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GEOCHEMISTRY, PHYSICOCHEMICAL CONTROLS, AND GENESIS OF THE EL MOCHITO ZN-PB-AG SKARN-HOSTED DEPOSIT, HONDURAS

Katherine M. Ault

Department of Earth and Planetary Sciences McGill University Montréal, Québec Canada

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Doctor of Philosophy

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ABSTRACT

The El Mochito mine, located in west-central Honduras, exploits a distal Zn-Pb-Ag skarn-hosted deposit. The bulk of economic mineralization, occurring either as steeply dipping pipes or flat-lying manto bodies, is hosted by Cretaceous Átima Formation limestone. Skarn mineralogy consists of early grossularitic garnet followed by andraditic garnet and hedenbergitic pyroxene, with pyroxene skarn the principal host to sphalerite mineralization. Ore minerals, which post-dated silicate precipitation, comprise sphalerite of variable Fe content, galena, magnetite, pyrrhotite, chalcopyrite, pyrite and trace amounts of arsenopyrite. The distribution of ore metals in the orebodies is zoned from Zn-Fe -rich cores to adjacent Pb- and Ag-rich zones reflecting the sequential saturation of sphalerite and galena in the fluid with decreasing temperature.

Skarn formation was accompanied by significant additions of Si, Fe, Mg, Al, and Mn and variable changes in Ca during early alteration. Apparent decreases in the concentrations of Ti and Zr suggest that the fluid:rock ratio was high. Variations in component activities of the hydrothermal fluid indicate that andraditic garnet skarn was stable at lower $\log(a_{Ca2+}/a_{H+2})$, $\log(a_{Al3+}/a_{H+3})$, and $\log a_{SiO_2(aq)}$, and higher $\log(a_{Fe3+}/a_{H+3})$ than its grossularitic garnet skarn precursor, whereas hedenbergitic pyroxene skarn was stable at lower $\log(a_{Ca2+}/a_{H+2})$ and $\log(a_{Fe3+}/a_{H+3})$ and higher $\log a_{SiO_2(aq)}$ than its andraditic skarn precursor.

 δ^{34} S values of sphalerite, galena and pyrrhotite cluster between -1 and +2‰, and their corresponding fluid δ^{34} S_{H2S} values ranged from -3.7 to + 5.4‰, indicating that the sulphur was primarily igneous in origin, and lead isotope ratios of galena are similar to those of the Miocene-Pliocene Padre Miguel ignimbrite. Variation in the δ^{34} S values of sphalerite and the whole-rock Pb isotope ratios of the host limestone are interpreted to reflect decreasing alteration toward the southwest.

Microthermometric measurements for garnet-, pyroxene- and sphalerite-hosted fluid inclusions indicate that two end-member fluids, a saline formational brine and a Ferich orthomagmatic fluid, formed skarn and ore at the deposit. The first, hosted by grossularitic garnet and low-Fe sphalerite, is characterized by homogenization temperatures ranging from 260 to 390°C, and salinities from 7 to 45 wt.% NaCl equivalent. The second, hosted by pyroxene, andraditic garnet, and medium-Fe sphalerite, is characterized by a higher homogenization temperature (320 to 400°C), lower salinity (1 to 15 wt.% NaCl equivalent) and an elevated Fe concentration. No evidence for boiling was observed, and all inclusions homogenized by vapour disappearance. Fluids were H₂O-dominant, with minor concentrations of CO₂, CH₄ and N₂. Laser ablation ICP-MS analyses of grossularitic garnet-, pyroxene- and sphalerite-hosted fluid inclusions indicate that Na, K, Ca and Fe are the dominant cations in solution and that fluids contained median values of Zn and Pb ranging from <1 to 373 ppm and from <1 to 706 ppm, respectively.

A genetic model is proposed in which formational waters and orthomagmatic fluids associated mixed progressively at depth to form the fluids associated with skarn and ore at the El Mochito deposit. Ore precipitation appears to have occurred by destabilization of metal-chloride complexes triggered by an increase in f_{s_2} during fluid mixing.

Résumé

La mine El Mochito, située dans le centre ouest du Honduras, exploite un gisement distal de Zn-Pb-Ag retrouvé dans un skarn. La majeure partie de la minéralisation économique, localisée soit dans des diatrèmes à pendage élevé ou dans des gisements de manto plts, se retrouve dans une calcaire Crétacée de la Formation Átima. La minéralogie du skarn consiste en un grenat grossulaire précoce suivi par un grenat andradite et un pyroxène hédenbergite, le skarn à pyroxène étant l'hôte principal de la minéralisation sphaléritique. Les minerais métalliques, formés après la précipitation des minéraux silicates, comprennent de la sphalérite à teneur en fer variable, de la galène, de la magnétite, de la pyrrhotine, de la chalcopyrite et de la pyrite, ainsi que des traces d'arsénopyrite. La distribution des minerais métalliques dans les gisements est zonée, allant de noyaux riches en Zn et Fe à des zones adjacentes riches en Pb at Ag dues à la saturation séquentielle de la sphalérite et de la galène dans le fluide lors d'une baisse de température.

La formation du skarn a été accompagnée d'enrichissements significatifs en Si, Fe, Mg, Al et Mn, alors que la Ca a été largement conservé durant l'altération précoce. Les baisses apparentes des concentrations en Ti et Zr, suggèrent que le rapport liquide/solide était élevé. Les variations dans les activités des composantes du liquide hydrothermal indiquent que le skarn grenatique andraditique était stable à des $log(a_{Ca2+}/a_{H+2})$, $log(a_{Al3+}/a_{H+3})$, et $loga_{SiO_2(aq)}$ plus bas, et à des $log(a_{Fe3+}/a_{H+3})$ plus élevés, que le skarn grenatique grossularitique précurseur, tandis que le skarn à pyroxène hédenbergitique était stable à des $log(a_{Ca2+}/a_{H+2})$ et $log(a_{Fe3+}/a_{H+3})$ et plus bas et des $loga_{SiO_2(aq)}$ plus élevés que le skarn andraditique précurseur.

Les valeurs de δ^{34} S de la sphalérite, la galène et la pyrrhotine se regroupent entre -1 et +2‰ et les valeurs de δ^{34} S_{H2S} du fluide correspondant vont de -3.7 à + 5.4‰, ce qui indique que le soufre était d'origine preincipalement ignée et que les rapport d'isotopes de plomb de la galène sont similaires à ceux de l'ignimbrite Padre Miguel du Miocène-Pliocène. La variation dans les valeurs de δ^{34} S de la sphalérite et les rapports des isotopes de plomb de la calcaire hôte, sont interprétés comme résultant d'une altération décroissante vers le sud-ouest.

Les résultats de micro-thermométrie pour les inclusions liquides dans les grenats, les pyroxènes et les sphalérites, indiquent que deux liquides, une saumure saline de formation et un liquide orthomagmatique riche en Fe, ont formé le skarn et le minerai du gisement. Le premier liquide, retrouvé dans le grenat grossulaire et la sphalérite pauvre en Fe, est caractérisé par des températures d'homogénéisation allant de 260 à 390°C et par des salinités allant de 7 à 45% par poids, équivalent NaCl. Le deuxième liquide, retrouvé dans des pyroxènes, des andradites, et des sphalérites à teneur modérée in Fe, est caractérisé par une température d'homogénéisation plus élevée (320 à 400°C), une salinité plus basse (1 à 15% par poids, équivalent NaCl) et une concentration en Fe élevée. Aucune évidence d'ebullition n'a été observée et toutes les inclusions ont été homogénéisées par disparition de la vapeur. Les liquides étaient composés principalement de H₂O, avec des quantités mineures de CO₂, CH₄ et N₂. Les analyses au ICP-MS à ablation laser des inclusions liquides retrouvées dans le grenat grossulaire, le pyroxène et la sphalérite, indiquent que le Na, K, Ca et le Fe étaient les cations dominants en solution et que les liquides contenaient des concentrations médianes en Zn and Pb allant de <1 à 373 ppm et de <1 à 706 ppm respectivement.

Un modèle génétique est proposé dans lequel les eaux de formation et les liquides orthomagmatiques associés avec l'ignimbrite Padre Miquel, se sont mélangés progressivement en profonduer pour former les liquides associés avec le skarn et le minerai dans le gisement El Mochito. Le mélange des liquides a déclenché une hausse dans la f_{s_2} et la précipitation du minerai a eu lieu lors de la déstabilisation de complexes de chlorure.

ACKNOWLEDGEMENTS

Several people deserve acknowledgment and thanks for the initiation and longwaited completion of this thesis. First and foremost, Dr. A.E. Williams-Jones warrants a great big thank you because without his direction, enthusiasm, and confidence this project would have never been realized.

Jim Clark, who often acted as a surrogate supervisor and manuscript editor, provided academic and technical assistance. Glenn Poirier, Shi Lang and Jim also provided invaluable help obtaining reliable electron microprobe data. Others who proved to be exceptionally tolerant to a near-constant barrage of questions regarding sample preparation and submission, and data acquisition were K. Klassen from the isotope lab at Queen's University, Dr. A. Simonetti and Professor C. Gariépy from GEOTOP, and J. Gagnon from GLIER at the University of Windsor.

Thanks also to M. Willis, A. Chouinard, K. Smuk, A. Kosowski, S. Archibald, C. Normand, M. Heiligmann, H. Young, G. Poirier, J. Gagnon, C. P. Mann, D. Dolejs, A. Migdisov and M. Mlynarczyk, as well as many others, who contributed toward a friendly and stimulating environment, both social and academic, at McGill. Meredith and Annick merit special recognition for all the stimulating discussions, mostly food-related, during our Wednesday night cooking club. The translated abstract was kindly provided by G. Bernier.

Financial assistance for this project was provided by SEG and GSA grants to K.M.A., NSERC and FCAR operating grants to A.E.W-J., and by Breakwater Resources. Breakwater also supplied logistical support, access to the mine and accommodation. Y. Vandermeer, K. Ball, F. Bailey and K. Bailey are particularly thanked for making my stay in Honduras both productive and enjoyable.

The constant support from my family has proven invaluable during this study. My great uncle, Dr. James Oscar Ault is also thanked for making sure I didn't have to live the life of a starving student. Finally, thanks to S. Archibald for all his love and encouragement.

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PREFACE

The research presented in this thesis was initiated after a discussion between the author and her supervisor, Prof. A.E. Williams-Jones, in the summer of 1997. The thesis is divided into 5 chapters, 3 of which are manuscripts and the remaining two the general introduction and conclusions. Chapter I has been submitted to Ore Geology Reviews, Chapter II is in press in *Economic Geology* and Chapter III will be submitted to Economic Geology. Each manuscript is co-authored by Prof. A.E. Williams-Jones who recommended the project, provided advice concerning research methodology, evaluation and interpretation of data, and critically reviewed the text. The third manuscript is also co-authored by J. Gagnon, I. Samson, and B. Fryer of Windsor University. The author carried out fieldwork and core-logging in the summer and spring of 1998 and 2001, The author also performed all petrographic analyses, fluid inclusion respectively. microthermometry, and gas chromatographic analyses of fluid inclusions. The scientific interpretations and ideas presented in the papers are for the most part the responsibility of the main author. LA-ICP-MS analyses were carried out with the assistance of J. Gagnon, University of Windsor (GLIER Institute), Windsor, Ontario under the supervision and advice of Drs. B. Fryer and I. Samson. Electron microprobe analyses were conducted with the assistance of S. Lang, G. Poirier and J. Clark at McGill University, major and trace element compositions of whole rocks were analyzed by X-ray fluorescence and ICP-MS at Activation Laboratories in Ancaster, Ontario. Sulfur and oxygen isotope compositions were determined by K. Klassen at the Queen's University stable isotope lab in Kingston, Ontario. Lead isotope ratios were determined by Prof. C. Gariépy and Dr. A. Simonetti of GEOTOP in Montréal, Québec. The following is an excerpt from the "Guidelines Concerning Thesis Preparation" as required by the Faculty of Graduate Studies and Research at McGill University:

Candidates have the option of including, as part of the thesis, the text of one or more papers submitted or to be submitted for publication, or the clearly duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis. If this option is chosen, connecting text that provide logical bridges between the different papers are mandatory. The thesis must be written in such a way that it is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.

The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation". **The thesis must include :** A Table of Contents, an abstract in English and French, an introduction which clearly states the rationale and objectives of the study, a review of the literature, a final conclusion and summer, and a thorough bibliography or reference list.

Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's best interest to make perfectly clear the responsibilities of all authors of co-authored papers.

<u>Chapter I</u>

General Introduction

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INTRODUCTION

Skarn-hosted deposits, important sources of base and precious metals, occur worldwide in a variety of tectonic settings. Although they are commonly considered to be the end product of the metasomatic replacement of a carbonate host rock, and the majority are hosted by limestone-bearing lithologies, they can form from a variety of protoliths. Economically exploitable skarns, which have also been referred to as high temperature carbonate replacement deposits may be classified into several sub-types based on the main ore metal, e.g., Fe-skarn, W-skarn, Cu-skarn, Mo-skarn, Sn-skarn and Zn-skarn (Einaudi et al., 1981).

The feature that distinguishes skarn deposits from other carbonate-replacement deposits such as Mississippi Valley Type and Irish Type is the presence of a hightemperature calc-silicate gangue that generally consists of grandite series garnet and hedenbergite-diopside series pyroxene. The formation of these deposits is a multistage process involving the infiltration, interaction and reaction of hydrothermal fluids with host rocks, usually carbonates, to form gangue silicates and sulphide ore. A number of parameters can potentially control alteration and mineralization in the skarn environment, including temperature, pH, f_{O_2} and the activities of fluid components such as Si, Al, and Fe. In principle, the relative importance of these different parameters can be evaluated qualitatively using a combination of isotope variations, fluid chemistry of silicates and sulphides and bulk rock geochemistry of skarns. Armed with these data, it should then be possible to develop a predictive genetic model that satisfactorily reconciles the proposed controlling parameters with the various observed geological features of skarn and ore. This study focuses on a distal Zn-Pb-Ag skarn, El Mochito, which like several others in its class is not spatially associated with a causative intrusion. Since El Mochito is a typical Zn-skarn deposit, it is hoped that by understanding how this deposit formed, we can gain insights to the formation of base metal skarns and aid in their exploration.

SKARN HOSTED ZN-PB-AG DEPOSITS: A REVIEW

Due to the irregular morphology and distribution of their orebodies, skarn deposits often make difficult exploration targets. This is particularly true for distal skarn deposits where no igneous association is observed. As a result, there is a large database of publications outlining the mineralogy, geochemistry and zonation patterns associated with skarns and skarn-hosted deposits, which attempt to identify the distinguishing features of each variety and how they can be applied in their exploration. Several excellent review articles provide detailed descriptions of the defining characteristics of each particular skarn variety (c.f. Dawson, 1996; Meinert, 1992; Megaw et al., 1988; Einaudi et al., 1981; Zharikov, 1970). The current section, however, deals solely with Zn (Pb-Ag) skarns.

Einaudi et al., (1981) have subdivided Zn skarn deposits into 1) Zn skarns formed near batholiths, 2) Zn skarns formed near dikes, and 3) Zn skarns formed distal to a probable or unknown igneous source. The common characteristic of these skarns is that they usually occur distal to their related intrusive source and occasionally no known igneous source is associated with the deposit, as is the case for the El Mochito deposit. Zinc skarn deposits typically contain from 1 to 10 Mt of ore with average grades of 10 to 15 wt.% Zn and Pb, and up to 300g/t Ag (Dawson, 1996). Notable Zn skarns occur at Naica, Santa Eulalia and Providencia, Mexico, the Central Mining District of New Mexico, Gilman and Leadville, Colorado, Nakatatsu, Japan, El Mochito, Honduras, Dal'negorsk, Russia and Dognecea, Romania. These deposits may also be transitional to massive limestone replacement deposits, similar to those occurring in Mexico, and because Zn skarns generally occur distal to their intrusive source, the regions may not be explored to their full potential (Megaw, 1998; Megaw et al., 1988; Einaudi et al., 1981). For example, where porphyry systems intrude carbonate-rich protoliths, high temperature base metal-rich skarns can form at a distance from the porphyry, e.g. Bingham, Utah, the Central Mining District, New Mexico and the Kassandra Mining District, Greece (Gilg, 1993). Most Zn skarns occur in continental settings associated with subduction and rifting, and the intrusive bodies are typically calc-alkaline, felsic to intermediate batholiths, stocks, dykes and sills that are granodioritic to quartz monzonitic in

composition (Dawson, 1996; Meinert, 1992; Einaudi et al., 1981). The orebodies form along lithologic contacts and structural pathways, and morphologically appear either as flat-lying stratigraphically controlled mantos or steeply dipping cylindrical chimneys, with extremely sharp contacts between skarn and protolith. The gangue mineralogy is Mn- and Fe-rich and consists primarily of grossular-andradite series garnet, hedenbergitediopside series pyroxene, and epidote. Calcite and quartz are ubiquitous in the skarn assemblage, with calcite predominating.

