. Biotite which has replaced amphibole (in the matrix of the rock) commonly contains inclusions of chalcopyrite.

Amphiboles in Sungun form subhedral prismatic phenocrysts up to 9 mm long, with blue to pale green pleochroism of variable intensity. The amphiboles have compositions intermediate between magnesio-hornblende and edenitic hornblende (based on the classification of Papike, 1988), with F/(F+Cl) values ranging from 0.20 to 0.80 (Table 3). In the deeper parts of the stock, biotite phenocrysts (Fe-rich) have been replaced by a complex aggregate consisting of pyrite + chalcopyrite + rutile + hydrothermal biotite (Mg-rich).

Petrographic observations and microprobe analyses indicate the presence of two generations of alkali feldspar within the potassic alteration zone: a) perthitic phenocrysts

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Sample No.	34-164	34-161	34-163	34-163	34-162	33-163	34-163	34-163	34-163	25-514	25-514	25-514	25-514	25-514	34-477	34-477
Dril-core No.	34	34	34	34	34	33	34	34	34	25	25	25	25	25	34	34
Туре '	Pro	Рто	Pro	Pro	Phc	Phc	Phe	Phc	Phc	K	КК	<u> </u>	<u>K</u>	K	Pro	Pro
SiO, (wt %)	30.09	29.94	30.39	30.45	29.89	29.18	31.11	29.91	30.06	30,75	27.90	27.64	29.63	28.70	29.91	29.89
TiO,	0.05	0.02	0.03	0.02	0.02	0.03	0.02	0,03	0.00	0.06	0.05	0.07	0.04	0.01	0.03	0.02
Al <sub>1</sub> O <sub>3</sub>	18.28	18.18	18.11	18.09	18.06	17.59	18.61	18.64	18.32	21.40	20,39	20.18	21.39	20.88	18.64	18.06
FeO <sup>2</sup>	14,32	13.70	14.47	13.57	14.74	14.07	13.10	15.18	13.85	16.44	17.02	16.72	11.22	12.06	15.18	14.74
MnO	0.20	0,24	0.15	0.17	0.21	0.24	0.17	0.16	0.21	0.05	0.08	0.08	0.11	0.15	0.16	0.21
MgO	24.50	24.40	24,16	24.15	24.18	24.04	22.87	23.76	24.60	18.42	21.48	21.04	23,85	25.24	23.76	24.18
CaO	0.05	0.05	0.07	0.07	0.04	0.06	0.09	0.08	0.06	0.08	0.07	0.06	0.03	0.04	0.08	0.04
Na <sub>2</sub> O	0,03	0.09	0.04	0,06	0.07	0.05	0.10	0.09	0.03	0.01	0.01	0.03	0.02	0.04	0.09	0.07
K₂O	0.09	0.07	0.15	0.35	0.19	0.10	0.26	0.07	0.09	1.32	0,04	0.03	0.66	0.14	0.07	0.19
F	0.28	0.27	0.35	0.37	0,31	0.27	0.35	. 0.30	0.19	0.16	0.36	0.20	0.39	0.17	0.30	0.31
Cl	0.02	0,06	0.02	0.05	0.01	0.03	0.04	0.06	0.02	0.01	0.00	0.01	0.01	0.01	0.06	0.01
Total	87.91	87.01	87.94	87.34	87.71	85.65	86.72	88.28	87.42	88.69	87.40	86.06	87,35	87.42	88.28	87.71
No. of atoms																
based on 11 O																
Si	2.96	2.97	2.99	3.00	2.96	2.95	3.07	2.94	2.97	3,10	2.80	2.82	2.88	2.81	2.94	2.96
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Al	2.13	2.14	2.11	2.12	2.12	2.11	2.18	2.18	2.15	2.50	2.43	2.44	2.47	2.43	2.18	2.12
Fe	1.18	1.14	1.19	1.12	1.22	1.19	1.08	1.25	1.14	1,35	1.43	1.43	0.91	0.99	1.25	1.22
Mn	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.02
Mg	3.59	3.61	3.54	3.55	3.57	3.63	3.36	3.48	3.62	2.70	3.20	3.20	3.46	3.68	3.48	3.55
Ca	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00
Na	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.00	0.00	0.01	0,00	0.01	0,02	0.01
К	0.01	0.01	0.02	0.04	0.02	0.01	0.03	0.01	0.01	0.17	0.01	0,00	0,08	0,02	0.01	0.02
F	0.09	0.08	0,11	0.12	0.10	0.09	0.11	0.09	0,06	0.05	0.11	0,06	0.12	0.05	0.09	0.10
CI	0.00	0.01	0.00	0.01	0,00	0.01	0.01	0.01	0.00	0.00	0.00	0,00	0.00	0,00	0.01	0.00
Total	10.00	10.00	9.99	9.99	10.02	10.03	9.88	10.00	9.99	9,88	10.00	9,99	9.93	10,00	10.00	10.00
F/(F+Cl)	1.00	0.89	1.00	0.92	1.00	0.90	0.92	0.90	1.00						0.90	
Fe/(Fe+Mg)	0.25	0.24	0.25	0.24	0.25	0.25	0.24	0.26	0.24	0.33	0.31	0.31	0.21	0.21	0.26	0.26

TABLE 2. Representative Electron	Microprobe Analyses of C	hlorite In the Sungun	Porphyry Co	opper Deposi
			_ , , , ,	

 ${}^{1}K$  = potassic zone, Phc = phyllic alteration zone, Pro = propylitic zone

<sup>2</sup> FeO = total Fe

**Figure 5.** A plot of Fe/(Fe+Mg) vs. F/(F+Cl) for biotite in the Sungun deposit based on microprobe analyses (see text).



14010	J. Repit	somative	Licchon	Microphy	500 / mail	303 01 1 H	inpiniooio	nomgia	noutoritie	TOURS III	uio bullg		<u>,,, cobb</u>	or Depos	
Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Dril-core No.	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23
Туре 1	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs
						_									
SiO <sub>2</sub> (wt %)	48.88	46.99	45.89	46.82	47.16	47.01	46.76	47.77	47.09	47.19	45.88	48.01	47.05	46.52	47.83
TiO <sub>2</sub>	1.18	1.45	1.50	1.34	1.28	1.43	1.33	1.12	1.11	1.20	1.36	1.13	1.25	1.31	1.16
Al <sub>2</sub> O <sub>3</sub>	6,29	7.10	7.78	7.24	6.81	7.22	7.11	7.04	7.00	6.83	7.84	6.71	7.37	7.34	6,80
FeO <sup>2</sup>	11.88	12.50	13.36	13.08	13.08	13.29	13.23	12.60	12.86	12.97	13.55	13.12	13,18	13.01	12.90
MnO	0.46	0,43	0.44	0.47	0.43	0.44	0.47	0.46	0.40	0.41	0.42	0.46	0.44	0,45	0,43
MgO	16.43	15.46	15.00	15,38	15.30	15.06	15.10	15.66	15,36	15.63	14.68	15.52	15.20	15.21	15.64
CaO	11.27	11.21	11.27	11.48	11,30	11.39	11.27	11.39	11.34	11.21	11.41	11.39	11.39	11.22	11.44
Na <sub>2</sub> O	1.33	1.85	1.57	1.51	1.67	1.50	1.55	1.43	1.68	1.52	1.78	1.48	1.49	1,68	1.43
K <sub>2</sub> O	0.39	0.85	0.63	0.57	0.70	0.54	0.52	0.52	0.65	0.54	0.82	0.54	0.59	0.61	0.53
F	0.11	0.14	0.06	0.14	0.21	0.17	0.07	0.17	0.05	0.07	0.19	0,06	0.14	0.09	0.09
CI	0.08	0.39	0.10	0.10	0,33	0.08	0.09	0.08	0.36	0.11	0.31	0.14	0.08	0.20	0.08
Total	98.284	98.369	97.576	98.12	98.26	98.113	97.48	98.216	97.901	97.661	98.232	98,543	98,183	97.633	98.315
No. of atoms								•							
based on 11 O															
Si	7.35	7.14	7.06	7.14	7.17	7.16	7.18	7.23	7.19	7.22	7.02	7.27	7.16	7.13	7.25
Ti	0.13	0.17	0.17	0.15	0.15	0.16	0.15	0.13	0.13	0.14	0.16	0.13	0.14	0.15	0,13
Al	1.12	1.27	1.41	1.30	1.22	1.30	1.29	1.26	1.26	1.23	1.41	1.20	1.32	1.33	1.22
Fe	1.49	1.59	1.72	1.67	1.66	1.69	1.70	1,60	1.64	1.66	1.73	1.66	1.68	1.67	1.64
Mn	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0,06	0.05	0.05	0.05	0.06	0,06	0.06	0,05
Mg	3.68	3.50	3.44	3.49	3.47	3.42	3.46	3,53	3,50	3.56	3.35	3,50	3.45	3.48	3,53
Ca	1.82	1.82	1.86	1.87	1.84	1.86	1.85	1.85	1.86	1.84	1,87	1.85	1.86	1.84	1.86
Na	0.39	0.55	0.47	0.45	0,49	0.44	0.46	0.42	0,50	0.45	0.53	0.43	0.44	0.50	0,42
к	0.07	0.16	0.12	0.11	0.14	0.10	0.10	0,10	0.13	0.10	0.16	0.10	0.11	0.12	0.10
F	0.05	0.07	0.03	0.07	0.10	0.08	0.03	0.08	0.02	0.03	0.09	0,03	0.07	0.04	0.04
CI	0.02	0.10	0.03	0.03	0.08	0.02	0.02	0.02	0.09	0.03	0.08	0.03	0.02	0.05	0.02
F/(F+Cl)	0.71	0.41	0.50	0.70	0.56	0.80	0.60	0.80	0.18	0.50	0,53	0.50	0.78	0.44	0.67
Fe/(Fe+Mg)	0,29	0.31	0.33	0.32	0.32	0.33	0.33	0.31	0.32	0.32	0,34	0.32	0.33	0,32	0.32

Table 3 Representative Electron Microprobe Analyses of Amphibole from granodioritic rocks in the Sungun Porphyry Copper Deposit

<sup>1</sup> Frs = fresh rock, <sup>2</sup> FeO = total Fe

of magmatic origin; and b) poikilitic overgrowths of hydrothermal origin. The bulk composition of the primary alkali feldspar is orthoclase-rich (Or/(Or+Ab+An) = 0.88-0.99), with variable but relatively high barium contents (BaO up to 1.74 wt %). The orthoclase and albite domains in magmatic perthite have compositional ranges of Or<sub>97</sub>Ab<sub>2</sub>An<sub>1</sub> to Or<sub>99</sub>Ab<sub>1</sub>, and Ab<sub>76</sub>Or<sub>1</sub>An<sub>23</sub> to Ab<sub>81</sub>Or<sub>3</sub>An<sub>16</sub>, respectively. These compositions require subsolidus exsolution at ~500 °C (Tuttle and Bowen, 1958). Albitic domains also contain small inclusions of primary biotite, plagioclase, and accessory minerals like apatite, titanite, and zircon. Hydrothermal K-feldspar is characterized by abundant inclusions of unaltered rock, and by the absence of perthite intergrowths. The composition of hydrothermal K-feldspar ranges from Or<sub>72</sub>Ab<sub>27</sub>An<sub>1</sub> to Or<sub>78</sub>Ab<sub>10</sub>An<sub>12</sub>.

Chlorite is fairly common in Type I mineralization, where it is found replacing mafic minerals such as amphibole and biotite. Based on microprobe analyses (Table 4), two types of chlorite have been identified; a) a clinochlore which is associatea with chalcopyrite mineralization, and b) diabanitic chlorite which formed mainly as small grains in the groundmass, and is unrelated to copper mineralization. Compositional variation between these two varieties of chlorite mainly consists of variations in FeO and MgO.

#### Types II and III Mineralization

Types II and III styles of mineralization host most of the copper in the deposit, which occurs both in veins (Group II) and as disseminations in rocks displaying intense phyllic alteration. The principal differences between Types II and III mineralization are

GROUP I	A : $Qtz + Mo + Anh + K$ -feldspar + Py ± Mt ± Bis B : $Qtz + Mo + Anh + Py \pm Po \pm Ccp \pm Brn$ C : $Qtz + Mo + Anh + Ser + Py \pm Ccp \pm Po \pm Hem$	Discontinuous, vary in thickness between 0.5 and 3 mm. Formed during early fracturing of the porphyry stock. Molybdenite occurs mainly along vein margins. K-feldspar, anhydrite, chalcopyrite, bornite and pyrite occur mostly in the central part of the veins. Bismuthinite, pyrite and chalcopyrite occur as inclusions in the molybdenite. Surrounded by potassic and less commonly phyllic and propylitic alteration zones.
GROUP II	<b>D</b> : $Qtz + Ccp + Py + Po \pm Mo$ <b>E</b> : $Qtz + Ccp + Py + Po \pm Mt \pm Hem \pm Tit$	Generally cross-cut and off-set group I veins. Well-developed sericitic alteration haloes, lack K-feldspar. Vein quartz is relatively coarse-grained and crystals tend to be oriented perpendicular to vein walls. Sulphide minerals located mainly in a narrow discontinuous layer in vein centers.
GROUP III	F: $Qtz + Py + Ser + Anh \pm Ccp \pm Mo \pm Rut$ G: $Qtz + Py + Cal + Anh \pm Ccp \pm Hem + Rut$ H: $Qtz + Py$ (massive) + Cal ± $Ser \pm Ccp \pm Gn \pm Sph$	Generally cross-cut both group I and II veins. Relatively continuous, polyphase, and vary in thickness from 3 to 50 mm. Quartz occurs mainly near vein margins, with anhydrite (gypsum), calcite and sulphides intergrown in the vein centers. Chalcopyrite, occurs as small blebs and inclusions in pyrite.
GROUP IV	I: $Qtz + Py$ J: $Qtz + Cal \pm Py$ K: Cal $\pm Py$ L: $Gyp \pm Py$	Cross-cut all other vein groups, and represent the youngest vein-forming event. Tend to be thick (up to 17 cm), and filled by quartz, and/or calcite, and/or gypsum. Surrounded by zones of silicification up to 3 cm wide.

# TABLE 4. Mineralogical Classification of Mineralized Quartz Veins in Sungun Deposit

Abbreviations: Qtz = quartz; Anh = anhydrite; Ccp = chalcopyrite; Py = pyrite; Bm = bornite; Cal = calcite; Ser = sericite; Gyp = gypsum; Hem = hematite; Bis = bismothinite; Gn = galena; Sph = sphalerite; Tit = titanite; Rut = nutile; Mt = magnetite; Mo = molybdenite; Po = pyrrhotite

Figure 6. Chlorite compositions from the phyllic and propylitic alteration zones (diagram after Hey, M. H., 1954).



the lack of pyrrhotite, magnetite and titanite in the latter. In veins, chalcopyrite is accompanied by pyrite (locally with partial to complete replacement by chalcopyrite), and traces of molybdenite. It is difficult to determine whether chalcopyrite formed directly or as a replacement of pre-existing disseminated pyrite in the host diorite/granodiorite. Sericite occurs as randomly oriented grains containing relict biotite and/or amphibole, with intergrowths of rutile and inclusions of zircon. The concentration of fluorine in the sericite ranges from below detection to ~0.9 wt % F, whereas the chlorine content is generally below the limit of detection.

Minor sphalerite and galena were deposited subsequent to pyrite-chalcopyrite in Type III mineralization. Sphalerite coats earlier pyrite, and galena fills vugs and surrounds chalcopyrite and pyrite (Fig. 7).

### PHYSICOCHEMICAL CONSTRAINTS

Thermodynamic data for ore and gangue minerals, water and aqueous species (SUPCRT92, Johnson et al., 1992, Table 5) were used to delineate the stability fields of the various alteration and mineralization assemblages as a function of the intensive parameters  $fS_2$ ,  $fO_2$ , and pH. Temperatures for early and late stages of alteration and mineralization have been estimated from fluid inclusion data (see Chapter III). These data indicate that Group II Cu-rich veins were deposited by a high salinity aqueous fluid (~55 wt % NaCl equivalent) in the temperature range 300 °C to 380 °C, with a mode at 360 °C. In contrast, the Group I Mo-rich veins formed at higher temperature (>400 °C). For the present calculations, we have adopted a K/Na ratio of 0.26, which falls within the

Figure 7. a). Scanning electron photomicrographs of galena and sphalerite in Group III vein mineralization. b). Galena fills vugs in the pyrite. Abbreviations: CP = chalcopyrite, GA = galena, SP = sphalerite, PY = pyrite.





range of values (0.19 to 0.35) determined by microthermometric analyses of fluid inclusions containing halite, chalcopyrite and sylvite daughter minerals from group I and II quartz veins (see Chapter III). These values are comparable to those of other porphyry copper deposits (e.g., Panguna, Eastoe, 1978; Tintic, Utah, Ramboz, 1979; Granisle and Bell, Wilson et al., 1980), and are consistent with values (0.25 and 0.29) estimated by Lagache and Weisbrod (1977) for an aqueous fluid in equilibrium with two feldspars at high temperature (500 bars, 600 to 650 °C). Total aqueous S and C concentrations were set to 0.1 molal. These estimates are consistent with analyses of the S content of fluid inclusion decrepitates and agree with previous estimates of their concentrations in porphyry fluids (e.g., Barnes, 1979). Total concentrations of other components (e.g., aqueous Cl, K, Ca) were chosen to be consistent with the fluid inclusion data (Chapter III). The speciation and chemical activities of the important aqueous species were obtained using the program EQBRM (Anderson and Crerar, 1993). Although EQBRM uses the Davies version of the extended Debye-Huckel equation, we found that the speciation calculations were relatively insensitive to the magnitude of the activity coefficients.

Isothermal  $fS_2$ - $fO_2$  (Figure 8) and  $fO_2$ -pH (Figure 9) diagrams have been constructed at 360 °C, the inferred temperature of deposition for most of the hypogene copper mineralization at the Sungun deposit (see Chapter III). Figure 8 shows the stability fields of pyrrhotite, pyrite, chalcopyrite, bornite, magnetite, titanite, rutile, and hematite, and alteration minerals such as K-feldspar, muscovite and hydrothermal biotite. The activity of the annite endmember in hydrothermal biotite was calculated based on microprobe analyses, following the methods outlined in Wood and Fraser (1977). The

Figure 8. LogfO<sub>2</sub>-logfS<sub>2</sub> diagram characterizing Type II mineralization and associated alteration (sericitization), showing the stability field of ore, silicate and oxide minerals at 360 °C and 500 bars. Mineral stabilities were calculated in the systems Cu-Fe-S-O and K-Al-Si-O-H, with ionic strength = 1,  $m \operatorname{Ca}^{+2} = 0.1$  to 0.001,  $aK^{+} = 0.04$  and  $aS = 10^{-1}$ . Activities were estimated from speciation calculations using compositional data from fluid inclusions. Phase boundaries and predominance fields of aqueous species were calculated using SUPCRT92 (Johnson et. al., 1992). Stability fields of pyrrhotite, pyrite, magnetite, chalcopyrite, bornite and hematite are separated by bold lines. The thin discontinuous lines represent constant pH, and the ticked continuous lines show the Kfeldspar-muscovite (pH = 5.05) and muscovite-pyrophyllite (pH = 3.18) transitions. Point "S" represents the Sungun conditions in terms of  $(\log fO_2 - \log fS_2)$  based on the observed mineral paragenesis in Group II and to some extent in Group III Cu-mineralized quartz veins. Abbreviations: CP = chalcopyrite, PO = pyrthotite, PY = pyrite, BN =bornite, Mt = magnetite, Hem = hematite, Qz = quartz, Mus = muscovite, Kspar = Kfeldspar, CV = covellite, CC = chalcocite.



**Figure 9.** Log  $fO_2$ -pH diagram showing approximate conditions (shaded areas) for Group II and III mineralized quartz veins, relative to mineral stabilities in the systems Cu-Fe-S-O, K-Al-Si-O-H, and calcite/anhydrite, calculated for same P-T and m Ca<sup>+2</sup>, aK<sup>+</sup> and aS conditions as in Figure 8. The inferred conditions of copper deposition at Sungun are shaded, labeled "A", and "B", and refer to the potassic and phyllic alteration zones, respectively. See text for further details and discussion. Abbreviations as in Figure 8.


		Log K			
#	Reaction	360 °C	450 °C		
1	$3Pyrrhotite + 2O_2 = Magnetite + 1.5S_2$	45.47	38.89		
2	$3Pyrite + 2O_2 = Magnetite + 3S_2$	31.89	29.70		
3	Annite $+ 0.5O_2 = Orthoclase + Water + Magnetite$	14.47	12.71		
4	$2Magnetite + 0.5O_2 = 3Hematite$	13.37	10.81		
5	Bornite + 4Pyrrhotite + $S_2 = 5$ Chalcopyrite	13.12	9.45		
6	4Muscovite + $4$ H <sup>+</sup> + $6$ Water = $6$ Kaolinite + $4$ K <sup>+</sup>	5.98	4.63		
7	$Pyrrhotite + 0.5S_2 = Pyrite$	4.53	3.10		
8	$2$ Covellite = Chalcocite + $0.5S_2$	-1.67	-0.68		
9	Bornite + 4Pyrite = 5Chalcopyrite + $S_2$	-4.99	-2.80		
10	Muscovite + $2K^+$ + $6Quartz = 3Orthoclase + 2H^+$	-7.30	-6.93		
11	Annite + $3S_2$ = Orthoclase + 3Pyrite + Water + $1.5O_2$	-17.15	-16.99		
12	Hematite $+ 2S_2 = 2Pyrite + 1.5O_2$	-25.71	-23.41		
13	Annite + $1.5S_2$ = Orthoclase + 3Pyrrhotite + Water + $1.5O_2$	-30.73	-26.17		
14	Bornite + 2Hematite + $3S_2 = \%$ chalcopyrite + $3O_2$	-56.41	-49.61		
15	$3Bornite + 4Magnetite + 9S_2 = 15Chalcopyrite + 8O_2$	-142.51	-127.21		
16	$H2S = H^+ + HS^-$	-7.85	-10.07		
17	$HS^{-} + 2O_2 = SO_4^{-2} + H^{+}$	47.22	36.24		
18	$0.5S_2 + 0.75O_2 + Water = SO_4^{-2} + 2H^+$	27.44	16.59		
19	$HSO_4 + SO_4^2 + H^+$	-6.72	-8.77		
20	$Hs^{-} = H^{+} + S^{-2}$	-8.62	-9.72		
21	$0.5S_2 + Water = HS^2 + H^2 + 0.5O_2$	-19.78	-19.66		
22	$15$ Chalcopyrite + $18$ Water + $35O_2 = 3B$ ornite + $4Magnetite + 18SO_4$	636.35	425.74		
23	5Chalcopyrite + 6Water + $12O_2$ = Bornite + 2Hematite + $6SO4^{-2}$ + 36	221.03	149.12		
24	2Pyrite + 4Water + 7.5O <sub>2</sub> = Hematite + $4HSO_4^{-} + 4H^{+}$	162.31	124.77		
25	2Pyrite + 4Water + 7.5O <sub>2</sub> = Hematite + $8H^{+}$ + $4SO_{4}^{-2}$	135.46	89.75		
26	Annite + $6HS^{+}$ + $6H^{+}$ + $1.5O_2$ = K-feldspar + 3Pyrite + 7Water	101.53	100.96		
27	$5$ Chalcopyrite + $2H_2S + O_2 = Bornite + 4FeS_2 + 2Water$	28.85	21.98		
28	$Pyrrhotite + Hs' + H^{+} + 0.5O_2 = Pyrite + Water$	27.32	26.11		
2 <del>9</del>	$Pyrrhotite + H_2S + 0.5O_2 = Pyrite + Water$	16.46	12.65		
30	Annite + 0.50 <sub>2</sub> = Magnetite + K-feldspar + Water	14.73	12.71		
31	$2Magnetite + 0.5O_2 = 3Hematite$	13.37	10.81		

Table	e 5.	Log	Κ	Contents	for 3	60-450	°C in	Costant	Pressure

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		Log K			
#	Reaction	360 °C	450 °C		
32	$Pyrrhotite + 0.5S_2 = Pyrite$	4.53	3.06		
33	$TiO_2 + SiO_2 + Ca + Water = SiCaTiO_5 + 2H^2$	-5.94	-5.80		
34	$3Pyrrhotite + 3Water + 0.5O_2 = Magnetite + 3HS^2 + 3H^2$	-13.87	-20.08		
35	5Chalcopyrite + $2HSO_4^-$ + $2H^+$ = Bornite + $4Pyrite$ + $2Water$ + $3O_7^-$	-63.31	-47.88		
36	$3Pyrite + 6Water = Magnetite + 6HS^{-} + 6H^{+} + O_{2}$	-86.79	-88.24		
37	$15$ Chalcopyrite + $18$ Water + $O_2 = 3B$ ornite + $4Mag$ netite + $18HS^2$ .	-225.58	-240.17		
38	Annite + $6SO_4^2$ + $6H^+$ = K-feldspar + 3Pyrite + 4Water + $12O_2$	-239.64	-167.58		
39	4Muscovite + $4$ H <sup>+</sup> + $6$ Water = $6$ Kaolinite + $4$ K <sup>+</sup>	5.98	4.63		
40	K-feldspar + Na <sup>+</sup> + H <sup>+</sup> = Albite + K <sup>+</sup> + H <sup>+</sup>	-0.86	-0.78		
41	Muscovite + $Na^+$ + $H^+$ = Paragonite + $K^+$ + $H^+$	-1.44	-1.33		
42	Muscovite + $2K^+$ + $6SiO_2$ = $3K$ -feldspar + $2H^+$	-7.30	-6.93		
43	$5$ Chalcopyrite + 2Water + $3O_2$ = Bornite + 4Pyrrhotite + 2HSO <sub>4</sub> +	55.18	41.23		
44	5Chalcopyrite + $2HS' + 2H^+ + O_2 = Bornite + 4Pyrite + 2Water$	44.55	42.12		
45	$Fe + HS' + H^+ + 0.5O_2 = Pyrrhotite + Water$	29.43	27.72		
46	$Fe + H_2S + 0.5O_2 = Pyrrhotite + Water$	21.58	17.66		
47	$Calcite + 2H^{+} = Ca^{+2} + CO_{2} + Water$	8.25	8.80		
48	5Chalcopyrite + 2Water = Bornite + 4Pyrrhotite + $2H_2S + O_2$	-36.98	-28.63		
49	5Chalcopyrite + $2SO4^{-2} + 4H^{+} = Bomite + 4Pyrite + 2Water + 3O_{2}$	-49.88	-30.37		
50	Anhydrite + $2H^* = Ca^{*2} + H_2S + 2O_2$	-49.90	-39.98		
51	5Chalcopyrite + 2Water = Bornite + 4Pyrrhotite + $2HS^{+} + 2H^{+} + O_{2}$	-52.68	-48.76		
52	Anhydrite + $H^* = Ca^{+2} + HS^2 + 2O_2$	-57.75	-50.05		
53	5Chalcopyrite + $2HSO_4^{+} + 2H^{+} = Bornite + 4Pyrite + 2Water + 3O_{1}^{-}$	-63.31	-47.88		
54	$3$ Annite + $3$ H <sup>+</sup> + $1.5O_2 = 3$ Magnetite + $3$ K <sup>+</sup> + $7.5$ SiO <sub>2</sub> + $4.5$ Water	53.29	47.70		
55	3Annite + $2$ H <sup>+</sup> + $1.5$ O <sub>2</sub> = Muscovite + $3$ Magnetite + $2$ K <sup>+</sup> + $6$ SiO <sub>2</sub> +	51.50	45.07		
56	Annite + 0.75O <sub>2</sub> = 1.5Hematite + K-feldspar + Water	21.42	18.12		
57	$3Pyrrhotite + 3Water + 0.5O_2 = Magnetite + 3H_2S$	9.68	10.12		
58	Annite + $3H_2S + 2/3K^+ + 3Pyrrhotite + 4Water$	5.74	3.35		
59	$2Muscovite + 2H^+ = 3Andalusite + 2K^+ + 3SiO_2 + 3Water$	3.48	5.25		
60	$3Pyrrhotite + 2K^{+} = 2Muscovite + 2H^{+} + 6SiO_{2}$	-3.59	-3.70		
61	Anhydrite + $H^+ = Ca^{+2} + HSO_4^-$	-3.82	-5.05		
62	$3Pyrite + 6Water = Magnetite + 6H_2S + O_2$	-39.67	-27.84		

### Table 5 (con'd)

value (log activity) obtained is -3.1. The stability field of pure annite (activity = 1) is also shown for comparison. The stability field of anhydrite has been contoured over a range of  $Ca^{+2}$  activity. The latter value was difficult to estimate. Although fluid inclusion decrepitate analyses indicate a high total Ca content (2 to 4 wt% Ca of the decrepitate, see Chapter III), most of this Ca will be ion paired with Cl<sup>-</sup> and other ligands at the temperature of interest (Williams-Jones and Seward, 1989).