Fluid inclusion studies indicate that the skarn and ore-related mineralization form at temperatures ranging from 200 to 500°C from CO₂-poor (X_{CO_2} <0.01) fluids with salinities varying from 1 to 60 wt% NaCl equivalent (Jamtveit and Anderson, 1993; Newberry et al., 1991; Kwak, 1986; Sawkins, 1964). Stable isotope investigations of sulphides, silicates and carbonates indicate that δ^{34} S, δ^{18} O and δ^{13} C values fall within the magmatic range (Newberry et al., 1991; Megaw et al., 1988; Taylor and O'Neil, 1977; Sawkins, 1964). Depleted δ^{18} O and δ^{13} C values have been noted in the surrounding carbonates, and have been used to infer the extent of hydrothermal alteration (Vázquez et al., 1998; Megaw et al., 1988; Sawkins, 1964).

The genetic model and evolution of Zn skarn systems based on the common patterns of skarn alteration and ore formation is described as follows based on descriptions by Dawson (1996) and Einaudi et al., (1981). An igneous intrusion initially causes the formation of marble and calc-silicate hornfels in the adjacent, typically carbonate-bearing, country rock. The separation of a magmatic-hydrothermal fluid from the crystallizing magma results in the formation of endoskarn and exoskarn, through the metasomatism of the pluton, and marble and calc-silicate hornfels, respectively. Depending of the nature of the protolith and resultant silicate mineralogy, the skarn could be classified as either magnesian or calcic. Calcic skarns result from the replacement of limestone by a mixture of Ca and Fe silicates, while magnesian skarns result from the replacement of a dolomitic host by Mg-silicates. This fluid can combine with metamorphic, meteoric or basinal fluids to transport Fe, Si, Al and the ore metals along igneous and stratigraphic contacts, fractures and other potential fluid conduits. During the later prograde stages the fluids become progressively enriched in S, Mn, and Fe, and sulphide and magnetite precipitation is initiated. The main period of ore formation,

however, occurs during retrograde or hydrous alteration of the prograde skarn silicates. Fluid conditions favour the transport of metals as chloride complexes and the fluids are relatively reduced and H_2S stable (Seward and Barnes, 1997). The model of distal Zn skarn formation is slightly different from the classic skarn model in that fluids are expected to have traveled some distance, there is generally no observable thermal aureole, and the mineralogy is Mn- and Fe-enriched compared to proximal skarn deposits.

Although numerous studies of skarn deposits have described their mineralogy, established their bulk compositions, compositional variations, and potential conditions of skarn and ore formation, this study addresses several aspects of skarn and ore-formation not previously discussed. These include, 1) the effect of an evolving precursor rather than a single protolith or a mixed protolith during progressive skarn alteration, 2) whether δ^{34} S values and Pb isotope ratios can be used to establish the direction of fluid flow and the extent of fluid:rock interaction, 3) the quantification of the amount of metals in solution by LA-ICP-MS analyses of fluid inclusions in skarn and ore minerals, and 4) whether the skarn and ore forming hydrothermal fluids were dominantly magmatic and meteoric.

THE EL MOCHITO ZN-PB-AG DEPOSIT

The El Mochito mine exploits a distal chimney-manto Zn-Pb-Ag limestone replacement deposit (skarn) located within west-central Honduras (15°N latitude, 88°W longitude), 85 Km southwest of San Pedro Sula. El Mochito is currently the largest mining operation in Central America, and has been in production since 1948, producing concentrates of Zn, Pb, and Fe, as well as significant quantities of Ag. The deposit was discovered in 1938 and subsequently acquired by the New York and Honduras Rosario Mining Company (Rosario Resources), and initial production of ~100 tonnes per day commenced in the upper zones of the deposit that are now collectively known as the Mina Vieja or "Old Mine". American Pacific Mining Corporation (AMPAC) purchased the property from Rosario (then a subsidiary of AMAX Inc.) in 1987; Breakwater

Resources purchased AMPAC in March 1990 and has operated the mine since (Bailey, 2004).

The deposit contains ~13 Mt of ore grading at 7 wt.% Zn, 2 wt.% Pb and 80g/t Ag (Byrd, 1997; Thalenhorst, 1994) with 3 Mt in reserve. The known ore-grade mineralization occurs in a volume of rock measuring ~2.5 Km by 1 Km, with the orebodies occupying ~0.3% (Thalenhorst, 1994). The deposit exhibits features typical of distal Zn skarns such as the occurrence of stratigraphically and structurally-controlled orebodies (i.e., mantos and chimneys), and a Fe- and Mn-rich silicate gangue consisting predominantly of grossular-andradite series garnet and hedenbergite-diopside series pyroxene (Einaudi et al., 1981). Most orebodies lack identifiable feeder structures, however, the majority occur along fault zones within the mine suggesting that the latter acted as fluid conduits for hydrothermal solutions.

The Salva Vida-Nacional trend, the focus of this study, is a ~600 m manto system containing ~3 Mt of ore located along the Salva Vida-Nacional fault zone. These readily accessible orebodies provided an excellent opportunity to observe whether changes in geochemistry along trend could be used to infer the direction of fluid flow, extent of fluid:rock interaction and source of metals for the deposit. The samples from the Salva Vida-Nacional trend were supplemented by samples taken from surficial exposures and additional parts of the deposit.

PREVIOUS WORK AT EL MOCHITO

Previous work at the mine includes an unpublished M.Sc. thesis (Dilles, 1982), two published articles outlining isotopic haloes in the host limestone as well as introducing the San Juan, Porvenir, Yojoa and Nueva orebodies, mine stratigraphy and mineralogy (Vázquez et al., 1998; Araya et al., 1977), two published abstracts discussing the isotopic zonation in garnets and limestone (Vázquez et al., 1993; Vennemann et al., 1993), a recent paper in preparation by F. Bailey describing the minerals of the deposit from a collectors' standpoint, and several unpublished company reports detailing orebody-specific lithology, geology and mineralogy. The thesis by Dilles details the mineralogy, paragenesis and metal zonation occurring within the Cantarannas Formation of the San Juan orebody and the flanking manto bodies. The results of the isotope studies suggest that the fluid responsible for the observed zonation was of mixed magmaticmeteoric origin, and that depletion in δ^{18} O and δ^{13} C occurred with increased distance toward the orebodies, due to increased fluid:rock interaction. The abstracts also deal with the isotope variations in garnet crystals providing evidence that the fluids were magmatic in origin and that there was a change in fluid conditions, evident from the core to rim δ^{18} O depletion of individual crystals. There are also published abstracts concerning mining and milling techniques that provide a basic introduction to the geology of the deposit (Byrd, 1997; Araya et al., 1977).

THESIS OBJECTIVES

The ultimate goal of this study is to determine how the El Mochito deposit formed. Since the deposit exhibits all the characteristics of a typical Zn skarn, the results determined during this study would be more applicable to other Zn skarns than if it was unique within its sub-type. Although variations in mineral chemistry, and mineral and metal zonation have proven to be useful tools in skarn exploration (Meinert, 1987; Newberry et al., 1981; Yun and Einaudi, 1981), establishment of an alternate exploration strategy based on a genetic model would prove extremely useful in the search for these difficult exploration targets where such zonation trends are not evident. Consequently, the current study has also attempted to determine whether any geochemical trends could be identified that would be of use in the exploration for these deposits. During the early part of the study, skarn types were identified and their mineralogy, paragenesis, and composition documented. Bulk chemical analyses of skarn varieties were compared to their individual precursors then related to the component activities of the hydrothermal fluids in order to better understand the alteration processes occurring during skarn formation. Investigations of the nature and extent of metal and mineral zonation within the deposit were carried out to determine whether discernable patterns could be identified that could be used to aid in exploration. The nature and potential location of fluid source,

and direction of fluid flow was established through the use of stable and radiogenic isotopes. The temperature, composition and evolution of skarn and ore-forming fluids were established through fluid inclusion microthermometry, gas chromatographic analyses and LA-ICP-MS of silicate and sulphide-hosted fluid inclusions. The results of each study were used to develop a model of skarn and ore-formation at El Mochito, which could potentially be applied in the exploration for other skarn-hosted Zn deposits not clearly related to an igneous source, as well as aid in the understanding of the processes of alteration and ore-formation in the skarn environment.

THESIS ORGANIZATION

This thesis is divided into five chapters: a general introduction, three manuscripts and the conclusions. Chapter II provides a review of the geology of the deposit, bulk chemistry of the skarn varieties, their mineralogy and compositional variation, and the metal zonation within the Salva Vida and Nacional orebodies. The stabilities of the skarn silicates at the inferred temperatures of formation were used to establish the potential X_{CO_2} and log f_{O_2} of the hydrothermal fluid. Variations in component activities of the hydrothermal fluid were also determined based on the compositional variation of the skarn silicates and compared to the mass changes determined from the bulk geochemistry of the skarn varieties. Changes in the FeS content of sphalerite were determined to be the result of the f_{O_2} buffering effects of the associated iron sulphide and oxide phases. The zonation within the orebodies, from central Zn and Fe to peripheral Pb and Ag is a reflection of decreasing temperature as the magmatic hydrothermal fluids cooled during outward and upward migration from the fault zones.

Chapter III reports the sulphur and lead isotope composition of the sulphides and whole rocks in the deposit, and establishes the nature and source of hydrothermal fluids in the deposit. δ^{34} S values of sphalerite, galena and pyrrhotite fall within the range expected for magmatic-derived sulphur while lead isotope ratios for galena are similar to Pb isotope ratios for the Miocene-Pliocene Padre Miguel ignimbrite. A progressive decrease in the δ^{34} S values of sphalerite and a corresponding increase in the whole-rock

Pb isotope ratios of the host limestone correlate with decreasing alteration from northeast to southwest along the trend of the Salva Vida and Nacional orebodies. These observations are interpreted to indicate that the fluid and lead source was located to the northeast of the deposit and that magma genetically related to the Padre Miguel ignimbrite produced the hydrothermal system, which formed the deposit.

Chapter IV establishes the geochemical controls on skarn and ore formation at the deposit, and makes inferences about the composition and evolution of the hydrothermal fluids through analyses of fluid inclusions by microthermometry, gas chromatography and LA-ICP-MS. This study is the first to quantitatively determine the composition of skarn and ore-fluids through the analyses of fluid inclusions by LA-ICP-MS analyses. The results of all these studies have been integrated in developing a genetic model that explains how skarn and ore formed at the El Mochito deposit. Liquid-vapour inclusions in garnet, pyroxene and sphalerite comprise two main populations, an early high salinity and lower temperature fluid and a later higher temperature and lower salinity fluid. Gas chromatographic analyses of volatiles contained in grossularitic garnet, andraditic garnet, pyroxene, and sphalerite-hosted fluid inclusions reveal that the fluids consist dominantly of H₂O, and that the fluids associated with grossularitic garnet and low-Fe sphalerite were reduced compared to those precipitating andraditic garnet, pyroxene and medium-Fe sphalerite. LA-ICP-MS analyses of fluid inclusions hosted in grossularitic garnet, pyroxene and sphalerite indicate that Na, K, Ca and Fe are the dominant cations in solution and that the hydrothermal fluids contained up to 5500 ppm Zn and 840 ppm Pb. Based on the results of fluid inclusion microthermometry, the $\delta^{34}S_{H_2S}$ of fluids precipitating sphalerite, galena and pyrrhotite was calculated to fall within the range expected for magmatic sulphur. A comprehensive genetic model of skarn and ore formation at El Mochito is proposed by combining the observed mineralogy, isotope values and fluid geochemistry. In this model, hydrothermal fluids, derived primarily from magmatic and basinal sources, flowed along the faults bounding the Mochito Graben, reacting and eventually equilibrating with the Átima limestone to form skarn and ore at the deposit.

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INTRODUCTION TO CHAPTER II

The following chapter "*Mineralogy and Geochemistry of the El Mochito Skarn-Hosted Zn Deposit, Honduras*" provides a more detailed description of the El Mochito deposit. The skarn and ore mineralogy are described and compositional variations of the skarn minerals are used to make inferences about the evolution of the hydrothermal fluids as alteration and ore formation progressed. Bulk rock geochemistry of the main skarn varieties is evaluated in terms of their individual precursors to determine how changes in fluid chemistry affected the resultant alteration assemblages. Metal zonation within the Salva Vida and Nacional orebodies was also investigated to determine whether it could reflect proximal versus distal locations with respect to heat and fluid source within each orebody. CHAPTER II

MINERALOGY AND GEOCHEMISTRY OF THE EL MOCHITO SKARN-HOSTED ZN DEPOSIT, HONDURAS

K.M. Ault and A.E. Williams-Jones

ABSTRACT

The El Mochito mine, located in west-central Honduras, exploits a distal Zn-Pb-Ag skarn deposit. The bulk of the economic mineralization, occurring either as steeply dipping pipes or flat-lying manto bodies, is hosted by Cretaceous limestone of the Átima Formation. The prograde silicate minerals consist predominantly of pyroxene (Hd₅₃. ₇₉Di₄₋₄₃Jo₅₋₄₁), and two types of garnet, an early grossularitic variety (Gr₅₂₋₇₁Ad₂₅₋₄₆Sp₁₋₉) and a later andraditic variety (Ad₅₀₋₈₃Gr₁₄₋₄₈Sp₁₋₆). Ore minerals comprise Fe-poor to Ferich sphalerite, galena, pyrite, pyrrhotite, and chalcopyrite, all of which post-date the main silicates. The distribution of ore metals within the Salva Vida and Nacional orebodies is zoned from Fe-Zn-rich cores to adjacent Pb-rich zones and outer zones rich in Ag.

Comparison of the bulk rock composition of the garnet and pyroxene skarns to their individual precursors indicates that significant additions in Si, Fe, Mg, Al, and Mn accompanied skarn formation. The only components that were lost in appreciable quantities were Ca and volatiles, although Ca may have been conserved during early skarn formation. Apparent decreases in the concentrations of Ti and Zr suggests that the fluid:rock ratio was high.

Based on the stabilities of garnet and pyroxene, the X_{CO_2} and log f_{O_2} of the hydrothermal fluid ranged from 0.001 to 0.015 and -25 to -22, respectively, between temperatures of 400 and 500°C. Variations in component activities of the hydrothermal fluid indicate that andraditic garnet skarn was stable at lower log(a_{Ca2+}/a_{H+2}), log(a_{Al3+}/a_{H+3}), and log $a_{SiO_2(aq)}$, and higher log(a_{Fe3+}/a_{H+3}) than its grossularitic garnet skarn precursor, whereas hedenbergitic pyroxene skarn was stable at lower log(a_{Ca2+}/a_{H+2}) and log(a_{Fe3+}/a_{H+3}) and higher log $a_{SiO_2(aq)}$ than its andraditic skarn precursor. The variations in component activities for each skarn type are consistent with the mass changes interpreted from the bulk rock geochemistry. Changes in the FeS content of sphalerite are thought to result from the f_{O_2} buffering effects of the associated iron sulphide and oxide phases. The zonation from Zn to Pb and the Ag reflects the sequential saturation of sphalerite and galena in the fluid with decreasing temperature as the magmatic hydrothermal fluids cooled during outward and upward migration from the fault zones.

INTRODUCTION

The formation of skarn-hosted ore deposits, important worldwide resources of base and precious metals, occurs through a complex, multistage process involving thermal metamorphism, metasomatism, and fluid:rock interaction (Einaudi et al., 1981). A distinguishing feature of skarn deposits is the presence of a high temperature calc-silicate gangue that is often compositionally and paragenetically zoned (Newberry et al., 1991; Meinert, 1998; Einaudi et al., 1981). This zonation is considered to result from increased fluid pH as the hydrothermal fluids were neutralized during reaction with the host carbonates, as demonstrated by studies defining the relationship between the compositional variation and stability of calc-silicate minerals to the component activities of their parental hydrothermal fluids (Bowman, 1998; Vander Auwera and Verkaeren, 1993; Luce et al., 1985; Einaudi et al., 1981; Rose and Burt, 1979; Korzhinskii, 1970). Similarly, a zonation in the ore metals, progressing from Zn-rich cores to Pb and Ag-rich peripheries, is also often noted, and is thought to result from a decrease in temperature as hydrothermal fluids proceed from their sources to the sites of deposition (Newberry et al., 1991; Meinert, 1987; Beaver, 1986; Yun and Einaudi, 1981).