In Figure 8, constant pH lines have been constructed within the different sulphur species fields to characterize the alteration silicate minerals in equilibrium with copper mineralization for different  $fO_2$  and  $fS_2$  conditions. These boundaries have been calculated for the dominant silicate and Ca-bearing minerals that co-exist with economic copper mineralization, i.e. orthoclase, muscovite, calcite, and anhydrite at a Ca<sup>+2</sup> molality of 0.1 to 0.01 (fluid inclusion data, see Chapter III). Muscovite formed at the expense of K-feldspar and biotite (evident from textural relationships) through progressive acidification, as shown by the arrows in Figure 8. The pH value at 360 °C for the muscovite field boundary is 5.05 at log  $fO_2$  of -25.5 (point "S" defined by coexisting muscovite and chalcopyrite; Fig. 8), and 3.18 at  $\log fO_2$  of -22 (at the muscovitepyrophyllite boundary). At point "S", all of the major ore and gangue minerals in the phyllic and potassic alteration zones at Sungun are stable. This includes the phases chalcopyrite, pyrite, hematite, muscovite, K-feldspar, anhydrite, and hydrothermal biotite. Only a slight deviation to higher  $fS_2$  values could explain the presence of bornite, a minor ore mineral at Sungun. Although not shown, molybdenite would also be stable at point "S". However, as discussed earlier, most of the molybdenite at Sungun was deposited at higher temperatures.

It is evident from Figure 8 that the stability field of hydrothermal biotite ( $a_{annite} = 10^{-3.1}$ ) is considerably larger than that of pure annite. If the pure annite endmember was used, it would not be possible to have the stable assemblage biotite + hematite, which is commonly observed in hypogene mineralization at Sungun.

Figure 9 is a  $fO_2$ -pH diagram drawn for the same conditions as those in Figure 8. The inferred conditions of copper deposition at Sungun are shaded and labeled "A", and "B", and refer to potassic, and phyllic alteration zones, respectively. Although the boundaries of these regions as drawn are fairly large, in reality the oxidation state of the hydrothermal fluids was probably close to the aqueous sulfide/sulfate boundary. Evidence for this includes the abundance of both anhydrite and metal sulfides, as well as limited sulfur isotopic data that supports an aqueous sulfate/sulfide ratio close to unity (Chapter III). Thus, the observed changes in alteration mineralogy can be explained by changes in pH (or  $K^+/H^+$  ratio), with little or no change in relative oxidation state (defined by the aqueous sulfide/sulfate buffer).

An interesting feature of Figure 9 is that the hydrothermal biotite field is supplanted by pyrite over much of the central portion of the diagram. Thus, although pyrite, chalcopyrite and hydrothermal biotite may coexist, this is only possible at fairly low S<sub>2</sub> fugacities. At higher S<sub>2</sub> fugacities (i.e., deeper into the center of the pyrite field), biotite is unstable with respect to pyrite. In fact, replacement of Fe-rich biotite by pyrite + chalcopyrite + rutile + Mg-rich biotite is a commonly observed texture in wellmineralized zones at Sungun. The stability fields of anhydrite and calcite are also shown in Figure 9, contoured for different Ca<sup>2+</sup> activities. Both minerals are present in hypogene ore at Sungun, although anhydrite is by far the more abundant phase, especially in the higher temperature stages of mineralization. This is consistent with the fact that the anhydrite insoluble boundary occurs at a much lower pH than that for calcite at any given  $aCa^{2+}$ . In fact, according to our calculations, calcite could only form at pH values above 5, assuming a maximum  $aCa^{2+}$  value of 0.1, and that our estimate of total C = 0.1 molal is correct. Thus, calcite should only form in the potassic zone. In contrast, calcite has been observed in phyllic alteration at Sungun, where it is invariably intergrown with anhydrite. Judging from Figure 9, this texture is best explained as a late replacement phenomenon, in which cooler fluids of possible meteoric origin partially converted the anhydrite to calcite.

Isothermal  $fS_2$ - $fO_2$  (Figure 10) and  $fO_2$ -pH (Fig. 11) diagrams were also drawn for 450 °C and 500 bars, which are the conditions estimated for most of the molybdenite (Type I) mineralization and associated potassic alteration at Sungun. The muscovite-Kfeldspar and muscovite-andalusite boundaries occur at pH values of 5.86 and 5.05, respectively. It should also be noted that magnetite may coexist with hydrothermal biotite at high temperatures (450 °C and higher), whereas at 360 °C and lower temperature hydrothermal biotite lies in the stability field of hematite (compare Figures 8 and 9). This is consistent with the observation that magnetite is much more abundant in Type I mineralization than in Types II and III, the latter containing hematite instead of magnetite.

Figure 12 illustrates the mineral stability fields for early potassic and later phyllic alteration on log  $(aK^+/aH^+)$  versus log  $(aNa^+/aH^+)$  diagrams. As fluids migrate away from an intrusive heat source and down a thermal gradient, the stability field of K-feldspar expands at the expense of albite, which is reflected by potassic alteration of wall-rock (Fig. 12a). The reverse reaction is operative when fluids migrate toward a heat

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**Figure 10.** Log  $fO_2$ -log  $fS_2$  diagram characterizing Type I mineralization and associated alteration (potassic), showing the stability field of ore, silicate and oxide minerals at 450 °C and 500 bars. The mineral stabilities were calculated in the systems Cu-Fe-S-O and K-Al-Si-O-H, with ionic strength = 1, m Ca<sup>+2</sup> = 0.1 to 0.01,  $aK^+$  = 0.004 and  $aS = 10^{-1}$  Activities were estimated from speciation calculations using compositional data observed from fluid inclusions. Phase boundaries predominance fields and stabilities of mineral aqueous species were calculated as described in Figure 8. Point "S" represents the Sungun conditions for type I mineralization based on observed mineral paragenesis.



**Figure 11.** Log  $fO_2$ -pH diagram showing the approximate condition (dark shaded area) of the Group I Mo-quartz veins, relative to mineral stabilities in the systems Cu-Fe-S-O and K-Al-Si-O-H, and anhydrite at 450 °C, 500 bars, ionic strength = 1,  $m \text{ Ca}^{+2} = 0.1$  to 0.01,  $aK^+ = 0.004$  and  $aS = 10^{-1}$ . Activities were estimated from speciation calculations using compositional data observed from fluid inclusions. Phase boundaries, predominance fields and stabilities of mineral aqueous species were calculated as described in Figure 8. Point "S1" represents the Sungun conditions for type I mineralization based on observed mineral paragenesis.



**Figure 12.** Log  $aK^+/aH^+$  versus Log  $aNa^+/aH^+$ diagram showing the thermal paths and stability relationships of minerals in the system K-Al-Si-OH, at different stages in the Sungun hydrothermal system. Diagram (a) is drawn for 380-450 °C and 500 bars. As fluids migrate away from the intrusive heat source and down a thermal gradient (solution retrograde), the Log  $aK^+/aH^+$  ratio increases, whereas the Log  $aNa^+/aH^+$  decreases. This expands the stability field of K-feldspar at the expense of albite, which is reflected by potassic alteration of wall rock. The reverse reaction is operative when the fluid migrates toward the heat source and up a thermal gradient (solution prograde). The albite stability field expands at the expense of K-feldspar. Diagram (b), illustrates the sericitic (phyllic) alteration which overprints the early-stage potassic alteration. Conditions are 240-400 °C, and 500 bars. Under solution retrograde conditions, the muscovite stability field expands at the expense of both K-feldspar and albite.



source, and the albite stability field expands at the expense of K-feldspar. Later phyllic alteration is superimposed on the early-stage potassic alteration by a continued decrease in temperature. In this case, the muscovite field of stability expands at the expense of both K-feldspar and albite.

#### **COPPER SOLUBILITY AND CHALCOPYRITE DEPOSITION**

Although there have been many detailed studies of the mineralogy, paragenesis and fluid evolution of porphyry copper deposits, few have attempted to quantify processes attending copper transport and deposition. Two notable exceptions are the studies of Brimhall (1980) and Crerar and Barnes (1976). Brimhall (1980) examined the chemical evolution of ore-forming fluids at Butte, Montana by constructing equilibrium diagrams based on the thermodynamic data base of Helgeson and coworkers (Brimhall, and Ghiorso 1983; Brimhall, 1980). However, Brimhall's calculations did not take into account the effect of complexation of copper with chloride ions. Crerar and Barnes (1976) measured the solubility of various copper-bearing mineral assemblages in chloride solutions to 350 °C, and applied these results to the formation of porphyry copper deposits. They concluded that chloride complexes of copper were of major importance in the formation of these ore deposits, and that CuCl(aq) was the dominant form of aqueous copper above 300 °C. However, subsequent work by Russian scientists (Var'yash and Rekharskiy, 1981; Var'yash, 1991; Zotov et al., 1995), as well as recent experimental work in our own laboratory at McGill University, (Gammons et al., 1996; Xiao et al., in prep.), indicates that  $CuCl_2$  is the dominant copper complex under the conditions of interest.

We have re-evaluated the solubility of copper in porphyry ore fluids, using as guides the physico-chemical conditions for ore formation at Sungun outlined above;  $aCI^{-1}$  (1.04 m) was estimated from speciation calculations using the computer program EQBRM and data from fluid inclusions (see earlier discussion). The results are summarized in Figure 13. The mineral solubility contours in this figure are based on the thermodynamic data of Zotov et al. (1995) for the following reaction:

$$Cu(s) + 2Cl' + H^{+} + \frac{1}{4O_2} = CuCl_2 + \frac{1}{2H_2O(l)}$$
(1)

Because native copper is absent in hypogene porphyry copper deposits, it is desirable to recast reaction (1) in terms of chalcopyrite. This is accomplished by adding the following reaction:

$$CuFeS_2(s) = Cu(s) + FeS_2(s)$$
(2)

to obtain:

$$CuFeS_{2}(s) + 2Cl' + H^{+} + \frac{1}{4}O_{2} = CuCl_{2}' + FeS_{2}(s) + \frac{1}{2}H_{2}O(l)$$
(3)

Thermodynamic data for reaction (2) were taken from SUPCRT92 (Johnson et al., 1992). The calculated value of log K<sub>3</sub> at 360 °C, and 500 bars is +9.20 (see Table 6 for logK<sub>1</sub>, logK<sub>2</sub> and logK<sub>3</sub>). One convenient feature of reaction (3) is that it is independent of the concentrations of aqueous sulphur and iron. However, this is no longer the case once

**Figure 13.** Log  $fO_2$ -pH diagram showing Cu solubility contours for Group II mineralized quartz veins at 360 °C (see text for details). Phase boundaries, predominance fields and stabilities of mineral aqueous species were calculated as described in Figure 8. The value of  $aCI^{-}$  (1.04 m) was estimated from speciation calculations using the computer program EQBRM and data from fluid inclusions. See text for more details.



mineral phase boundaries are crossed. For example, in the bornite + pyrite field, reaction(3) is rewritten:

$$Cu_{5}FeS_{4}(s) + 10Cl^{-} + 5H^{+} + 1/4O_{2}(g) =$$

$$5CuCl_{2}^{-} + FeS_{2}(s) + 2H_{2}S(aq) + 1/2H_{2}O(l) \qquad (4)$$

which is dependent on H<sub>2</sub>S concentration. The inflections in slope of the solubility contours shown in Figure 13 have been calculated from the stoichiometry of the relevant reactions. For example, for reaction (4),  $d{O_2}/d{pH} = +20$ .

As is evident from reaction (3), copper solubility for the assemblage pyrite + chalcopyrite is highest at conditions of high  $fO_2$ , low pH and high chloride concentration. The range in these physico-chemical conditions for the Sungun deposit has been determined previously (shaded regions of Figure 13). Within this range, copper solubility varies over several orders of magnitude, from almost 1,000 to less than 1 ppm. The former value is close to the estimated copper content of the initial fluid at Sungun (1200 to 3800 ppm, Type I fluid inclusions), based on SEM/EDS analyses of fluid inclusion decrepitates and the volume of chalcopyrite daughter minerals (see Chapter III). As shown in Figure 13, copper solubility decreases rapidly with increase in pH. Such an increase could occur, for example, during mixing of acidic magmatic waters with heated meteoric waters of lower salinity and near-neutral pH. Mixing would also serve to dilute the aqueous phase with respect to Cl<sup>-</sup> ion, further augmenting the precipitation of chalcopyrite. A sudden increase in pH could also result from boiling, due to the partitioning of acidic components (e.g., HCl, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S) into vapour during phase

Table 6. Log k Values Used to Calculate the Chalcopyrite Solubility Diagram																		
Reactions	_	Pressure = 500 (bars)																
	No.	T °C	300	310	320	330	340	350	360	370	380	390	400	410	420	430	440	450
$CuFeS_{2(0)} = Cu_{(0)} + FeS_{2(0)}$	1	Log K <sub>1</sub>	-3.672	-3.656	-3.640	-3.625	-3.611	-3.598	-3.585	-3.573	-3.561	-3,550	-3.540	•3.530	-3.520	-3.511	-3.503	-3.495
$Cu_{(s)} + 2CI_{(s_1)} + 0.25 O_{2(s)} + H^* = CuCI_{2(s_2)}^2 + 0.5 H_2O_{(l)}$	2	Log K <sub>1</sub>	12.47	12.49	12.53	12,57	12.62	12.70	12.77	12.87	13.00	13.15	13.35	13.56	13.81	14.11	14.46	14.86
CuFeS <sub>2 (1)</sub> + 2Cl <sup>*</sup> <sub>(a1)</sub> + 0.25 O <sub>2 (2)</sub> + H <sup>+</sup> = CuCl2- (aq)+ FeS2 (s)+ 0.5 H2O (1)	3	Log K <sub>3</sub>	8,80	8.84	8.89	8.95	9.01	9.10	9.19	9.30	9.44	9.60	9.81	10.03	10.29	10.60	10.95	11.37
$KAI_{3}Si_{3}O_{10}(OH)_{2} + 2K^{+} + 6SiO_{2} = 3KAISi_{3}O_{2} + 2H^{+}$	4	Log K <sub>4</sub> pH	•7.58 5.79	-7.53 5.76	-7.48 5.74	-7.43 5.71	-7.37 5.69	-7.32 5.66	-7.30 5.65	-7.26 5.63	-7.21 5.61	-7.17 5.59	-7.13 5.57	-7.09 5.55	-7.05 5.53	-7.01 5.51	-6.98 5.49	•6.93 5.47
$3Fe_2O_3 = 2Fe_3O_4 + 0.5 O_2(a)$		Log K <sub>5</sub> fO <sub>2</sub>	-15.5 -31.00	-15.11 -30.23	-14.74 -29.48	-14.38 •28.76	•14.03 •28.06	•13.69 •27.39	-13.37 -26.73	-13.05 -26.10	-12.74 -25.48	-12.44 -24.88	•12.15 •24.30	-11.87 -23.74	•11.59 •23,19	-11.33 -22.65	•11.066 •22.13	-10.81 -21.63
		CuCl'2 (ppm)	1	2	4	7	13	25	45	89	183	395	931	2229	5908	17033	53963	196038

K1, K4 and K3 values from SUPCRT92, K2 values from Zotov et al., 1995, K3 = K1 + K2

separation (Drummond and Ohmoto, 1985). Both these processes, boiling and fluid mixing, are inferred to have been important in the genesis of the Sungun deposit, based on fluid inclusion and ore petrology constraints (see Chapter III).

As discussed earlier, there was a transition from early molybdenite precipitation to later copper deposition, which could imply that decreasing temperature was an important control of mineralization. The temperature dependence of copper solubility for a solution with  $aCI^{-} = 1$  m (at 360 °C  $aCI^{-}$  is estimated to have been 1.04 m, see earlier discussion) and P = 500 bars is shown in Figure 14. The calculations are based on equation 3, and therefore assume equilibrium between chalcopyrite and pyrite. Oxygen fugacity was fixed by coexistence of magnetite and hematite, both of which are present in hypogene alteration/mineralization at Sungun. The pH was calculated assuming coexistence of muscovite, K-feldspar and quartz, with  $aK^+$  set to 0.01 (see preceding discussion). Thermodynamic data for copper solubility were taken from Zotov et al. (1995), and all other reactions from SUPCRT92 (Johnson et al., 1992, Table 6).

Figure 14 indicates that chalcopyrite solubility under the pH and  $fO_2$  conditions at Sungun is strongly dependent on temperature, decreasing from a high of > 100,000 ppm at 450 °C, to a low of ~1 ppm at 300 °C. Estimates of the copper content of the early ore fluids that formed the Sungun deposit range from 0.02 to 0.06 molal, which corresponds to 1200 to 3800 ppm (Chapter III). Comparing these data with Figure 14 indicates that ore fluids at Sungun would have been highly undersaturated with chalcopyrite at the onset of hydrothermal activity. If mineral deposition was due simply to a temperature decrease, saturation would have occurred at about 400 °C. This agrees well with the observation that veins formed at T >400 °C contain molybdenite but rarely chalcopyrite, whereas the

Figure 14. Solubility of chalcopyrite as a function of temperature at  $aCI^{-} = 1$  m (see text for details of calculations). Note that chalcopyrite solubility under the Sungun conditions is very strongly dependent on temperature, decreasing from >100,000 ppm at 450 °C, to ~1 ppm at 300 °C.



bulk of chalcopyrite deposition at Sungun occurred in Group II veins between approximately 300 and 380 °C (Chapter III).

#### DISCUSSION

In a previous paper (Chapter III), we proposed a model in which orthomagmatic, copper-rich fluids evolved during cooling and crystallization of the Sungun parental magma (a high K andesitic liquid with a composition similar to continental arc calcalkaline magmas). The presence of biotite and hornblende on the liquidus from the monzonite/quartz-monzonite to diorite/granodiorite stages of intrusion suggests that the magma initially contained >3 wt. % H<sub>2</sub>O, and therefore almost certainly saturated with water soon after emplacement (Whitney, 1989; Burnham, 1979). Resorbed phenocrysts of quartz are best explained by rapid changes in fluid pressures accompanying second boiling and subsequent brecciation and stockwork development (Whitney, 1989). The fluid inclusion study of Hezarkhani and Williams-Jones (see Chapter III) also documented the presence of Cu-rich hypersaline fluid inclusions in early and main-stage Cu-(Mo) mineralization. In addition, the distribution and style of alteration at Sungun is typical of porphyry Cu deposits in calc-alkaline volcano-plutonic arcs. Thus, there is little doubt that magmatic/hydrothermal processes played a very important role in the origin of the Sungun deposit.

One of the main objectives of this study was to try to define in some detail the physico-chemical conditions attending mineralization at Sungun (see preceding section). A second objective was to try to combine these thermodynamic constraints with the

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results of the fluid inclusion study of Hezarkhani and Williams-Jones (see Chapter III) to build a chemical model describing the process of ore deposition. This proved a much more difficult task, largely because the inherent complexity of porphyry Cu systems can lead to non-unique solutions. For example, our analysis of chalcopyrite solubility (see reaction 3) indicates that this mineral could have deposited in response to: (1) a decrease in  $fO_2$ ; (2) an increase in pH; (3) a decrease in temperature; and (4) a decrease in chloride concentration. To determine which of these processes was most responsible, it is necessary to re-evaluate all of the fluid inclusion, thermodynamic and paragenetic evidence.

The first process, reduction, can probably be ruled out. There is little evidence for significant redox reactions in the mineral assemblages at Sungun. If anything, the transition in the dominant Fe-oxide from magnetite at high temperature to hermatite at low temperature suggests an increase in relative oxidation state with reaction progress.

The second process, pH increase, could have been important during fluid boiling and resultant potassic alteration. However, we have demonstrated that at the inferred temperature of potassic alteration at Sungun, the ore fluids were probably highly undersaturated with respect to chalcopyrite, or any other copper mineral for that matter. Moreover, we have shown that most of the main-stage mineralization at Sungun appears to be associated with phyllic, rather than potassic alteration. Thus, although boiling may have played an important role as a means of generating a highly saline, copper-rich brine, little copper deposition appears to have taken place in response to pH changes induced by this initial boiling.

In contrast, the third process, temperature decrease, almost certainly played an important role. A significant drop in temperature occurred between early potassic alteration (~ 450 °C) and later phyllic alteration and main-stage Cu mineralization (~ 360 °C). This fact, combined with our thermodynamic analysis of chalcopyrite solubility, suggests that deposition of copper was delayed until the metal-rich brine had cooled several hundred degrees below the temperature at which it exited the parent magma. Cooling may also indirectly have served to lower the acidity of the ore fluid. Although the boiled brine was in equilibrium with K-feldspar and hydrothermal biotite at high temperature, a decrease in temperature would eventually have placed the fluid composition in the stability field of muscovite (Fig. 12 ... see also Burnham, 1981; and Burnham and Ohmoto, 1980). Because the conversion of feldspar to muscovite consumes protons, the acidity of the brine would have tended to decrease with cooling, provided that the system remained rock-buffered. Any increase in pH would have served to reinforce the drop in solubility due to cooling alone.

Cooling may also have played an important role as a means of increasing the  $H_2S$  content of the ore fluid via hydrolysis (disproportionation) of magmatic SO<sub>2</sub>. The reaction in question can be written:

$$4SO_{2}(g) + 4H_{2}O(l) = H_{2}S(aq) + 3H_{2}SO_{4}(aq)$$
(5)

Theoretical studies (e.g., Burnham, 1979) have shown that this reaction proceeds from left to right with decrease in temperature, especially below 400 °C. The aqueous sulfide produced could then combine with dissolved copper and iron to precipitate chalcopyrite:

$$CuCl_2$$
 + FeCl<sub>2</sub>(aq) + 2H<sub>2</sub>S + 1/4O<sub>2</sub> = CuFeS<sub>2</sub> + 4Cl<sup>-</sup> + 3H<sup>+</sup> + 1/2H<sub>2</sub>O (6)

However, it should be noted that the production of  $H^+$  by dissociation of sulfuric acid in reaction (5) could largely outweigh the effect of increasing H<sub>2</sub>S concentration on chalcopyrite solubility according to reaction (6), especially if the immediate wallrocks have no pH-buffering capacity (e.g., all feldspar already converted to muscovite). For this reason, hydrolysis of SO<sub>2</sub> could actually lead to the dissolution of chalcopyrite, rather than its precipitation.

The final mechanism, decrease in Cl concentration, is also of potential importance. The fluid inclusion study of Hezarkhani and Williams-Jones (see Chapter III), presented evidence that significant mixing did indeed occur between hypersaline brines of magmatic origin and lower salinity fluids of presumed meteoric origin. Any such mixing would decrease the Cl concentration of the metal-carrying fluid, thus destabilizing the CuCl<sub>2</sub><sup>-</sup> complex and depositing chalcopyrite. If the meteoric water was cooler than the magmatic water, mixing would also have resulted in a temperature decrease, further promoting metal deposition, as discussed above. Although no H stable isotope data was collected in this study, previous studies have indicated a major involvement of circulating meteoric fluids in the origin of other porphyry Cu deposits (references). In fact, Brimhall (1980) argued that circulating meteoric fluids could play a key role by remobilizing copper "protore" and increasing the grade of an otherwise subeconomic deposit to something similar to Butte, Montana. However, although this model is compelling for Butte, it does not appear to be satisfactory for Sungun. It is clear

from our previous fluid inclusion study that, although low salinity fluids were involved in the mineralization process, the bulk of the copper was introduced and deposited from hypersaline brines.

#### CONCLUSIONS

The following conclusions can be drown from our study of the Sungun porphyry copper deposit:

1) The main stage of Cu mineralization at Sungun occurred in Group II and III veins, and occurred as a result of the precipitation of chalcopyrite from high salinity aqueous fluids (~55 wt % NaCl equivalent) in the temperature range 300 °C to 380 °C (with a mode of 360 °C).

2) Group I Mo-rich veins formed at higher temperatures (>400 °C) from similarly derived orthomagmatic fluids, prior to the cooling that led to chalcopyrite saturation.

3) Thermodynamic modeling of the stability fields for alteration and mineralization phases support the interpretation that Cu deposition occurred at a temperature of <400 °C.

4) Cu solubilities established for the assemblage chalcopyrite-pyrite are highest at conditions of high  $fO_2$ , low pH and high chloride concentration. At Sungun, fluid conditions varied from >400 °C, initially to ~300 °C; corresponding copper saturation varied from ~1000 to less than 1 ppm. Solubility decreases rapidly with increasing pH, and mixing of acidic magmatic waters with heated meteoric waters of lower salinity and near-neutral pH could have caused chalcopyrite deposition. A sudden increase in pH

could also result from boiling. Both processes, may have been important in the genesis of the Sungun deposit.

5) Chalcopyrite solubility at  $aC\Gamma = 1$  m and 500 bars is strongly dependent on temperature, decreasing from >100,000 ppm at 450 °C, to ~1 ppm at 300 °C (the copper content in the initial Sungun ore fluids was 1200 to 3800 ppm). Ore fluids at Sungun were initially undersaturated with chalcopyrite, and saturation occurred at about 400 °C. This agrees well with the observation that Group I veins which formed at T >400 °C contain molybdenite but rarely chalcopyrite, whereas the bulk of the chalcopyrite deposition at Sungun occurred in Group II veins between approximately 300 and 380 °C.

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# **CHAPTER VI**

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## **CHAPTER VI**

### **GENERAL CONCLUSIONS**

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#### CONCLUSIONS

The Sungun porphyry copper deposit is hosted by a diorite/granodiorite to monzonite/quartz-monzonite stock, which intruded Eocene volcanosedimentary and Cretaceous carbonate rocks to a paleodepth of <2000 metres in Northwestern Iran. Bulk chemical analyses of least altered intrusive rocks classified the corresponding magma as being syncollisional, medium to high K, calc-alkaline and generated in a continental arc setting. The multiple intrusions of diorite/granodiorite to monzonite/quartz-monzonite indicate a long-lived intrusive episode associated with repeated fracturing and hydrothermal activity. The presence of hydrous minerals like hornblende in the freshest diorite/granodiorite indicate that the corresponding magma initially contained >3 wt percent H<sub>2</sub>O. This high water content coupled with the shallow emplacement of the magma, led to its saturation with water and the exsolution of fluids at an early stage of crystallization (which is characterized by the replacement of early hornblende with biotite), and subsequently Mo and then Cu mineralization in the stock (see Chapters II, IV and V).

The degree of fractionation was estimated using a Rayleigh fractionation equation which related the concentrations of Zr, Nb and Y in the least altered sample to their concentrations in progressively more evolved samples. The results of these calculations indicate that the compositions of the various rock types can be explained by up to 24 % fractionation of a diorite/granodiorite magma to produce a more evolved monzonite/quartzmonzonite suite.