Although bulk geochemical studies have shown that the formation of skarn deposits is associated with significant gains in Si, Fe, Al, Mg and the ore metals, and losses in Ca and CO₂ and other volatiles (Lentz et al., 1995; Ochiai, 1987; Kwak, 1978; Reid, 1978; Nielsen, 1970), a factor not considered in these studies has been the potential change in protolith composition with evolution of the skarn system. Another issue often overlooked is the fact that by the time the ore fluids are introduced there is little to no original carbonate left to react with the ore-forming solutions. Clearly, the lack of original carbonate protolith would strongly reduce the possibility that fluid neutralization is the main factor controlling mineral zonation, compositional variation, and ore deposition in skarn deposits. Therefore, consideration must be given to the possibility that other factors and processes may control formation of skarns and related ores.

The El Mochito deposit exhibits features typical of distal Zn skarns, such as the location of manto and chimney orebodies along fault zones, a calc-silicate gangue of grossular-andradite series garnet and hedenbergitic-diopside series pyroxene, the lack of a metamorphic aureole, and a Mn and Fe-rich mineralogy (Vázquez et al., 1998; Dilles, The current study reviews the geology and mineralogy of the deposit and 1982). examines how compositional variations of the main skarn types at El Mochito reflect the evolution of the skarn-forming fluid. Mass gains and losses were assessed for garnet and pyroxene skarns to establish the chemical changes that occurred during alteration of each successive mineralogic zone. The variations in individual mineral compositions and component activities were evaluated as a complement to the mass balance study to make inferences as to how the skarn fluids changed as alteration progressed. Metal zonation was also investigated to determine whether specific patterns could be identified that could provide clues to the location of the heat and fluid source and also what factors influenced ore mineral precipitation. Based on the observed geochemical variations a general model of skarn formation at the El Mochito deposit was produced.

GEOLOGIC SETTING

The El Mochito mine, located in west-central Honduras, exploits a Zn-Pb-Ag skarn deposit containing ~15 Mt of ore grading 7% Zn, 2% Pb and 80g/t Ag (Vázquez et al., 1998; Thalenhorst, 1994). The largest operating mine in Central America, El Mochito is located in the Central Cordillera of Honduras (Figure 2-1). The region forms part of the Chortis block, a major geologic province of the Caribbean plate composed dominantly of Precambrian and Paleozoic phyllites and schists which, in Honduras, is cut by a staggered series of major NE- to NW-trending faults and grabens (Draper et al., 1994; Malfait and Dinkelman, 1972; Williams and McBirney, 1969; Mills et al., 1967). These structures, known collectively as the Honduras Depression, are considered to represent a major zone of extensional intraplate deformation, which formed during the mid-Tertiary (Mills et al., 1967; Williams and McBirney, 1969; Malfait and Dinkelman, 1972; Mann and Burke, 1984; Gordon, 1990; Aldrich et al., 1991). El Mochito lies in the

Figure 2-1. Location, tectonic setting and geology of the El Mochito deposit. PMSZ=Polochic Motagua suture zone. (Modified from Williams and McBirney, 1969). Mochito graben, a smaller structure off the Yojoa graben (Fig. 2-1), both of which are related to development of the Honduras Depression (Malfait and Dinkelman, (1972).



Tertiary

Padre Miguel Group rhyolitic ignimbrites

Matagalpa Formation

Cretaceous



Atima Formation

limestone

The closest outcrops of igneous rocks occur at Lago de Yojoa, a volcanic centre located 13 km to the northeast (Fig. 2-1). These rocks comprise andesitic to basaltic lavas and pyroclastic flows of the Eocene-Oligocene Matagalpa Formation, rhyolitic ignimbrites of the Miocene-Pliocene Padre Miguel Group, and basaltic flows and scoria cones of the Quaternary-Recent Yojoa Eruptive Complex (Williams and McBirney, 1969).

Lithologic Units

Sedimentary rocks in the mine area comprise quartz sandstone of the (Jurassic?) Todos Santos Formation, limestone and shale of the Cretaceous Yojoa Group and redbeds of the Tertiary Valle de Angeles Group. The only igneous rocks are diabase dykes dated at 16.7 ± 0.7 , 9.7 ± 0.4 , and 9.4 ± 0.4 Ma (K/Ar whole-rock; Dilles, 1982). Based on these age determinations as well as those for other igneous rocks in the region, intrusion of the dykes appears to have coincided with extrusion of the Padre Miguel ignimbrite at Lago de Yojoa.

Skarn and ore formed mainly in the Atima Formation and to a lesser extent in the underlying Cantarannas Formation, both members of the Yojoa Group, and occur in manto and chimney bodies (Figure 2-2A), which are commonly located along or near fault zones (Fig. 2-2B). Some poorly mineralized skarn also developed in the Todos Santos Formation, the basal unit in the mine area. The contact between the Todos Santos and Cantarannas Formations is unconformable and the lithology is gradational, consisting of interbedded limey and clastic units. The Átima Formation is a medium to dark grey massive micritic limestone containing abundant foraminifera and ostracod fossils. This unit hosts abundant calcite veins and stylolitic structures; unaltered limestone consists almost entirely of calcite, and contains minor clay-rich layers and interbeds of siltstone and mudstone. Organic matter was not observed, and staining of limestone with potassium ferrocyanide confirmed the lack of dolomite. The Átima limestone is separated into an upper and lower member by the Mochito shale. When altered, the limestone appears bleached and contains recrystallised calcite, abundant carbonate veins and epidote along the stylolitic sutures. The minor mudstone and siltstone interbeds within the Atima Formation are very similar, and consist of very fine- to fine-grained
Figure 2-2. A) Cross-section through the El Mochito deposit. Orebodies are shaded, major faults are shown as large dotted lines and the Cantarannas contact is shown as a continuous dashed line. B) Plan view of the El Mochito deposit (2500 level composite) illustrating the association of most orebodies (shaded) with fault zones (dotted lines). SVN=Salva Vida-Nacional, SJ=San Juan, PR=Port Royal, NPO=Nispero, MN=Main, POR=Porvenir.



rounded quartz grains hosted in a matrix of clay and carbonate, and fine-grained subround quartz grains within a matrix of clay and carbonate, respectively. These units, when altered to skarn, contain mostly epidote, quartz, calcite, and clay, with minor garnet, pyroxene, magnetite, biotite, and K-feldspar. The Cantarannas Formation consists of thinly bedded calcareous shale, limestone, siltstone, and sandstone (Mills et al., 1967). The Todos Santos Formation is a white to grey quartz sandstone, consisting of fine- to medium-grained, sub-round quartz grains accompanied by minor chlorite, epidote and magnetite. This sandstone unit, when altered, contains abundant quartz with interstitial epidote, clay minerals and minor garnet and pyroxene. The Mochito diabase dykes consist predominantly of medium-grained plagioclase phenocrysts (An₇₃₋₈₀Ab₂₀₋₂₇) in a fine-grained matrix of plagioclase, sericite and chlorite. The dykes are intensely altered where in contact with ore-bearing skarn mineralization but are not mineralized (Smith, 1975). The stratigraphic sequence at El Mochito is shown on Figure 2-3.

Skarn Types

The main skarn types at El Mochito are hedenbergitic pyroxene skarn and andraditic garnet skarn, and are accompanied by epidote, magnetite, grossularitic garnet, chlorite, and sulphide skarns (Figure 2-4). Garnet and pyroxene skarns occur throughout the deposit and there is a general zonation from garnet skarn to pyroxene skarn with distance from fault zones in each orebody. Magnetite and sulphide skarns usually occur within the centre of each orebody, whereas epidote and chlorite skarns are usually found along the peripheries, close to stratigraphic contacts or within fault zones. Pyroxene skarns contain radiating aggregates/clusters of euhedral to subhedral lath-shaped crystals of hedenbergitic pyroxene ranging from 30µm to 3 cm in length (Fig. 2-4A). The pyroxene is variably pale to dark green, black or pink/brown due to variations in the proportions of diopside, hedenbergite and johansennite. Sphalerite occurs mostly in pyroxene skarn, and proportions of magnetite, epidote, and chlorite are also highest in pyroxene skarn. Andraditic garnet skarns consist mainly of euhedral to subhedral yellow-green garnet crystals ranging in diameter from 80µm to 1.5 cm (Fig. 2-4B) and also commonly contain disseminated sphalerite, galena, magnetite, calcite, pyrite and epidote. Grossularitic garnet skarn contains euhedral to subhedral crystals of red-pink-

Figure 2-3. Stratigraphy at the El Mochito deposit showing the occurrence of chimney and manto orebodies hosted mainly in the Átima limestone. (Modified from Mills et al., 1967).



Figure 2-4. Skarn varieties at El Mochito. A) Pyroxene skarn with magnetite and interstitial calcite. B) Andraditic garnet skarn with interstitial calcite. C) Epidote skarn with stringers of sphalerite and interstitial chlorite and calcite. D) Magnetite skarns with pyroxene, sphalerite, epidote and calcite. E) Grossularitic garnet skarn containing interstitial sphalerite and magnetite. F) Pyrrhotite skarn containing interstitial epidote and clay, veinlets of chalcopyrite and blebs of sphalerite and magnetite. G) Chlorite skarn with interstitial epidote, and calcite with blebs of galena and stringers of sphalerite. Gr=grossularitic garnet, Ad=andraditic garnet, Px=pyroxene, Epi=epidote, Sp=sphalerite, Gal=galena, Cc=calcite, Mt=magnetite, Po=pyrrhotite, Chl=chlorite.



orange grossularitic garnet ranging in diameter from 40µm to 1 cm (Fig. 2-4E). Magnetite, pyrite, calcite, quartz, epidote and sphalerite are commonly present in grossularitic garnet skarn. Epidote skarns are a characteristic apple green colour and fine-grained, with crystals ranging from 10 to 200µm in diameter (Fig. 2-4C); calcite and chlorite are abundant in epidote skarn. Magnetite skarns comprise fine- to medium-grained, hypidiomorphic to allotriomorphic magnetite (Fig. 2-4D), and typically contain pyroxene, epidote, garnet, sphalerite, and pyrrhotite. Chlorite skarns are green to pale green in colour (Fig. 2-4G) and do not contain appreciable quantities of ore. Skarns labeled as sulphide commonly consist of mixtures of sphalerite and pyrrhotite, and contain interstitial calc-silicate minerals (Figure 2-4F).

The general distribution of skarn types within orebodies varies from centrally located magnetite and sulphide skarns to peripheral garnet and pyroxene skarns (Figure 2-5). Pyroxene and epidote skarns typically occur in the basal parts of the orebodies, whereas garnet skarns are concentrated in the upper parts.

SKARN AND ORE MINERALOGY

Silicates

There are two types of garnet, an early dark pinkish-brown variety and a later, much more abundant, yellow-green variety, both of which exhibit sector or oscillatory zoning in thin section (Figure 2-6A,B). Electron microprobe analyses indicate that the former is grossular-rich with an average composition of $Gr_{55}Ad_{41}Sp_4$ and the latter andradite-rich with an average composition of $Ad_{72}Gr_{25}Sp_3$ (Table 2-1A). Garnet is locally altered to a retrograde assemblage of epidote, magnetite or hematite, calcite, quartz, chlorite and smectitic clay, particularly in the cores of crystals. Grossularitic garnet was the earliest of the silicates to form and commonly displays turbid cores surrounded by zoned andradite-rich rims (Fig. 2-6A). Andraditic garnet occurs either as zoned rims on grossularitic garnet or as discrete crystals and masses, cutting and replacing previously formed grossularitic garnet. Pyroxene, which formed after garnet

Figure 2-5. Distribution of skarn in the central sections of the Salva Vida (9900) and Nacional (9400) orebodies. Skarns rich in magnetite, pyrrhotite and massive sphalerite appear within the cores of each orebody while garnet pyroxene and epidote are distributed more peripherally. Garnet skarn occurs at higher elevations in the sections, closer to the limestone contact, whereas pyroxene and epidote are more abundant in the basal portions. The 5% Zn contour is shown in red and delineates the orebodies.



Figure 2-6. Photomicrographs of skarn silicates in thin section. Scale bar is 0.5 mm. A, B, F, and G were taken under plane polarized light and C, D, E, and H under transmitted light. Gr=grossularitic garnet, Ad=andraditic garnet, Px=pyroxene, Epi=epidote, Sp=sphalerite, Gn=galena, Cc=calcite. A) Early grossularitic garnet replaced by later finely zoned andraditic garnet. The grossularitic core is partly altered to a mixture of calcite and epidote. B) Late, poorly zoned, andraditic garnet mantling early grossularitic garnet; alteration minerals comprise a mix of chlorite and carbonate. C) Lath of pyroxene cutting earlier-formed andraditic garnet. D) Well-developed bladed and interlocking pyroxene crystals. E) Pyroxene rosette cored by magnetite. F) Crystals of prograde epidote replacing pyroxene. G) Alteration of garnet and pyroxene by a finegrained mixture of retrograde epidote and smectite. H) Bladed bustamite at the skarn limestone contact.



Table 2-1. Representative analyses of garnet (A), pyroxene (B) and epidote (C) compositions. The total number of analyses is shown in brackets. Sample locations are shown in Appendix 1 and all electron microprobe analyses are listed in Appendix 2.

(A)	SV2650-23 (6)	5215-303 (4)	4520-50 (4)	5213-196 (4)	SV2550-19 (6)	NM98-2 (2)
SiO	37.01	36.89	35.93	35.61	35.84	34.67
Al ₂ O ₃	13.87	9.19	8.60	4.47	5.90	2.45
Cr ₂ O ₃	0.00	0.00	0.01	0.00	0.00	0.01
TiO	0.11	0.28	0.13	0.01	0.36	0.16
Fe ₂ O ₁ *	12.37	18.56	19.99	25.32	23.44	28.51
MnO	1.16	0.60	0.99	1.62	2.64	1.28
MgO	0.06	0.03	0.02	0.07	0.03	0.01
CaO	34.24	34.20	33.32	32.34	31.78	32.95
Total	98.81	99.76	98.99	99.45	99.99	100.04
<u>End-Member (</u>	Compositions					
Andradite	27.5	46.2	49.7	70.7	62.9	83.1
Grossular	70.8	52.2	48.6	25.2	35.4	15.3
Spessartine	1.4	1.4	1.4	3.8	1.4	1.3
Uvarovite	0.0	0.0	0.0	0.0	0.0	0.0
Ругоре	0.2	0.3	0.3	0.3	0.3	0.3
Almandine	0.0	0.0	0.0	0.0	0.0	0.0
(B)	SV2550-27 (7)	SV2650-26 (5)	NAC2350-3 (2)	NAC2450-6 (3)	6198-155 (11)	-
SiO ₂	50.28	49.01	50.64	48.62	50.19	
Al ₂ O ₃	0.49	0.05	0.09	0.52	0.00	
TiO ₂	0.03	0.01	0.00	0.01	0.16	
FeO*	16.40	17.82	17.70	23.16	20.75	
MnO	1.49	6.74	2.89	1.64	1.40	
MgO	7.45	2.94	5.68	2.56	4.25	
CaO	23.85	23.24	23.71	23.39	23.34	
Na ₂ O	0.06	0.02	0.02	0.05	0.06	
K ₂ O	0.00	0.03	0.02	0.03	0.00	
Total	100.04	99.86	100.74	99.98	100.15	
<u>End-Member (</u>	Compositions					
Hedenbergite	52.6	59.6	57.6	78.8	69.8	
Diopside	42.6	17.6	32.9	15.6	25.5	
Johannsenite	4.8	22.8	9.5	5.7	4.8	_
(C)	NAC2450-1 (3)	NAC2350-3 (4) SV2550-27 (1)	SV2650-21 (3)	6466-207 (3)	-
SiO ₂	37.58	37.57	37.67	37.74	37.84	
TiO ₂	0.15	0.09	0.24	0.03	0.05	
Al ₂ O ₃	22.89	22.09	22.50	23.62	22.79	
Cr ₂ O ₃	0.01	0.02	0.00	0.00	0.00	
Fe ₂ O ₃ *	13.21	13.54	14.00	12.32	13.25	
MnO	0.18	0.28	0.01	0.14	0.20	
MgO	0.05	0.05	0.05	0.02	0.01	
CaO	23.34	23.34	23.18	23.64	23.32	
Na ₂ O	0.01	0.00	0.00	0.00	0.02	
K ₂ O	0.03	0.01	0.00	0.02	0.01	
Total	97 44	97.00	97.63	97.52	97.49	

Jeol JXA-8900L electron microprobe analyses using ZAF correction; 15 kV, 30 nA; 20 s peak counts; 5 μ m beam. Typical lower detection limits at 3-sigma are 0.02 wt% for SiO₂, Al₂O₃, MgO, Na₂O and K₂O; 0.03 wt% for CaO; 0.04 wt% for FeO and MnO; and 0.05 wt% for TiO₂. (A) Andradite and pyrope standards were used for major elements. (B) A diopside-based standard for major elements. (C) Diopside and orthoclase standards were used for major elements. *Total Fe as Fe₂O₃ (Fig. 2-6C), is fine- to coarse-grained, variably pale to dark green, black or pink/brown, and occurs either as large, bladed, interlocked crystals (Fig. 2-6D) or radiating masses/rosettes with cores of magnetite (Fig. 2-6E). Electron microprobe analyses (Table 2-1B) indicate that the principal pyroxene component is hedenbergite, and that the diopside and johannsenite proportions are variable, ranging from Jo5-40 and Di4-43. Although the garnet compositions are similar to those analysed previously from the San Juan orebody (Dilles, 1982), the composition of pyroxene in the Salva Vida and Nacional orebodies is more hedenbergitic. Pyroxene is altered locally, especially along cleavage planes, to a retrograde assemblage that includes epidote, chlorite, ilvaite, quartz, calcite, Mn-actinolite, tremolite, magnetite or hematite and smectitic clay. No systematic variations in pyroxene composition were noted along the Salva Vida-Nacional trend and there was no evident zonation within individual crystals, although pyroxene occurring close to the skarn-limestone contact tends to have a higher johannsenite component than elsewhere. The compositions of both pyroxene and garnet fall within the expected range for Zn skarns (Einaudi et al., 1981) and are similar to those analysed from the San Juan orebody (Dilles, 1982).

Epidote occurs predominantly as a retrograde phase; prograde epidote is characterized by small, euhedral crystals and tends to be coarser-grained than its retrograde equivalent (Fig. 2-6F,G). Compositions of both prograde and retrograde varieties are fairly uniform (Table 2-1C). Alteration of epidote typically produced smectite and magnetite or hematite.

Bustamite, biotite and K-feldspar occur in very minor quantities, bustamite at the skarn-limestone contact (Fig. 2-6H) and biotite and K-feldspar from alteration of minor mudstone and siltstone layers and diabase dykes. Calcite, chlorite, ilvaite, sericite, quartz and tremolite are retrograde minerals, occurring interstitially, as part of alteration assemblages of silicates, or within late veins.

Sulphide and Oxide Mineralogy

Textural relationships among oxides and sulphides are shown in Figure 2-7. Magnetite was the earliest of the oxide and sulphide phases to form, occurring as feathery masses (Fig. 2-7A), mantles on earlier-formed silicates (Fig. 2-7B), disseminated grains,

Figure 2-7. Photomicrographs (reflected light) of sulphide textures in polished thin sections. Scale bar is 0.1 mm. A) Feathery magnetite followed by sphalerite, galena and chalcopyrite with interstitial calcite; pyroxene replaced by sulphides. B) Epidote mantled by magnetite with later sphalerite, pyrrhotite, pyrite and chalcopyrite. The pyrrhotite is earlier than sphalerite and the pyrite is the latest sulphide, and appears to replace pyrrhotite. C) Early cube of pyrite replaced by pyrrhotite. D) Early magnetite partially replaced by pyrrhotite. The magnetite and pyrrhotite appear to have replaced garnet, as shown by the relict textures. E) Sphalerite breaking apart and infilling fractures in andraditic garnet. F) Pyrrhotite with late galena and traces of sphalerite filling fractures. G) Pyrrhotite replaced by chalcopyrite, galena and native bismuth. H) Composite galena-chalcopyrite blebs hosted in sphalerite.



interlayered with pyroxene, and as cores from which bladed rosettes of pyroxene radiate. Pyrite was the earliest sulphide to form, occurring as early euhedra cut by the later sulphides (Fig. 2-7C), as rims on silicates, and as late euhedra surrounded by calcite and quartz. Pyrrhotite occurs either as massive aggregates or as veins cutting magnetite and pyrite, and is associated with pyrite, minor magnetite, and sphalerite, replacing pyrite and magnetite and predating sphalerite (Fig. 2-7B,C, D).

Sphalerite was subdivided into three sub-types based on its color in hand specimen: S1 (pale yellow-brown), S2 (orange-red) and S3 (black), the most common variety being the S2 sub-type. Electron microprobe analyses of sphalerite (Table 2-2A) indicate that the color classification reflects variations in iron concentration, and permits the sub-types to be distinguished chemically as follows: S1 (<5% Fe), S2 (>5 to 10% Fe) and S3 (>10% Fe). The relative timing of sphalerite sub-types cannot be ascertained directly as more than one sub-type has not been noted to occur in the same sample, however, it can be inferred from the associated Fe sulphides. The S1 sub-type commonly occurs with pyrite, whereas the S2 and S3 sub-types occur primarily with pyrrhotite, which as noted above postdated formation of pyrite. These associations and the Fe content of the sphalerite are also consistent with a trend of decreasing f_{O_2} and/or f_{S_2} from S1 to S3 sphalerite. Most of the sphalerite in the deposit is hosted by pyroxene skarn, where it fills interstices among pyroxene grains, occurs along grain boundaries, or crosscuts earlier-formed silicate and oxide phases (Fig. 2-7A,B,E).

Galena occurs most commonly as blebs in sphalerite (Fig. 2-7H), and also fills fractures in sphalerite and pyrrhotite (Fig. 2-7F). Galena post-dated sphalerite and crystallized contemporaneously with chalcopyrite, commonly forming composite blebs with chalcopyrite in sphalerite (Fig. 2-7H). Electron microprobe analyses indicate that galena (Table 2-2B) frequently contains significant concentrations of Ag and Bi, up to 1.7 and 2.19 wt. %, respectively, and that these concentrations are positively correlated.

Chalcopyrite occurs as late veinlets, composite blebs with galena in sphalerite, scattered blebs in sphalerite (Fig. 2-7B,F,H), along cleavage traces in sphalerite or as overgrowths on sphalerite and pyrrhotite. Formation of chalcopyrite post-dated that of sphalerite and appears to have been contemporaneous with crystallization of galena.

Table 2-2. Representative compositions of sphalerite sub-types (A) and galena (B) from the El Mochito deposit. Total number of analyses in brackets, otherwise a single analyses was performed. Sample locations are shown in Appendix 1 and all analytical results are listed in Appendix 2.

(A)				S2			<u> </u>			
	2450-10	5615-75	6466-207	5215-5	2650-24	2650-25	4365-526	5226-176	2650-23	SV2A
	(6)	(8)	(10)	(4)	(6)	(3)	(5)	(7)	(9)	
Zn	62.9	65.0	62.2	62.84	60.1	61.3	57.4	53.8	54.4	49.91
Fe	4.1	1.4	3.9	3.20	6.6	5.5	8.8	11.8	11.8	15.19
Cd	0.6	0.8	0.6	0.51	0.6	0.6	0.6	0.4	0.5	0.56
Mn	0.0	0.2	0.3	0.00	0.0	0.0	0.0	0.0	0.0	0.00
Cu	0.0	0.0	0.0	0.02	0.0	0.0	0.1	0.0	0.0	0.01
S	32.9	33.1	33.0	33.04	33.3	33.5	33.3	33.4	33.7	33.62
Total	100.5	100.6	100.0	99.60	100.5	100.8	100.2	99.5	100.4	99.28
Atomic pro	portions									
Zn	0.96	0.99	0.95	0.96	0.92	0.94	0.88	0.82	0.83	0.76
Fe	0.07	0.03	0.07	0.06	0.12	0.10	0.16	0.21	0.21	0.27
Cd	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	1.03	1.03	1.03	1.03	1.04	1.05	1.04	1.04	1.05	1.05
mol% FeS	7.1	2.5	6.9	5.6	11.4	9.4	15.2	20.5	20.3	26.3
(B)	2450-8	6466-207	5226-176	5615-564	2650-25	4360-102	NAC2450-6	4502-34	5615-75	SV2550-19
	(2)	(3)	(3)	(5)	(5)		(5)	(4)	(4)	(4)
Pb	83.71	82.53	86.48	87.08	86.47	86.83	83.34	83.48	87.04	84.62
Bi	1.31	1.82	0.00	0.00	0.00	0.00	0.99	1.36	0.01	0.78
Ag	1.05	1.45	0.07	0.04	0.00	0.00	0.60	1.09	0.08	0.59
S	13.52	13.64	13.31	13.53	13.22	13.33	13.44	13.36	13.34	13.38
Total	99.60	99.44	99.86	100.65	99.69	100.16	98.38	99.29	100.46	99.38
Atomic pro	portions									
РЬ	0.48	0.47	0.42	0.42	0.42	0.42	0.40	0.40	0.42	0.41
Bi	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Ag	0.01	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01
S	0.50	0.50	0.42	0.42	0.41	0.42	0.42	0.42	0.42	0.42

Jeol JXA-8900L electron microprobe analyses using CITZAF correction; 20 kV, 40 nA; 45 s peak counts, except 20 s for Fe and Mn; 2 µm beam. Typical lower detection limits at 3-sigma are 0.01 wt.% for Cd and S; 0.03 wt.% for Fe and Mn; 0.04 wt.% for Zn; 0.05 wt.% for Cu; 0.02 wt.% for Ag and S; 0.08 wt.% for Bi; and 0.09 wt.% for Pb. (A) Sphalerite standard was used for major elements. (B) Galena standard was used for major elements.

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There are minor variations in sulphide mineralogy with skarn type; S1 and S2 sphalerites occur in both garnet and pyroxene skarn, however high Fe sphalerite (S3) rarely occurs in garnet skarn, and pyrrhotite occurs almost exclusively with high Fe sphalerite. A summary of the general silicate, oxide and sulphide paragenesis is presented in Figure 2-8.

METAL ZONATION

Contour maps showing the distribution of metals in the central part (9900N and 9400N) of the Salva Vida and Nacional orebodies are presented on Figures 2-9 and 2-10. These sections can be subdivided into three zones: an upper zone of unaltered Átima limestone and marble, a central zone of skarn and ore, and a lower zone of variably altered Todos Santos sandstone. However, only the Todos Santos contact, faults, the distribution of metals, and the 5% zinc contour are shown.

Salva Vida Section 9900N - Metal zonation and associated skarns

On the 9900N section of the Salva Vida orebody, the highest Zn contents (>20 wt.%) are in the central zone, commonly within the vicinity of the Salva Vida-Nacional fault (Fig. 2-9). These Zn-rich rocks comprise pyroxene, magnetite, and pyrrhotite skarn (Fig. 2-5A). The highest Pb grades (>12%) occur in the basal portion of the section, near the Todos Santos sandstone contact, whereas the bulk of the Pb mineralization occurs in the upper part of the orebody close to the limestone contact. The Pb-rich skarns contain garnet, magnetite and epidote. Silver contours correlate positively with those of Pb, and most Ag-rich zones straddle fault zones within the upper parts of the orebody, in garnet or epidote skarn. Iron-rich zones overlap the Zn-rich zones within the central section of the orebody. Overall, the Salva Vida orebody has relatively Fe-rich rocks along its western margin and at depth, Zn-rich rocks in the centre, and Pb-Ag-rich rocks at the peripheries. Contoured data for the 9700N and 10100N sections of the Salva Vida orebody (not shown) demonstrate similar distributions of metals and skarn types.

Figure 2-8. Simplified paragenetic sequence for silicate, sulphide and oxide minerals at El Mochito.

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Early Late

Silicates

Garnet (Gr>50) Garnet (Ad>50) Pyroxene Epidote

Sulphides and Oxides

Magnetite	
Pyrrhotite	•
Pyrite	• •
Sphalerite	
Galena	
Chalcopyrite	

Figure 2-9. Distribution of Zn, Fe, Pb and Ag on the 9900N section of the Salva Vida orebody. A 5% Zn lower cut-off was used to define the limits of the orebody (outlined areas). Faults are delineated by solid lines and a dashed line traces the Todos Santos contact. Values are in wt. % for Zn, Pb, and Fe, and g/t for Ag.



Easting

Figure 2-10. Distribution of Zn, Fe, Pb and Ag on the 9400N section of the Nacional orebody. A 5% Zn lower cut-off was used to define the limits of the orebody (outline areas). Faults are delineated by solid lines and a dashed line traces the Todos Santos contact. Values are in wt. % for Zn, Pb, and Fe, and g/t for Ag.



Easting

Nacional Section 9400N - Metal zonation and associated skarns

Rocks with the highest Zn contents are centrally located on section 9400N (Fig. 2-10). As in the case of the Salva Vida orebody, the Zn-rich skarns are composed mainly of magnetite, pyrrhotite, and pyroxene (Fig. 2-5B). The zone richest in Pb occurs near the eastern margin of the orebody in garnet- and pyroxene-bearing skarn. Silver-rich zones do not coincide with those of Pb and instead occur peripheral to Zn-rich zones. This could be due to the presence of Ag in phases other than galena, e.g., acanthite and native silver, which are reported to occur in the shallower parts of the deposit (Araya et al., 1977), however none of these phases were found during the current study. As is the case for Pb-rich zones, garnet skarns and pyroxene skarns host Ag-rich zones. The centrally located Zn-rich zone is marked by high concentrations of Fe, but the most Ferich rocks occur at slightly higher elevations than those of Zn-rich zones characterize the Nacional orebody. Sections 9200N and 9600N of the Nacional orebody were also contoured and similar metal zonation and skarn trends were noted.

WHOLE-ROCK GEOCHEMISTRY

Whole-rock geochemical analyses were performed in order to evaluate chemical changes during the formation of garnet and pyroxene skarns. Major and trace element compositions were determined for skarns (mineralized and unmineralized) and unaltered Átima limestone. Major element concentrations were determined by fusion-ICP and trace element concentrations by a combination of INAA and ICP methods. The chemical compositions of limestone, and garnet and pyroxene skarns are reported in Table 2-3. Given that the mudstone and siltstone units are volumetrically negligible compared to the limestone, they are presumed to have made a minor contribution to skarn composition.

Quantitative Evaluation of Alteration at El Mochito

Mass gains and mass losses were evaluated using the isocon method of Grant (1986). Átima limestone was assumed to be the precursor for the grossularitic garnet

Table 2-3. Chemical composition of limestone, grossularitic garnet, and raditic garnet and pyroxene skarns. All sample locations are shown in Appendix 1 and all bulk rock geochemical data is presented in Appendix 3. Major element values in italics were normalized to Zn and Pb-free compositions.