Mineralogical, fluid inclusion and isotopic analyses from the deposit indicate that hydrothermal activity involved three distinct fluids. The first hydrothermal fluid caused

potassic alteration and Cu-Mo mineralization. This fluid was characterized by generally high temperatures and moderate to high salinities, and was magmatically derived. It was responsible for the wide distribution of Group I and II mineralized quartz veins, at temperatures ranging from 360 ° to >500 °C, and boiled episodically. The data from oxygen and sulfur isotope analyses suggest a magmatic source for the hydrothermal mineralization in those veins. The second hydrothermal fluid (Fluid II) is of mixed origin, representing the mixing of magmatic fluid, at moderate to low temperatures (up to 420 °C). with a predominantly, meteoric fluid (Fluid III). This fluid boiled extensively and was responsible for transition and phyllic alteration zones (phyllic), and also partly Cu remobilization/ deposition (see below) in the deeper and shallower parts, of the stock respectively. The third hydrothermal fluid (Fluid III) consisted of low temperature, low to moderate salinity (1 to 9 wt % NaCl equiv.) and oxidized meteoric water, which was responsible for peripheral propylitic alteration in a zone outside the core of potassically altered rock, and possibly argillic alteration when it was allowed to penetrate into the core. The later hydrothermal evolution was controlled by the incursion of dilute meteoric fluids into the permeable stockwork system (source of Fluid II). This addition of external fluids increased Na/K ratios in the progressively heated fluids, and caused the remobilization of previously precipitated copper sulfides through acidification and oxidation, and their redeposition in highly fractured zones. This is evident from the occurrence of chalcopyrite as overgrowths on earlier grains of chalcopyrite.

During magmatic evolution, Cu behaved as an incompatible element, i.e., it did not enter the crystal structure of mafic phases. At a late stage of magma evolution, a sharp drop in the pressure, due to shallow emplacement (2000 m) caused a fluid (fluid *I*) phase to

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separate. This fluid was initially in equilibrium with magmatic phases like quartz and two alkali-feldspars, and copper partitioned into it as a chloride complex. Subsequent interaction of this fluid with the host rocks caused potassic alteration and Mo-Cu mineralization. The second, lower temperature fluid (fluid *II*) produced phyllic alteration at lower temperature (with a mode of 360 °C) and was responsible for partial remobilization and deposition of Cu in the upper part of the stock, and in Group II and III quartz veins. During the various alteration episodes, elements like Na, K, Mg, Mn and Ca were mobile.

Calculations of gains and losses of components showed that during potassic alteration K was added at the expense of Na and Ca. Magnesium and iron were also depleted and, predictably, copper was enriched. In the transition zone, Ca was added and K and Cu depleted. During phyllic alteration the most important changes were addition of Si and Cu, the latter having been remobilized from the transition zone, and depletions of Na, K . and Fe.

Based on the thermochemical conditions evaluated from fluid inclusion and alteration studies, and from calculations using the SUPCRT92 thermodynamic data base (Johnson et al., 1992) and the data of Zotov et al., (1995), we were able to re-evaluate the solubility of Cu in the Sungun ore fluid as a function of T,  $fO_2$  and pH. At 450 °C, the  $fO_2$  was between -20 and -23, and the pH between 5.5 and 6.5, and at 360 °C the corresponding values were -31 to -27, and 4 to 8, respectively. Copper solubility for the assemblage pyrite + chalcopyrite is highest at conditions of high  $fO_2$ , low pH and high chloride concentration. Within the above range of  $fO_2$  and pH conditions, copper solubility varies over several orders of magnitude, from almost 1,000 to less than 1 ppm. It decreases rapidly with increases in pH. The pH increased during mixing of acidic magmatic waters

with heated meteoric waters of lower salinity and near-neutral pH. Mixing may also have served to dilute the aqueous phase with respect to Cl<sup>-</sup> ions, further augmenting the precipitation of chalcopyrite. A sudden increase in pH could also have resulted from boiling, due to the partitioning of acidic components (e.g., HCl, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S) into vapour during phase separation. Based on fluid inclusion and ore petrology constraints, both these processes, boiling and fluid mixing, are inferred to have been important in the genesis of the Sungun deposit. Chalcopyrite solubility under the pH and  $fO_2$  conditions at Sungun is most strongly dependent on temperature, decreasing from a high of > 100,000 ppm at 450 °C, to ~1 ppm at 300 °C. It is concluded that the ore fluids at Sungun were highly undersaturated with chalcopyrite at the onset of hydrothermal activity, and that saturation was due simply to a temperature decrease and occurred at about 400 °C. This agrees well with the observation that veins formed at T >400 °C contain molybdenite (not economic) but rarely chalcopyrite, whereas the bulk of chalcopyrite deposition at Sungun occurred in Group II veins between approximately 300 and 380 °C.

A schematic of representation of the alteration and related mineralization processes within the Sungun porphyry copper deposit is shown in Figure 1. During crystallization of the diorite/granodiorite to monzonite/quartz-monzonite magma, fracturing in the upper part of the system caused a drop in pressure and allowed the fluid *I* phase to separate, and also boil. This fluid was responsible for potassic alteration and the mineralization of molybdenite in the core of the intrusion and copper peripheral to the core. It also produced cupriferous skarns in the Cretaceous marls and carbonate rocks. Mixing of the magmatic fluid with meteoric fluids (which formed fluid *II*) caused transition alteration at depth and phyllic alteration at higher levels. This mixing also caused copper remobilization from the

Figure 1. (a) formation of potassic alteration within the central part of the diorite/granodiorite pluton. (b) phyllic and transition alteration zones, formed by decreasing the temperature and mixing the magmatic fluid with meteoric fluids. The overall fluid migration is in the upper part of the pluton. (c) present surface following erosion of the Lower Tertiary volcanic and volcanoclastic rocks. Note that argillic alteration occurred after erosion and is therefore of supergene origin.







potassically altered core to the phyllic alteration zone.

#### CONTRIBUTIONS TO KNOWLEDGE

The following are the most important contributions to knowledge from this thesis:

1- This is the first study to quantitatively evaluate the hydrothermal evolution and comprehensively investigate the origin and controls of mineralization in a porphyry copper deposit in the Middle East generally, and specifically in Iran.

2- This study is the first to determine the origin of the mineralizing fluid and the ore metals in an Iranian porphyry copper deposit.

3- The study suggests that porphyry copper mineralization in Iran is associated with H<sub>2</sub>O-rich diorite/granodiorite magmas that evolved by fractional crystallization from a high .
 K calc-alkaline magma produced in an arc setting.

4- The thesis presents data demonstrating that boiling commenced early in the evolution of the Sungun hydrothermal system and was particularly vigorous during phyllic alteration. This boiling caused a decrease in temperature and increases in  $fO_2$  and pH.

5- This is the first study to use modern data on Cu mineral solubility to quantitatively evaluate the conditions of chalcopyrite saturation in a porphyry system. Calculations show that decreasing temperature and increasing pH were the main controls of Cu mineralization.

6- The thesis presents a model which satisfactorily explains the origin of the Sungun porphyry copper deposit. This model calls for the emplacement of a watersaturated dioritic/granodioritic magma at high crustal levels, exsolution of orthomagmatic chloride-rich brines from the magma, partitioning of Cu into these brines as chloride complexes, and deposition of chalcopyrite as a result of decreasing temperature and increasing pH in response to boiling and mixing with meteoric fluids.

#### **RECOMMENDATIONS FOR FUTURE WORK**

This study has characterized the evolution of a representative porphyry copper type deposit in the Middle-East, but was limited by analytical methods and a lack of key thermodynamic data. For example, we depended on microthermometric analyses of fluid inclusions, and SEM-EDS analyses on the decrepitated residues, combined with mineral chemistry, to characterize the chemical composition of the ore-forming fluid. This approach has very large associated errors. We need to be able to analyze the composition of the ore-forming fluids directly to reliabley, constrain the physicochemical conditions. Newly available techniques for the analysis of individual fluid inclusions, e.g., laser ablation ICP-MS, synchrotron X-ray fluorescence or PIXE (Proton Induced X-ray Emission) and PIGE (Proton Induced y-ray Emission), could provide valuable additional quantitative information on the chemistry of the fluids and thus help to better understand the processes responsible for alteration and copper mineralization in the Sungun deposit and porphyry copper deposits generally. Experimental data on fluid-melt, mineral-melt and fluid-mineral partitioning of copper would greatly aid future modeling of these systems, as would improved data on the speciation of the metals in the aqueous phase. The latter is particularly true for Mo.

Only one porphyry system has been investigated in the Sahand-Bazman belt at the level of detail required to quantitatively model porphyry Cu metallogenesis; others (i.e., Sar-Cheshmeh, Meidok and Shahre-Babak) which are part of the same metallogenic event, should be investigated to further characterize this style of mineralization. Basic documentation of the other deposits is required and in the case of Sar-Cheshmeh detailed-fluid inclusion and alteration studies are necessary to permit comparison with Sungun. In order to understand the metallogeny of the belt, more studies are needed to better understand the tectonics and igneous petrology.

Skarn-related alteration and mineralization in the Sungun area has been investigated using petrography and mineral chemistry (not presented in this thesis). Unfortunately, fluid inclusions which provide an important source of data for reconstructing fluid evolution were absent in the samples available from Sungun. It is recommended that further sampling of the skarn be undertaken with the purpose of finding material suitable for a fluid inclusion study. Armed with such data, it might be possible to relate the changing skarn mineralogy to changes in the porphyry system, and in turn, develop a better understanding of the metallogeny of the entire porphyry-skarn system.

The upper parts of porphyry copper deposits (which could contain epithermal gold mineralization) have been eroded in the cases of most well-known porphyry copper deposits in other parts of the world, and consequently it is rarely possible to investigate the relationship between epithermal precious metal and deeper porphyry copper mineralization. In Iran, where the tops of several of these systems have been preserved, there is an excellent opportunity to determine the links between these two environments. We recommend

strongly that the Shahre-Babak and Meidok deposits, which contain the "tops and bottoms"

of porphyry systems be investigated with this purpose in mind.

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Zotov A. V., Kudrin A. V., Levin K. A., Shikina N. D. and Var'yash L. N. (1995), Experimental studies of the solubility and complexing of selected ore elements (Au, Ag, Cu, Mo, As, Sb, Hg) in aqueous solutions. *In* (K.I. Shmulovich, B. W. D. Yardley, and G. G. Gonchar, eds.) Fluids in the Crust: Equilibrium and Transport Properties. Chapman & Hall, 323pp.

## WHOLE-ROCK GEOCHEMICAL DATA FROM SUNGUN

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M;	Major (wt %) and Trace Element (ppm) Analyses of Representative Fresh and Altered Rocks from the Sungun Porphyry Copper Deposit Granodiorite														
							Grano	diorite							
Sample r	58-140	58-146	58-71	30-149	30-138	70-141	34-282	70-175	30-168	21-32	26-277	44-345	44-371	44-409	44-429
Туре	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	<u> </u>	<u> </u>	<u> </u>	K	K	<u> </u>	<u> </u>
SiO <sub>2</sub>	54.15	49.21	56.04	60.53	60.54	59.02	61.68	58.84	61.89	57.76	64,8	64.12	65.92	59.07	62.92
TiO <sub>2</sub>	0.8	0.83	0.73	0.57	0.58	0.59	0.57	0.62	0.58	0.47	0,68	0.48	0.49	0,58	0.56
$Al_2O_3$	16.31	16.78	16.41	15.88	15.96	15.74	16.02	16.12	15.89	14.42	16.45	15.57	15.56	15.43	15.85
Fe <sub>2</sub> O <sub>2</sub> <sup>1</sup>	6.93	7.2	6.34	4.94	4.91	5.1	4.94	5.51	3.52	5.04	1.27	2.12	1.71	4.07	1.7
MnO	0.13	0.13	0.12	0.1	0.1	0.09	0.09	0.11	0.08	0.07	0.03	0.04	0.01	0.09	0.03
MgO	4.25	4.28	3.73	2.56	2.61	2.59	2.52	3.52	2.06	2.27	1.13	1.43	1.35	2.32	1.67
CaO	6.28	7	6.39	4.98	4.66	5.06	4.64	5.11	4.38	3.77	2.04	2,35	1.85	4.46	2,98
Na <sub>2</sub> O	3.83	3.32	3.55	4.04	3.96	3.57	3,85	4.14	1.03	1.71	0.23	1.87	0.98	3.38	0.21
K₂Ō	2.44	3.7	2.32	2.48	2.63	2.12	2,58	2.38	3.76	6.28	6.32	5.95	6.94	2.87	5.71
P2O5	0.24	0.25	0.23	0.24	0.24	0.25	0.24	0.23	0.25	0.25	0.35	0.26	0.26	0.24	0.3
L.O.I.	5.53	7.85	4.71	4.14	4.37	6.16	3.63	3.92	6.54	5.38	5.07	3.47	3,56	7.76	6.66
Total	100,99	100.72	100.67	100.56	100.56	100.43	100.9	100.65	99.98	98.06	99.66	99.33	99.74	100.37	99.35
Ba	748	1138	684	835	833	787	944	857	175	2044	1305	1059	1629	558	1216
Cc	64	57	61	80	53	59	58	51	87	192	110	130	67	48	132
Co	13	25	24	21	12	15	19	14	10	16	13	19	24	20	18
$Cr_2O_3$	56	61	57	49	56	47	64	131	48	44	123	52	55	47	76
Cu	98	56	81	98	64	201	224	127	50	3327	9080	13050	7845	196	5160
Ni	49	50	42	22	27	29	25	41	29	35	17	15	26	23	40
Sc	23	26	26	18	19	19	16	27	14	11	5	6	2	11	4
V	154	154	141	85	95	98	99	110	84	61	87	66	59	89	79
Zn	59	60	58	53	50	55	52	49	50	640	1640	2353	1420	122	962
Ga	18	17	18	17	17	17	17	17	17	17	12	14	13	16	16
Nb	7	13	5	10	9	13	10	9	16	17	18	19	18	11	20
Pb	14	24	17	16	14	11	13	12	13	21	13	28	9	11	11
Rb	49	89	50	58	64	56	56	52	98	118	100	118	125	81	112
Sr	785	461	1334	699	664	210	715	673	283	418	633	1035	849	326	951
Th	8	1	10	9	9	7	10	8	11	22	11	21	17	2	20
U	0	2	0	0	0	0	0	0	0	D/L	D/L	D/L	D/L	D/L	D/L
Y	22	19	20	18	18	19	17	19	16	18	12	8	9	15	11
Zr	111	115	96	104	99	115	105	103	119	116	168	118	130	105	120

<sup>1</sup>Total Fe as  $Fe_2O_3$ , D/L = Below detection limit,

Frs = Fresh, K = Potassic alteration zone, Trn = transition alteration zone, Phc = Phyllic alteration zone, Arg = argillic alteration zone, L.O.I = Loss on ignition, \* = Rock analyses from Mehrpartou, 1993

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							<u>(Con</u>	<u>'d)</u>							
<u></u>							Granod	iorite	<u> </u>						
Sample no.	25-122	29-195	25-517	34-163	25-453	7-150.6	25-522	30-200	25-239	25-275	33-281	26-237	25-371	26-239	25-134
Туре	Tm	K	К	<u>K</u>	K	<u> </u>	Тп	Tm	Phc	Phc	Phc	Phc	Phc	Phc	Arg
SiO <sub>2</sub>	61.66	64.47	62.94	63,31	61.51	58,88	61.98	61.66	71.09	69,09	57.25	68,80	68.01	67.38	63.71
TiO <sub>2</sub>	0.51	0.49	0.46	0.76	0.48	0.49	0.49	0,47	0.64	0.58	0.56	0.42	0.51	0.51	0,40
Al <sub>2</sub> O <sub>3</sub>	15.92	16	15.02	15.21	15.86	15.98	15,88	15.91	15.98	15,69	15.63	12,99	15.88	14.21	18.61
Fe <sub>2</sub> O <sub>2</sub> <sup>1</sup>	3.88	3.36	4.58	2.97	4.02	4.51	3.44	3.91	2.40	2.26	4.83	1.62	2.68	2.79	0.10
MnO	0.14	0.05	0.02	0.05	0.04	0.02	0.13	0.13	0.02	0.01	0.02	0.01	0.05	0.10	0.01
MgO	2.04	1.87	1.29	3.45	2.36	1.35	1.76	1.85	1.59	1.03	1.54	1.50	3.41	2.81	0.67
CaO	4.14	3.12	2,56	4.77	2.72	2.65	4.19	3.25	1,69	1.55	3.57	2,51	4.23	3,54	1.00
Na <sub>2</sub> O	3.54	4.49	2.45	4.61	3.87	2.46	3.48	3.11	0.08	2,23	1.08	0.99	0,91	1.87	0.04
K <sub>2</sub> O	3.07	4.02	4.70	4.50	4.03	4,60	3.85	3.96	4.48	4.78	4.00	4.88	3,56	3.22	4.93
P2O5	0.25	0.25	0.24	0.51	0.25	0.25	0,26	0.22	0.33	0.28	0.30	0,20	0.12	0.20	0.05
L.O.I.	5.85	2.43	4.59	3.81	2.85	5.27	5.14	5.68	2.12	3.61	7.05	4.18	2,56	3.21	6.11
Total	100.75	100.73	99.24	99.38	99.74	99.13	100.06	99.53	100.42	99,53	98.82	99.24	101.80	99.84	95,63
Ba	981	1219	1266	667	1497	1288	1203	863	485	739	1105	1264	657	853	412
Cc	81	111	78	74	123	79	93	75	81	68	75	63	74	43	43
Со	10	1	18	11	9	3	12	10	20	0	45	18	12	11	12
Cr <sub>2</sub> O <sub>3</sub>	40	83	63	269	132	63	46	83	111	40	105	80	279	26	76
Cu	36	140	2312	615	619	1826	43	87	691	872	2566	8257	715	467	12
Ni	44	36	24	91	91	33	25	43	67	14	73	84	93	47	67
Sc	13	9	15	19	15	10	15	13	11	11	10	3	12	13	14
V	74	65	61	95	71	61	70	66	106	62	80	51	18	54	63
Zn	115	25	21	42	60	29	61	62	17	6	516	1494	95	85	56
Ga NIL	1/	17	10	19	18	19	1/	18	1/	1/	18	11	39	10	17
	26	15	14	14	12	20	14	50	12	13	19	15	21	23	19
го Rh	- 30 77	76	102	61	20 74	102	08	112	103	00	111	01	61	63	23 71
Sr.	352	900	1102	206	867	365	730	430	66	60	202	91	271	560	56
Th	13	23	27	13	27	26	17	18	8	20	19	16	13	16	18
U	2	23	6	4	5	10	5	5	1	0	D/I	D/I	4	3	3
Ÿ	14	ที่	12	15	12	13	13	13	12	4	13	7	14	ทั	9
Żr	114	112	108	151	109	112	117	110	137	133	158	89	151	149	135

							<u>APPEN</u>	<u>DIX 1</u>							
							(Cor	<u>it'd)</u>						•	
<u></u>									Andesit	ic Dykes					
Sample no.	25-171	25-213	34-137	34-241	25-167	30-283	44-413	30-102	38-183	34-445	25-395	30-227	25-394	38-167	81-509
Туре	Arg	Arg	Arg	Arg	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs
SiO <sub>2</sub>	64.89	70,48	68.18	71.12	56.61	58.25	58.71	58.01	57.71	59.91	58.36	56.71	57.81	56.24	61.42
TiO <sub>2</sub>	0.52	0.42	0.64	0,50	0.68	0.66	0.65	0.65	0.65	0.71	0.71	0.72	0.69	0.77	0.7
Al <sub>2</sub> O <sub>3</sub>	19.30	18.31	17.54	16.53	15.51	15.98	15.79	15.91	15.49	16,11	16.11	15.59	15.99	17.19	16.6
Fe-O-1	4 32	4 20	3.11	2.98	5.41	5.69	5.67	5.77	6.01	6.01	5.89	5.39	5.89	5.83	5.71
MnO	0.02	0.19	0.01	0.01	0.08	0.09	0.08	0.08	0.09	0.09	0.09	0.1	0.1	0.13	0.08
MgO	1.12	0.31	1.12	0.73	2.67	3.7	3.8	3.8	3.31	4.01	4.23	2.59	4.22	3.99	2.83
CaO	0.43	0.67	0.51	0,12	6.97	6.21	5.71	6.01	5,42	5.41	5,65	6.98	5.64	5,91	2.79
NanO	4.21	0.17	0.11	1.00	3.12	3.51	3,51	3.52	3.4	4.01	4	3.11	3,99	3.68	4.31
- K₁O	1.21	0.10	4.21	1.53	2.1	2.3	2.3	2.41	2.52	2.39	2.35	2.07	2.32	4.7	1.02
P2O5	0.32	0.30	0.08	0.17	0.28	0.26	0.27	0.25	0.26	0.25	0.26	0.25	0.25	0,27	0.26
L.O.I.	4.37	5.23	4.10	6.10	5.53	4.23	3.57	3.67	5.67	1.54	3.25	5.91	3.21	2.13	3.74
Total	100.71	100.38	99.61	100.79	98.96	100.88	100.06	100.08	100.53	100.44	100.9	99.42	100.11	100.84	99,46
Ba	532	894	971	647	1241	708	710	681	840	701	733	1298	731	1922	721
Ce	51	43	121	64	23	34	41	34	63	22	23	35	31	45	29
Со	11	10	18	13	1	3	1	7	2	1	4	3	5	0	0
$Cr_2O_3$	68	101	78	54	81	104	79	101	105	79	102	83	101	61	83
Cu	84	451	59	84	33	41	41	44	41	39	32	55	41	30	131
Ni	34	71	13	26	51	45	37	41	33	44	43	39	51	24	27
Sc	15	18	21	3	1	1	2	1	1	1	2	2	4	110	1
V	68	89	19	132	114	119	91	117	108	140	139	109	140	113	130
Zn	02	/8	90	45	10	33 10 5	52	35	29	55 14	05	00	05	9/	98
Ga	10	10	18	10	10	10,5	12,1	11.1	1/	14	15	10	15	10	10
ND DL	12	20	14	12	12	12	10	12	11	10	11	13	11	11	12
PO Dh	45	11	10	100	24 61	15	10	10	13	20 50	59	51	13	1/1	41 60
K() S-	20 71	04 175	20	08	1521	1080	01 947	49	601	940 940	250	1520	20 791	520	601
SI Th	14	140	ענ רג	20 22	21	1709	047 147	107	10	047	139	1550	12	J47 11	16
11	7	3	22	8	D/I	D/I	D/I	D/I		D/I	, D/I	D/I	D/I	D/L	10
Ÿ	, 9	6	ñ	12	15	16.5	18.5	11	9	17	12.1	14	15.2	14	15
Zr	79	141	171	150	133	123	121	121	117	120	110	121	114	128	129

APPENDIX	I
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				_			((	Cont'd)							
		<u> </u>	Monz	onite to C	Quartz-mo	nzonite					Mineralized Dykes           1*         2*         3*         4*         5*           K         K         K         K         K           64.93         61.1         57.93         57.45         70.73           0.71         0.63         0.99         0.82         0.39           5.64         17.64         18.84         17.12         14.1				ي المربية المربية المربية
Sample nc	81-490	81-298	64-137	64-114	106-383	106-158	64-151	64-116	64-189	1*	2*	3*	4*	5*	6*
Туре	Frs	Frs	<u> </u>	Frs	Frs	Frs	Frs	Frs	Frs	<u> </u>	K	K	K	<u>K</u>	K
SiO <sub>2</sub>	61.98	61.13	63.98	67.71	68.61	59.98	61	60.98	61.41	54.93	61.1	57.93	57.45	70.73	64.59
$TiO_2$	0.6	0.59	0.62	0.61	0.49	5.9	0.58	0.59	0.6	0.71	0.63	0.99	0.82	0.39	0.54
$AI_2O_3$	16.51	16	16.43	16.11	17.67	16.29	16.26	16.33	16.61	15.64	17.64	18.84	17.12	14.1	16.06
Fe <sub>2</sub> O <sub>2</sub> <sup>1</sup>	5.23	5.31	2.5	2.59	2.19	5.3	5.49	3.41	5.13	5.3	5.27	6.99	6.61	3.2	6.38
MnO	0.09	0.11	0.08	0.04	0.05	0.09	0.07	0.07	0.08	0.09	0.14	0.09	0.12	0.05	0.03
MgO	2.54	2.54	3.71	2	1.02	3.01	2.71	3.02	2.82	5.62	2.94	3.27	3.8	1.65	1.96
CaO	4.42	4.13	0.84	0.73	0.72	5.1	5	5.01	5.27	7.58	0.79	4	2	0.67	0.42
Na <sub>2</sub> O	3.95	4.51	5.01	4.69	3.36	4.01	3.75	4	4.11	3.11	5.74	4,12	6.03	4.01	3,25
K <sub>2</sub> O	2.61	2.35	1.93	1.01	3.98	2,33	2.38	2.29	2.71	5.34	1.71	1.66	1.65	3.05	3.3
P2O5	0.28	0.26	0.28	0.25	0.22	0.25	0.26	0.27	0.27	0.22	0.28	0.42	0.35	0.18	0.3
L.O.I.	2.39	4.11	4.78	4.81	1.93	3.02	3.11	4.23	1.6						
Total	100.6	101.04	100.16	100.55	100.24	100.18	100.61	100.2	100.61	98.54	96.24	98.31	95,95	98.03	96.83
Ba	812	799	812	698	1079	741	801	731	741	1439	1379	536	952	1061	653
Cc	42	49	98	45	46	68	20	46	51	141	75	22	14	65	63
Co	2	1	1	1	0	2	0	1	2	16	0	0	0	0	0
$Cr_2O_3$	89	75	89	109	71	111	79	69	84	167	58	55	72	228	59
Cu	63	359	112	121	32	61	57	51	43	41	44	552	58	132	37
Ni	22	25	41	44	11	20	32	32	31	96	27	18	46	93	51
Sc	2	l	3	1	1	1	3	1	3					. – .	
V	89	99	82	73	53	113	98	99	98	123	100	185	157	174	53
Zn	81	108	52	49	43	10	69	82	65	112	93	9/9	98	113	225
Ua Nh	10	14	14	13	17	10	10	10	12	170	0	12	11	10	14
Dh	23	13	23	21	28	22	51	23	22	12.0	9 1/1	25	11	10	25
Rh	65	61	45	81	105	48	63	62	40	70	43	34	30	42	83
Sr	687	653	473	501	508	648	601	661	664	672	354	830	456	700	326
Th	24	12	18	33	29	21	20	19	21	14	11	16	11	12	20
U	2	D/L	3	2	4	1	1	0	1	2	0	0	0	0	0
Y	12	13	14	5	10	15	15	18	14	14.2	17	12	18	15	11
Zr	130	121	125	133	152	131	134	121	122	169	114	123	136	111	129