	Limestone			Grossularitic		Andraditic			Pyroxene skarn		
				garne	t skarn	garnet skarn					
	Unalt-1	Unalt-2	Unalt-6	2650-26	2550-21	2290-10	2550-18	SJ2350-4	2550-27	2450-6	NM98-3
wt%			· · · · ·								
SiO ₂	2.83	1.25	3.77	40.72	34.70	35.20	32.73	26.01	40.72	39.12	58.68
Al ₂ O ₃	0.47	0.41	1.01	6.41	7.40	2.16	3.11	1.25	5.99	9.60	0.34
TiO ₂	0.01	0.00	0.03	0.70	0.43	0.12	0.09	0.09	0.19	0.45	0.10
Fe ₂ O ₃	0.23	0.12	0.54	15.98	19.14	25.71	28.22	28.46	22.34	20.61	13.11
MnO	0.02	0.01	0.01	3.30	1.25	2.11	0.77	1.00	1.07	1.76	4.91
MgO	0.59	0.63	0.87	2.55	0.46	0.73	0.12	15.99	5.02	1.41	1.52
CaO	55.11	55.51	53.60	28.96	34.33	31.54	33.12	23.81	18.97	21.98	16.52
Na ₂ O	0.04	0.03	0.03	0.04	0.01	0.03	0.01	0.01	0.02	0.04	0.03
K ₂ O	0.14	0.15	0.33	0.00	0.04	0.01	0.06	0.03	0.11	0.05	0.04
P ₂ O ₅	0.01	0.01	0.01	0.15	0.06	0.02	0.03	0.09	0.05	0.15	0.02
LOI	41.51	42.10	40.56	1.86	2.18	1.49	2.35	3.28	5.52	4.84	4.15
Total	100.95	100.21	100.75	100.67	100.00	99.11	100.61	100.00	100.00	100.00	99.42
ppm											
Zn	28	82	2	950	-	3673	619	-	-	-	9599
Pb	<5	<5	<5	2911	-	1130	420	-	-	-	6558
Cu	2.0	2.0	2.0	4.9	521	57	5.93	4299	333	2240	4
Ag	5	<0.4	<0.4	12	52	23	42.48	270	17	181	11
Sb	3.9	1.1	7	8	6	5	7.90	11	101	79	22
Ba	11	7	120	4	3.1	2.0	3.95	4.3	25	4.0	5
As	104	5	51	44	149	118	101	264	35	31	6
Cd	<0.5	<0.5	<0.5	9	352	35	5	1958	5729	1046	94
Cr	<5	<5	7	96	47	16	16	<5	35	50	22
Sc	0.8	0.5	1.6	15	4.6	2.8	1.3	1.0	5	11	2.2
V	10	11	14	85	44	21	19	21	45	73	10
Sr	235	274	232	22	17	6	19	3	88	184	27
Rb	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15
Th	0.5	0.3	0.5	7	4	1.2	1.88	2	2.0	4.2	1.4
U	3.3	2.9	2.6	2.0	1.9	2.5	0.89	<0.5	6	4.2	0.7
Y	2.0	2.0	2.0	16	12	4.0	4.0	2.1	9	17	1.0
Zr	9	7	14	264	50	33	40	34	58	113	52

Major elements were analysed by fusion-ICP with detection limits of 0.01%, except for TiO2 and MnO which had detection limits of 0.001%. Trace elements were analysed by a combination of INAA and ICP methods and had detection limits of 1ppm for Zn, Cu, Ba, Co, Mn, Sr, W, and Y; 3 ppm for Pb, 00.3 ppm for Ag and Cd, 0.01 ppm for Sb and Sc, 2 ppm for Cr and V, 0.5 ppm for As and U, 15 ppm for Rb, and 0.2 ppm for Th.

skarn as the latter was the earliest skarn silicate to form. However, as andraditic garnet clearly replaced grossularitic garnet and hedenbergitic pyroxene replaced andraditic garnet, grossularitic garnet skarn and andraditic garnet skarn were assumed to be the precursors for andraditic garnet skarn and hedenbergitic pyroxene skarn, respectively. This approach contrasts with that adopted in most studies, which have attributed differences in skarn mineralogy to differences in protolith composition, and accordingly evaluated chemical changes during skarn formation using one or more independent protoliths rather than a single evolving protolith as the precursor or precursors. For example, Kwak (1978) noted that the precursors to skarn at the King Island scheelite deposit were hornfels and marble, while Lentz et al. (1995) assumed that the protolith at the Millstream Cu-Fe skarn deposit consisted of a mixture of 60% metasedimentary rocks and 40% limestone.

In addition to the problem of precursor selection, assumptions about possible volume change and very high fluid:rock ratios can be problematic in evaluating mass changes in skarn forming systems (Lentz, 2000). Based on the consistency of bedding thickness from limestone to skarn at both hand sample and outcrop scales (Figure 2-11) any volume change during formation of the El Mochito skarns was small. Lindgren (1924) and Kwak (1978) came to the same conclusion for the Bingham and King Island skarns based on similar bedding features. The constant volume assumption, which is adopted in the present study, removes the need to perform calculations based on the immobility of a specific element.

Isocon diagrams based on this assumption indicate that all elements analysed, including those normally considered immobile, underwent considerable mass change. Zinc and lead were not included as the ore minerals occur interstitially and precipitated after skarn formation, hence it was assumed that all major elemental variations occurred prior to ore formation. During formation of grossularitic garnet skarn, there were significant increases in Si, Al, and Fe and losses of Ca, Ba, and K, (Table 2-4, Figure 2-12A). The relatively small loss of CaO (-9%) indicates that this element may have been conserved during alteration to grossularitic garnet skarn, and the proximity of CaO to the constant volume isocon confirms this observation. Formation of andraditic garnet skarn was accompanied mainly by an appreciable addition of Fe, a small addition Si and a

Figure 2-11. Photographs demonstrating the continuity of bedding features in outcrop, hand-specimen and core from El Mochito. A) Continuity of primary bedding textures across a sharp contact between garnet skarn and limestone. B) Epidote skarn that has replaced beds in limestone and still shows evidence of primary bedding features. C) Primary textures of limestone mimicked by skarn.



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	Garnet (G	r _{>50}) skarn	Garnet (Ad	l _{>50}) skarn	Pyroxene (Hd _{>55}) skarn		
SiO ₂	48	2034	2	5	21	61	
Al_2O_3	10	1663	-5	-62	-2	-88	
TiO ₂	1	4154	-0.3	-75	-0.01	-12	
Fe ₂ O ₃	30	9875	10	51	-15	-55	
MnO	2	18140	0	23	3	217	
MgO	-0.1	-7	-0.01	-1.3	1	233	
CaO	-5	-9	0	1	-17	-52	
Na ₂ O	-0.01	-47	0	113	0	40	
K ₂ O	-0.1	-65	-0.01	-14	0	16	
LOI	-38	-92	-0.1	-6	2	101	
Ba	-33	-88	0	3	3	94	
V	54	512	-23	-52	5	26	
Sr	-227	-90	-4	-22	-11	-89	
Y	16	776	-8	-65	44	1117	
Zr	62	549	-11	-23	-36	-99	

Table 2-4. Absolute and relative mass changes (%) for grossularitic garnet ($Gr_{>50}$), and raditic garnet ($Ad_{>50}$) and pyroxene skarns compared to their respective precursors (limestone, grossularitic garnet skarn and andraditic garnet skarn, respectively).

Figure 2-12. Isocon diagrams comparing the composition of grossularitic garnet, andraditic garnet and pyroxene skarns relative to that of their precursors. The solid line shows the constant volume isocon and the dotted line the constant Zr isocon. The limestone composition is an average of 4 samples (Unalt 1,2,3,6), the grossularitic garnet skarn composition is from 1 sample (SV2550-21), the andraditic garnet skarn composition is the average of 2 samples (SV2550-18, NAC2290-10) and the pyroxene composition is from 2 samples (SV2550-27, NAC2450-6).





modest loss of Al (Table 2-4, Fig. 2-12B). Calcium plots very close to the constant volume line and shows a small increase (1%), showing that it was essentially conserved during alteration of grossularitic skarn to andraditic garnet skarn. Substantial gains in Si, Mg, Mn and losses of Ca, Fe, and a modest loss of Al characterize alteration of andraditic garnet skarn to hedenbergitic pyroxene skarn (Table 2-4, Fig 2-12C). The loss of Ca is in sharp contrast to the behaviour of this element during other skarn stages where it appears to have been conserved.

The results of the bulk chemical study indicate that the formation of garnet and pyroxene skarns corresponded mainly to changes in the quantities of Fe, Al, Si, Mg, Mn, and Ca. The variations in the major elements are reflected by the mineralogy, whereas changes in LOI are due either to decarbonation reactions or commencement of retrograde alteration and/or formation of hydrous phases.

DISCUSSION

Evolution of the Skarn-Forming Fluid

The application of aqueous activity diagrams has proven to be especially useful in explaining mineral zoning in hydrothermal systems, particularly in skarns (Bowman, 1998; Vander Auwera and Verkaeren, 1993; Johnson and Norton, 1985; Bird et al., 1984; Einaudi, 1977; Korzhinskii, 1959). The evolution of the El Mochito skarn forming system was evaluated in terms of the activities of Fe³⁺, Al³⁺, SiO_{2(aq)}, Mg²⁺, Ca²⁺, and H⁺, components that experienced appreciable mobility. The calculations were performed for temperatures of 400 and 500°C, the minimum and maximum temperatures of trapping of fluid by grossularitic garnet, andraditic garnet, and hedenbergitic pyroxene, assuming a pressure of 1 kb (Vázquez et al., 1998; Ault and Williams-Jones, unpublished data). The pressure was estimated from stratigraphic reconstruction of the sedimentary cover during the late Tertiary (from 1.5-3 km; Dilles, 1982; Williams and McBirney, 1969; Mills et al., 1967). No evidence of boiling was detected during fluid inclusion microthermometry and, as a result, the pressure regime is considered to have been lithostatic. The X_{CO2} and log f_{O2} conditions of the skarn-forming fluid were estimated from the stabilities of the

main skarn silicates. Mineral activities were calculated for garnet, pyroxene and wollastonite using the computer program AX (Holland and Powell, 1998), assuming nonideal solid solution mixing models for garnet and pyroxene, and ideal mixing between wollastonite and bustamite. The bustamite activity was calculated based on compositional data obtained by Dilles (1982) and the garnet and pyroxene activities from the compositional data obtained during this study. The log K's for all reactions (Table 2-5) were calculated using the software package Hch (Shvarov and Bastrakov, 1999), incorporating the updated SUPCRT92 database (Shock, 1998; Johnson et al., 1992). From the stability of bustamite and the assumed temperatures and pressure of skarn formation, the X_{CO_2} is estimated to have been ~0.008±0.007 (Figure 2-13A). The value of log f_{O_2} ranged from -22 to -25 based on the stability of andraditic garnet and hedenbergitic pyroxene (Fig. 2-13B).

The activities of Fe^{3+} , Al^{3+} , $SiO_{2(aq)}$, Mg^{2+} , and Ca^{2+} were estimated from phase relations in the system Ca-Si-Mg-Fe-Al-H2O-CO2-O2, and the effect of their variations on mineral stabilities is shown on Figure 2-14. The earliest stage of alteration, characterized by the formation of grossularitic garnet (labeled either as Gr55 or Ad41), occurred at high values of $\log(a_{Ca2+}/a_{H+2})$, $\log(a_{Al3+}/a_{H+3})$, moderate $\log(a_{Fe3+}/a_{H+3})$, and variable but relatively high loga_{SiO₂(aq)}. The next alteration stage, featuring and raditic garnet (labeled either as Ad₇₂ or Gr₂₅), occurred at lower $log(a_{Ca2+}/a_{H+2})$ and $log(a_{Al3+}/a_{H+3})$, higher $log(a_{Fe3+}/a_{H+3})$ and a generally lower, more restricted, range of $loga_{SiO_2(aq)}$ compared to the earlier, grossularitic garnet-rich skarn stage. Alteration to hedenbergitic pyroxene skarn appears to have occurred at lower $\log(a_{Ca2+}/a_{H+2})$, $\log(a_{AI3+}/a_{H+3})$, $\log(a_{Fe3+}/a_{H+3})$ and higher $\log_{SiO_2(aq)}$ and $\log(a_{Mg2+}/a_{H+2})$ values than during the preceding stages. With the exception of Ca²⁺/H⁺ during the first stage of skarn formation, these ratios are consistent with the mass gains and losses estimated to have occurred during the formation of grossularitic garnet, and raditic garnet and hedenbergitic pyroxene skarn. The high $\log(a_{A13+}/a_{H+3})$, $\log(a_{Fe3+}/a_{H+3})$ and relatively high $\log a_{SiO_2(aq)}$ during grossularitic garnet skarn formation are matched by substantial addition of Al, Fe, and Si to the rock; the

Table 2-5. Reactions and corresponding log K values, between 300 and 500°C, used toconstruct Figure 13.

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		log K						
	Reaction	300	350	400	450	500		
[1]	Quartz + Calcite = Wollastonite $(Wo_{44}Bu_{66}) + CO_2$	-1.8	-1.0	-0.3	0.4	1.0		
[2]	3 Andradite(Ad ₇₂) + 9CO ₂ = 3 Magnetite + 9Calcite + 9Quartz + $\frac{1}{2}O_2$	-9 .0	-13.3	-17.3	-20.9	-24.2		
[3]	3Hedenbergite(Hd ₆₄) + $3CO_2$ = Magnetite + $3Calcite + 6Quartz + \frac{1}{2}O_2$	21.0	16.8	13.2	9.9	7.0		
[4]	6Andradite(Ad ₇₂) + 9CO ₂ = 9Hedenbergite(Hd ₆₄) + Magnetite + 9Calcite + 2.5O ₂	-80.9	-77.2	-7 4.2	-71.7	-69.4		
[5]	And radite(Ad ₇₂) + Quartz + CO ₂ = 2Hedenbergite(Hd ₆₄) + Calcite + $\frac{1}{2}O_2$	-17.0	-15.7	-14.5	-13.6	-12.7		
[6]	Andradite(Ad ₇₂) + Magnetite + Quartz + CO_2 = 2Hedenbergite(Hd ₆₄) + $2O_2$	71.9	63.9	56.9	50.8	45.2		
[7]	2Magnetite + $\frac{1}{2}O_2$ = 3Hematite	-16.8	-14.9	-13.1	-11.6	-10.2		

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Figure 2-13. A) T-log X_{CO_2} diagram showing the conditions of bustamite stability. The range of X_{CO_2} is 0.001 to 0.014 for the temperatures at which the El Mochito skarns are interpreted to have formed (400-500°C). The bustamite activity ($a_{Bu} = 0.66$, assuming ideal mixing) is based on electron microprobe analyses of bustamite by Dilles (1982). The SUPCRT database does not contain bustamite data; therefore stability conditions were calculated from data for wollastonite. B) T-log f_{O_2} diagram showing mineral stability relationships in the system Fe-Si-Al-O-S. Andradite and hedenbergite with compositions of those at El Mochito (Ad₅₀₋₈₃, Hd₅₃₋₇₉) are stable at temperatures between 400 and 500°C, and log f_{O_2} ranges from -22 to -25.





Temperature (°C)

Figure 2-14. Activity diagrams showing the stability fields of skarn silicates at 400 and 500°C for the CaO-MgO-Fe₂O₃-Al₂O₃-SiO₂-H₂O-CO₂ system. Grossular, andradite and diopside stability fields were calculated for garnet and pyroxene compositions corresponding to those of average grossularitic garnet (Gr₅₅Ad₄₁Sp₄), and raditic garnet (Ad₇₂Gr₂₅Sp₃) and hedenbergitic pyroxene (Hd₆₄Di₂₀Jo₁₆). The dotted line indicates calcite saturation, and the dashed line on E and F magnetite saturation, and on G and H, quartz saturation. Gr-grossular, Ad-andradite, Hd-hedenbergite, Di-diopside, Wowollastonite, Qtz-quartz, Cc-calcite, Tlc-talc, Fo-forsterite, Mtc-monticellite, Tremtremolite, Ghl-gehlenite, Marg-margarite, Act-actinolite, Fay-fayalite, Anthanthophyllite, Larn-larnite. Arrows indicate the progression from andradite stability to hedenbergite stability.



lower $log(a_{Al3^+}/a_{H^+}^3)$ and higher $log(a_{Fe3^+}/a_{H^+}^3)$ during formation of andraditic garnet skarn are matched by a strong depletion in Al and enrichment in Fe; and the lower $log(a_{Ca2^+}/a_{H^+}^2)$, $log(a_{Al3^+}/a_{H^+}^3)$ and $log(a_{Fe3^+}/a_{H^+}^3)$ during hedenbergite skarn formation are matched by the large corresponding depletions in Ca, Al, and Fe, and correspondingly additions of SiO₂ and Mg. The high activity of Ca²⁺/H⁺ associated with formation of the early grossularitic garnet skarn is a reflection of the neutralization of the hydrothermal fluid by reaction with the limestone. This would have rapidly consumed H⁺ thereby giving the impression of higher Ca²⁺, whereas the mass bulk chemical data indicate that Ca may have been conserved or even slightly depleted.

Skarn formation appears to have been an essentially isovolumetric process and most elements underwent notable gains during this process. The possibility exists that some components were derived from the intercalated limey siliciclastic units, either through diffusion or homogenization of the protolith through metasomatism (Lentz, 1995). However, as these units comprise a minor proportion of the limestone package (<10%), their contributions would have been small relative to the mass of elements added during skarn formation. Whereas elements such as Si and the ore metals are invariably enriched strongly during skarn formation (Barton et al., 1991), Ca is generally lost despite formation of calc-silicate minerals (Einaudi and Burt, 1982). However, there are examples in which Ca content was unaffected or even increased (Lentz et al., 1995; Vander Auwera and Verkaeren, 1995; Kwak, 1978). Variations in elements like Ti and Zr, which are immobile, suggests that skarn formation involved high fluid:rock ratios.