	Volcanics           ople nc         1*         2*         3*         4*         5*         6*         7*         8*         9*											Highly	Mineraliz	ed Dykes		,
Sample no	1*	2*	3*	4*	5*	6*	7*	8*	9*	10*	1*	2*	3*	4*	5*	
Туре	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Altered	Altered	Altered	Altered	Altered	,
SiO <sub>2</sub>	58.01	57.49	57.91	57.75	57.85	57.66	56.89	58.27	57.55	58.31	54.83	61.1	57.93	57,45	70.73	
TiO <sub>2</sub>	0.97	0.97	0.96	0.96	0.98	0.97	0.97	0.95	0.97	0.97	0.77	0,63	0.99	0.82	0.39	
Al <sub>2</sub> O <sub>2</sub>	18.02	17.75	17.73	17.91	17.94	17.76	18.23	17.62	17.77	17.99	14.64	17.64	18.84	17.12	14.1	
Fe <sub>2</sub> O <sub>2</sub> <sup>1</sup>	5.53	5.79	5.78	5.59	5.71	5.72	5.82	5.79	5.41	5.73	6.3	5.27	6.99	6.61	3.2	
MnO	0.07	0.08	0.08	0.09	0.08	0.08	0.08	0.08	0.07	0.08	0.11	0.14	0.09	0.12	0.05	
MgO	2.11	2.88	2.82	2.84	2.24	3.07	2,75	3.06	2.75	2.54	5.6	2.94	3.27	3.8	1.65	
CaO	6.95	7.11	7.2	7.21	7.11	7	6.84	7.11	7.03	7.16	7.63	0.79	4	2	0.67	
Na <sub>2</sub> O	5.02	4.95	5.1	5.02	5.27	4.59	4.77	5,04	4.97	4.86	2.21	5.74	4.12	6.03	4.01	
к <sub>1</sub> О	1.73	1.75	1.75	1.71	1.8	1.76	1.75	1.7	1.75	1.76	5.21	1.71	1.66	1.65	3.05	
P2O5	0.6	0.56	0.6	0.57	0.63	0.57	0.62	0.59	0.57	0.61	0.52	0.28	0.42	0.35	0.18	
L.O.I.		412.0												0120		
Total	99.01	99.33	99.93	99.65	99.61	99.18	98.72	100.21	98.84	100.01	97.82	96,24	98.31	95,95	98.03	
Ba	580	561	554	571	558	561	605	564	547	582	1513	1379	536	952	1061	
Cc	0	64	72	58	63	54	95	83	105	63	139	75	22	14	65	
Со	nd	nd	nd	1	nd	nd	nd	nd	nd	nd	0	0	0	0	0	
$Cr_2O_3$	67	53	58	72	63	46	48	76	63	54	194	58	55	72	228	
Cu	56	73	54	49	54	39	56	54	45	82	37	44	552	58	132	
Ni	21	23	14	21	18	21	33	23	16	8	121	27	18	46	93	
Sc																
V	133	136	123	114	122	118	134	111	133	129	115	100	185	157	174	
Zn	83	89	84	81	85	91	90	83	72	83	113	93	979	98	113	
Ga	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Nb	20	20	17	21	19	18	18	16	17	34	21	9	13	11	10	
Pb	10	13	12	20	9	23	4	1	10	6	18	14	25	11	11	
Rb	28	30	29	32	40	29	30	28	25	40	88	43	34	39	42	
SI	1231	1238	1220	1233	1218	1200	1209	1232	1217	1144	000	354	830	456	/00	
111	10	12	11	24 2	14	17	10	20	9	11	29		10	11	12	
v	12	15	13	2 15	30	10	14	15	0	26	12	U 17	12	U 19	15	
1 7r	176	165	15	179	161	164	172	161	165	146	174	114	12	136	111	
	170					107	1/4	101	105	170	۲"/۱ 		143	120		

(Cont'd)

				(C	ont'd)				
	Hig	hly Miner	ralized Dy		S	ub-minera	ilized Dyl	kes	
Sample no Type	6* Altered	7* Altered	8* Altered	9* Altered	1()* Altered	1* Altered	2* Altered	3* Altered	4* Altered
SiO <sub>2</sub>	64.59	57.05	49.63	63.86	64.64	69,87	61.83	65.76	63.06
TiO <sub>2</sub>	0.54	0.17	0.91	0.45	0.45	0.61	0,6	0.42	0.55
$AI_2O_3$	16.06	16.88	15.51	15.46	15.41	17.38	16.44	15.04	15.47
Fe <sub>2</sub> O <sub>3</sub> <sup>1</sup>	6.38	6.28	7.54	6.47	3,56	3.48	5,1	3.2	3.48
MnO	0.03	0.11	0.15	0.13	0.06	0.02	0.08	0.11	0.07
MgO	1.96	3.6	5.68	1.7	1.41	1.4	2.65	1.22	1.24
CaO	0.42	2.67	6,45	0.59	2,95	0.09	4.56	3.83	3.64
Na <sub>2</sub> O	3.25	4,29	4.16	4.33	4.8	0.15	4.21	4.16	3.84
K <sub>2</sub> O	3.3	2.63	1.97	2.68	3.45	5.32	2.62	2,93	2.97
P2O5	0.3	0.34	0.3	0.22	0.2	0.27	0.28	0.21	0.28
L.O.I.								·	
Total	96.83	94.02	92.3	95.89	96.93	98.59	98.37	96.88	94.6
Ba	653	842	1677	1320	838	520	943	871	1442
Cc	63	70	50	94	94	57	75	52	33
Co	0	0	0	0	0	0	0	0	0
$Cr_2O_3$	59	78	79	85	77	81	83	68	76
Cu	37	8258	35	182	47	224	39	20	42
Ni	51	45	17	33	11	2	25	17	30
Sc									
γ	53	123	68	70	64	79	95	61	62
Zn	225	304	331	136	58	13	64	87	52
Ga	0	0	0	0	()	0	0	0	0
Nb	14			17	12	17	9	14	19
PD	30	12	20	52	25	37	15	30	10
KD C	83 226	29 620	20	13	93 206	141	29 200	80 711	80
<b>ა</b> ნ უს	020 20	029	4/3	331	390 22	152	עעס 19	/[]	191
111	20	22 0	20	סכ ה	23 0	21	0 10	1/	28 0
v	11	23	11	5	5	נ 6	16 16	1	9 12
Zr	129	127	123	137	116	138	129	132	153

### **FLUID INCLUSION DATA FROM SUNGUN VEINS**

Sanıple	Chip #	Origin	Туре	1./V%	Component	Te (° C)	Tm (° C) fm (° C) HI	Th (° C) Halite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Salinity LVHS types	Salinity LV and VL types
		GR	OUP I VE	LINS	······						<u></u>		
25-421	1	\$	LV	85/15	L+V+O	-25.0	-3.2			266.5			5.2
25-421	1	S	LV	75 / 25	L+V+Ω	-28.0	-4.6			270.0			7.3
106-627	2	S	LV	85/15	L+V	-25.3	-3.4			279.0			5,5
106-627	2	S	LV	80/20	L+V	-24.0	-4.1			249.0			6.6
106-627	2	5	LV	70/30	L+V	-26.2	-2.1			287.0			3.5
25-421	1	S	LV	80/20	L+V+O	-22.0	-6.1			299,8			9.4
25-421	2	S	LV	70/30	1.+V	-23.0	-2.1			255.0			3.5
106-627	1	S	1.V	85/15	L+V	-23.6	-3.9			275.0			6.3
25-500	1	S	LV	80/20	L+V+0	-23.2	-7.3			310,0			10.9
25-421	1	S	LV	80/20	L+V	-25.0	-3.9			287,0			6.3
25-421	4	S	LV	70/30	L+V+U1	-24.2	-6.3			292.0			9.6
25-421	5	s	LV	60/40	L+V	-20.0	-8,1			398.0			11.9
25-421	4	s	1.V	70/30	L+V+UI	-23,7	-6.3			410.0			9.6
25-421	1	s	LV	80/20	L+V	-29.1	-1,3			255.0			2.2
106-627	1	s	LV	85/15	L+V	-23.0	-5.3			278.0			8.3
25-421	5	s	LV	70/30	L+V	-16.0	-6.2			437.9			9.5
25-421	4	р	VL	30/70	V+L+U+O	-21.7	-1.3				485.0		2.2
25-421	5	p	VL	30/70	V+L+O	-21,0	-6.3				437.0		9.6
106-627	5	p	VL.	30/70	V+L+O	-27.0	-8.2				470.0		12.0
25-421	5	p	VL.	30/70	V+L+O	-23.1	-6.2				421.0		9.5
25-421	5	p	VL.	30/70	V+L+O	-20,3	-4.8				600.0		7.6
25-421	5	р	VI.	15/85	V+L	-23.0	-5,3				503.0		8.3
25-421	5	р	VL.	15/85	V+L	-23.9	-9.0				433.0		12.9
25-421	5	р	VI.	15/85	V+L	-27.0	-13.1				410.0		17.0
25-421	5	ь р	VI.	30/70	V+L	-24,8	-8,3				423.0		12.1
25-421	5	n D	VI.	15/85	V+L	-23.2	-11.3				421.0		15.3
25-421	5	DS I	VI.	30/70	V+L+O	-21.0	-7.1				398.0		10.6
25.421	5	1~~	VI	15/85	V+L	-29.0	-10.3				450.0		11.3
25-421	5	1~ n	VI	10/90	V+L+0	-18.0	-9.9				481.0		13.0
106-627	2	r n	VI	10/90	V+L+O	-19.7	.4 9				433.0		77
106-627	2	r D	vi	25/75	V+L+O	-24.2	-11.5				490.0		15.5
106-627	2	r n	VI.	30/70	V+1.	-25.1	-4.7				583.0		74
106-627	2	r D	VI.	15/85	V+L	-27.3	-9.1				557.0		13.0
25-421	4	I' DS	VI.	15/85	V+L+O	-40.1	-7.8				415.0		11.5
25.421	4	۲* n	vi	30/70	V+I	-39.0	-3.9				432.0		63
25-421	Å	Р 17	VI	30/70	V-1	.37 1	-9.4				422.0		4.D
25-421	7	P De	VI	30/70		-415	- 4.7				460.0		-1.0
25-421	4	- n - n		15/85		-32.0	-5.2				442.0		121
22-721	7	P	¥L. \Л	20/70	V.I	-32,9 A3 6	-0.1				430.0		7,4 16 A

Sample	Chip#	Origin	Туре	L/V %	Component	Te (° C)	Tm (° C) Tm ('	° C) 111	Th (° C) Halite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Salinity LVHS types	Salinity I.V and VL types
25-421	4	p	VI.	15/85	V+L	-37.3	-4,1					401.0		6,6
25-421	4	ps	VL.	15/85	V+L	-27.1	-13.4					471.0		17.3
25-421	4	hz	VL.	30/70	V+L	-29.3	-12.1					575.0		16.1
25-421	4	bz	VL.	15/85	V+L+O	-35.3	-6.8					610.0		10,3
25-421	4	ps	VI.	30/70	V+L+O	-48.7	-9.1					601.0		13,0
25-421	4	$\mathbf{p}_{\mathbf{z}}$	VI.	30/70	V+L+O	-30,5	-12.9					620.0		16.8
25-421	1	$\mathbf{p}_{\mathbf{s}}$	VL.	15/85	V+L	-48.0	-13.0					465,0		16.9
25-421	3	р	VL	30/70	V+L+O	-46.0	-12.0					487		16.0
25-421	4	р	VL.	35765	V+L+O	-47.0	-7.1					478.0		10.6
25-421	3	S		10/50	V+L+U V-L+O	-47.0	-0,8				2/1.2			10.3
25-421	з 2	p	VI. VI	40700	V+L+U V-1	+34.0	-3.0				400.0	262.0		4.9
25-421	5	e Îvu	VI	40/60	V+L V+L	-19.0	-1.7					406.0		2,9
25-421	4	DS	VI.	40/60	V+L+O	-20.5	-1.3				428.0	100,0		2.2
25-421	5	S	VL	45/55	V+L	-17.0	-1.1					412.0		1.9
25-421	4	ps	LVHS <sub>1</sub>	60 / 40	L+V+H+Cep±An±U1	-40.0	-23.0	5.4	310.0		335.0		38.9	
25-421	2	р	LVHSI	80/20	L+V+II+Ccp±U1	-57.0	-25.0	9.8	350,0		283,0		42.4	
25-421	3	ps	LVHS <sub>1</sub>	75/25	L+V+II+Ccp±U1	-44.7	-22.0	6.0	347.0		289.0		42.1	
25-421	2	р	LVHS,	80/20	L+V+II+Ccp±An±U1	-49.0	-25,0	6.3	335.0		297.0		41.0	
25-421	l	p	LVHS	80/20	L+V+H+Ccp±An±U1	-51.3	-22.0	8,0	405.0		273.5		48.0	
25-421	3	s	LVHS <sub>1</sub>	75/25	L+V+H+Ccp±An±U1	-63.0	-13.4		390,0		425.0		46.4	
25-421	1	р	LVHS <sub>1</sub>	80 / 20	L+V+II+Cep±An±UI	-50.7	-8.0		350.0		280.0		42.4	
25-421	3	ps	LVHS <sub>1</sub>	80/20	L+V+H+Ccp±U1	-42.1	-23.0	7.2	320.0		372.0		39.8	
25-421	I	ps	LVHS <sub>1</sub>	85715	L+V+H+Ccp±U1	-51.0	-8,5		298.0		309.0		38.0	
25-421	3	ps	LVHS <sub>1</sub>	80/20	L+V+II+Ccp±U1	-43.0	-22.0	6.9	310.0		291.0		38.9	
25-421	4	р	LVHS <sub>1</sub>	75/25	L+V+H+Ccp±U1	-43.0	-7.0		392.0		343.0		46.6	
25-421	3	р	LVHS <sub>1</sub>	80/20	L+V+H+Ccp±UI	-44.0	-6,4		398.3		290.0		47.3	
25-421	4	р	LVHS <sub>1</sub>	75 / 25	L+V+H+Ccp±An±U1	-42.5	-7.3		401.5		283.0		47.6	
25-421	3	р	LVHS <sub>1</sub>	80/20	L+V+H+Ccp±An±U1	-63,0	-12.0		453.0		282.0		53.6	
25-500	1	bz	LVHS <sub>1</sub>	80/20	L+V+H+Ccp±U1	-46.3	-8.0		403.0		348.3		47.8	
25-500	l	ps	LVHS <sub>1</sub>	90/10	L+V+II+Ccp±U1	-41.3	-10.2		291.0		293.0		37.5	
25-421	4	р	LVHS <sub>1</sub>	75/25	L+V+H+Ccp±U1	-60.0	-12.7		331.0		372.0		40.7	
25-421	4	hz.	LVHS <sub>1</sub>	70/30	L+V+II+Ccp±U1	-52.0	-11.8		405.6	79	260.7		48.1	
25-421	3	р	LVHS <sub>2</sub>	80/20	.+V+H+Sy+Ccp±An±U1±(	-44.0	-21.0	5	300.0	60.5	364,0		38.2	
25-421	5	р	LVHS <sub>2</sub>	75 / 25	L+V+H+Sy+Ccp±An±O	-56.2	-13.3		414.6	90.1	400.0		49.1	
25-421	5	р	LVHS <sub>2</sub>	70/30	L+V+H+Sy+Ccp±U1±O	-59.4	-10.3		456.2	96	393,0		54.0	
25-500	1	р	LVHS <sub>2</sub>	80 / 20	L+V+II+Sy+Ccp±An±O	-64.0	-25.2		257.0	57.5	237.0		35,1	

Sample	Chip#	Origin	Туре	L/V%	Component	Te (° C)	Tm (° C) fn	ν (° C) ΗΙ	Th (° C) Halite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Salinity LVHS types	Salinity LV and VL types
25-500	1	р	LVHS <sub>2</sub>	70/30	L+V+II+Sy+Cep±An±O	-47.0	-11.0		457.0	n.d.	398.0		54.1	
25-500	1	р	LVHS <sub>2</sub>	80/20	L+V+H+Sy+Cep±An±O	-53.2	-12.1		339.0	n.d.	471.5		41.4	
25-500	J	р	LVHS <sub>2</sub>	75 / 25	L+V+II+Sy+Cep±An±O	-46.7	-6.4		318.0	n.d.	437.0		39.6	
25-500	1	Р	LVHS <sub>2</sub>	70/30	L+V+H+Sy+Ccp±U1±O	-57.7	-21.0		350,0	98	471.0		42,4	
25-500	1	Р	LVHS <sub>2</sub>	70/30	L+V+11+Sy+Ccp±U1±O	-54.0	-16.9		358,0	72	446.0		43.2	
25-421	4	S	LVHS <sub>2</sub>	75 / 25	L+V+II+Sy+Ccp±An±O	-51.2	-8,0		280,0	50.3	395.0		36.7	
25-421	4	р	LVHS <sub>2</sub>	80/20	L+V+H+Sy+Cep±An±O	-48,8	-22.0	7	336,0	62	487.0		41.1	
25-421	5	р	LVHS <sub>2</sub>	80 / 20	L+V+H+Sy+Cep±An±O	-63.0	-12.3		356.6	75	392.6		43.0	
25-421	5	р	LVHS <sub>3</sub>	85715	L+V+II+Sy+Cep±UI±O	-59.0	-30.0	13	390.0	73	353,0		46.4	
25-421	1	р	LVHS <sub>3</sub>	80/20	L+V+H	-49.3	•11.0		298,0				38.0	
25-421	2	р	LVHS <sub>3</sub>	40/60	V+L+H	-51.7	-8.0		384.0		327.0		45.7	
25-421	3	s	LVHS <sub>3</sub>	45/55	V+L+H+O	-43.8	-6.5		298.0			327	38,0	
25-421	2	s	LVHS <sub>3</sub>	75/25	L+V+11	-50.0	-7.3		364.0		305.0		43,7	
25-421	2	р	LVHS <sub>3</sub>	85/15	L+V+H	-49,1	-7.3		283.0		304.0		36.9	
25-421	4	p	LVHS <sub>3</sub>	60/40	L+V+II	-58,0	-12.8		307.0		430.0		38.7	
25-421	5	p	LVHS <sub>3</sub>	70/30	L+V+H	56,0	-10.6		369.0		350,0		44.2	
25-421	1	р	LVHS <sub>3</sub>	70/30	L.+V+H	-55.0	-12.0		390.0		298.0		46.4	
25-421	2	р	LVHS <sub>3</sub>	65/35	L+V+H	-37.0	-3.6		430.0		307.0		50.8	
25-421	3	ps	LVHS <sub>3</sub>	80/20	1.+V+11	-44.0	-28.0	7	435.0		383.0		51,4	
106-627	1	ps	LVHS <sub>3</sub>	85/15	L+V+H	-67.4	-17.0		381,0		233.0		45.4	
25-421	3	р	LVHS <sub>3</sub>	70 / 3 <b>0</b>	L+V+H+O	-50.0	-11.4		306.5		225.0		38,7	
25-421	5	р	LVHS <sub>3</sub>	70/30	L+V+H+O	-59.7	-13,1		341.7		384.7		41.6	
25-421	3	ps	LVIIS <sub>3</sub>	45 / 55	V+L+H+O	-41.0	-4.3		356.0			470	43,0	
25-421	2	p	LVIIS <sub>3</sub>	65/35	1.+V+H+O	-59,0	-14.0		410.0		435,0		48.5	
25-421	5	p	LVHS <sub>3</sub>	70/30	L+V+II+O	-53,2	-15.5		410.5		376.0		48.6	
25-421	2	р	LVHS <sub>3</sub>	65/35	L+V+11+O	-58,3	-12.2		450.0		397.0		53,3	
25-500	1	p	LVHS <sub>3</sub>	75/25	L+V+II+O	-43.0	-8.2		398.0		261.0		47.2	
25-500	1	р	LVHS <sub>3</sub>	70/30	L+V+11+O	-58.1	-12.2		236.0		610.0		33,8	
25-421	2	s	LVIIS <sub>3</sub>	75/25	L+V+H±U±O	-61.0	-12.4		389,0		329.0		46.3	
106-627	l	be	LVIIS3	75/25	L+V+H±U±O	-65.0	-18,5		359.1		215.0		43,3	
	GR	OUP II VE	EINS											
25.466	4	S	LV	80/20	L+V	-48,1	-8.9				280,1			12.8
25-478	1	р	LV	70/30	L+V+O	-33,5	-4.3				305.0			8.0
25.466	3	ps	LV	60/40	L+V	-27,0	•2.6				288,9			4.3

Sample	Chip #	Origin	Туре	L/V %	Component	Te (" (')	Tm (° C) Fm (° C) HI	Th (° C) Halite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Safinity LVHS types	Salinity LV and VL types
25-478	1	S	LV	85/15	1.+V	·22.0	-1.3			271.0			2.2
25-487	1	р	LV	60/40	L+V	-20.1	-1.9			365.7			3.2
25-487	1	ps	L.V	60/40	L+V	-23.1	-5.8			510.0			9.0
25-487	1	s	LV	65/35	L+V	-22,0	-1.5			316.6			2.6
25-487	1	s	LV	90/10	L+V	•20.0	-2.3			317.5			3.9
25-478	1	S	LV	85715	L+V	-19.8	-1.9			255.5			3.2
25.466	3	ps	LV	65/35	I.+V	-22,0	-1.2			269.0			2.1
25-478	1	s	LV	65/35	L+V	-19,0	-4.2			278.1			6,7
25,466	3	ps	LV	90/10	L+V	-21.0	-9.7			256.0			13,7
25-478	1	S	1.V	85/15	L+V+0	-17.0	-3.8			326.5			6.1
25.466	3	ps	LV	95/5	L+V	-22.0	-3.2			245.0			5.2
25-487	1	125	LV	60/40	L+V	-21.0	-7.5			282.7			11.1
25-487	1	s	LV	85/15	L+V	-16.0	-4.1			330.0			6.6
33-473	2	ps	L.V	85/15	L+V+11	-55.0	-10.5	275		288,0			14,5
33-473	1	p	LV	55745	L+V+H	-58.0	-9.8	487		450.0			13.8
25.466	1	ps	VI.	20/80	V+1,	-56.6	-7.4				379.0		11.0
25-307	1	ps	VL.	30/70	V+L	-46.0	-7.0				387.0		10,5
25-307	1	ps	VL.	50/50	V+1.	-39.2	-5.2			384.0			8.1
25-307	3	S	VI.	45 / 50	V+L	-24.0	-9.2				405.6		13,1
25-307	3	s	VL.	50/50	V+L	· ·21.4	-2.1				398.0		3,5
25-307	3	S	VL.	55 / 45	V+1.	-23.0	-6.9				343.0		10.4
25.466	1	s	VI.	20/80	V+L	-31.8	-2.1				373.0		3,5
25-307	2	S	VL.	15/85	V+L	•19.0	-10.5				327.0		14.5
25-307	2	р	VL.	40 / 60	V+L	-23,5	-6.3				411.2		9.6
25-307	1	р	VL.	15/85	V+L	-26,3	-11.7				377.0		15.7
25-307	3	S	VL.	50/50	V+L	-25,7	-5.9				320.0		9.1
25-233	1	р	VL.	45 / 55	V+1.	-27,5	•13.2				398.0		17.1
25-233	1	Р	VI.	50/50	V+L	-26.1	-14.9				420.0		18.6
25-233	1	р	VI.	15/85	V+L	-30,6	-12.6				383.0		16.6
25-233	1	р	VL	30/70	V+1.	-28.0	-7.3				315.0		10.9
25-233	1	р	VI.	30/70	V+L	-29,3	-7.9				337.0		11.6
25-233	1	р	VI.	30/70	V+1.	-23.7	-4.2				318.0		6.7
25-307	3	S	VI.	45 / 55	V+I.	-26.4	-1.2				356.0		2.1
25-307	3	S	VL.	50/50	V+1.	-23.0	-1.2				341.8		2.1
25-307	1	р	VL.	15785	V+1.	-25.0	-1.1				450.0		1.9
25-487	1	ps	VL.	30/70	V+L	·26.2	-7.2				620.0		10.8
25-307	3	S	VL.	20/80	V+L	-24.0	-0.9				450.5		1.6
25-307	1	р	VL	30/70	V+L	-23,0	-0.9				350.0		1.6
25-307	3	5	VL.	30 / 70	V+L	-22.0	-0.8				364.4		1.4
25-307	1	ps	VL	20/80	V+L	-21.6	-0,8				360.0		1.4