Implications of Metal Zonation

The distribution of metals in the Salva Vida and Nacional orebodies is strikingly similar, suggesting that the processes controlling ore mineral deposition were the same in both orebodies. A similar zonation was also observed previously in the San Juan orebody (Dilles, 1982). The fault control of orebody location at El Mochito is obvious and the coincidence of Zn, Pb, Ag and Fe anomalies with fault zones reinforces this observation. From the solubility of Zn, Pb, and Ag, it can be demonstrated that cooling, an increase in pH, or a decrease in log f_{O_2} would favour the sequential precipitation of sphalerite, followed by galena and finally acanthite (Figure 2-15). If the fluid underwent

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Figure 2-15. A) T-pH diagram showing the solubility of sphalerite, galena and acanthite. The sequence in which these minerals saturate with decreasing temperature and increasing pH duplicates the corresponding metal zonation from the centre to the margins of the Salva Vida and Nacional orebodies. Log f_{O_2} -pH diagrams at 400°C (B) and 500°C (C) showing the stability of minerals in the Fe-S-O system, sulphur species predominance fields, and contours of sphalerite, galena and acanthite stability. The metal zonation and mineral solubility is pH controlled in the low f_{O_2} region and f_{O_2} controlled in the more oxidized region. Precipitation of the sulphides results from destabilization of the metalchloride complexes $ZnCl_2^{\circ}$, PbCl₃, and $AgCl_2^{\circ}$ (Akinfiev and Zotov, 2001; Ruaya and Seward, 1986; Seward, 1984). Concentration of metals was 1000 ppm for Zn and Pb and 1 ppm for Ag, and $\Sigma S=0.1m$. Metal zonation cannot be explained by variations in f_{S_2} ; decreasing the f_{S_2} shifts the ore mineral boundaries to higher pH and lower f_{O_2} , whereas increasing the f_{S_2} has the opposite effect.



progressive neutralization as it reacted with the host limestone, the resulting zonation from Zn to Pb and finally Ag, would be as observed at El Mochito. However, as all orebodies were altered to skarn prior to ore formation, there would have been little original carbonate available to neutralize the fluid, therefore another mechanism must have produced the observed zonation. Although a decrease in log f_{O_2} could also cause the metal zonation, this would require that the fluid was fairly oxidized initially, i.e. located in either the HSO₄ or SO₄²⁻ predominance fields, which is considered unlikely given the elevated temperatures and reduced log f_{O_2} interpreted from mineral stabilities. We therefore conclude that the metal zonation of the Salva Vida and Nacional orebodies resulted from cooling of the ore fluid as it infiltrated the skarns. This zonation is similar to that of other skarn deposits (e.g. Darwin, Newberry et al., 1991; Groundhog, Meinert, 1987; Yeonhwa-Ulchin District, Yun and Einaudi, 1982) where it has also been interpreted to reflect decreased temperature during the upward and outward movement of hydrothermal fluids.

Compositional Variation of Skarn and Ore Minerals

The change in the garnet composition, from early grossularitic to later and raditic is common to many skarn systems, and is considered to represent a progression from a rock-dominated to a fluid-dominated setting and concomitant evolution of fluids to higher Fe concentrations (Jamtveit et al., 1995; 1993). The wide range in the Fe content of the sphalerite (3 to 26 mol% FeS) can be the result of several factors including variations in temperature and pressure, f_{O_2} , and f_{S_2} and a_{Fe} (Vaughan and Craig, 1997).

However, as Fe-poor sphalerite is most often seen with pyrite or magnetite and Fe-rich sphalerite with pyrrhotite or magnetite, the change in Fe content of sphalerite is thought to result primarily from variations in log f_{O_2} due to the different buffering effects of the associated iron sulphide and oxide minerals. Thus the higher f_{O_2} conditions implied by pyrite and magnetite stability promoted formation of low Fe sphalerite and the lower f_{O_2} conditions of pyrrhotite stability the formation of high Fe sphalerite. Alternatively, the oxidation state of Fe in the minerals associated with sphalerite could also influence which variety of sphalerite precipitated. Low-Fe sphalerite is also often seen in association with

garnet, which contains Fe^{3+} whereas medium and high-Fe sphalerite are more often seen with pyroxene, which contains Fe^{2+} . Since the Fe incorporated into the sphalerite structure would be as Fe^{2+} , those varieties with excess Fe may have been influenced by the oxidation state of Fe in the associated Fe-bearing phases. Formation of low Fe sphalerite would also have been influenced by the high f_{S_2} implied by pyrite stability, and formation of high Fe sphalerite by the low f_{S_2} implied by pyrrhotite stability. Fluid inclusion microthermometry of sphalerite shows that low Fe sphalerite has a lower homogenization temperature than the higher Fe varieties (Ault and Williams-Jones, unpublished data), which is consistent with phase equilibria that favor a reduction of the FeS content of sphalerite with decreasing temperature (Vaughan and Craig, 1997). Ag and Bi are positively correlated in galena reaching concentrations up to 14500 and 18200 ppm, respectively. These are common trace elements in galena and their concentrations can be related to temperature, with higher formation temperatures favouring increased proportions of Bi and Ag (Foord and Shaw, 1998; Van Hook, 1950).

CONCLUSIONS

Hydrothermal alteration of relatively pure limestone at El Mochito produced skarns dominated by grossular-andradite series garnet and hedenbergite-diopside series pyroxene, which were replaced by ore minerals. Skarn alteration appears to have proceeded in a series of steps in which limestone was transformed successively into grossularitic garnet skarn, andraditic garnet skarn, and pyroxene skarn. The mass losses and gains determined from the bulk rock chemistry and mineral stabilities in terms of component activities are in general agreement and appear to document an early neutralization of the hydrothermal fluid related to increased interaction with the host carbonate and increasing fluid:rock ratios in the skarn and ore-forming system at El Mochito.

Zinc-lead-silver mineralization post-dated skarn formation and is zoned from Zn to Pb and the Ag, reflecting the sequential saturation of sphalerite and galena in the fluid with decreasing temperature. Sphalerite shows a wide range in Fe content from Fe-rich

in contact with pyrrhotite to Fe-poor in contact with pyrite and magnetite, due either to the f_{O_2} buffering effects of the associated iron sulphide and oxide phases or oxidation state of Fe in the associated Fe-bearing phases. A model is proposed in which hydrothermal fluids, utilizing faults as fluid conduits, reacted with carbonates of the Átima and Cantarannas formations, to form skarns dominated by grossular-andradite series garnets and hedenbergitic pyroxene and eventually precipitate sphalerite and galena as the fluid cooled during outward and upward migration from the fault zones.

ACKNOWLEDGMENTS

Financial support was provided by SEG and GSA grants to K.M.A., NSERC and FCAR grants to A.E.W-J., and by Breakwater Resources Ltd. The authors wish to thank the staff at El Mochito mine for providing logistical support for this project. Thanks also to J. Clark and G. Poirier for assisting with electron microprobe analyses and D. Dolejs for helping with mass-balance calculations. This manuscript benefited from a review by J. Clark.

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INTRODUCTION TO CHAPTER III

The previous chapter outlined the gross chemical changes associated with each skarn zone and showed that alteration at the El Mochito deposit occurred at apparently high water:rock ratios which introduced significant quantities of Si, Fe, Mn, Al, Mg and the ore metals. Compositional variation of the main gangue minerals, andraditic garnet and hedenbergitic pyroxene, appears to document neutralization of the hydrothermal fluid as well as remobilization of mineral components with increased interaction with the host carbonate. The following chapter "Sulphur and Lead Isotope Study of the El Mochito Zn-Pb-Ag deposit" applies the isotope compositions of the sulphides, local igneous rocks, and host carbonate to the problem of fluid source.

The source of fluid and metals for the El Mochito deposit was previously not known, however, convincing isotopic evidence demonstrates that the hydrothermal fluids were predominantly magmatic in origin and related to the magma that formed the Miocene Padre Miguel ignimbrite. An apparent decrease in sulphur isotope compositions and increasing Pb compositions along the Salva Vida-Nacional trend appears to define the direction of fluid flow and further supports the association of the Padre Miguel ignimbrite magmas with the hydrothermal fluids that formed the deposit. **CHAPTER III**

SULPHUR AND LEAD ISOTOPE STUDY OF THE EL MOCHITO ZN-PB-AG DEPOSIT

K.M. Ault and A.E. Williams-Jones

ABSTRACT

The El Mochito mine, located in west-central Honduras, exploits a Zn-Pb-Ag skarnhosted deposit. Sulphide minerals comprising sphalerite, galena, pyrrhotite, and pyrite postdate a gangue consisting mainly of pyroxene in the hedenbergite-diopside series and garnet in the andradite-grossular series. A strong structural control is apparent, with most mineralization located along or near fault zones. No igneous body, which could have contributed to the formation of the skarn, appears spatially associated with the El Mochito deposit, and a source of fluid and metals has not been identified previously.

 δ^{34} S values of sphalerite, galena and pyrrhotite cluster between -1 and +2 per mil, suggesting that the sulphur at El Mochito was primarily igneous in origin. Lead isotope ratios for galena have mean values of 18.766, 15.616, and 38.572 for ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb, respectively, and are similar to Pb isotope ratios for the Miocene-Pliocene Padre Miguel ignimbrite. A progressive decrease in the δ^{34} S values of sphalerite and a corresponding increase in the whole-rock Pb isotope ratios of the host limestone are correlated to decreasing alteration from northeast to southwest along the trend of the Salva Vida and Nacional orebodies. These observations are interpreted to indicate that the fluid, sulphur, and lead source was located to the northeast of the deposit and that magma genetically related to the Padre Miguel ignimbrite produced the hydrothermal system, which formed the deposit.

INTRODUCTION

Zinc skarns are typically distal in location with respect to their assumed igneous source, and commonly a relationship to an igneous body is not evident (Einaudi et al., 1981). Frequently, the location and nature of the fluid source can be deduced from the spatial distribution of garnet:pyroxene ratios, ore metal ratios, and the Fe and Mn content of sphalerite (Yun and Einaudi, 1982; Meinert, 1987; Megaw et al., 1988; Pearson et al., 1988; Newberry et al., 1991; Vázquez et al., 1998). At El Mochito, however, except for the Cu/(Zn+Pb) ratio, which generally decreases toward the southwest (K.M. Ault and A.E. Williams-Jones, unpublished data), evidence of such zoning is lacking, and the above ratios

cannot be used to make inferences about location of the heat source, the fluid source and the direction of fluid flow. On the other hand, sulphur and lead isotope ratios vary spatially with respect to mineralization, suggesting that they may not only indicate the nature of the ore-forming fluid but also provide vectors to the source of hydrothermal activity.

The sulphur and lead isotopic compositions of ore mineral separates and the various rock types occurring in the El Mochito district were evaluated and the data used to infer that the fluids and metals originated in a magmatic system several kilometers to the northeast of the deposit. This preliminary study indicates that sulphur and lead isotope analyses could provide a valuable tool in the exploration for distal Zn-Pb-Ag skarn deposits, particularly in those cases where other zoning is not evident.

GEOLOGY AND STRATIGRAPHY

El Mochito, the largest operating mine in Central America, is located in the Central Cordillera of Honduras and exploits a Zn skarn containing 13 Mt of ore grading 7% Zn, 2% Pb and 80g/t Ag (Vázquez et al., 1998; Thalenhorst, 1994,). Geologically, the region forms part of the Chortis block, a major province of the Caribbean plate, which in Honduras is cut by a series of mid-Tertiary en echelon NE- to NW-trending faults and grabens known collectively as the Honduras Depression (Mills et al., 1967; Williams and McBirney, 1969; Malfait and Dinkelman, 1972; Mann and Burke, 1984; Aldrich et al., 1991). El Mochito lies in one of the smaller of these structures, the Mochito Graben (Figure 3-1).

The stratigraphic sequence at El Mochito comprises quartz sandstones and conglomerates of the Jurassic (?) Todos Santos Formation, limestones and shales of the early Cretaceous Yojoa Group, and late Cretaceous redbeds of the Valle de Angeles Group (Figure 3-2). The Yojoa Group, which hosts the deposit, consists of a basal unit of interbedded, noncalcareous shale and shaly/argillaceous limestone (the 34 m-thick Cantarannas Formation), and an overlying unit of limestone (the 1250 m-thick Átima Formation). The bulk of the ore is in the Átima Formation, which is subdivided by the 115 m-thick Mochito Shale into upper and lower limestone units. Igneous rocks proximal to the deposit are

Figure 3-1. Location, tectonic setting and geology of the El Mochito deposit. PMSZ-Polochic-Motagua suture zone (modified from Williams and McBirney, 1969). Numbers denote sample localities for (1) limestone from Santa Bárbara Mountain, (2) unaltered Átima limestone, (3 and 4) Padre Miguel ignimbrite, (5) Yojoa basalt, and (6) Matagalpa Formation tuff.

Figure 3-2. Stratigraphy at the El Mochito deposit, showing the location of chimney and manto orebodies hosted in the Átima limestone. (Modified after Mills et al., 1967).

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restricted to diabase dikes exposed solely in the mine. The dikes, which range in age from 9.4 \pm 0.4 to 16.5 \pm 0.7 Ma (K-Ar whole rock ages; Dilles, 1982), are invariably altered, and intensely so where in contact with skarn mineralization (Smith, 1975) but are not mineralized. The altered nature of the dikes indicates that they were emplaced prior to or during mineralization. The closest surface exposures of igneous rocks occur at Lago de Yojoa, 13 km to the northeast (Fig. 3-1). These comprise andesitic to basaltic lavas and pyroclastic flows of the Eocene to Oligocene Matagalpa Formation (37.4 \pm 0.3 Ma ⁴⁰Ar/³⁹Ar age of hydrothermal biotite in andesite: Bargar, 1991), rhyolitic ignimbrites of the Miocene to Pliocene Padre Miguel Group (18.9 \pm 0.2 to 15.0 \pm 0.2 Ma whole-rock K/Ar ages: Williams and McBirney, 1969), and basalts of the Quaternary Yojoa Eruptive Complex (0.196 \pm 0.052 to 5.2 \pm 0.2 Ma whole-rock K/Ar age: Eppler et al., 1987). All volcanism at Lago de Yojoa appears to be related to the development of the Honduras Depression (Williams and McBirney, 1969; Malfait and Dinkelman, 1972; Wadge and Wooden, 1982; Aldrich et al., 1987).

Three main fault sets occur in the mine (Figure 3-3). The oldest faults trend eastnortheast, dip steeply to the north, and are locally cut by diabase dikes (Araya et al., 1977; Dilles, 1982). Ore chimneys beneath the Mochito shale appear to be rooted along these faults, which are thought to be rejuvenated basement structures related to movement along the Polochic-Motagua suture zone connecting the North American and Caribbean plates (Vázquez et al., 1998). A second fault set, including the Main and Porvenir faults, was important in localizing mineralizing fluids for the Yojoa, El Pie and San Juan ore bodies (Dilles, 1982). This second fault set trends 20 to 40° NE, dips steeply to the NW, and is considered to be a vestige of Laramide tectonism. The youngest set of faults, which controlled most of the mineralization investigated (the Salva Vida-Nacional and Port Royal orebodies) comprises steeply dipping N-NE-trending faults that are related to the formation of the Mochito graben (Araya et al., 1977).

The age of the El Mochito deposit is constrained by the pre/syn-ore dikes discussed above to be less than 16.5 Ma in age and likely formed during late Miocene to early Pliocene faulting which accompanied formation of the Mochito graben (Malfait and Dinkelman, 1972). This age clearly excludes a magma cogenetic with the Matagalpa Formation as a possible source of fluids for the deposit, whereas the magmas forming the Padre Miguel

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Figure 3-3. Plan view of the El Mochito deposit (2500 level) illustrating the association of most orebodies (shaded) with fault zones (solid lines). SVN-Salva Vida-Nacional; SJ-San Juan; PR-Port Royal; NPO-Nispero; MN-Main; POR-Porvenir.

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Group, Yojoa Eruptive Complex, and diabase dikes are possible candidates, based on their younger ages. Given that the source of the basaltic magma likely contained little water, the magmas producing the diabase dikes and Yojoa basalts are unlikely sources for the El Mochito fluids (Holloway and Blank, 1994). This leaves the rhyolitic to trachy-dacitic Padre Miguel ignimbrite (Table 3-1), which is compositionally similar to igneous rocks typically associated with Zn skarns (Meinert, 1995). Thus, if skarn and ore mineralization were produced by hydrothermal fluids of magmatic origin, the only plausible source for these fluids was the magma responsible for Padre Miguel volcanism.

MINERALIZATION AND PARAGENESIS

The mineralogy of the El Mochito deposit is typical of Zn skarns (Einaudi et al., 1981) and comprises a silicate gangue of pyroxene and garnet, and a later ore mineral assemblage of sphalerite, galena, pyrite, pyrrhotite, chalcopyrite, magnetite and trace arsenopyrite (Figure 3-4). There are two generations of garnet (Fig. 3-4A), an early grossularitic ($Gr_{55}Ad_{41}Sp_4$) variety and a later variety that is more andraditic ($Ad_{72}Gr_{25}Sp_3$) in composition (Dilles, 1982; Vázquez et al., 1998; Ault and Williams-Jones, submitted). Both generations of garnet are replaced by hedenbergitic ($Hd_{64}Di_{20}Jo_{16}$) pyroxene (Fig. 3-4B) and finally epidote. Examination of the skarn minerals on multiple levels of the mine indicates that there is no obvious variation in their spatial distribution within the deposit. Calcite and subordinate quartz are interstitial to the two dominant silicate minerals. Other gangue silicates, all of which occur in minor amounts, include bustamite, biotite, and K-feldspar.