	Sample	Chip #	Origin	Туре	L/V %	Component	Te (° C)	Tm (° C)	) HI – Th (° C) Halite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Salinity LVHS types	Salinity LV and VL types
25-487         1         pc         VL         50 / 50         V-L         -23.0         -45.7         20.0           33-473         2         s         VL         50 / 70         V-L         -20.2         -3.2         -60.0           33-473         1         p         VL         50 / 50         V-L         -5.2         -60.0         -287.8           33-473         1         p         VL         50 / 50         V-L         -5.2         -5.3         -5.0         -285.0         45.3           25.466         2         p         L/VIIS, 72 / 52         L+V+II+Cqp2AnaEU         -6.7         432.7         283.0         51.2           25.466         3         p         L/VIIS, 80 / 20         L+V+II+Cqp2AnaEU         -5.0         450.0         29.3         33.3           25.466         3         p         L/VIIS, 80 / 20         L+V+II+Cqp2AnaEU         -5.0         450.0         29.0         350.0         35.2           25.307         5         p         L/VIIS, 87 / 15         L+V+II+Cqp2AnaEU         -50.0         381.0         44.2           25.307         5         p         L/VIIS, 87 / 15         L+V+II+Cqp2AnaEU         -46.0         384.4	25-307	1	р	VI.	50/50	V+L	-23.1	-0,6				376.0		1.0
25-871psVL30/70V-L-7.2	25-487	1	ps	VL.	50/50	V+1.	-23.0	-0.5			293.0			0.9
33.4732sV.50/50V+L-3.30-9.8211.0287.823.4731pV.L50/50V+L-32.0-5.445.00427.025.4662pL.VIIS,75/25L+V+II+Cqp+AntUI-9.2-5.3380.0285.045.325.4664pL.VIIS,75/25L+V+II+Cqp+AntUI-41.0-12.3413.0276.048.925.4663pL.VIIS,80/20L+V+II+Cqp+AntUI-46.919.245.029.353.325.4664pL.VIIS,80/20L+V+II+Cqp+AntUI-52.0-21.5373.0277.244.625.3075pL.VIIS,85/15L+V+II+Cqp+AntUI-52.0-21.5373.0277.244.625.3075pL.VIIS,85/15L+V+II+Cqp+AntUI-52.0-21.5373.0277.047.125.3075pL.VIIS,80/20L+V+II+Cqp+AntUI-51.0369.0381.044.225.3075pL.VIIS,80/20L+V+II+Cqp+AntUI-47.3389.0357.046.325.3075pL.VIIS,80/20L+V+II+Cqp+AntUI-47.0-16.0385.4359.045.925.3075pL.VIIS,80/20L+V+II+Cqp+AntUI-47.0-16.0385.4359.045.025.3075pL.VIIS,80/20L+V+II+Cqp+AntUI-47.0-16.0	25-487	1	ps	VL.	30/70	V+L	-20.2	-3.2				609.0		5.2
33-131pV.50/30V+L-32.0-3.445.00427.025.4663pLVIIS,87/25L+V+II+Cqp2AnEU-5.3380.025.045.325.4663pLVIIS,87/25L+V+II+Cqp2AnEU-6.0432.728.051.225.4663pLVIIS,80/20L+V+II+Cqp2AnEU-6.7432.728.051.225.4663pLVIIS,80/20L+V+II+Cqp2AnEU-5.3373.0277.244.625.4663pLVIIS,87/15L+V+II+Cqp2AnEU-5.1373.0277.244.625.3075pLVIIS,85/15L+V+II+Cqp2AnEU-5.121.0410.0354.048.525.3075pLVIIS,85/15L+V+II+Cqp2AnEU-5.121.0410.0357.046.325.3075pLVIIS,80/20L+V+II+Cqp2UI-47.317.3380.0357.046.325.3075pLVIIS,80/20L+V+II+Cqp2UI-47.2-15.7366.0340.047.025.3075pLVIIS,80/20L+V+II+Cqp2UI-47.2-15.7366.0340.047.025.3075pLVIIS,80/20L+V+II+Cqp2UI-47.2-15.7366.0340.047.025.3075pLVIIS,80/20L+V+II+Cqp2UI-47.2-15.7366.0340.047.0 <tr< td=""><td>33-473</td><td>2</td><td>S</td><td>VI.</td><td>50/50</td><td>V+1.</td><td>-53.0</td><td>-9.8</td><td>271.0</td><td></td><td></td><td>287.8</td><td></td><td>13.8</td></tr<>	33-473	2	S	VI.	50/50	V+1.	-53.0	-9.8	271.0			287.8		13.8
23.460         3         p         LVIIs, LVIIs, 15,466         4         p         LVIIs, LVIIs, 15,25         1.4V4114CqptAuEU1         -9.2         -3.3         38.00         28.00         49.3           25.466         4         p         LVIIs, LVIIs, 15,25         1.4V4114CqptAuEU1         -10.2         413.0         276.0         48.9           25.466         3         p         LVIIs, LVIIs, 15,266         1.4V4114CqptAuEU1         -52.0         -12.3         413.0         276.0         48.9           25.466         4         p         LVIIs, 16/20         1.4V4114CqptAuEU1         -52.0         -21.5         373.0         277.2         41.6           25.307         5         p         LVIIS, 16/15         87/15         1.4V4114CqptAuEU1         -53.0         23.00         381.0         44.2           25.307         5         p         LVIIS, 16/15         87/15         L+V4114CqptAuEU1         -48.0         -19.4         397.3         297.0         47.1           25.307         5         p         LVIIS, 16/15         87/15         L+V4114CqptAuEU1         -48.0         -19.4         397.3         46.3           25.307         5         p         LVIIS, 16/15         1.4V4114CqptAuEU1	33-473	1	р	VL,	50750	V+L	-52.0	-5.4	450,0		427.0			8.4
23.4662pL VIIS L VIIS 	25.466	3	р	LV1151	15125	L+V+H+Ccp±An±UI	-39.2	-5.3	380.0		285.0		45.3	
22.4664pL.VIIS, L.Y.J.S.L.Y.J.S. L.Y.VIIKCPERLI-64.9-19.242.0390.0300.025.4663pL.VIIS, L.Y.J.S.807.20L.V.VIIKCPERABUI-6.7432.728.051.225.4664pL.VIIS, L.Y.J.S.707.00L.Y.VIIKCPERABUI-52.0-21.5373.0277.244.625.3075pL.VIIS, L.Y.J.S.857.15L.Y.VIIKCPERABUI-52.0-21.0410.0354.048.525.3075pL.VIIS, L.Y.J.S.857.15L.Y.VIIKCPERABUI-50.4-13.0309.0381.044.225.3075pL.VIIS, L.Y.J.S.807.20L.Y.VIIKCPERABUI-44.0-19.4397.3297.047.125.3075pL.VIIS, L.Y.J.S.807.20L.Y.VIIKCPERABUI-44.0-17.3-17.3389.0357.046.325.3075pL.VIIS, L.Y.J.S.807.40L.Y.VIIKCPERABUI-44.0-26.0377.1-348.745.025.3075pL.VIIS, L.Y.J.S.807.40L.Y.VIIKCPERABUI-44.0-26.0377.1348.745.025.3075pL.VIIS, L.Y.J.S.85.15L.Y.VIIKCPERABUI-45.4-23.4384.8371.445.825.3075pL.VIIS, L.Y.J.S.85.15L.Y.VIIKCPERABUI-45.0-25.1405.0278.145.025.4664p <td< td=""><td>25.466</td><td>2</td><td>р</td><td>LVHS<sub>1</sub></td><td>80720</td><td>L+V+H+Cep±UI</td><td>-51.0</td><td>-12.3</td><td>413.0</td><td></td><td>276.0</td><td></td><td>48.9</td><td></td></td<>	25.466	2	р	LVHS <sub>1</sub>	80720	L+V+H+Cep±UI	-51.0	-12.3	413.0		276.0		48.9	
23.4663pL/VIS, L/VIS, B/20L/VIS, L/VIS, L/VIS, L/VIS, D/30L/VIS, L/VIS, L/VIS, L/VIS, L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/15L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, L/VIS, S/145L/VIS, L/VIS, L/VIS, L/VIS, S/155L/VIS, L/VIS, L/VIS, L/VIS, S/155L/VIS, L/VIS, L/VIS, L/VIS, S/155L/VIS, L/VIS, L/VIS, L/VIS, S/155L/VIS, L/VIS, L/VIS, L/VIS, S/155L/VIS, L/VIS, L/VIS, L/VIS, L/VIS, S/155L/VIS, L/	25,466	4	р	LVHS	75725	L+V+II+Ccp±UI	-64.9	- 19.2	423.0		390,0		50.0	
25.466       3       p       LVIIS,       807.00       1.4+11+Cop2An2U1       -45.8       -5.0       450.0       299.3       53.3         25.466       4       p       LVIIS,       857.15       1.4+11+Cop2An2U1       -52.0       -21.5       377.0       277.2       44.6         25.307       5       p       LVIIS,       857.15       1.4+11+Cop2An2U1       -52.0       -21.0       410.0       354.0       48.5         25.307       5       p       LVIIS,       857.15       L+V+H+Cop2An2U1       -50.4       -13.0       360.0       381.0       44.2         25.307       5       p       LVIIS,       857.45       L+V+H+Cop2U1       -49.6       -16.0       385.4       359.0       45.9         25.307       5       p       LVIIS,       807.40       L+V+H+Cop2U1       -47.2       -15.7       396.0       349.0       47.0         25.307       5       p       LVIIS,       807.00       L+V+H+Cop2U1       -47.2       -15.7       396.0       349.0       47.0         25.307       5       p       LVIIS,       807.15       L+V+H+Cop2Ma2U1       -45.4       -23.4       384.8       371.4       45.0	25.466	3	Р	LVHS	80720	L+V+H+Cep±An±UI	-40.2	-6.7	432.7		283.0		51.2	
23.4664pLVIIS,07.30L+V+H+Cqp2AnzUI-24.337.8027.1244.625.3075pL.VIIS,85.715L+V+H+Cqp2AnzUI-53.0-23.0230.0330.033.525.3075pL.VIIS,87.75L+V+H+Cqp2AnzUI-50.4-13.0369.0381.044.225.3075pL.VIIS,80.70L+V+H+Cqp2UI-48.0-19.4397.3297.047.125.3075pL.VIIS,80.70L+V+H+Cqp2UI-47.3-17.3389.0357.046.325.3075pL.VIIS,80.70L+V+H+Cqp2UI-47.2-15.7396.0349.047.025.3075pL.VIIS,80.720L+V+H+Cqp2UI-47.2-15.7396.0349.047.025.3075pL.VIIS,80.720L+V+H+Cqp2AnzUI-44.0-26.0377.1348.745.025.3075pL.VIIS,80.720L+V+H+Cqp2AnzUI-44.0-45.032.4384.8371.445.833.4731pL.VIIS,85.745L+V+H+Cqp2AnzUI-51.1405.0278.145.025.4664pL.VIIS,85.745L+V+H+Cqp2AnzUI-51.012.2216.0320.032.042.225.4664pL.VIIS,85.745L+V+H+Cqp2AnzUI-50.0-13.0441.0322.852.225.425.4781	25.466	3	р		80720	L+V+II+Ccp±An±UI	-+J.8 52.0	-5.0	450.0		299.3		53,3	
23-307       5       p       LVHS1       83/1.3       L+V+H+Chr2Miell       -35.0       24.0       350.0       35.1         25-307       5       p       L,VHS1       85/1.5       L+V+H+Chr2Miell       -52.1       -21.0       410.0       354.0       44.2         25-307       5       p       L,VHS1       80/1.5       L+V+H+Chr2Miell       -48.0       19.4       397.3       297.0       47.1         25-307       5       p       L,VHS1       80/20       L+V+H+Chr2Miell       -47.3       17.3       389.0       357.0       46.3         25-307       5       p       L,VHS1       80/20       L+V+H+Chr2Miell       -47.2       -15.7       396.0       349.0       47.0         25-307       5       p       L,VHS1       80/20       L+V+H+Chr2Maull       -44.0       -26.0       377.1       348.7       45.0         25-307       5       p       L,VHS1       80/20       L+V+H+Chr2Maull       -44.0       -26.0       377.1       348.7       45.0         25-307       5       p       L,VHS1       85/15       L+V+H+Chr2Maull       -58.0       -51.1       405.0       278.1       48.0         25-487	20,400	+ c	р	LVHS	107.30	L+V+H+Cep±Au±UI	-52.0	•21.5	375.0		211.2		44.0	
25-307       5       p       LVIIS, 80/13       L+V+H+Cpr2MI2U       -50.4       -11.0       40.0       534.0       48.3         25-307       5       p       LVIIS, 80/20       L+V+H+Cpr2MI2U       -50.4       -13.0       369.0       381.0       44.2         25-307       5       p       LVIIS, 80/20       L+V+H+Cpr2UI       -47.3       -17.3       389.0       357.0       46.3         25-307       5       p       LVIIS, 80/20       L+V+H+Cpr2UI       -47.2       -15.7       366.0       349.0       47.0         25-307       5       p       LVIIS, 80/20       L+V+H+Cpr2ntul       -44.0       -26.0       377.1       348.7       45.0         25-307       5       p       LVIIS, 80/20       L+V+H+Cpr2ntul       -42.6       -23.4       384.8       371.4       45.8         33.473       1       p       LVIIS, 85/15       L+V+H+Cpr2ntul       -42.6       -28.0       12.2       216.0       320.0       32.7         25.466       4       p       LVIIS, 85/15       L+V+H+Cpr       -40.0       -10.3       369.0       352.0       44.2         25.466       4       p       LVIIS, 70/30       L+V+H+Cpr	23-307	נ ב	p	1.0116	03/13	L+V+H+Cqr±An±U1	-55.0	-23.0	230.0		220.0		33,5	
22-3075pL VIIS1 L VIIS1 $60720$ L+V+II+Cqp±UI L+V+II+Cqp±UI $41.0$ $48.0$ $19.4$ $307.3$ $307.0$ $361.0$ $41.2$ $44.2$ 25-3075pL.VIIS1 LVIS1 $55745$ L+V+II+Cqp±UI L+V+II+Cqp±UI $47.3$ $49.6$ $16.0$ $385.4$ $359.0$ $45.9$ 25-3075pL.VIIS1 LVIS1 $80720$ L+V+II+Cqp±UI $49.6$ $41.2$ $16.0$ $385.4$ $359.0$ $45.9$ 25-3075pL.VIIS1 R $80720$ 	25-307	2	p		80/10	L+V+H+Ccp±An±UI	-52.1	-21.0	410.0		304.0		48.5	
25.1075p1.7115,55/431.74 × H+CcpzU144.017.457.327.044.125.3075p1.VIIS,80/201.+V+H+CcpzU147.3-17.3389.0357.046.325.3075p1.VIIS,80/201.+V+H+CcpzU147.2-15.7396.0349.047.025.3075p1.VIIS,80/201.+V+H+CcpzAnzU144.0-26.0377.1348.745.025.3075p1.VIIS,80/201.+V+H+CcpzAnzU1-46.4-23.4384.8371.445.825.3075p1.VIIS,85/151.+V+H+CcpzAnzU1-58.0-5.1405.0278.148.025.4664p1.VIIS,85/151.+V+H+CcpzU1c0-42.6-28.012.2216.0320.032.725.4664p1.VIIS,70/301.+V+H+Ccp-63.0-13.0441.0322.852.225.4664p1.VIIS,70/301.+V+H+Ccp-42.2-11.0369.8342.044.325.4781p1.VIIS,70/301.+V+H+Ccp-55.6-11.6357.927743.125.4781p1.VIIS,65/351.+V+H+Ccp-55.6-11.6357.927743.125.4781p1.VIIS,75/351.+V+H+Ccp-55.6-11.6357.927743.125.4781p1.VIIS,7	23-307	2	P	L VIIoj	60720		19.0	-15.0	207.2		201.0		44.2	
25-3075pLVIIs LVIIS LVII	25-307	5	р	1.4191	22/42 80/20	L+V+II+Cep±UI	-40.0	-19,4	397.3		297.0		47.1	
25-3075p1.7151537/431.4*V+11+Cqp2U1-49.6-16.0383.4359.045.925-3075p1.VIIS180/201.4*V+11+Cqp2U1-47.2-15.7396.0349.047.025-3075p1.VIIS180/201.4*V+11+Cqp2AnzU1-44.0-26.0377.1384.745.025-3075p1.VIIS180/201.4*V+11+Cqp2AnzU1-45.4-23.4384.8371.445.833-4731p1.VIIS185/151.4*V+11+Cqp2AnzU1-46.6-28.012.2216.0320.032.725.4664p1.VIIS155/451.4*V+11+Cqp-49.0-10.3369.0352.044.225.4664p1.VIIS170/301.4*V+11+Cqp-63.0-13.0441.0322.852.225.4871p1.VIIS170/301.4*V+11+Cqp-41.0-9.0268.0258.035.925.4871p1.VIIS170/301.4*V+11+Cqp-41.0-9.0268.0258.035.925.4781p1.VIIS165/351.4*V+11+Cqp-57.0-15.3395.075330.046.925.4781p1.VIIS145/551.4*V+11+Cqp-55.6-11.6357.927743.125.4781p1.VIIS275/251.4*V+11+Sq+Cqp2Anz0-56.0-16.1446.098398.052.8 <t< td=""><td>25-307</td><td>5</td><td>р</td><td></td><td>80/20</td><td>L+V+H+Cep±UI</td><td>-47.3</td><td>-17.3</td><td>.389.0</td><td></td><td>357.0</td><td></td><td>40.3</td><td></td></t<>	25-307	5	р		80/20	L+V+H+Cep±UI	-47.3	-17.3	.389.0		357.0		40.3	
25-3075pLVHS180/20L+V+H+Cq2DI-41/2-15/7350.0349.047/025-3075pLVHS180/20L+V+H+Cq2DAn±UI-44.0-26.0377.1348.745.025-3075pLVHS180/20L+V+H+Cq2DAn±UI-45.4-23.4384.8371.445.833-4731pLVHS185/15L+V+H+Cq2DAn±UI-58.0-5.1405.0278.148.025-4871pLVHS185/15L+V+H+Cq2DU±O-42.6-28.012.2216.0320.032.725.4664pLVHS170/30L+V+H+Cq2DU±O-42.6-28.012.2216.0320.0352.044.225.4664pLVHS170/30L+V+H+Cq2-63.0-13.0441.0322.852.225.4871pLVHS170/30L+V+H+Cq2-41.0-9.0268.0258.035.035.925.4781pLVHS165/35L+V+H+Cq2-16.3395.07530.046.925.4781pLVHS145/55L+V+H+Cq2-55.6-11.6357.927743.125.4781pLVHS275/25L+V+H+Cq2-55.6-11.6357.927743.125.4781pLVHS275/25L+V+H+Sy+Cq2An±O-56.0-16.3271.0n.d425.036.125.3072p	25-307	5	р	L VII51	22/42		-49.0	-10.0	383,4		339,0		45.9	
25-3075p1.VHS1 1.VHS160/201.+V+H+Ccp±An±U1 L+V+H+Ccp±An±U1-20.0317.1348.7448.725-3075p1.VHS1 1.VHS170/301.+V+H+Ccp±An±U1-58.0-23.4384.8371.445.833-4731p1.VHS1 1.VHS185/151.+V+H+Ccp±An±U1-58.0-5.1405.0278.148.025-4871p1.VHS1 	25-307	2	р —	1.VH81	80/20	L+V+H+Cep±01	-47,2	-13.7	0,00		249.0		47.0	
25-3075pLVHS1 LVHS1 $10730$ L+V+H+Cqp±AngU1 $-3.4$ $-58.0$ $56.8$ $57.4$ $-58.0$ $57.4$ $-58.0$ $57.4$ 	25-307	2	р -	LVDO	70/20	L+V+H+Ccp±An±UI	44.0	-20.0	377.1		248.7		45.0	
3.5-4731p $1.V1S_1$ $85/13$ $1.+V+H+Ccp2AnzOI$ $-58.0$ $-51.1$ $405.0$ $27.6$ $44.0$ 25-4871p $1.V1S_1$ $85/15$ $1.+V+H+Ccp2AnzOI$ $-42.6$ $-28.0$ $12.2$ $216.0$ $320.0$ $32.7$ 25.4664p $1.V1S_1$ $55/45$ $1.+V+H+Ccp2AnzOI$ $-49.0$ $-10.3$ $369.0$ $352.0$ $44.2$ 25.4664p $1.V1S_1$ $70/30$ $1.+V+H+Ccp$ $-63.0$ $-13.0$ $441.0$ $322.8$ $52.2$ 25.4871p $1.V1S_1$ $70/30$ $1.+V+H+Ccp$ $-44.0$ $-9.0$ $268.0$ $258.0$ $35.9$ 25.4781p $1.V1S_1$ $70/30$ $1.+V+H+Ccp$ $-42.2$ $-11.0$ $369.8$ $342.0$ $44.3$ 25.4781p $1.V1S_1$ $65/35$ $1.+V+H+Ccp$ $-55.6$ $-11.6$ $357.9$ $277$ $43.1$ 25.4781p $1.V1S_2$ $75/25$ $1.+V+H+Ccp$ $-55.6$ $-11.6$ $357.9$ $277$ $43.1$ 25.4781p $1.V1S_2$ $70/30$ $1.+V+H+Sy+Ccp2An20$ $-56.0$ $-16.1$ $446.0$ $98$ $398.0$ $32.8$ 25.3072p $1.V1S_2$ $70/30$ $1.+V+H+Sy+Ccp2An20$ $-57.3$ $-15.1$ $243.0$ $n.d$ $398.0$ $34.2$ 25.3072p $1.V1S_2$ $70/30$ $1.+V+H+Sy+Ccp2An20$ $-46.5$ $-17.4$ $340.2$ $n.d$ $401.0$ $4$	23-307	5	p	LVII0]	107 30	L+V+H+Cep±An±UI	-42,4 69.0	-23.4	304.0		371,4		45.8	
25-487       1       p       LVHS1       85/15       L+V+H+CqEOFEO       -42.6       -28.0       12.2       216.0       320.0       32.7         25.466       4       p       LVHS1       55/45       L+V+H+CqEOFEO       -49.0       -10.3       369.0       352.0       44.2         25.466       4       p       LVHS1       70/30       L+V+H+CqP       -63.0       -13.0       441.0       322.8       52.2         25.487       1       p       LVHS1       70/30       L+V+H+CqP       -44.0       -9.0       268.0       258.0       35.9         25.487       1       p       LVHS1       70/30       L+V+H+CqP       -57.0       -15.3       395.0       75       330.0       46.9         25.478       1       p       LVHS1       45/55       L+V+H+CqP       -55.6       -11.6       357.9       277       43.1         25.478       1       p       LVHS2       75/25       L+V+H+Sy+CqptAn±O       -56.0       -16.1       446.0       98       398.0       52.8         25.307       2       p       LVHS2       90/10       L+V+H+Sy+CqptAn±O       -56.0       -16.3       271.0       n.d       498.0	33-473	1	p	LVD9	05/15		-26.0	-0.1	405,0		270,1		48,0	
25.4664p $LVIS_1$ $55/45$ $L+V+II+Cep$ $-49.0$ $-10.3$ $369.0$ $352.0$ $44.2$ 25.4664p $LVIS_1$ $70/30$ $L+V+II+Cep$ $-63.0$ $-13.0$ $441.0$ $322.8$ $52.2$ 25.4871p $LVIS_1$ $70/30$ $L+V+II+Cep$ $-44.0$ $-9.0$ $268.0$ $258.0$ $359.0$ $35.9$ 25.4871p $LVIS_1$ $70/30$ $L+V+II+Cep$ $-42.2$ $-11.0$ $369.8$ $342.0$ $44.3$ 25.4781p $LVIS_1$ $65/35$ $L+V+II+Cep$ $-57.0$ $-15.3$ $395.0$ $75$ $330.0$ $46.9$ 25.4781p $LVIS_1$ $45/55$ $L+V+II+Cep$ $-55.6$ $-11.6$ $357.9$ $277$ $43.1$ 25.4781p $LVIS_2$ $75/25$ $L+V+II+Sy+Cep\pmAn\pm0$ $-56.0$ $-16.1$ $446.0$ $98$ $398.0$ $52.8$ 25.3072p $LVIS_2$ $90/10$ $L+V+II+Sy+Cep\pmAn\pm0$ $-56.0$ $-16.3$ $271.0$ $n.d$ $49.0$ $34.2$ 25.3072p $LVIS_2$ $70/30$ $L+V+II+Sy+Cep\pmAn\pm0$ $-56.0$ $-16.3$ $271.0$ $n.d$ $401.0$ $41.5$ 25.3072p $LVIS_2$ $70/30$ $L+V+II+Sy+Cep\pmAn\pm0$ $-46.5$ $-17.4$ $340.2$ $n.d$ $401.0$ $41.5$ 25.3072p $LVIS_2$ $80/20$ $L+V+II+Sy+Cep\pmAn\pm0$ $-46.5$ $-17.4$ $340.2$ $n$	25-487	1	p	LAUS	65/15		++2.0	-28.0 12.2	210.0		320.0		32.7	
25.400       4       p       LVHS1       70730       L+V+H+Ccp       -63.0       -13.0       441.0       522.8       52.2         25-487       1       p       LVHS1       70730       L+V+H+Ccp       -44.0       -9.0       268.0       258.0       35.9         25-487       1       p       LVHS1       70730       L+V+H+Ccp       -42.2       -11.0       369.8       342.0       44.3         25-478       1       p       LVHS1       65735       L+V+H+Ccp       -57.0       -15.3       395.0       75       330.0       46.9         25-478       1       p       LVHS2       75/25       L+V+H+Ccp       -55.6       -11.6       357.9       277       43.1         25-478       1       p       LVHS2       75/25       L+V+H+Sy+Ccp±An±O       -56.0       -16.1       446.0       98       398.0       52.8         25-307       2       p       LVHS2       90/10       L+V+H+Sy+Ccp±An±O       -56.0       -16.3       271.0       n.d       425.0       36.1         25-307       2       p       LVHS2       70/30       L+V+H+Sy+Ccp±An±O       -46.5       -17.4       340.2       n.d       401.0	25.400	4	p	1.0116	20120	L + v + n + C cp	·49.0	-10.3	309.0		332.0		44.2	
25-487       1       p       1.V131       70730       1.+V+H+Ccp       -44.0       -9.0       268.0       258.0       35.9         25-487       1       p       LVHS1       70730       L+V+H+Ccp       -42.2       -11.0       369.8       342.0       44.3         25-478       1       p       LVHS1       65735       L+V+H+Ccp       -57.0       -15.3       395.0       75       330.0       46.9         25-478       1       p       LVHS2       75725       L+V+H+Sy+Ccp±An±O       -56.0       -16.1       446.0       98       398.0       52.8         25-307       2       p       LVHS2       75725       L+V+H+Sy+Ccp±An±O       -56.0       -16.3       271.0       n.d       425.0       36.1         25-307       2       p       LVHS2       90/10       L+V+H+Sy+Ccp±An±O       -57.3       -15.1       243.0       n.d       398.0       342.2         25-307       2       p       LVHS2       60/40       L+V+H+Sy+Ccp±An±O       -46.5       -17.4       340.2       n.d       401.0       41.5         25-307       2       p       LVHS2       80/20       L+V+H+Sy+Ccp±An±O       -47.1       -15.0	25.400	4	P	L VIIO]	707 30	L+V+H+Cep	-03,0	-13.0	441.0		322,8		32.2	
25-487       1       p       LVHS1       70730       L+V+H+Ccp       -42.2       -11.0       369.8       342.0       44.3         25-478       1       p       LVHS1       65/35       L+V+H+Ccp       -57.0       -15.3       395.0       75       330.0       46.9         25-478       1       p       LVHS1       45/55       L+V+H+Ccp       -55.6       -11.6       357.9       277       43.1         25-478       1       p       LVHS2       75/25       L+V+H+Sy+Ccp±An±O       -56.0       -16.1       446.0       98       398.0       52.8         25-307       2       p       LVHS2       70/30       L+V+H+Sy+Ccp±An±O       -56.0       -16.3       271.0       n.d       425.0       36.1         25-307       2       p       LVHS2       70/30       L+V+H+Sy+Ccp±An±O       -57.3       -15.1       243.0       n.d       398.0       34.2         25-307       2       p       LVHS2       60/40       L+V+H+Sy+Ccp±An±O       -46.5       -17.4       340.2       n.d       401.0       41.5         25-307       2       p       LVHS2       80/20       L+V+H+Sy+Ccp±An±O       -47.1       -15.0       <	23-487	1	P	LVD	707.30	L+V+II+Cep	-14.0	-9.0	208.0		208.0		35.9	
25-478       1       p       LVIIS1       05755       L+V+II+Ccp       -57.0       -15.3       395.0       75       330.0       46.9         25-478       I       p       LVIIS1       45755       L+V+II+Ccp       -55.6       -11.6       357.9       277       43.1         25-478       I       p       LVIIS2       75725       L+V+II+Sy+Ccp±An±O       -56.0       -16.1       446.0       98       398.0       52.8         25-307       2       p       LVIIS2       90/10       L+V+II+Sy+Ccp±An±O       -56.0       -16.3       271.0       n.d       425.0       36.1         25-307       2       p       LVIIS2       70/30       L+V+II+Sy+Ccp±An±O       -56.0       -16.3       271.0       n.d       498.0       34.2         25-307       2       p       LVIIS2       70/30       L+V+II+Sy+Ccp±An±O       -46.5       -17.4       340.2       n.d       401.0       41.5         25-307       2       p       LVIIS2       80/20       L+V+II+Sy+Ccp±An±O       -47.1       -15.0       297.0       n.d       378.0       37.9         25-307       1       p       LVIIS2       80/20       L+V+II+Sy+Ccp±An±O	25-487	1	þ	LVD	10730	L+v+n+Cep	-42.2	-11.0	309.8	76	342.0		44.3	
25-478       1       p       LVHS1       43755       L+V+H+Cp       -55.6       -11.6       357.9       277       43.1         25-478       1       p       LVHS2       75725       L+V+H+Cp       -56.0       -16.1       446.0       98       398.0       52.8         25-307       2       p       LVHS2       90/10       L+V+H+Sy+Ccp±An±O       -56.0       -16.3       271.0       n.d       425.0       36.1         25-307       2       p       LVHS2       70/30       L+V+H+Sy+Ccp±An±O       -57.3       -15.1       243.0       n.d       398.0       34.2         25-307       2       p       LVHS2       60/40       L+V+H+Sy+Ccp±An±O       -46.5       -17.4       340.2       n.d       401.0       41.5         25-307       2       p       LVHS2       80/20       L+V+H+Sy+Ccp±An±O       -47.1       -15.0       297.0       n.d       378.0       37.9         25-307       1       p       LVHS2       80/20       L+V+H+Sy+Ccp±An±O       -41.0       -49       258.0       55.3       320.0       35.2         25-307       1       p       LVHS2       90/10       L+V+H+Sy+Ccp±An±O       -54.2	25-478	1	P	TAU2	03/35	L+V+H+Cep	-57.0	-15.3	395.0	د/	330,0	077	46.9	
25-476       1       p       L/1152       1/7 L/1152 <td>25-478</td> <td>L I</td> <td>р</td> <td>LVHS</td> <td>43/33</td> <td></td> <td>-22.0</td> <td>-11.0</td> <td>357.9</td> <td>ΛV</td> <td>209.0</td> <td>211</td> <td>43.1</td> <td></td>	25-478	L I	р	LVHS	43/33		-22.0	-11.0	357.9	ΛV	209.0	211	43.1	
25-307       2       p       LVHS2       90 / 10       L+V+H+Sy+Ccp±An±O       -36.0       -16.5       271.0       n.d       425.0       36.1         25-307       2       p       LVHS2       70 / 30       L+V+H+Sy+Ccp±An±O       -57.3       -15.1       243.0       n.d       398.0       34.2         25-307       2       p       LVHS2       60 / 40       L+V+H+Sy+Ccp±An±O       -46.5       -17.4       340.2       n.d       401.0       41.5         25-307       2       p       LVHS2       80 / 20       L+V+H+Sy+Ccp±An±O       -47.1       -15.0       297.0       n.d       378.0       37.9         25-307       1       p       LVHS2       80 / 20       L+V+H+Sy+Ccp±An±O       -41.0       -4.9       258.0       55.3       320.0       35.2         25-307       1       p       LVHS2       90 / 10       L+V+H+Sy+Ccp±An±O       -54.2       -16.2       385.0       74.0       375.0       45.8	20-478	1	P	1. 41102	13/23	L+V+H+Sy+Ccp±An±O	•24.0	-10.1	440.0	۵۷ - ما	398.0		52.8	
25-307       2       p       LVHS2       70730       L+V+H+Sy+Ccp±An±O       -37.3       -15.1       243.0       n.d       398.0       54.2         25-307       2       p       LVHS2       60/40       L+V+H+Sy+Ccp±An±O       -46.5       -17.4       340.2       n.d       401.0       41.5         25-307       2       p       LVHS2       80/20       L+V+H+Sy+Ccp±An±O       -47.1       -15.0       297.0       n.d       378.0       37.9         25-307       1       p       LVHS2       80/20       L+V+H+Sy+Ccp±An±O       -41.0       -4.9       258.0       55.3       320.0       35.2         25-307       1       p       LVHS2       90/10       L+V+H+Sy+Ccp±An±O       -54.2       -16.2       385.0       74.0       375.0       45.8	25-307	2	p	1. 1102	70/10	L+V+H+Sy+Ccp±An±O	-30,0	-10.3	2/1.0	n.a	423.0		30.1	
25-307       2       p       LVIIS2       00/40       L+V+II+Sy+Ccp±An±O       -40.5       -17.4       340.2       n.d       401.0       41.5         25-307       2       p       LVIIS2       80/20       L+V+II+Sy+Ccp±An±O       -47.1       -15.0       297.0       n.d       378.0       37.9         25-307       1       p       LVIIS2       80/20       L+V+II+Sy+Ccp±An±O       -41.0       -4.9       258.0       55.3       320.0       35.2         25-307       1       p       LVIIS2       90/10       L+V+II+Sy+Ccp±An±O       -41.0       -4.9       258.0       55.3       320.0       35.2         25-307       1       p       LVIIS2       90/10       L+V+II+Sy+Ccp±An±O       -54.2       -16.2       385.0       74.0       375.0       45.8	23-307	2	Р	1.01162	60140		•37,5 A6 E	-13.1	243,0	n.a	101 C		34.2	
25-307       2       p       L VH32       80 / 20       L + V + H + Sy + Cep±An±O       - 47.1       - 15.0       297.0       n.d       378.0       37.9         25-307       I       p       L VHS1       80 / 20       L + V + H + Sy + Cep±An±O       - 41.0       - 4.9       258.0       55.3       320.0       35.2         25-307       I       p       L VHS2       90 / 10       L + V + H + Sy + Cep±An±O       - 54.2       - 16.2       385.0       74.0       375.0       45.8	23-307	2	P	1 11102	00/40	L+v+II+Sy+Cip±All±U	-40.3	-17.4	340.2	п.a	401.0		41.5	
25-307       1       p       L V H 31       80 / 20       L V H 1 + Sy + Cep±An±O       -41.0       -4.9       258.0       55.3       320.0       35.2         25-307       1       p       L VH 32       90 / 10       L + V + H + Sy + Cep±An±O       -54.2       -16.2       385.0       74.0       375.0       45.8	25-307	2	P	LV1152	80720	L+V+II+Sy+Cep±An±O	-4/.1	-12.0	297.0	11.d	378,0		37.9	
25-307 I p LVII52 90710 L+V+H+Sy+Cep±An±O -54.2 -16.2 385.0 74.0 375.0 45.8	25-307	1	Р	LVHS	80720	L+V+H+Sy+Cep±An±O	-41.0	-4.9	258.0	22.3	320,0		35.2	
	25-307	1	р	LVHS <sub>2</sub>	90710 00.117	L+V+H+Sy+Ccp±An±O	-54.2	-16.2	385.0	74.0	375.0		45.8	