Sphalerite, galena, and magnetite are the main ore minerals, followed in order of abundance by chalcopyrite, pyrrhotite, pyrite, and trace arsenopyrite. These minerals occupy interstices between silicates of the skarn assemblage or occur in veins, and are commonly accompanied by calcite and/or quartz. Magnetite was the earliest of the ore minerals to form and commonly mantles skarn silicates or has replaced these minerals (Fig. 3-4C). Pyrite was the earliest sulphide to form followed by pyrrhotite, then sphalerite. Sphalerite contains from 3 to 26 mol% FeS (Ault and Williams-Jones, submitted); both sphalerite and pyrrhotite replace magnetite, and sphalerite also replaces pyrrhotite (Fig. 3-4C,F). Chalcopyrite and

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	Basalt	Basalt Ignimbrite ¹		Mochito Dike		
	Yojoa Gp.	KA-IGN-1	KA-IGN-2	5528-540	3676-450	
wt%						
SiO ₂	45.89	67.57	76.73	48.50	46.91	
Al ₂ O ₃	17.78	12.82	12.40	18.31	17.99	
TiO ₂	2.66	0.18	0.18	1.24	1.47	
Fe ₂ O ₂	11.92	2.13	0.99	10.97	8.29	
MnO	0.18	0.06	0.01	0.17	0.28	
ΜσΟ	4 43	0 39	0.08	5.23	7.47	
C•O	7 17	2.89	0.25	7.48	9.95	
Na-O	3.64	2.89	1 38	2.66	2.02	
K O	1 49	4.52	4.01	1 14	1.56	
R ₂ O	0.56	4.52	4.01	0.27	0.29	
P ₂ O ₅	0.56	0.04	0.05	0.27	0.23	
LOI	4.11	6.29	3.64	3.53	3.51	
Total	99.84	99.79	99.73	99.49	99.75	
ppm		1.0		~~	1.50	
Zn	102	163	>> 22	11	158	
PD	4	23	33	4	24	
Cu A a	25	4	2 ~5	16	11	
Ag Sh	1	190	1	<5 1	1 22	
50 Do	1 250	4	1	244	22 452	
	250	130	550 6	7	111	
rs Cd	2 <05	<05	<05	′ <0.5	<0.5	
Ce	53	90	51	24	27	
Co	37	13	10	28	42	
Cr	39	13	-* <5	16	189	
Ni	21	3	2	1	90	
Sc	26	5	5	25	30	
v	280	13	14	215	186	
Sr	442	101	48	671	562	
Rb	<15	128	114	32	99	
Th	3	13	10	1	1	
U	1	3	3	<0.5	<0.5	
Y	22	49	17	16	18	
Zr	251	337	187	109	156	

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Table 3-1. Bulk rock composition of local igneous rocks. Locations of dike samples shown in Appendix 1.

Major elements were analyzed by fusion-ICP with detection limits of 0.01%, except for TiO₂ and MnO which had detection limits of 0.001%. Trace elements were analyzed by a combination of INAA and ICP methods and had detection limits of 1ppm for Zn, Cu, Ba, Co, Mn, Sr, W, and Y; 3 ppm for Pb, 00.3 ppm for Ag and Cd, 0.01 ppm for Sb and Sc, 2 ppm for Cr and V, 0.5 ppm for As and U, 15 ppm for Rb, and 0.2 ppm for Th.

¹The composition of the Padre Miguel ignimbrite is the closest match to igneous rocks typically associated with Zn skarns.

Figure 3-4. Photomicrographs of mineral textures showing paragenetic relationships among the silicate, sulphide, and oxide phases. Figures A and C were taken under polarized light, B and D under transmitted light and E-H under reflected light. The scale bar is 0.1mm. Gr-grossularitic garnet, Ad-andraditic garnet, Px-pyroxene, Epi-epidote, Sp-sphalerite, Gngalena, Cc-calcite, Mt-magnetite, Po-pyrrhotite, Py-pyrite, Chl-chlorite. A) Early grossularitic garnet partly replaced by later, zoned andraditic garnet. The fine-grained alteration phases comprise a mixture of chlorite and calcite. B) Pyroxene after andraditic garnet; a lath of pyroxene can be seen breaking apart an earlier formed garnet crystal. C) Pervasive epidote alteration after pyroxene; sphalerite occurs as an interstitial phase. D) Early epidote mantled by magnetite followed by sphalerite; sphalerite occurs along fractures in pyrrhotite and contains blebs of pyrrhotite; the magnetite also mantles epidote. Both magnetite and pyrrhotite were followed by sphalerite and later chalcopyrite.



galena precipitated penecontemporaneously, as shown by composite grains aligned along healed fractures in sphalerite (Fig. 3-4E). Both chalcopyrite and galena also form separate inclusions in sphalerite (Fig. 3-4C,F,D), and chalcopyrite commonly replaces pyrrhotite (Fig. 3-4F). Pyrite was also the final sulphide to crystallize and either replaces pyrrhotite (Fig. 3-4C) or occurs as late cubes accompanying calcite. A paragenetic sequence that reflects these textures is presented in Figure 3-5.

SAMPLING AND METHODOLOGY

Twenty-four sulphide samples, comprising separates of sphalerite, galena and pyrrhotite, were analyzed for their sulphur isotopic composition. These samples were collected mainly from the Salva Vida-Nacional trend, a 600 m zone of semicontinuous mineralization containing 2.7 million tonnes of ore and representing the most extensive zone of mineralization along a single structure within the mine. Samples were hand-picked under a binocular microscope, and yielded fourteen separates of sphalerite, eight of galena and two of pyrrhotite. Analyses of the sulphur isotopic compositions were performed at Queen's University (Kingston, Ontario) using a Finnigan Mat 252 isotope ratio mass spectrometer. Sulphur isotopic compositions are expressed in standard notation relative to Cañon Diablo troilite (δ^{34} S value of 0 ‰: Shima et al., 1963) with a precision of ±0.2 per mil.

Lead isotope analyses were performed on fourteen galena separates and twenty-one whole-rock samples from the Salva Vida, Nacional, Yojoa, San Juan, Main and Nueva orebodies. The whole-rock samples were of altered and unmineralized Átima limestone (evident bleaching and veining but without noticeable skarn mineralization), altered and nonmineralized Todos Santos sandstone (no completely unaltered samples were found), diabase from the mine, and a sample of unaltered limestone from an outcrop in the mine area. Samples of Padre Miguel ignimbrite, basalt from the Yojoa Eruptive Complex, and one altered limestone sample from Santa Bárbara Mountain were also analyzed. Hand-picked galena separates were treated using standard dissolution methods, and whole-rock samples were prepared by crushing in an agate puck-mill, followed by digestion in either a mixture of HF and concentrated HNO₃ (for silicates) or 6N HCl and concentrated HNO₃ (for

Figure 3-5. Paragenetic sequence of silicate, sulphide and oxide crystallization at El Mochito.

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Early

Late

<u>Silicates</u>

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Garnet (Gr>50)	
Garnet (Ad>50)	
Pyroxene	
Epidote	

Sulphides and Oxides

Magnetite	
Pyrrhotite	•
Pyrite	• •
Sphalerite	\bullet
Galena	
Chalcopyrite	

carbonates) and separation of Pb using anion-exchange chromatography, as described by Manhès et al. (1980). Lead isotopic compositions were measured at the University of Québec, Montréal, using an IsoProbe MC-ICP-MS, and have a maximum 2σ uncertainty of ± 0.006 per ratio.

RESULTS AND DISCUSSION

Sulphur Isotopes

The sphalerite, galena and pyrrhotite mineral separates have δ^{34} S values between -3.5 and +5.6 per mil (Table 3-2 and Figure 3-6) and a mode at +0.5 per mil. Although galena, sphalerite and pyrrhotite coexist, galena is paragenetically later than the other two minerals, and sphalerite postdates pyrrhotite, indicating that these minerals were not in equilibrium during ore deposition. The sulphur isotopic data could therefore not be used to reliably estimate temperatures of sulphide formation. The sulphur isotopic composition of El Mochito sulphides falls within the range of -5 to +5 per mil reported for other Zn skarn deposits (Bowman, 1998). This range encompasses that of igneous rocks (-3 to +3‰, Ohmoto and Rye, 1979), and as many of these deposits have a known igneous association, the data have been interpreted to reflect a magmatic source for the sulphur. We suggest that the source of sulphur for the El Mochito sulphides was also magmatic.

The δ^{34} S values for sphalerite demonstrate an overall decrease from northeast to southwest along the trend of the Salva Vida, Nacional and Port Royal orebodies, the only orebodies, other than the Yojoa, for which more than one sample was analyzed (Figure 3-7). This trend is tentatively interpreted to reflect progressive interaction of the limestone with a hydrothermal fluid originating in the northeast; an increase in pH by 1 log unit could decrease δ^{34} S of the sulphides by up to 3 per mil at the conditions interpreted for formation of the deposit (c.f. Ohmoto, 1972).

Lead Isotopes

The Pb isotope compositions of galena separates and whole-rock samples are listed in Table 3-3. The ratios of ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb for the galena separates have

Table 3-2. δ^{34} S values for sulphide minerals at El Mochito. Sample locations shown in Appendix 1.

Sample	Orebody	Mineral	δ ³⁴ S ‰	Sphalerite Fe (wt%)
4526-128	Nacional	sphalerite	-2.4	2.6
2450-8	Nacional	sphalerite	-1.2	3.7
5382-898	Main-Nueva	sphalerite	1.3	1.5
6673-419	Porvenir	sphalerite	3.0	3.6
6622-1067	Santo Nino	sphalerite	-0.4	5.9
6001-425	Port Royal	sphalerite	1.6	5.6
5615-89	Yojoa	sphalerite	-1.8	5.9
2550-19	Salva Vida	sphalerite	0.4	3.7
2450-6	Nacional	sphalerite	-3.2	9.2
4512-27	Nacional	sphalerite	0.2	7.9
5197-92	Salva Vida	sphalerite	3.9	6.6
4360-102	Nacional	sphalerite	0.5	4.8
3795-135	San Juan	sphalerite	3.1	10.2
1868-105	Yojoa	sphalerite	5.6	10.7
Avg. Sphalerite		+0.8		
2450-3	Nacional	galena	2.0	
5197-92	Salva Vida	galena	0.3	
2650-D	Salva Vida	galena	0.5	
4526-128	Nacional	galena	1.1	
2550-19	Salva Vida	galena	0.3	
4360-102	Nacional	galena	-0.6	
5382-898	Main-Nueva	galena	0.8	
5615-89	Yojoa	galena	-0.6	
Avg. Galena	-	-	+0.5	
4557-26	Nacional	pyrrhotite	-2.5	
5203-138	Salva Vida	pyrrhotite	-3.5	
Avg. Pyrrhotite		-3.0		
Avg. sulphides			+0.4	

Figure 3-6. Histogram of sulphide δ^{34} S values. The samples cluster between -1 and +2% and have a mode occurring at +0.5%.





Figure 3-7. (A) Sphalerite δ^{34} S values at El Mochito and (B) an enlargement of the area in (A) showing the Salva Vida-Nacional trend. The decrease in δ^{34} S values of sphalerite from NE to SW is interpreted to indicate a trend of decreasing fluid:rock ratio and the direction of fluid flow. Orebodies are shaded and faults are shown as solid lines. Different symbols mark samples from different orebodies or structural trends. • Salva Vida, Nacional and Port Royal, • San Juan \blacktriangle Yojoa, •Porvenir, + Santo Niño, *Main Nueva.




Sample	Description	Orebody/Location ¹	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
5230-172	galena	Salva Vida	18.755	15.608	38.549
5215-243	galena	Salva Vida	18.770	15.616	38.577
5224-158	galena	Salva Vida	18.754	15.599	38.493
2650-8	galena	Salva Vida	18.761	15.608	38.544
5197-12	galena	Salva Vida	18.765	15.618	38.583
2450-3	galena	Nacional	18.766	15.619	38.570
4526-128	galena	Nacional	18.759	15.614	38.567
2290-7	galena	Nacional	18.769	15.622	38.598
4500-47	galena	Nacional	18.762	15.608	38.543
4365-799	galena	Nacional	18.770	15.618	38.582
2350-12	galena	Nacional	18.757	15.611	38.567
5615-75	galena	Yojoa	18.773	15.624	38.595
6643-1662	galena	Nueva East	18.789	15.634	38.628
5382-901	galena	Main-Nueva	18.775	15.625	38.612
Avg.			18.766	15.616	38.572
Yojoa Group	basalt	Lago de Yojoa (4)	18.639	15.592	38.334
Padre Miguel-1	ignimbrite	Lago de Yojoa (23)	18.715	15.597	38.483
Padre Miguel-2	ignimbrite	Lago de Yojoa (33)	18.806	15.612	38.580
C	0	••••	18.761	15.605	38.532
6461-596	dike	Port Royal	18.681	15.623	38.468
3676-450	dike	Nueva East (24)	18.695	15.634	38.559
5419-1020	dike	S. section of mine	18.727	15.644	38.594
Avg.			18.701	15.634	38.540
6139-529	quartz sandstone	El Pie (19)	18.728	15.639	38.602
UNALT-1	unaltered limestone	Quarry (3)	23.107	15.824	38.541
Santa Bárbara	altered limestone	Sta. Barbara Mtn. (2)	18.703	15.621	38.466
SV2600-1	altered limestone	Salva Vida	18.520	15.535	37.861
SV2650-17	altered limestone	Salva Vida (12)	18.820	15.603	38.525
NM-98-1	altered limestone	N. Manto (49)	18.792	15.628	38.637
NAC2450-4	altered limestone	Nacional (39)	23.717	15.681	38.534
NAC2290-9	altered limestone	Nacional	19.007	15.627	38.587
5483-850	altered limestone	Port Royal	18.772	15.650	38.673
5735-693	altered limestone	Yojoa	18.805	15.659	38.737
5393-1070	altered limestone	Nueva	18.755	15.642	38.628
6402-675	altered limestone	Porvenir	18.753	15.643	38.610
6246-805	altered limestone	San Juan	18.758	15.645	38.645
6510-879	altered limestone	S. section of mine	18.775	15.623	38.611
5419-1010	altered limestone	S. section of mine	18.724	15.634	38.569
Avg. (least altered)			18.771	15.626	38.553

Table 3-3. Pb-isotopic compositions of galena and whole-rock samples from the El Mochito deposit and vicinity. Sample locations shown in Appendix 1.

¹Values in brackets are the Pb content in ppm.

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a narrow range, with mean values of 18.766, 15.616 and 38.572, respectively. Comparison of the isotopic values obtained for the Yojoa basalt, Padre Miguel ignimbrite, diabase dike, Átima limestone, and Todos Santos sandstone with the average galena values indicates that the Pb isotope composition of the ores most closely matches that of the Padre Miguel ignimbrite. The host limestone could not have been a significant source of lead in the ores because its lead is much more radiogenic than that of the galena separates. The Pb isotope ratios of the Yojoa basalt sample also differ from those of the galena separates, although less appreciably so. The Pb isotope ratios of the diabase dikes and Todos Santos sandstone are similar to those of the ore lead, but they are consistently less radiogenic. As the samples representing these units are altered, it is difficult to assess to what extent their present Pb isotope ratios reflect their original composition.

The Pb isotope ratios of galena from El Mochito are similar to those of other Central American galena samples, particularly samples collected from magmatic-hydrothermal deposits within the Chortis block, as shown on plots of ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb ratios (Figure 3-8). The Pb isotope ratios of the El Mochito galena and Padre Miguel ignimbrite fall on or close to the orogenic growth curve of Zartman and Haines (1988), demonstrating that the Pb reservoirs for both included a mixture of mantle and crustal sources. Significantly, the primary igneous geochemistry of the Padre Miguel ignimbrite indicates mixing of mantle and crustal magmas (Williams and McBirney, 1969; Patino et al., 1997). The similarity of the Pb isotope signature of the El Mochito galena to that of the Padre Miguel ignimbrite suggests that the Padre Miguel magmas may have been the source of the Pb in the deposit. This interpretation is consistent with that of Sundblad et al., (1991) who concluded that the Pb isotope composition of galena in ore deposits hosted by the Chortis block reflects that of the associated intrusions.