APPENDIX II

ويستنكر ويستغيره مستا						APPE	NDIX II					نور بسند المسالي ا		
Sample	Chip #	Origin	Туре	1.7V %	Component	Te (° C)	Tm (° C) Tm (° C	C) HE-11	n (° C) Talite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Salinity LVHS types	Salinity LV and VL types
25-307	2	p	LVHS <sub>2</sub>	90/10	L+V+II+Sy+Ccp±An±O	-54,3	-14.9	•	145.0	91.0	430.0		52.6	
25-307	1	р	LVHS <sub>2</sub>	70/30	L+V+H+Sy+Ccp±UI±O	-53.0	-9.5		469.0	91.3	451.0		55.7	
25.466	3	р	LVHS <sub>2</sub>	60740	l.+V+ll+Sy+Ccp±U1±O	-30,4	-3.5	:	363.0	80.0	380,0		43.6	
33-473	2	р	LVHS <sub>2</sub>	80/20	L+V+H+Sy+Ccp±U1±O	-51.0	-7.1		437.3	85.0	430,0		51.7	
33.473	1	p	LVHS <sub>2</sub>	80/20	.+V+H+Sy+Ccp±An±U1±(	-56.0	-9.8		451.0	91.0	478.0		53,4	
33-473	2	p	LVHS <sub>2</sub>	70/30	L+V+H+Sy+Ccp±U1±O	-49,0	-8.7		453.0	98.0	410,0		53.6	
33-473	2	р	LVHS <sub>2</sub>	80 / 20	L+V+H+Sy+Ccp±U1±O	-53.2	-14.9		498.0	119.0	485,0		59.5	
25-307	1	p	LVHS <sub>3</sub>	35/75	L+V+H	-62.0	-13.9		430.0			393	50.8	
25-307	2	р	LVHS <sub>3</sub>	80/20	L+V+11	-40.0	-7.0		463.0		350,0		54.9	
25.466	2	5	LVHS <sub>3</sub>	80/20	L+V+H	-45.0	-15.9	:	280.0		245.0		36.7	
25,466	3	р	LVHS <sub>3</sub>	80/20	L+V+H	-41.0	-6,6		373.0		305.0		44.6	
25.466	1	р	LVHS <sub>3</sub>	80/20	L+V+H	-60.0	-14.0		425.0		277.0		50.3	
25-478	1	р	LVHS <sub>1</sub>	85/15	L+V+H	-49.6	-17.0		291.0		289.0		37.5	
25-307	2	р	LVHS,	70/30	L+V+H+O	-38.0	-3.7		485.0		363.0		57.8	
25-307	J	p	LVHS	50/50	L+V+H+O	-53.6	-11.0		500			485	59.8	
25.466	2	, D	LVHS	60/40	L+V+H+O	-55.0	-15.0	;	297.0		320.0		37.9	
25.466	1	ns	LVHS	70/30	L+V+II+O	-54.4	.13.9		310.0		278.0		38.9	
33-473	1	5 1	LVHS	70/30	L+V+H+Cen	-53.0	.33.0 11	2	295.0		307.0		37.8	
33-473	-	n	LVHS	60/40	L+V+H+Cm	-57.0	-14 5		385.0		398.0		45.8	
25-307		DS	LVHS	35 / 75	V+L+H+UI	-46.5	-5.6		458.0		2211.0	366	54.3	
25-487	1	р.	LVIIS	75/25	V+L+11+U1	-41.3	-8.3		373.0		262.7		44.6	
	GR	OUP III V	EINS											
25-280	I	р	LV	65/35	L+V	-21.6	-6.3				248.0			9.6
25-280	1	р	LV	80/20	L+V	-18.5	-5.1				241.0			8.0
25-280	1	ps	LV	80/20	L+V	-22.0	-4.2				233.0			6.7
25-233	1	р	LV	90 / 10	L+V	-23.1	-7.2				302.0			10.8
25-233	1	р	LV	85715	L+V	-24.0	-8.5				295.0			12.3
25-233	2	ps	LV	85715	L+V	-23.1	-9.4				330.0			13.3
25-233	2	р	LV	80/20	L+V	-20.5	-12.3				345.0			16.3
25-233	2	he su	LV	80/20	1.+V	-23.0	-10.3				337.0			14.3
25-233	2	ps	1.V	65/35	1.+V	-19.9	-2.5				312.0			4.2
25-233	1	р		65/35	L+V	-19.6	-5.5				328,0			8.6
25-233	1	р		80720	L+V	-21.8	-3.6				312.0			5.8
23-233	1	P		80/20		-20.0	-2.9				292.0			4.8
20.200	1	3	L.¥	03733	LT V	-19.7	-2.1				230,0			3.2

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Sample	Chip#	Origin	Туре	L/V %	Component	Te (° C)	Tm (° C) fm (° C) 111	Th (° C) Halite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Salinity LVHS types	Salinity LV and VL types
25-233	2	ps	LV	80/20	L+V	-25.0	-6.3			321.0			9.6
25-233	2	ps	LV	90710	L+V	-23.5	-9.2			310.0			13.1
25-233	2	ps	LV	85/15	I.+V	-19.0	-11.1			298.0			15.1
25-233	2	15	LV	65/35	L+V	-27.0	-5,2			293.5			8.1
25-233	2	ps.	LV	85715	L+V	-31.1	-4.8			271.0			7.6
25-233	2	)ns	1.V	90/10	I.+V	-27.5	-3.1			237.0			5.1
25-233	2	ps	LV	75/25	L+V	-22.1	-2.9			225,0			4.8
25-280	1	125	L.V	85715	L+V	-21.7	-4.3			235.0			6.9
25-280	1	р	L.V	65/35	L+V	-22.0	-7.2			273.0			10.8
25-280	1	ps	LV	85715	L+V	-21.3	-6.2			254.0			9.5
25-280	1	p	L.V	90/10	1.+V	-20.0	-3.8			269.0			6.1
25-273	1	p	1.V	90710	1.+V	-24.9	-1.3			235.0			2.2
25-280	1	p	L.V	85715	I.+V	-19.8	-2.9			255.5			4.8
25-280	2	125	1.V	65/35	I.+V	-22.0	-6.2			269.0			9.5
25-280	1	ps	LV	75/25	L+V	- 19.4	-4.1			225.0			6.6
25-280	3	, p	VI.	20/80	V+L+O	-28.0	-7.2			432.0			10.8
25-280	3	р	VI.	30/70	V+1.	-25.0	-0.9			520.0			1.6
25-280	3	p	VL.	50/50	V+L	-30.6	-4.2			387.0			6.7
25-280	3	• p	VL	45/50	V+L+O	-29.3	-1.2			478.0			2.1
25-280	3	p	VI.	50/50	V+L	-26.2	-13.2			493.0			17.1
25-280	3	p	VL	55/45	V+L	-26,4	-12.6			605.0			16.6
25-280	3	p	VL.	20/80	V+L	· -24.0	-7.3			510.6			10.9
25-280	3	p	VI.	20/80	V+L+O	-23.5	-11.0			420.0			15.0
25-280	3	р	VL.	30/70	V+L	-23.7	-7.9			381.0			11.6
25-273	1	р	LVHS <sub>3</sub>	90/10	L+V+II+O	-41.0	-9.0	310.9		268,0		39.0	
25-273	2	р	LVHS <sub>3</sub>	70/30	L+V+H	-39.5	-11.0	265.0		251.0		35.6	
25-273	2	s	LVHS <sub>3</sub>	80 / 20	L+V+H	-42.0	-10.2	260.0		245.0		35.3	
25-273	3	р	LVHS	65/35	1.+V+II	-36.0	-8.0	245.0		230.0		34.4	
25-273	3	p	LVHS	85/15	L+V+H	-35,7	-6.2	251.0		245.0		34.7	
25-273	3	ı D	LVHS	90/10	L+V+H	-36.8	-7.0	214.0		258.0		32.6	
25-273	3	r D	LVHS.	75/25	L+V+H	-38.0	-9.0	247.0		293.0		34.5	
25.273	4	P P	I VHS.	85/15	1+V+H	.33.0	-5.0	211.0		276.0		32.4	
25-273	л А	P	I VHS.	75/25	1 4 1 4 1 1	20.0	-5,8	2010		201.0		38.0	
22.273	7	P	1 1/103	75/25		-29.0		296.0		291.0		30.0	
23-213	4	P	L VII33	12142		-32,4	-3,4	241.0		280.0		34.1	
25-273	4	р	LVHS3	90710	L+V+11	-31.0	-5,0	235.0		215.0		33.8	
25-307	1	bz	LVHS <sub>3</sub>	85/15	L+V+H	-32.0	-9.1	321.0		250,0		39.8	
25-307	1	ps	LVHS3	75/25	L+V+H	-36.8	-6.8	373.0		258.0		44.6	
25-307	1	ba	LVHS3	85715	L+V+H	-31.7	-8,4	342.0		240.0		41.7	

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Sample	Chip#	Origin	Туре	L/V %	Component	Te (° C)	Tm (° C) I'm (° C) Hł	Th (° C) Halite	Th (° C) Sylvite	Th (° C) Liquid	Th (° C) Vapour	Salinity LVHS types	Salinity LV and VL types
25-307	1	ps	LVHS <sub>3</sub>	70/30	L+V+H	-43.0	-12.1	381.0		300.0		45.4	
25-273	4	р	LVHS <sub>3</sub>	85/15	L+V+H	-30,5	-6.5	298.0		320.0		38.0	
25-273	4	р	LVHS <sub>3</sub>	70/30	L+V+H	-28.7	-6.6	231.0		252.0		33.5	
25-273	4	р	LVHS <sub>3</sub>	70/30	L+V+H	-26.0	-4.1	236.0		293.0		33.8	
25-273	4	р	LVHS <sub>3</sub>	90/10	L+V+H	-32.0	-6.0	230.0		261.0		33.5	
25-273	3	р	LVHS <sub>1</sub>	85715	1.+V+H	-38.5	-6.8	291.0		326.0		37.5	
25-273	3	S	LVHS <sub>3</sub>	80/20	L+V+H	-40.3	-12.0	271.0		320,0		36.1	
25-273	3	р	LVHS <sub>3</sub>	85/15	L+V+H	-39.0	- 8.4	264.0		258.0		35.6	
25-273	3	р	LVHS <sub>3</sub>	85/15	L+V+H	-37.3	-8,2	216.0		251.0		32.7	
25-273	1	р	LVHS <sub>3</sub>	85/15	L+V+II+O	-42,0	-8.0	325,0		329,0		40.2	
25-273	2	p	LVHS <sub>3</sub>	85 \ 15	L+V+II+O	•41.0	-9.0	273.0		261.0		36.2	
25-273	3	ps	LVHS <sub>3</sub>	80/20	L+V+H+O	-41.0	-6.3	259.0		231.0		35.3	
25-273	1	p	LVHS <sub>3</sub>	70/30	L+V+H+O	-38,0	-6.4	351.0		345.0		42.5	

### **ELECTRON MICROPROBE DATA FROM SUNGUN**

### **MINERALS**

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<u></u>				Electron	Microprobe	Analyses o	f Amphibole	s in the Sun	gun Granod	orite				<u></u>
Sample no. Dril-core no. Tuna <sup>1</sup>	1 23-158 Era	2 23-158 Era	3 23-158 Em	4 23-158 Free	5 23-158 Em	6 23-158 Fra	7 23-158 Fra	8 23-158 Vire	9 23-158 Em	10 23-158 Em	11 23-158 Em	12 23-158 Fm	13 23-158 Ere	14 23-158 Em
Type	<u> </u>	<b>F15</b>	<b>F18</b>	148	<u></u>	<u>F15</u>	118	148	ris	148	rts	LIS	FIS	<u> </u>
SiO, (wt %)	48.88	46.99	45.89	46.82	47.16	47.01	46.76	47.77	47.09	47.19	45.88	48.01	47.05	46.52
TiO,	1.18	1.45	1.50	1.34	1.28	1.43	1.33	1.12	1.11	1.20	1.36	1.13	1.25	1.31
Al <sub>2</sub> O <sub>1</sub>	6.29	7.10	7.78	7.24	6.81	7.22	7.11	7.04	7.00	6,83	7,84	6.71	7.37	7.34
FeO <sup>2</sup>	11.88	12.50	13.36	13.08	13.08	13.29	13.23	12.60	12,86	12.97	13,55	13.12	13.18	13.01
MnO	0.46	0.43	0.44	0.47	0.43	0.44	0,47	0.46	0.40	0.41	0.42	0.46	0.44	0,45
MgO	16.43	15.46	15.00	15.38	15.30	15.06	15.10	15,66	15.36	15.63	14.68	15.52	15,20	15.21
CaO	11.27	11.21	11.27	11.48	11.30	11.39	11.27	11.39	11.34	11.21	11.41	11.39	11.39	11.22
Na <sub>2</sub> O	1.33	1.85	1.57	1.51	1.67	1,50	1.55	1.43	1.68	1.52	1.78	1.48	1.49	1.68
K,O	0,39	0.85	0.63	0.57	0.70	0.54	0.52	0.52	0.65	0.54	0.82	0.54	0.59	0.61
F	0.11	0.14	0.06	0.14	0.21	0.17	0.07	0.17	0.05	0.07	0.19	0.06	0.14	0.09
- Cl	0.08	0.39	0.10	0.10	0.33	0.08	0.09	0.08	0.36	0.11	031	0.14	0.08	0.20
Total	08.78	08 37	07.58	08.12	08.26	08.11	07 48	0,00	07.00	07.66	09.23	08 54	0,00	07.63
No of store	70,20	20,37	21.20	<i>70.12</i>	20.20	90.11	21,40	20.22	51.50	97.00	20,43	20.34	20,10	27.05
based on 24 O														
based on 24 O														
Si	7.35	7.14	7.06	7.14	7.17	7.16	7.18	7.23	7.19	7.22	7.02	7.27	7.16	7.13
Ti	0.13	0.17	0.17	0.15	0.15	0.16	0.15	0.13	0.13	0.14	0.16	0,13	0.14	0.15
Al	1.12	1.27	1.41	1.30	1.22	1.30	1.29	1.26	1.26	1.23	1.42	1.20	1.32	1.33
Fe	1.50	1.59	1.72	1.67	1.66	1.69	1.70	1.60	1.64	1.66	1.74	1.66	1,68	1.67
Mn	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.05	0.06	0.06	0.06
Mg	3,68	3.50	3.44	3.49	3.47	3.42	3.46	3,54	3.50	3,56	3,35	3,50	3.45	3,48
Ca	1,82	1,82	1,86	1.87	1.84	1.86	1.85	1.85	1.86	1.84	1.87	1,85	1.86	1.84
Na	0.39	0.55	0.47	0.45	0.49	0.44	0.46	0.42	0.50	0.45	0.53	0.43	0.44	0.50
к	0.07	0.16	0.12	0.11	0,14	0,11	0.10	0.10	0.13	0,11	0,16	0,11	0.12	0.12
F	0,05	0,07	0.03	0.07	0.10	0.08	0.03	0.08	0.02	0.03	0.09	0.03	0.07	0.04
Cl	0.02	0.10	0.03	0.03	0.09	0.02	0.02	0.02	0.09	0.03	0.08	0.04	0.02	0.05
	0.70	0.40		0.70		0.70	0.60	0.0-	0.10	0.5.1	0.64	0.45	0.74	0.44
F/(F+Cl)	0,70	0,40	0.51	0,72	0.54	0.79	0.59	0.81	0,19	0.54	0.54	0.45	0.76	0,44
I'C/(I'C+Mg)	0.29	0.31	0.33	0.32	0.32	0.33	0.33	0.31	0.32	0.32	0.34	0.32	0,33	U, J //

<sup>1</sup> Frs = fresh rock <sup>2</sup> FeO = total Fe

				in collected in the		Amp	hiboles (con	.)						
Sample no.	15	16	17	18	19	20	22	23	24	25	26	27	28	29
Dril-core no.	23-158	23-158	23-158	23-158	23-158	23-158	23-158	23-158	23-158	23-158	23-158	23-158	23-158	23-158
Type 1	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs	Frs
Si(), (wt %)	47.83	46.04	48.29	47.49	47.65	47.06	46.86	47.19	48.58	48.23	45.58	46.75	47.03	46.73
TiO,	1.16	1.48	1.09	1.34	1.32	1.43	1.50	1.39	1.15	1.25	1.13	1.39	1.29	1.33
ALO	6.80	8.16	6.45	7.15	6.70	7.17	7.46	7.32	6.33	6.42	6.05	7.40	7.01	7.36
FeO <sup>2</sup>	12.90	13.34	12.72	13.48	13.37	13.10	13.32	12.87	11.87	11.80	12.06	13.12	12.98	12.87
MnO	0.43	0.39	0.45	0.48	0.45	0.41	0.46	0.40	0.46	0,47	0.41	0.46	0.44	0.46
MgO	15.64	14.79	15.72	15.16	15.44	15.10	15,13	15.39	16.27	16.37	15,27	15.13	15.25	15.24
CaO	11.44	11.47	11.35	11.26	11.23	11.20	11.16	11.37	11.13	11.28	11.20	11.43	11.42	11.34
Na <sub>2</sub> O	1.43	1.88	1.38	1.48	1.53	1.71	1.70	1.63	1.54	1.54	2,43	1.73	1.57	1.68
K <sub>1</sub> O	0.53	0.76	0.50	0.53	0.49	0.80	0,66	0,64	0.53	0.45	1.10	0.63	0.58	0.62
F	0.09	0.09	0.07	0.10	0.22	0.10	0.13	0.09	0.12	0.18	0.15	0.09	0.11	0.10
CI	0.08	0.25	0.07	0.11	0.08	0.28	0.25	0.20	0.28	0.10	0.87	0.19	0.09	0.15
Total	98.32	98.65	98.07	98.57	98.48	98.35	98.62	98.50	98.25	98.09	96.25	98.31	97.77	97.88
No. of atoms														
hased on 24 O														
Si	7.25	7.01	7.33	7.20	7.22	7,16	7.11	7.16	7.32	7.28	7.11	7.12	7.19	7.14
Ti	0.13	0.17	0.12	0.15	0.15	0.16	0.17	0.16	0.13	0.14	0.13	0.16	0.15	0.15
	1.22	1.47	1.15	1.28	1,20	1.29	1.33	1.31	1.12	1.14	1.11	1.33	1.26	1.33
Fe	1,64	1.70	1.61	1.71	1,70	1.67	1.69	1.63	1.50	1.49	1.57	1.67	1.66	1.64
Mn	0.06	0.05	0.06	0.06	0.06	0.05	0.06	0.05	0.06	0.06	0.06	0.06	0.06	0.06
Mg	3.54	3.36	3.56	3.43	3.49	3,43	3.42	3.48	3.66	3.69	3.55	3.44	3.48	3.47
Ca	1.86	1.87	1.85	1.83	1.82	1.83	1.82	1.85	1,80	1.83	1.87	1.87	1.87	1.86
Na	0.42	0.56	0.41	0.44	0.45	0.50	0.50	0.48	0.45	0.45	0.74	0.51	0.47	0.50
к	0.10	0.15	0.10	0.10	0.10	0.16	0.13	0.12	0.10	0.09	0.22	0.12	0.11	0.12
F	0.04	0.04	0.03	0.05	0.11	0.05	0.06	0.05	0,06	0.09	0.08	0.04	0.05	0.05
Cl	0.02	0.07	0.02	0.03	0.02	0.07	0.06	0.05	0.07	0.03	0.23	0.05	0.02	0.04
F/(F+Cl)	0.68	0.40	0.62	0.65	0.84	0.40	0.49	0.47	0.45	0.78	0.25	0.47	0.68	0.55
Fe/(Fe+Mg)	0.32	0.34	0.31	0.33	0.33	0.33	0.33	0.32	0.29	0.29	0.31	0.33	0.32	0.32

				Electron Mic	roprohe Analy	ysis of Feldspar	s from Sungu	<u>a Porphyry Co</u>	pper Deposit				
Sample no. Dril-core no. Stage	l 33-437 K	2 33-437 K	3 33-437 K	4 33-437 K	5 33-437 K	6 33-437 K	7 33-437 K	8 33-437 K	9 33-354 K-Tm	10 33-354 K-Tm	11 33-354 K-Tm	12 33-354 K-Tm	13 33-354 K-Tm
SiO2	66.74	62.93	64.37	63.74	64.68	69.18	63.99	64.26	64.49	67.51	64.43	64.24	65.59
A12O3	17.64	19.79	18.53	18.71	18.51	19.18	18.69	18,48	18.72	19.08	18.47	18,54	18.92
FeO	0.03	1.28	0.06	0.08	0.12	0.13	0.10	0.07	0.09	0.09	0.09	0.07	0.22
MgO	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
CaO	0.01	0.05	0.01	0.06	0.10	0.13	0.06	0,03	0.42	0.38	0.13	0.09	0.65
Na2O	0.39	1.85	0.80	1.28	2.02	1.62	1.31	0.92	1.64	1.32	1.27	1.20	2.72
K2O	15.84	13.05	16.19	15.33	13.61	9.69	14.95	15.56	14.52	11.60	15.06	15,36	13.33
BaO	0.99	0.71	0,85	1.08	1.34	1.32	1,05	1.40	1.00	1.05	0.92	0.74	0.14
Total	101.64	99.67	100.82	100.28	100.39	101.23	100.14	100.72	100.87	101.03	100.37	100,24	101.57
No. of atoms													
based on 8 O													
Si	3.04	2.92	2.98	2.96	2,98	3.06	2.97	2.98	2.97	3.03	2.98	2.98	2.97
Al	0.95	1.08	1.01	1.02	1.00	0.98	1.02	1.01	1.01	1.01	1.00	1.01	1.01
Fe	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0,00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0,00	0.00	0,00	0,00
Ca	0,00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.01	0.01	0.03
Na	0.04	0.17	0.07	0.12	0.18	0.14	0.12	0.08	0.15	0.12	0.10	0.11	0.24
К	0.94	0.77	0.96	0.91	0.80	0.55	0.89	0.92	0.85	0.66	0.89	0.91	0.77
Ba	0.02	0.01	0.02	0,02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.01	0.00
Sum	4.99	5.00	5.04	5.03	4.98	4.75	5.02	5.02	5.02	4.85	5.00	5.03	5.02
sum of cations	0.98	0.94	1.03	1.03	0.98	0.69	1.01	1.00	1.02	0.80	1.00	1.03	1.04
Or	95.92	81.91	93.20	88.35	81.63	79.71	88.12	92.00	83,33	83.31	89.00	88.35	74.04
Ab	4.08	18.09	6,80	11.65	18.37	20.29	11.88	8.00	14.71	14.43	10.00	10.68	23.08
An	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1,96	2.26	1.00	0.97	2.88
Or/(Or+Ab+An)	0.96	0.82	0.93	0.88	0.82	0.80	0.88	0.92	0.83	0.83	0.89	0.88	0.74

 $\frac{Or/(Or+Ab+An)}{^{1}} \text{ Frs} = \text{fresh rock, } K = \text{potassic zone, } K\text{-Trn} = \text{potassic-transition zone, } Phc = \text{phyllic}$ 



						Feld	spars (cont.)	-						
Sample no. Dril-core no. Stage	14 33-354 K-Tm	15 25-444 <u>K</u>	16 25-444 K	17 25-444 K	18 25-444 K	19 25-444 K	20 25-444 K	21 25-444 K	22 25-444 K	23 25-444 <u>K</u>	24 25-444 K	25 25-421 K	26 25-421 K	27 25-421 K
SiO2	65.08	64.60	64.95	64.81	64.41	64.86	65.72	64,43	64.95	65.92	64.68	66.72	65.09	64.79
AI2O3	18,31	18.59	18.73	18.41	18.34	18.43	17,89	18,70	18.39	17.71	18.31	17,79	18.26	18.52
FeO	0.07	0.09	0.04	0.09	0.09	0.05	0.04	0.09	0.08	0.20	0.07	0.06	0.08	0.05
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0,00
CaO	0.00	0.01	0.02	0.03	0.05	0.00	0.00	0,18	0.08	0.08	0.05	0.06	0.00	0.04
Na2O	0.95	1.03	1.06	1.10	1.08	0.88	0.12	1.92	1.30	0 95	1.02	1.35	0.89	1.22
K2O	15.87	15.68	15.73	15.48	15.57	16.00	17.44	13.84	15.10	15.68	15.86	14.73	16.03	15.40
BaO	0.53	0.85	0.99	0.85	1.02	0.88	0.16	1.33	0.98	0.32	0.65	0.98	0.64	0.75
Tota)	100.80	100.85	101,52	100.78	100.56	101.10	101.37	100,49	100.89	100.87	100.63	101.70	100.98	100.76
No, of atoms														
hased on 8 O														
Si	2.99	2.98	2.98	2.99	2.98	2.99	3.01	2.97	2.99	3.02	2.99	3.03	2.99	2.98
Al	0.99	1.01	1.01	0,98	1.00	0.98	0.96	1.01	1.00	0.96	0.99	0.99	0.98	1.00
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.10	0.10	0.09	0.09	0.10	0.07	0.01	0.17	0.12	0.08	0.09	0.12	0.10	0.11
К	0.92	0.92	0.92	0.92	0.92	0.94	1.02	0.82	0.89	0.92	0.93	0.84	0.92	0.90
Ba	0.01	0.02	0.02	0.02	0.02	0.02	0.00	0.02	0.02	0.01	0.01	0.02	0.01	0.01
Sum	5.01	5.03	5.02	5,00	5.02	5.00	5.00	5.00	5.02	5,00	5.01	5,00	5,00	5.00
sum of cations	1.02	1.02	1.01	1.01	1.02	1.01	1.03	1.00	1.01	1.00	1.02	0.96	1.02	1.01
Or	90.20	90.20	91.09	91.09	90,20	93.07	99.03	82.00	88.12	92.00	91.18	87,50	90.20	89.11
Ab	9,80	9.80	8.91	8.91	9.80	6.93	0.97	17.00	11.88	8,00	8.82	12.50	9.80	10,89
An	0.00	0.00	0.00	0,00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Or/(Or+Ab+An)	0.90	0.90	0.91	0.91	0.90	0.93	0.99	0.82	0.88	0.92	0.91	0.88	0.90	0.89



						Feld	spars (cont.)							
Sample no.	28	29	30	31	32	33	34	35	36	37	38	40	41	42
Dril-core no.	25-421	25-421	25-421	25-421	25-421	7-275	7-275	7-275	7-275	7-275	7-275	7-275	7-275	7-275
Stage	<u>K</u>	К	К	к	к	Phc	Phe	Phc	Phe	Phc	Phc	Phe	Phe	Phe
		<	60.00	<i>( )</i> <b>7</b> 0		<i>(</i> <b>) -</b>	( <b>a</b> a (	(0.0)		<i></i>				( <b>a</b> a (
SiO2	64.64	64.00	63.83	64.70	64,70	62.72	62,96	63,04	63,14	63,62	70,14	75.92	65.84	63.06
AI2O3	18.23	18.52	18.53	18.46	18,39	23.00	22.95	22.62	22.85	22.37	19.40	17,60	21.96	22.50
FeO	0.10	0.11	0.05	0.06	0.07	0.18	0.14	0.15	0.17	0.17	0.03	0,18	0.45	0.21
MgO	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.02	0.00	0.03	0,41	0.01
CaO	0.00	10.0	0.03	0.02	0.10	4.78	4.63	4.51	4.75	4.36	0.61	0,77	0.52	4.38
Na2O	0.66	1.05	0.91	1.13	1.10	8.41	8.50	8.36	8.72	8.84	10.83	8.67	7.89	8,01
K2O	16.54	15.47	15.50	15.15	15.62	0.29	0.48	0.65	0.18	0.22	0.15	0.43	2.74	1.12
BaO	0.67	1.03	1.74	1.54	0.72	0.13	0.04	0.08	0.03	0.00	0.00	0,00	0.00	0.09
Total	100.83	100,18	100.59	101.06	100.71	99.52	99.70	99.41	99.85	99.60	101.17	103.61	99.82	99.38
No, of atoms														
based on 8 O														
Si	2.99	2.97	2.97	2.98	2.98	2.81	2.81	2.81	2.80	2.82	3.01	3.15	2.90	2.81
AI	0.99	1.00	1.00	1,00	0,98	1.20	. 1.20	1.19	1.19	1.18	1.00	0.86	1.14	1.18
Fe	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.02	0.01
Me	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Ca	0.00	0.00	0.00	0.00	0.01	0.23	0.22	0.22	0.23	0.22	0.03	0.03	0.02	0.21
Na	0.06	0.09	0.08	0,10	0.10	0.73	0.73	0.73	0.76	0.76	0.95	0,70	0,67	0.69
К	0.98	0.92	0.92	0.89	0.92	0.02	0.03	0.04	0.01	0.01	0.01	0,02	0.15	0.06
Ba	0.01	0.02	0.03	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0,00	0.00	0.00
Sum	5.03	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	4,77	4.93	4.96
sum of cations	1.04	1.01	1.00	0.99	1.03	0.98	0.98	0.99	1.00	0.99	0.99	0.75	0.84	0.96
Or	94.23	91.09	92.00	89.90	89.32	2.04	3.06	4.04	1.00	1.01	1.01	2.67	17.86	6.25
Ab	5.77	8.91	8,00	10.10	9.71	74.49	74.49	73.74	76.00	76.77	95,96	93,33	79.76	71.88
An	0.00	0.00	0.00	0.00	0.97	23.47	22.45	22.22	23.00	22.22	3.03	4.00	2.38	21.88
Or/(Or+Ah+An)	0.94	0.91	0.92	0.90	0.89	0,02	0.03	0.04	0.01	0.01	0.01	0,03	0.18	0.06

						Feld	spars (cont.)							ويوفقك ويجبعه
Sample no. Dril-core no. Stage	43 7-275 Phc	44 7-275 Phe	45 7-275 Phe	46 7-275 Phe	47 7-275 Phe	48 7-275 Phe	49 7-275 Phc	50 7-275 Phe	51 34-322 K	52 34-322 K	53 34-322 K	54 34-322 K	55 34-322 K	58 34-322 K
														<b></b>
SiO2	62.86	62.66	67.17	62.84	58,74	63.15	79.10	62.09	63.45	61.74	60,87	63.17	63.14	58.75
A12O3	22.84	22.48	21.68	23.02	25.00	22.54	13.59	22.89	22.33	23.44	23.93	22.66	22.46	20.08
FeO	0.18	0.18	0.05	0.16	0.18	0.17	0.06	0.14	0.16	0.20	0.14	0.16	0.13	0.24
MgO	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0,00	0.00	0,00
CaO	4.90	4.77	3.05	4.87	7.55	4.64	0.58	4.99	4.30	5.25	6.03	4.52	4.30	4.36
Na2O	7.80	7.86	9.05	7.94	6,69	7.90	5.46	7.86	8.22	7.79	7.49	8,15	8.41	8,18
K2O	1.01	1.07	0,55	1.00	0.53	1.10	3.86	0.85	0,95	0.76	0.66	0.94	0,85	0,34
BaO	0.06	0.05	0.02	0,05	0.06	0.12	0.11	0.06	0.04	0.08	0.05	0.04	0.04	0.01
Total	99.66	99.08	101.57	99.89	98.75	99.61	102,76	98.88	99.44	99.27	99.18	99.63	99.33	91.95
No. of atoms hased on 8 O														
Si	2.80	2.81	2.90	2.79	2.66	2.81	3.32	2.79	2.82	2.76	2.73	2.81	2.82	2.83
Al	1.20	1.18	1.10	1.20	1.33	1.20	0.70	1.21	1.20	1.23	1.26	1.20	1.18	1.14
Fe	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0,00	0.00	0.00
Ca	0.23	0.23	0.14	0.22	0.37	0.22	0.26	0.24	0.20	0,25	0.29	0.22	0.21	0.23
Na	0.67	0.68	0.76	0.68	0.59	0.70	0.44	0.68	0.71	0.68	0,66	0,70	0.73	0.76
к	0.06	0.06	0,03	0.10	0.03	0.06	0.21	0.01	0.05	0.04	0.04	0,05	0.05	0.02
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0,00	0.00	0,00
Sum	4.97	4.97	4.93	5.00	4.99	5.00	4.93	4.94	4.99	4.97	4.99	4.99	5,00	4.99
sum of cations	0.96	0.97	0.93	1.00	0.99	0.98	0.91	0.93	0,96	0.97	0.99	0.97	0,99	1.01
Or	6.25	6.19	3.23	10.00	3.03	6.12	23.08	1,08	5.21	4.12	4.04	5.15	5.05	1.98
Ab	69.79	70.10	81.72	68.00	59.60	71.43	48,35	73.12	73,96	70.10	66.67	72.16	73,74	75.25
An	23,96	23.71	15.05	22.00	37.37	22.45	28.57	25,81	20.83	25,77	29.29	22.68	21.21	22.77
Or/(Or+Ab+An)	0.06	0.06	0.03	0.10	0.03	0.06	0.23	0.01	0.05	0.04	0.04	0.05	0.05	0.02

<u></u>			<u></u>			Feld	spars (cont.)							( <u></u>
Sample no. Dril-core no.	59 34-322	60 34-322	61 34-322	62 34-322	63 34-322	64 34-322	65 34-322	66 34-322	67 34-322	68 34-322	69 34-322	70 34-322	71 34-322	72 34-322
Stage	К	K-Tm	K-Tm	K-Tm	K-Tm	K-Tm	K-Tm	K-Tm	K-Tm	K-Tm	K-Tm	К•Тпі	K-Tm	K-Tm
2:00	62.52	67.16	67.94	61.21	62.18	61 17	62 51	61 55	62.07	Z1 91	60.74	61.09	<b>41</b> 91	62.60
A12(22	22.32	03.10	02.04	22.03	22.10	17 51	224	22.35	22.07	22.61	22.00	22.00	22.45	22,00
A1205 Esc)	0.21	0.07	018	0.18	0.18	0.04	0.16	014	D 14	017	0.16	£2.02 0.17	014	013
Mat	0.21	0.07	0.10	0.10	0.01	0.04	0.10	0.00	0.14	0.17	0.10	0.17	0.14	0,15
MgO CaO	5.08	1 38	4.60	5.43	4 86	0.01	4.62	1.75	5.02	1.88	5.43	5 3.1	5.00	4.81
	.J.UG 7 99	4,30	7.00	5.45 7 V7	7.00	0.00	7.86	8.05	7.80	7.00	7.55	7.74	7 80	7.01
Naz()	1.00	0.20	1.10	0.67	0.00	16.12	1.03	0.07	0.02	0.06	0.86	0.01	0.00	0.00
N20	1,02	0,56	0.02	0.07	0.99	0.78	0.10	0.02	0.92	0,90	0.00	0.91	0.90	0.99
BaO	0.10	0,00	0.0.5	0.06	0.11	0,78	0.10	0.05	0.02	0,08	0.06	0.04	0.05	0.02
Total	99.63	98.87	99.39	98.45	98.52	99.55	98.98	97.83	98.62	98.43	97.69	98.12	98.24	99.09
No. of atoms														
hased on 8 O														
Si	2.79	2.82	2.81	2.77	2.80	3.02	2.80	2.79	2.79	2.79	2.76	2.77	2.79	2.80
AL	1.20	1.17	1.18	1.22	1.18	0.96	1.19	1.19	1.19	1,20	1.23	1.22	1.19	1,19
Fe	0.01	0.00	0.01	0.01	0.01	0.00	. 0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Me	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.24	0.21	0.22	0.26	0.23	0.00	0.22	0.23	0.24	0.24	0.26	0.26	0.24	0.23
Na	0.68	0.74	0.69	0.69	0.69	0.03	0.68	0.71	0,69	0.69	0.67	0.68	0.69	0.69
к	0.06	0.02	0.06	0.04	0,06	0.98	0.06	0.06	0.05	0.06	0.05	0.05	0.05	0.06
Ba	0.00	0.00	0.00	0.00	0.00	0,00	0.00	0.00	0.00	0.00	0,00	0.00	0.00	0.00
Sum	4.98	4.96	4.97	4.99	4.97	4.99	4,96	4.99	4.97	4.99	4.98	4.99	4.97	4.98
sum of cations	0.98	0.97	0.97	0.99	0.98	1.01	0,96	1.00	0.98	0.99	0.98	0.99	0.98	0,98
Or	6.12	2.06	6.19	4.04	6.12	97.03	6.25	6.00	5,10	6.06	5.10	5.05	5.10	6.12
Ab	69,39	76.29	71.13	69.70	70.41	2.97	70.83	71.00	70.41	69.70	68.37	68,69	70.41	70.41
An	24.49	21.65	22.68	26,26	23.47	0.00	22.92	23.00	24,49	24,24	26.53	26.26	24.49	23.47

0.06

0.04

0.06

0.97

0.06

0.06

0.05

0.06

0.05

0.05

0.05

0.06

APPENDIX\_III

Or/(Or+Ab+An)

0.06

0.02

Feldspars (cont.)														
Sample no. Dril-core no. Stage	73 34-322 K-Tm	74 44-481 K	75 44-481 K	76 44-481 K	77 44-481 K	78 44-481 K	79 44-481 K	80 44-481 K	81 44-481 K	82 44-481 K	83 44-481 K	84 44-481 K	85 44-481 K	86 44-481 K
SiO2	55.73	62.41	66.54	66.90	65.05	78.54	62.07	58.36	87.89	71.31	70.02	61.13	58,98	62.94
AI2O3	19.28	22.75	17.57	18.13	17.87	13.03	22.50	25.64	6.47	15.02	19.50	23.18	20.78	22.64
FeO	0.17	0.14	0.21	0.05	0,10	0.02	0.16	0.20	0.17	0.12	0.07	0.17	0.16	0.19
MgO	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.33	0.00	0.03	0.00	0.01	0.00
CaO	4.05	4.96	0.03	0.08	0.38	0.19	5.03	8.00	0.28	0.11	1.07	5.37	4.50	4.70
Na2O	8.03	7.99	0.58	3.21	2.57	1.24	8.06	6.52	2.89	1.26	9.86	7.73	7.39	8.10
K2O	0.97	0.98	16.26	12.88	12.74	10.03	0.88	0.50	0.43	12.22	0,58	0.85	0.88	1.01
BaO	0.03	0.07	0.23	0.07	0.17	0.10	0.05	0.05	0.01	0.39	0.05	0.05	0.08	0.05
Total	88.26	99.28	101.41	101.31	98.87	103.16	98.77	99.27	98.46	100.44	101.18	98.48	92.78	99.64
No, of atoms														
based on a O														
Si	2.81	2.79	3.04	3.02	3.01	3.34	2.79	2.63	3.68	3.19	3.02	2,76	2.82	2.80
Al	1.14	1.21	0.94	0.96	0.97	0.95	1,20	1.36	0.32	0.79	0.99	1.23	1.17	1.19
Fe	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01
Mg	0,00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
Ca	0.22	0.24	0.00	0.00	0.02	0.01	0.24	0.39	0.23	0.00	0.05	0.26	0.23	0.22
Na	0.79	0.69	0,05	0.28	0.23	0.10	0.70	0.57	0.23	0.11	0.82	0.68	0.69	0.70
к	0.06	0.06	0.95	0.74	0.75	0.55	0.05	0.03	0.02	0.70	0.03	0.05	0.05	0.06
Ba	0.00	0.00	0,00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0,00
Sum	5.03	5.00	4.99	5.00	4.98	4.95	4.99	4.99	4.51	4.80	4.91	4.99	4.97	4.98
sum of cations	1.07	0.99	1.00	1.02	1.00	0.66	0.99	0.99	0.48	0.81	0.90	0.99	0.97	0.98
Or	5.61	6.06	95.00	72.55	75.00	83.33	5.05	3.03	4.17	86,42	3.33	5.05	5.15	6.12
Ab	73.83	69.70	5,00	27.45	23.00	15.15	70.71	57.58	47.92	13.58	91.11	68.69	71.13	71.43
An	20.56	24.24	0.00	0.00	2.00	1.52	24.24	39.39	47.92	0.00	5.56	26.26	23.71	22.45
Or/(Or+Ab+An)	0.06	0.06	0.95	0.73	0.75	0.83	0.05	0.03	0.04	0.86	0.03	0.05	0.05	0.06
AP	PE	NDĽ	х Ш											
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-	_													

	Feldspars (cont.)													
Sample no. Dril-core no. Stage	87 44-481 K	88 166-529 Frs	89 166-529 Frs	90 166-529 Frs	91 166-529 Frs	92 166-529 Frs	93 166-529 Frs	94 166-529 Frs	95 166-529 Frs	96 166-529 Frs	97 166-529 Frs	98 166-529 Frs	99 166-529 Frs	100 166-529 Frs
<u>~</u>														
SiO2	62.25	55.87	62,56	59,28	56.60	58.16	59.25	58.82	57.29	57.12	59,27	59.54	59.65	58.94
AI2O3	22.96	20.27	22.71	25.57	24.84	25.94	24.82	25.69	26.15	26.24	25.21	25.20	24.69	24.98
FeO	0,14	0,18	0,20	0.23	0.26	0,20	0.27	0.17	0.22	0.22	0.24	0.23	0.23	0.19
MgO	0.01	0.01	0.01	0.02	0.01	0.02	0.00	0.03	0.01	0.02	0.02	0.01	0,00	0.02
CaO	5.00	4.58	4.58	7.73	7.18	8.08	7.02	7.59	8.38	8,38	7.11	7,30	6.66	7.07
Na2O	7.87	7,86	8.09	6,93	7.12	6.63	7.23	6.96	6.51	6.45	7.10	7.04	7.28	7.11
K2O	0.98	0,88	0.99	0.49	0.56	0.46	0.59	0.49	0.38	0.48	0.56	0.55	0.58	0.53
BaO	0.08	0,08	0.10	0.00	0.00	0.00	0.00	0.00	0,00	0.00	0,00	0.00	0.00	0.00
Total	99.30	89.73	99.24	100,26	99.58	99.48	99,18	99.75	98.94	98.91	99.48	99.86	99.09	98.83
No. of atoms hased on 8 O														
Si	2,78	2.78	2.80	2.65	2.63	2.62	2.67	2.64	2.60	2.59	2,66	2.66	2.69	2.66
Al	1.21	1.19	1.19	1.34	1,36	1.37	1.32	1.35	1.39	1.40	1.33	1.33	1.31	1.33
Fe	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.24	0.24	0.22	0.37	0.36	0.39	0.34	0.37	0.41	0.41	0.34	0.35	0.32	0.34
Na	0,68	0.76	0,70	0,60	0.64	0.58	0.63	0.61	0.57	0.57	0.62	0.61	0.64	0.62
К	0.06	0.06	0,06	0.03	0.03	0.03	0.03	0.03	0.02	0,03	0.03	0,03	0.03	0.03
Ba	0.00	0,00	0.00	0.00	0,00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	4,98	5.04	4.98	5.00	5.03	5.00	5.00	5.01	5.00	5.01	4.99	4.99	5.00	4.99
sum of cations	0.98	1.06	0.98	1.00	1.03	1.00	1.00	1.01	1.00	1.01	0.99	0,99	0.99	0.99
Or	6,12	5.66	6.12	3.00	2.91	3.00	3.00	2.97	2.00	2.97	3.03	3.03	3.03	3.03
Ab	69.39	71.70	71.43	60,00	62.14	58.00	63.00	60.40	57.00	56.44	62.63	61.62	64.65	62.63
An	24.49	22.64	22.45	37.00	34.95	39.00	34.00	36.63	41.00	40.59	34.34	35.35	32.32	34.34
Or/(Or+Ab+An)	0.06	0.06	0,06	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.03

### <u>APPENDIX III</u>

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Feldspars (cont.)									
Sample no. Dril-core no. Stage	101 166-529 Frs	102 166-529 Frs	103 166-529 Frs	104 166-529 Frs	105 166-529 Frs	106 166-529 Frs			
SiO2	58.47	58.41	58.46	60.31	58.61	58.66			
A12O3	25.68	25.81	25.82	24.94	25.74	24.72			
FeO	0.25	0.24	0.18	0.23	0.18	0.23			
MgO	0.00	0.01	0.00	0.03	0.01	0.00			
CaO	7.83	7.94	8.09	7.08	7.94	6.85			
Na2O	6.62	6.66	6.56	5.24	6,58	7.27			
K2O	0.48	0.43	0.48	0.58	0.48	0.55			
BaO	0.00	0.00	0.00	0,00	0.00	0.00			
Total	99.33	99.50	99.59	98.41	99.52	98.28			
No, of atoms		•							
based on 8 O									
Si	2.63	2.63	2.63	2.71	2.63	2.67			
Al	1.36	1,36	1.36	1.32	1.36	1.32			
Fe	0.01	0.01	0.01	0.01	0.01	0.01			
Mo	0.00	0.00	0.00	0.00	0.00	0.00			
Ca	0.38	0.38	0.39	0.34	0.38	0.33			
Na	0.58	0.58	0.57	0.46	0.57	0.64			
K	0.03	0.03	0.03	0.03	0.03	0.03			
Ba	0.00	0,00	0.00	0.00	0.00	0.00			
Sum	4.99	4.99	4.99	4.87	4.98	5,00			
sum of cations	0.99	0.99	0.99	0.83	0.98	1.00			
Or	3.03	3,03	3.03	3.61	3.06	3.00			
Ab	58.59	58.59	57.58	55.42	58.16	64.00			
An	38.38	38.38	39.39	40.96	38.78	33.00			
Or/(Or+Ab+An)	0.03	0.03	0.03	0.04	0.03	0.03			

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Representative microprobe analysis of apatite crystals from the Sungun deposit											
Sample no.	l	2	3	4	5	6	7				
Dril-core no	33-437	33-437	33-437	33-437	33-437	33-437	33-437				
Туре	_K_	K	K	_ K	K	К	K				
SiOz	0.21	0.13	0.12	0.15	0.21	0.87	0.17				
Al <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.01	0.00	0.17	0.63	0.00				
MgO	0.01	0.02	0.01	0.01	0.02	0.05	0.00				
MnO	0.02	0.05	0.06	0.04	0.03	0.04	0.00				
FeO	0.01	0.11	0.06	0.07	0.09	0.05	0.27				
CaO	54.54	55.12	55.19	54.80	54.30	55.21	54.95				
CeO2	0.25	0.08	0.17	0.16	0.18	0.00	0.19				
Nd <sub>2</sub> O <sub>3</sub>	0.13	0.05	0.08	0.07	0.09	0.01	0.12				
Cl	0.00	0.25	0.33	0.32	0.38	0.16	0.25				
La <sub>2</sub> O <sub>3</sub>	0.15	0.10	0.06	0.14	0.12	0.04	0.66				
ThO <sub>2</sub>	0.01	0.00	0.02	0.01	0.02	0.01	0.00				
UO2	0.00	0.00	0.00	0.01	0.01	0.01	0.00				
SO3	0.65	0.14	0.15	0.15	0.21	0.04	0.35				
F	3.85	2.97	2.73	2.96	2.86	2.94	2.22				
Na <sub>2</sub> O	0.27	0.05	0.08	0.05	0.08	0.10	0.14				
P <sub>2</sub> O <sub>5</sub>	40.88	42.18	40.33	42.30	41.60	42.55	41.39				
Y103	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
SrO	0.44	0.05	0.05	0.06	0.04	0.04	0.03				
Total	101.17	100.98	99.17	101.02	99.88	101.08	100.30				
No. of atoms											
based on 12 (	0										
F	0.80	0.62	0.58	0.62	0.60	0.60	0.47				
Na	0.04	0.01	0.01	0.01	0.01	0.01	0.02				
P	2.27	2.35	2.30	2.36	2.34	2.34	2.35				
Ý S-	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
Sr Cr	5.21	0.00	0.00	0.00 5.79	0.00	0.00	0.00				
Ca Ca	0.01	0.00	0.01	3.38	0.01	0.00	J.49				
Nd	0.01	0.00	0.01	0.01	0.01	0.00	0.01				
	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
	0.00	0.03	0.04	0.04	0.04	0.02	0.03				
La	0.00	0.00	0.00	0.00	0.00	0.00	0.02				
T T	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
S	0.03	0.00	0.00	0.01	0.01	0.00	0.02				
Si	0.01	0.01	0.01	0.01	0.01	0.06	0.01				
AI	0.00	0.00	0.00	0.00	0.01	0.05	0.00				
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
Fe	0.00	0.01	0.00	0.00	0.01	0.00	0.02				
SUM	8.53	8.45	8.52	8.44	8.45	8.42	8.43				

K = potassic alteration zone

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	Microp	robe Analyse	es of Biotite	in the Sungu	n Deposit	19 <sup>17</sup>	يعد وير والمريد
Drill Core no.	25-514	34-477	34-163	34-163	34-164	33-437	33-437
Mineral	Biotite	Biotite	Biotite	Biotite	Biotite	Biotit <del>e</del>	Biotite
No.	1	2	3	4	5	6	7
SiO2	38.58	37.27	36.60	38.58	37.27	38.54	38.28
TiO2	3.82	4.27	0.95	3.82	4.27	3.26	3.09
Al2O3	14.55	13.53	22.86	14.55	13.53	15.45	15.42
FeO	15.69	16.38	13.51	15.69	16.38	13.23	12.88
MnO	0.17	0.18	0.06	0.17	0.18	0.06	0.03
MgO .	14.34	14.40	12.39	14.34	14.40	15.00	14.94
CaO	0.03	0.01	0.13	0.03	0.01	0.00	0.00
Na2O	0.30	0.30	0.09	0.30	0.30	0.10	0.11
K2O	9.35	9.41	2.26	9.35	9.41	10.25	10.23
F	0.38	0.33	0.38	0.38	0.33	1.03	0.85
Cl	0.20	0.17	0.05	0.20	0.17	0.19	0.22
Total	97.21	96.07	89.11	97.21	96.07	96.63	95.63
Stoichiometry elements base on 11 O	of ed						
Si	2.81	2.77	2.72	2.81	2.77	2.77	2.78
Ti	0.21	0.24	0.05	0.21	0.24	0.18	0.17
Al	1.26	1.20	2.02	1.26	1.20	1.32	1.33
Fe	0.96	1.02	0.84	0.96	1.02	0.80	0.78
Mn	0.01	0.01	0.00	0.01	0.01	0.00	0.00
Mg	1.56	1.60	1.37	1.56	1.60	1.61	1.62
Ca	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na	0.04	0.04	0.01	0.04	0.04	0.01	0.02
K	0.90	0.89	0.01	0.87	0.89	0.94	0.95
F	0.09	0.08	0.09	0.09	0.08	0.23	0.20
Cl	0.02	0.02	0.01	0.02	0.02	0.02	0.03
Sum	7.86	7.87	7.33	7.83	7.87	7.89	7.88
F/(F+Cl)	0.82	0.80	0.90	0.82	0.80	0.92	0.87
Fe/(Fe+Mg)	0.38	0.39	0.38	0.38	0.39	0.33	0.33
<sup>IV</sup> Al (apfu)	0.26	0.20	1.02	0.26	0.20	0.32	0.33

			Biotite (cont	'd)			
Drill Core Mineral No.	33-437 Biotite 8	33-437 Biotite 9	33-437 Biotite 10	34-477 Biotite 11	25-431 Biotite 12	25-431 Biotite 13	25-431 Biotite 14
SiO2 TiO2	37.70 4.00	38.34 3.98	37.79 4.03	43.72 2.65	41.29 2.02	39.25 2.17	39.03 2.11
FeO MnO	15.30 0.05	14.17 15.42 0.06	14.85 14.17 0.04	3.87 0.01	2.53 0.00	4.17 0.04	4.18 0.01
MgO CaO	14.94 0.00	15.07 0.00	14.78 0.00	17.41 0.05	23.18 0.00	21.50 0.00	21.58 0.04
Na2O K2O F	0.10 10.16	0.13 10.05 0.73	0.11 10.21	0.15 9.94	0.14 10.51 2.60	0.18 10.43	0.17 10.25 2.10
Cl Total	0.22 97.31	0.23 98.18	0.82 0.23 97.02	0.08 96.97	0.04 97.35	0.09 95.29	0.08 95.09
Stoichiometr elements ba on 11 O	ry of sed						
Si Ti	2.75	2.77	2.75	2.94	2.77	2.75	2.72
Al Fe	1.22 0.93	1.22 0.93	1.28 0.86	1.37 0.22	1.20 0.14	1.28 0.24	1.29 0.24
Mn Mg	0.00 1.63	0.00 1.62	0.00 1.60	0.00 1.74	0.00 2.32	0.00 2.23	0.00 2.24
Ca Na	0.00	0.00	0.00	0.00 0.04	0.00	0.00	0.00 0.02
F Cl	0.95 0.17 0.03	0.93 0.17 0.03	0.95 0.19 0.03	0.95 0.41 0.01	0.90	0.93 0.43 0.01	0.91 0.46 0.01
Sum F/(F+Cl)	7.91 0.85	7.90 0.85	7.89 0.86	7.81 0.98	8.00 1.00	8.00 0.98	8.00 0.98
Fe/(Fe+Mg) <sup>IV</sup> Al (apfu)	0.36 0.22	0.36 0.22	0.35 0.28	0.11 0.37	0.06 0.20	0.10 0.28	0.10 0.29
<sup>vi</sup> Al (apfu)	1.00	1.00	1.00	1.00	1.00	1.00	1.00

			Biotite (cont	d)			
Drill Core	25-431	34-477	34-477	34-477	34-477	34-477	34-477
Mineral	Biotite	Biotite	Biotite	Biotite	Biotite	Biotite	Biotite
No.	15	16	17	18	19	20	20
SiO2	38.74	41.29	38.74	39.25	39.03	38.74	37.09
TiO2	3.91	2.02	3.91	2.17	2.11	3.72	3.97
Al2O3	15.53	15.05	15.53	15.50	15.54	15.81	14.80
FeO	4.79	2.53	4.79	4.17	4.18	7.54	6.74
MnO	0.02	0.00	0.02	0.04	0.01	0.00	0.19
MgO	21.39	23.18	21.39	21.50	21.58	18.38	20.55
CaO	0.04	0.00	0.04	0.00	0.04	0.02	0.07
Na2O	0.20	0.14	0.20	0.18	0.17	0.24	0.22
K2O	10.34	10.51	10.34	10.43	10.25	10.52	10.02
F	1.87	2.60	1.87	1.96	2.10	1.58	2.40
Cl	0.07	0.04	0.07	0.09	0.08	0.15	0.09
Total	96.91	97.35	96.91	95.29	95.09	96.71	96.14
Stoichiometry elements base on 11 O	of d						
Si	2.68	2.77	2.67	2.73	2.72	2.72	2.71
Ti	0.20	0.10	0.20	0.11	0.11	0.20	0.21
Al	1.27	1.20	1.27	1.28	1.29	1.32	1.30
Fe	0.28	0.14	0.28	0.24	0.24	0.44	0.34
Mn	0.00	0.00	0.00	0.00	0.00	0.00	.0.00
Mg	2.20	2.32	2.21	2.23	2.24	1.94	2.19
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.03	0.02	0.03	0.04	0.02	0.03	0.02
K	0.91	0.90	0.92	0.93	0.91	0.94	0.94
F	0.41	0.55	0.41	0.43	0.46	0.39	0.37
Cl	0.01	0.00	0.01	0.01	0.01	0.02	0.02
Sum	7.99	8.00	8.00	8.00	8.00	8.00	8.00
F/(F+Cl)	0.98	1.00	0.98	0.98	0.98	0.95	0.95
Fe/(Fe+Mg)	0.11	0.06	0.11	0.10	0.10	0.18	0.13
<sup>IV</sup> Al (apfu)	0.27	0.20	0.27	0.28	0.29	0.32	0.28
<sup>VI</sup> Al (apfu)	1.00	1.00	1.00	1.00	1.00	1.00	1.00

M	croprobe A	nalysis of M	uscovite and	Phengite in the	Sungun Dep	osit	
		Phengite			Muse	ovite	
Drill Core	33-437	33-437	33-437	25-514	25-514	25-514	25-514
Mineral	Phegite	Phegite	Phegite	Muscovite	Muscovite	Muscovite	Muscovite
No.	1	2	3	1	2	3	4
SiO2	42.70	43.29	47.24	49.96	46.39	50.96	48.38
TiO2	0.98	0.74	0.69	0.07	0.07	0.10	0.09
A12O3	21.35	23.59	29.51	28.62	26.28	28.45	25.85
FeO	8.80	7.80	3.43	1.02	0.73	0.92	1.23
MnO	0.02	0.03	0.00	0.02	0.00	0.01	0.00
MgO	11.65	10.45	3.52	2.29	2.08	2.74	2.62
CaO	0.00	0.03	0.02	0.13	0.19	0.18	0.12
Na2O	0.12	0.07	0.16	0.12	0.17	0.09	0.12
K2O	10.18	10.10	9.55	8.39	7.13	8.84	8.92
F	0.98	1.01	0.22	0.53	0.44	0.73	0.62
Cl	0.08	0.05	0.03	0.15	0.30	0.13	0.24
Total	96.85	97.16	94.36	91.29	83.79	93.15	88.19
Stoichiometry of elements base	of d						
\$	2.05	2.05	3 10	3 38	3.40	3 38	3 41
Ti	2.95	2.95	0.04	0.00	0.00	0.00	0.00
Δ1	1 75	1.01	0.04	2 31	2.00	2.00	217
Fe	0.51	0.44	0.19	0.06	0.05	0.05	0.07
Mn	0.01	0.44	0.00	0.00	0.00	0.00	0.07
Ma	1 20	1.06	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.01	0.02	0.01	0.01
Na	0.00	0.00	0.00	0.02	0.02	0.01	0.02
ĸ	0.90	0.88	0.82	0.02	0.62	0.75	0.80
F	0.21	0.00	0.05	0.11	0.10	0.15	0.14
CI	0.01	0.01	0.00	0.02	0.04	0.01	0.03
Sum	7 60	7 52	7.04	6.87	6.87	6.88	6.93
F/(F+CI)	0.95	0.96	1.00	0.85	0.71	0.94	0.82
Fe/(Fe+Mg)	0.30	0.29	0.35	0.21	0.18	0.16	0.20
<sup>rv</sup> Al (apfu)	0.75	0.91	1.37	1.31	1.29	1.25	1.17

### <u>APPENDIX III</u>

apfu = atom per formula unit

		M	luscovite (co	nťd)			
				Muscovite			
Drill Core	34-477	34-477	34-477	34-477	34-477	25-514	34-477
Mineral	Muscovite	Muscovite	Muscovite	Muscovite	Muscovite	Muscovite	Muscovit <del>e</del>
No.	5	6	7	8	9	10	11
SiO2	47.34	46.95	46.19	51.31	50.54	44.58	61.91
TiO2	0.22	0.33	0.15	0.11	0.12	0.21	0.09
AI2O3	28.30	31.36	33.75	28.13	27.34	27.17	18.67
FeO	2.76	1.72	0.81	1.14	1.22	5.61	0.04
MnO	0.03	0.01	0.00	0.00	0.01	0.03	0.02
MgO	3.92	2.87	1.02	3.55	3.77	7.84	0.00
CaO	0.02	0.01	0.01	0.13	0.11	0.05	0.00
Na2O	0.31	0.38	0.37	0.16	0.13	0.07	0.80
K2O	11.40	11.17	11.03	9.52	9.52	7.75	15.67
F	0.40	0.40	0.22	0.83	0.90	0.35	0.00
Cl	0.05	0.08	0.05	0.12	0.10	0.01	0.02
Total	94.74	95.28	93.59	94.99	93.76	93.64	97.21
Q+=1-1 *							
Stoichiometry	01						
elements base	20						
0n 14 U	2 21	2.14	2 10	2 26	2 26	2.06	1.06
	5.21	5.14	3.12	5.50	5.50	3.00	4.00
11	0.01	0.02	0.01	2.10	0.01	0.01	0.00
AI Ea	2.20	2.49	2.72	2.19	2.10	2.22	1.40
Mn	0.10	0.10	0.05	0.00	0.07	0.02	0.00
Ma	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C.	0.40	0.29	0.10	0.00	0.01	0.00	0.00
Na Na	0.00	0.00	0.00	0.01	0.02	0.00	0.00
K	0.04	0.05	0.05	0.02	0.02	0.01	131
F	0.09	0.95	0.95	0.30	0.19	0.70	0.00
	0.03	0.09	0.05	0.17	0.15	0.00	0.00
Sum	7 19	714	7.05	6.08	7.01	7 20	6.00
F/(F+Cl)	0.90	0 00	0.83	0.90	0.95	1.00	0.75
$Fe/(Fe+M_{\theta})$	0.29	0.26	0.33	0.15	0.16	0.29	0.00
Fa/Fa+Ma	1 28	1 40	1 70	1 10	1 16	1.22	0.00
Fe/Fe+Mg	1.28	1.49	1.72	1.19	1.16	1.22	0.46

	Microp	robe Analysi	s of Chlorite	in the Sungu	n Deposit		
Drill Core Mineral No.	341-63 Chlorite 1	341-63 Chlorite 2	341-63 Chlorite 3	341-63 Chlorite 4	341-63 Chlorite 5	341-63 Chlorite 6	341-63 Chlorite 7
SiO2 TiO2 Al2O3 FeO MnO MgO CaO Na2O K2O F Cl Total	30.13 0.02 17.07 14.09 0.19 24.54 0.06 0.08 0.12 0.35 0.03 86.68	30.09 0.05 18.28 14.32 0.20 24.50 0.05 0.03 0.09 0.28 0.02 87.91	30.06 0.00 18.32 13.85 0.21 24.60 0.06 0.03 0.09 0.19 0.02 87.42	29.94 0.02 18.18 13.70 0.24 24.40 0.05 0.09 0.07 0.27 0.06 87.01	29.15 0.02 18.28 15.61 0.16 21.83 0.03 0.08 0.08 0.08 0.32 0.03 85.58	30.39 0.03 18.11 14.47 0.15 24.16 0.07 0.04 0.15 0.35 0.02 87.94	30.45 0.02 18.09 13.57 0.17 24.15 0.07 0.06 0.35 0.37 0.05 87.34
Stoichiometry elements bas	y of sed				0.5.120		
Si Ti Al Fe Mn Mg Ca Na K F Cl	3.00 0.00 2.02 1.17 0.02 3.65 0.01 0.01 0.02 0.11 0.01	2.96 0.00 2.13 1.18 0.02 3.59 0.01 0.01 0.01 0.09 0.00	2.97 0.00 2.15 1.14 0.02 3.62 0.01 0.01 0.01 0.06 0.00	2.97 0.00 2.14 1.14 0.02 3.61 0.00 0.02 0.01 0.08 0.01	2.97 0.00 2.21 1.33 0.01 3.31 0.00 0.01 0.01 0.10 0.01	2.99 0.00 2.11 1.19 0.01 3.54 0.01 0.01 0.02 0.11 0.00	3.00 0.00 2.12 1.12 0.01 3.55 0.01 0.01 0.04 0.12 0.01
Sum F/(F+Cl) Fe/(Fe+Mg) <u>Fe/Fe+Mg</u>	10.02 0.92 0.24 8.30	10.00 0.25 0.25	9.99 0.24 <u>0.24</u>	10.00 0.89 0.24 0.24	9.96 0.91 0.29 0.29	9.99 0.25 0.25	9.99 0.92 0.24 0.24

		(	Chlorite (con	:'d)			
Drill Core Mineral No.	341-63 Chlorite 8	341-63 Chlorite 9	341-63 Chlorite 10	341-63 Chlorite 11	341-63 Chlorite 12	341-63 Chlorite 13	341-63 Chlorite 14
SiO2 TiO2 Al2O3 FeO MnO MgO CaO Na2O K2O F Cl	29.89 0.02 18.06 14.74 0.21 24.18 0.04 0.07 0.19 0.31 0.01 87.71	29.18 0.03 17.59 14.07 0.24 24.04 0.06 0.05 0.10 0.27 0.03 85.65	29.23 0.05 17.30 14.15 0.20 23.22 0.14 0.08 0.08 0.08 0.06 0.03 84.52	29.92 0.02 17.49 14.98 0.15 23.79 0.05 0.05 0.05 0.09 0.37 0.02 86.92	29.88 0.04 16.79 13.51 0.19 23.64 0.10 0.10 0.28 0.29 0.06 84.87	31.11 0.02 18.61 13.10 0.17 22.87 0.09 0.10 0.26 0.35 0.04 86.72	29.91 0.03 18.64 15.18 0.16 23.76 0.08 0.09 0.07 0.30 0.06 88.28
Stoichiometry elements bas on 14 O	of ed	02.02	51.52	00.72	01.07	00.72	00.20
Si Ti Al Fe Mn Mg Ca Na K F Cl	2.96 0.00 2.12 1.22 0.02 3.57 0.00 0.01 0.02 0.10 0.00	2.95 0.00 2.11 1.19 0.02 3.63 0.01 0.01 0.01 0.09 0.01	3.00 0.00 2.11 1.22 0.02 3.56 0.02 0.01 0.01 0.02 0.00	2.99 0.00 2.07 1.25 0.01 3.54 0.01 0.01 0.01 0.12 0.00	3.04 0.00 2.03 1.15 0.02 3.58 0.01 0.02 0.04 0.09 0.01	3.07 0.00 2.18 1.08 0.01 3.36 0.01 0.02 0.03 0.11 0.01	2.94 0.00 2.18 1.25 0.01 3.48 0.01 0.02 0.01 0.09 0.01
Sum F/(F+Cl) Fe/(Fe+Mg) Fe/Fe+Mg	0.25 0.25	10.02 0.90 0.25 0.25	9.97 0.26 0.26	10.01 0.26 0.26	9.99 0.90 0.24 0.24	9.89 0.92 0.24 0.24	10.00 0.90 0.26 0.26

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		(	Chlorite (con	ťd)			
Drill Core Mineral No.	341-63 Chlorite 1	341-63 Chlorite 2	341-63 Chlorite 3	341-63 Chlorite 4	341-63 Chlorite 5	341-63 Chlorite 6	341-63 Chlorite 7
SiO2 TiO2 Al2O3 FeO MnO MgO CaO Na2O K2O F Cl Total	30.82 0.01 17.53 14.67 0.17 23.40 0.07 0.02 0.39 0.02 0.01 87.10	30.56 0.04 17.84 14.65 0.22 24.18 0.06 0.05 0.29 0.07 0.01 87.94	30.25 0.05 17.20 14.78 0.16 23.79 0.13 0.04 0.13 0.00 0.01 86.54	30.51 0.00 17.68 14.40 0.09 23.82 0.13 0.01 0.12 0.04 0.01 86.80	29.97 0.00 17.73 14.32 0.14 24.14 0.12 0.06 0.10 0.10 0.01 86.69	30.42 0.03 18.58 14.09 0.14 23.31 0.10 0.02 0.03 0.05 0.01 86.75	31.18 0.01 17.97 14.60 0.10 23.79 0.12 0.05 0.30 0.05 0.30 0.05 0.01 88.16
Stoichiometry elements base	of ed						
Si Ti Al Fe Mn Mg Ca Na K F Cl Sum F/(F+Cl)	3.08 0.00 2.08 1.22 0.01 3.48 0.01 0.00 0.05 0.00 0.00 9.93	3.02 0.00 2.09 1.21 0.02 3.57 0.01 0.01 0.04 0.00 0.00 9.97	3.04 0.00 2.05 1.24 0.01 3.57 0.01 0.01 0.02 0.00 0.00 9.96	3.05 0.00 2.10 1.20 0.01 3.55 0.01 0.00 0.01 0.00 0.00 9.93	3.00 0.00 2.11 1.20 0.01 3.61 0.01 0.01 0.01 0.00 0.00 9.97	3.03 0.00 2.20 1.17 0.01 3.46 0.01 0.00 0.00 0.00 0.00 9.90	3.07 0.00 2.10 1.20 0.01 3.49 0.01 0.01 0.04 0.00 0.00 9.93
Fe/(Fe+Mg) Fc/Fe+Mg	0.26 0.26	0.25 0.25	0.26 0.26	0.25 0.25	0.25 0.25	0.25 0.25	0.26 0.26

		(	Chlorite (cont	ťd)			ور تجریح اشداد است.
Drill Core Mineral No.	341-63 Chlorite 8	341-63 Chlorite 9	341-63 Chlorite 10	341-63 Chlorite 11	341-63 Chlorite 12	341-63 Chlorite 13	341-63 Chlorite 14
SiO2 TiO2 Al2O3 FeO MnO MgO CaO Na2O K2O F Cl Total	30.28 0.01 17.68 14.32 0.14 23.53 0.11 0.05 0.11 0.06 0.01 86.30	30.37 0.02 17.05 14.97 0.17 23.26 0.08 0.03 0.29 0.03 0.01 86.27	29.55 0.00 18.15 14.53 0.23 24.11 0.05 0.01 0.08 0.04 0.01 86.75	29.89 0.01 17.47 14.94 0.22 24.27 0.05 0.03 0.12 0.04 0.01 87.03	29.61 0.00 17.98 14.91 0.17 23.64 0.08 0.03 0.15 0.06 0.01 86.64	29.76 0.00 18.25 14.60 0.18 23.96 0.06 0.01 0.06 0.08 0.01 86.97	30.05 0.00 18.12 14.74 0.20 23.88 0.04 0.02 0.09 0.05 0.01 87.20
Stoichiometry of elements based							
Si Ti Al Fe Mn Mg Ca Na K F Cl Sum F/(F+Cl)	3.04 0.00 2.11 1.20 0.01 3.53 0.01 0.01 0.01 0.00 0.00 9.93	3.07 0.00 2.05 1.26 0.01 3.50 0.01 0.01 0.04 0.00 0.00 9.95	2.96 0.00 2.16 1.22 0.02 3.60 0.01 0.00 0.01 0.00 0.00 9.99	$\begin{array}{c} 3.00\\ 0.00\\ 2.08\\ 1.25\\ 0.02\\ 3.63\\ 0.01\\ 0.01\\ 0.02\\ 0.00\\ 10.00\\ \end{array}$	2.98 0.00 2.15 1.26 0.01 3.55 0.01 0.01 0.02 0.00 0.00 9.98	2.98 0.00 2.17 1.22 0.02 3.57 0.01 0.00 0.01 0.00 0.00 9.97	3.00 0.00 2.15 1.23 0.02 3.55 0.00 0.00 0.01 0.00 0.00 9.96
Fe/(Fe+Mg) Fe/Fe+Mg	0.25	0.26 0.26	0.25 0.25	0.26	0.26	0.25 0.25	0.26

		(	Chlorite (con	:'d)			
Drill Core Mineral	341-63 Chlorite						
	15	10	L /	10	19	20	21
SiO2 TiO2 Al2O3 FeO MnO	29.72 0.02 17.20 15.10 0.19	30.40 0.02 17.68 14.78 0.17	30.74 0.04 17.45 14.53 0.14	30.82 0.04 17.23 14.49 0.13	31.03 0.05 18.16 14.90 0.13	37.14 0.05 22.60 12.28 0.05	31.86 0.02 18.35 15.11 0.08
MgO	23.47	23.95	23.95	22.90	23.71	16.02	22.11
CaO Na2O K2O F	0.04 0.03 0.25 0.03	0.06 0.02 0.16 0.05	0.08 0.03 0.37 0.04	0.06 0.04 0.80 0.04	0.08 0.02 0.39 0.02	0.12 0.04 1.57 0.05	0.07 0.05 0.64 0.02
CI	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Total	86.06	87.27	87.37	86.55	88.50	89.91	88.32
Stoichiometry of elements based on 14 O	of d						
Si	3.02	3.03	3.06	3.10	3.05	3.47	3.13
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AI	2.07	2.09	2.06	2.06	2.12	2.51	2.14
Fe	1.28	1.23	1.21	1.22	1.22	0.96	1.24
Mn	0.02	0.01	0.01	0.01	0.01	0.00	0.01
Mg	3.55	3.56	3.55	3.43	3.47	2.23	3.24
Ca	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Na	0.01	0.00	0.01	0.01	0.00	0.01	0.01
ĸ	0.03	0.02	0.05	0.10	0.05	0.19	0.08
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CI Sum	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	9.99	9.96	9.90	9.90	9.94	9.39	9.80
Fel(FelMa)	0.27	0.26	0.25	0.26	0.26	0.30	0.28
Fe/Fe+Mg	0.27	0.26	0.25	0.26	0.26	0.30	0.28

Chlorite (cont'd)							
Drill Core	341-63	341-63	341-63	341-63	341-63	341-63	341-63
Mineral	Chlorite	Chlorite	Chlorite	Chlorite	Chlorite	Chlorite	Chlorite
No.	22	23	24	25	26	27	28
SiO2	39.62	30.42	30.72	30.11	30.02	30.60	30.36
TiO2	0.06	0.01	0.06	0.05	0.00	0.05	0.00
Al2O3	23.50	18.80	17.80	17.91	17.50	18.05	17.58
FeO	10.61	13.55	14.46	14.99	14.48	14.83	14.45
MnO	0.04	0.21	0.19	0.10	0.16	0.10	0.17
MgO	13.52	23.16	24.61	23.02	23.82	21.62	23.58
CaO	0.11	0.12	0.08	0.09	0.10	0.10	0.06
Na2O	0.03	0.02	0.05	0.01	0.04	0.05	0.04
K2O	2.39	0.07	0.04	0.24	0.19	0.50	0.19
F	0.02	0.06	0.01	0.06	0.03	0.04	0.04
Cl	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Total	89.90	86.42	88.01	86.58	86.34	85.94	86.48
Stoichiometry elements base	of ed						
Si	3.66	3.03	3.03	3.03	3.02	$\begin{array}{c} 3.10\\ 0.00\\ 2.17\\ 1.25\\ 0.01\\ 3.26\\ 0.01\\ 0.01\\ 0.06\\ 0.00\\ 0.00\\ 9.88 \end{array}$	3.05
Ti	0.00	0.00	0.00	0.00	0.00		0.00
Al	2.58	2.23	2.08	2.14	2.09		2.09
Fe	0.82	1.13	1.19	1.26	1.22		1.21
Mn	0.00	0.02	0.02	0.01	0.01		0.01
Mg	1.86	3.44	3.61	3.45	3.58		3.53
Ca	0.01	0.01	0.01	0.01	0.01		0.01
Na	0.01	0.00	0.01	0.00	0.01		0.01
K	0.28	0.01	0.01	0.03	0.02		0.02
F	0.00	0.00	0.00	0.00	0.00		0.00
Cl	0.00	0.00	0.00	0.00	0.00		0.00
Sum	9.22	9.88	9.96	9.94	9.97		9.94
Fr/(F+Cl) Fe/(Fe+Mg) <u>Fe/Fe+Mg</u>	0.31 0.31	0.25 0.25	0.25 0.25	0.27 0.27	0.25 0.25	0.28 0.28	0.26 0.26

		(	Chlorite (con	t'd)			
Drill Core Mineral No.	341-63 Chlorite 29	25-514 Chlorite l	25-514 Chlorite 2	25-514 Chlorite 3	25-514 Chlorite 4	25-514 Chlorite 5	34-477 Chlorite 6
SiO2 TiO2 Al2O3 FeO MnO MgO CaO Na2O K2O F Cl Total	30.52 0.02 17.95 14.50 0.17 22.51 0.08 0.05 0.56 0.04 0.01 86.40	30.75 0.06 21.40 16.44 0.05 18.42 0.08 0.01 1.32 0.16 0.01 88.69	27.90 0.05 20.39 17.02 0.08 21.48 0.07 0.01 0.04 0.36 0.00 87.40	27.64 0.07 20.18 16.72 0.08 21.04 0.06 0.03 0.03 0.03 0.20 0.01 86.06	29.63 0.04 21.39 11.22 0.11 23.85 0.03 0.02 0.66 0.39 0.01 87.35	28.70 0.01 20.88 12.06 0.15 25.24 0.04 0.04 0.04 0.14 0.17 0.01 87.42	29.18 0.03 17.59 14.07 0.24 24.04 0.06 0.05 0.10 0.27 0.03 85.65
Stoichiometry elements bas on 14 O	v of red						
Si Ti Al Fe Mn Mg Ca Na K F Cl Sum F/(F+Cl)	3.07 0.00 2.14 1.22 0.01 3.38 0.01 0.01 0.01 0.07 0.00 0.00 9.92	3.10 0.00 2.50 1.35 0.00 2.70 0.01 0.00 0.17 0.05 0.00 9.88	2.80 0.00 2.43 1.43 0.01 3.20 0.01 0.00 0.01 0.11 0.00 10.00	2.82 0.01 2.44 1.43 0.01 3.20 0.01 0.01 0.00 0.06 0.00 9.99	2.88 0.00 2.47 0.91 0.01 3.46 0.00 0.00 0.00 0.08 0.12 0.00 9.93	2.81 0.00 2.43 0.99 0.01 3.68 0.00 0.01 0.02 0.05 0.00 10.00	2.95 0.00 2.11 1.19 0.02 3.63 0.01 0.01 0.01 0.01 0.09 0.01 10.03 1.01
Fe/(Fe+Mg) Fe/Fe+Mg	0.27	0.33	0.31	0.31	0.21	0.21	0.25 0.25

	(	Chlorite (cont	(d)		
Drill Core Mineral No.	34-477 Chlorite 7	34-477 Chlorite 8	34-477 Chlorite 9	34-477 Chlorite 10	34-477 Chlorite 11
SiO2 TiO2 Al2O3 FeO MnO MgO CaO Na2O K2O F	29.91 0.03 18.64 15.18 0.16 23.76 0.08 0.09 0.07 0.30	29.15 0.02 18.28 15.61 0.16 21.83 0.03 0.08 0.08 0.08 0.32	29.89 0.02 18.06 14.74 0.21 24.18 0.04 0.07 0.19 0.31	33.21 0.12 22.00 15.21 0.06 15.72 0.05 0.04 2.06 0.27	36.60 0.95 22.86 13.51 0.06 12.39 0.13 0.09 2.26 0.38
Cl Total	0.06 88.28	0.03 85.58	0.01 87.71	0.00 88.76	0.05 89.29
Stoichiometry of elements based on 14 O	of 1				
Si Ti Al Fe Mn Mg Ca Na K	2.94 0.00 2.18 1.25 0.01 3.48 0.01 0.02 0.01	2.97 0.00 2.21 1.33 0.01 3.31 0.00 0.01	2.96 0.00 2.12 1.22 0.02 3.55 0.00 0.01 0.02	3.23 0.01 2.54 1.24 0.00 2.28 0.01 0.01 0.26	3.47 0.07 2.57 1.07 0.00 1.75 0.01 0.02 0.27
F Cl Sum F/(F+Cl) Fe/(Fe+Mg) Fe/Fe+Mg	0.01 0.09 0.01 10.00 0.90 0.26 0.26	0.01 0.10 0.01 9.96 0.91 0.29 0.29	0.02 0.10 0.00 10.00 0.26 0.26	0.26 0.08 0.00 9.66 0.35 0.35	0.27 0.11 0.01 9.35 0.92 0.38 0.38

## <u>APPENDIX III</u>

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IMAGE EVALUATION TEST TARGET (QA-3)





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