Similar to the sulphur isotope data, Pb isotope values of the host limestone change systematically along the trend of the Salva Vida, Nacional and Port Royal orebodies (Figure 3-9). The lowest Pb isotope ratios, which occur in the northeast, are similar to those of average galena, whereas the southwesternmost sample yielded ratios similar to those of unaltered limestone. We therefore propose that the variation in the Pb isotope ratios of the limestone along the Salva Vida-Nacional trend reflects interaction of limestone with a hydrothermal fluid originating in the northeast and decreasing fluid:rock ratios southwards.

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Figure 3-8. Comparison of El Mochito galena Pb isotope compositions to that of galena from other deposits in Central America and the Padre Miguel ignimbrite. (1) Kesler and Ascarrunz-K, (1973), (2) Cumming et al., (1981), (3) Sundblad et al., (1991). The Orogene curve of Zartman and Haines (1988) is included for reference and shown as a dotted line.





Figure 3-9. (A) Pb isotope ratios of altered and non-mineralized limestone at El Mochito and (B) an enlargement of the area in (A) showing the Salva Vida-Nacional trend. Wholerock 206 Pb/ 204 Pb, 207 Pb/ 204 Pb and 208 Pb/ 204 Pb values for limestone decrease from SW to NE, approaching galena values. This trend is interpreted to represent increased alteration toward the NE and a southwesterly fluid flow. Orebodies are shaded and faults are shown as solid lines. Different symbols mark samples from different orebodies or structural trends. • Salva Vida, Nacional and Port Royal, • San Juan \blacktriangle Yojoa, •Porvenir, *Main Nueva, \checkmark North Manto, X south section of mine.



B)



CONCLUSIONS

The δ^{34} S values of sphalerite, galena and pyrrhotite indicate that their sulphur was derived from a magmatic sulphur source. This is also suggested by the Pb isotope ratios of galena, which are most similar to those of the Padre Miguel ignimbrite. The correspondence of both sets of values with the orogenic growth curve of Zartman and Haines (1988) suggests further that both mantle and crustal sources contributed to the lead in the magma. Systematic variation in the Pb isotope ratios of the altered limestone and the δ^{34} S values of sphalerite along the Salva Vida-Nacional trend suggest that the source of fluid and metals was to the northeast. These data support a model in which fluids exsolved from the Padre Miguel parent magma were responsible for formation of the El Mochito deposit. Future research involving the measurement of fluid inclusion homogenization temperatures and salinities will be undertaken to test this model.

ACKNOWLEDGMENTS

Financial support was provided by SEG and GSA grants to K.M.A., NSERC and FCAR operating grants to A.E.W-J., and by Breakwater Resources Ltd. The authors wish to thank the staff at El Mochito mine for providing support for this project. Thanks also to K. Klassen at Queen's University for performing stable isotope analyses and Prof. C. Gariépy and Dr. A. Simonetti of GEOTOP for performing Pb analyses. The manuscript benefited from critical reviews by J. Clark, R. Brathwaite and L. Meinert.

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INTRODUCTION TO CHAPTER IV

Previous chapters have established the gross chemical changes that occurred during alteration to skarn and formation of ore, metal zonation within the orebodies, compositional variations of the skarn minerals, the magmatic nature of the source fluids and the potential source of hydrothermal fluids. The following chapter "Skarn and Ore Formation at the El Mochito Zn-Pb-Ag Skarn Deposit: Fluid Composition and Evolution" describes the chemistry of the skarn and mineralizing fluids through detailed analyses of fluid inclusions by microthermometry, gas chromatography and LA-ICP-MS. Based on the results of fluid inclusion microthermometry the fluid $\delta^{34}_{H_2S}$ values were also determined. The evolution of the hydrothermal fluids is documented and a model of skarn and ore formation at El Mochito produced.

CHAPTER IV

SKARN AND ORE FORMATION AT THE EL MOCHITO ZN-PB-AG SKARN DEPOSIT: Fluid Composition and Evolution

K.M. Ault¹, A.E. Williams-Jones¹, J. E. Gagnon^{1,2}, I.M. Samson², B. J. Fryer²

¹McGill University, Department of Earth and Planetary Sciences, 3450 University St. Montreal, Quebec Canada H3A 2A7 ²University of Windsor, Department of Earth Sciences, Windsor, Ontario Canada N9B 3P4

ABSTRACT

The El Mochito Zn-Pb (Ag) skarn deposit, located in west-central Honduras is a typical example of a distal skarn-hosted base metal deposit. The deposit is hosted by Cretaceous limestone of the Átima Formation, and skarn and ore formation were related to extrusion of a nearby ignimbrite unit. The skarn mineralogy is characterized by early grossularitic garnet followed by andraditic garnet and hedenbergitic pyroxene, with pyroxene the main silicate and host to the bulk of the sphalerite mineralization. Ore minerals, which post-dated precipitation of silicates, comprise sphalerite of variable Fe content, galena, magnetite, pyrrhotite, chalcopyrite, pyrite, and trace amounts of arsenopyrite.

Liquid-vapour inclusions in garnet, pyroxene and sphalerite comprise two main populations. The first occurs mainly in grossularitic garnet and low-Fe sphalerite, and is characterized by homogenization temperatures ranging from 262 to 394°C, and salinities from 7.2 to 20.8 wt. % NaCl equivalent. By contrast, the second fluid inclusion population, which is associated with paragenetically later pyroxene and medium-Fe sphalerite, is characterized by a higher homogenization temperature (321 to 406°C), lower salinity (1.1 to 14.8 wt. % NaCl equivalent) and an elevated concentration of Fe. Grossularitic garnet also hosts several LVS inclusions that have compositions ranging from 12.1 to 22.1 wt. % NaCl and 23.2 to 25.8 wt. % CaCl₂, and homogenize at temperatures ranging from 334 to 466°C. No evidence for boiling was observed, and all inclusions homogenized by vapour disappearance.

The $\delta^{34}S_{H_2S}$ values of fluids precipitating sphalerite, galena and pyrrhotite were calculated to range from -3.7 to + 5.4‰ with a mean value of +0.7‰. These values suggest that the source of sulphur in the fluids was magmatic. Variation in the $\delta^{34}S$ values of sphalerite precipitating from hydrothermal fluids with a mean $\delta^{34}S$ value of 0.7‰ is interpreted to have resulted from an increase in pH as the fluid:rock ratio decreased.

Gas chromatographic analyses of inclusions hosted by grossularitic garnet, andraditic garnet, pyroxene, and sphalerite reveal that the fluids consist dominantly of H₂O, with minor quantities of CO₂ and negligible CH₄ and N₂. Based on these analyses, the X_{CO_2} of the skarn and ore-forming fluids ranged from 0.0001 to 0.005 and based on the CO₂/CH₄ ratios, log f_{O_2} values ranged from -30.6 to -24.9.

Laser ablation ICP-MS analyses of fluid inclusions hosted in grossularitic garnet, pyroxene and sphalerite indicate that Na, K, Ca and Fe are the dominant cations in solution and that the hydrothermal fluids contained median values of Zn ranging from <1 to 373 ppm and Pb from <1 to 706 ppm. A positive correlation between ore metal content and salinity suggests that the metals were chloride complexed and that ore deposition occurred by destabilization of these complexes during water:rock interaction. A model is proposed in which two end-member fluids, a saline formational brine and Ferich orthomagmatic fluid, progressively mixed at depth to form skarn and ore at the El Mochito deposit.

INTRODUCTION

The El Mochito mine, Honduras, the largest operation of its type in Central America (Figure 4-1), exploits a skarn-hosted Zn-Pb-Ag deposit containing ~15 Mt of ore grading 7 wt.% Zn, 2 wt.% Pb and 80g/t Ag (Vázquez et al., 1998; Thalenhorst, 1994). In earlier papers on the deposit, Ault and Williams-Jones (in press and submitted) have shown that formation of grossularitic garnet, andraditic garnet, and hedenbergitic pyroxene skarn was accompanied by significant additions of Si, Fe, Mg, Al, and Mn and that the only components lost in appreciable quantities were Ca and volatiles. The fluid:rock ratio is inferred to have been high based on apparent decreases in the concentrations of Ti and Zr. Sulphide precipitation post-dated crystallization of the main skarn silicates and produced ore bodies that have Zn- and Fe-rich cores and Pb- and Agrich peripheries. On the basis of sulphur and lead isotope data, fluids and metals are interpreted to have originated from a magmatic centre located northeast of the deposit (Ault and Williams-Jones, in press). The current paper focuses on the evolution of the hydrothermal fluids at El Mochito and how this controlled the processes of skarn and ore formation.

Figure 4-1. Location, tectonic setting and geology of the El Mochito deposit. PMSZ-Polochic-Motagua suture zone. (Modified from Williams and McBirney, 1969).



Tertiary

Padre Miguel Group rhyolitic ignimbrites

Matagalpa Formation

Cretaceous



Atima Formation limestone

The El Mochito deposit exhibits several features that characterize it as a typical Zn skarn, such as distal location with respect to its inferred fluid source, the structural and/or stratigraphic control on the location of chimney and manto-shaped orebodies (Figure 4-2), a calc-silicate gangue dominated by hedenbergite-diopside series pyroxene and grossular-andradite series garnet, and an overall Fe and Mn-rich mineralogy (Einaudi et al., 1981). However, it differs from other Zn skarns in several important aspects; there is no obvious zoned distribution of silicate minerals, there appears to be an evolving precursor rather than a single protolith and the Fe-overprint occurs at a higher temperature than the preceding low-Fe silicate stage. As in the earlier papers, the focus of this paper is the Salva Vida-Nacional trend (Fig. 4-2B), a 600 m zone of semicontinuous mineralization containing ~3Mt of ore. The physico-chemical parameters of the hydrothermal fluids were determined from fluid inclusion microthermometry, gas chromatographic analyses, sulphur isotopic analyses, and LA-ICP-MS analyses of garnet, pyroxene and sphalerite. By combining the results of these analytical methods with the results of our previous studies, the composition and evolution of hydrothermal fluids responsible for skarn and ore formation were deduced and a genetic model of the El Mochito deposit was generated.

GEOLOGIC SETTING AND STRATIGRAPHY

The El Mochito deposit, and most of Honduras, is located in the Chortis block, a major geologic province of the Caribbean plate, which is composed mainly of Precambrian and Paleozoic phyllites and schists (Draper et al., 1994; Mills et al., 1967). In Honduras, the Chortis block is cut by a staggered series of major NE- to NW-trending faults and grabens (Malfait and Dinkelman, 1972; Williams and McBirney, 1969; Mills et al., 1967), known collectively as the Honduras Depression. El Mochito lies in the Mochito graben, a smaller structure off the Yojoa graben, both of which are related to development of the Honduras Depression (Fig. 4-1).

The local stratigraphy consists of a basement of quartz sandstone belonging to the Todos Santos Formation (Jurassic?), which is overlain unconformably by Cretaceous

Figure 4-2. A) Cross-section through the El Mochito deposit. Orebodies are shaded and faults are shown as dotted lines. The Cantarannas contact is shown as a dotted line. B) Plan view of the deposit showing the location of most orebodies with fault zones.

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Yojoa Group limestones and shales, and in turn by the Tertiary Valle de Angeles Group redbeds (Figure 4-3). The Átima Formation, which is part of the Yojoa Group, hosts most of the ore and skarn, and is separated by the Mochito shale into upper and lower limestone members. The only igneous rocks in the deposit are rare pre-ore porphyritic diabase dykes dated at 16.7, 9.7, and 9.4 Ma (whole-rock K/Ar ages; Dilles, 1982). Based on these age determinations, emplacement of the dykes appears to have been synchronous with extrusion of the Padre Miguel ignimbrite (18.9 ± 0.2 to 15.0 ± 0.2 Ma, whole-rock K/Ar ages: Williams and McBirney, 1969) at Lago de Yojoa, and either predated or coincided with Zn-Pb-Ag mineralization in the deposit.

SKARN AND ORE MINERALOGY

The skarn consists mainly of garnet and pyroxene, but locally can contain high proportions of magnetite, epidote, chlorite and pyrrhotite. Commonly the skarn contains a single dominant mineral, and it is therefore possible to subdivide it on this basis. In decreasing order of abundance the following are the skarn types recognized in the deposit: pyroxene, andraditic garnet, epidote, magnetite, grossularitic garnet, chlorite, pyrrhotite. However, it is important to note that there are also gradations among skarn types. This is particularly the case for garnet and pyroxene skarns, which are zonally distributed, with garnet skarn grading into pyroxene skarn with increasing distance from fault zones in each orebody. Magnetite and sulphide skarns usually occur within the core of each orebody, whereas epidote and chlorite skarns are usually found along the peripheries, close to stratigraphic contacts or within fault zones.

Grossularitic garnet ($Gr_{55}Ad_{41}Sp_{4}$) was the earliest silicate to form followed by andraditic garnet ($Ad_{72}Gr_{25}Sp_{3}$), hedenbergitic pyroxene ($Hd_{64}Di_{20}Jo_{16}$) and finally, epidote (Figure 4-4). A change in garnet composition, from early grossularitic to later andraditic is typical in skarn-forming systems, and is thought to correspond to a progression from a rock-dominated to a fluid-dominated setting and concomitant evolution of fluids to higher Fe concentrations (Jamtveit et al., 1995; 1993). Interstitial

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Figure 4-3. Stratigraphy at the El Mochito deposit; orebodies are shown as shaded areas. (Modified after Mills et al., 1967).



Figure 4-4. Photomicrographs of silicate textures in skarn samples. A) Early grossularitic garnet core surrounded by a zoned andraditic rim. B) Andraditic garnet cutting early grossularitic garnet. C) Early garnet with later pyroxene and epidote. D) Late, pervasive epidote alteration. Gr-grossularitic garnet, Ad-andraditic garnet, Px-pyroxene, Epi-epidote, Gn-galena. Scale bar is 0.1 mm.



calcite and lesser quartz accompany the skarn silicates. Other silicate minerals in the deposit not mentioned previously, all of which occur in very small proportions, include bustamite, which occurs locally at the contact between limestone and skarn, biotite, smectitic clay, sericite, K-feldspar and ilvaite.

The main ore minerals are sphalerite, magnetite, and galena, and are accompanied by lesser pyrrhotite, pyrite, chalcopyrite, and trace arsenopyrite (Figure 4-5). Ore formation postdated silicate formation as shown by the largely interstitial nature of the sulphide minerals to garnet and pyroxene. Magnetite was the earliest of the ore minerals to form, and occurs as feathery masses, intergrown with pyroxene, as mantles on earlierformed silicates or as inclusions in sphalerite. Pyrrhotite formed after magnetite and is usually seen either as blebs in sphalerite or as veins cut by later phases. Although there was an early generation of pyrite, it is minor, and most of the pyrite occurs as late cubes associated with calcite. Sphalerite was the next phase to precipitate after pyrrhotite and has a FeS content ranging from 3 to 26 mol%. Based on composition and colour, sphalerite was subdivided into low-Fe (pale yellow/orange, <10 mol% Fe), medium-Fe (red, 10-15 mol% Fe) and high-Fe (black, >15 mol% Fe) varieties. Although the wide range in the Fe content of the sphalerite can be the result of several factors including variations in temperature and pressure, f_{O_2} , and f_{S_2} and a_{Fe} (Vaughan and Craig, 1997), evidence presented in Ault and Williams-Jones (submitted) indicate that it resulted primarily from variations in log f_{O_2} due to the different buffering effects of the associated iron sulphide and oxide minerals. Galena and chalcopyrite appear to have co-precipitated after sphalerite, and commonly occur as composite blebs in sphalerite. Galena is also often seen lining fractures in earlier formed sulphides, while chalcopyrite occurs mostly as blebs in sphalerite. A simplified paragenetic sequence of silicate, sulphides and oxides for El Mochito is presented in Figure 4-6.

The distribution of metals in the Salva Vida and Nacional orebodies is zoned from Zn and Fe-rich cores to Pb and Ag-rich peripheries (Ault and Williams-Jones, submitted). From the solubility of Zn, Pb, and Ag, it appears that either cooling, an increase in pH, or a decrease in log f_{O_2} would favour the sequential precipitation of sphalerite, followed by galena and finally acanthite. The metal zonation is concluded to have resulted from cooling of the ore fluid as it infiltrated the skarns during its upward and outward

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Figure 4-5. Photomicrographs of textures showing paragenetic relationships among the sulphide and oxide phases. A) Early feathery magnetite with interstitial calcite, and later sphalerite, chalcopyrite and galena. B) Early magnetite mantling epidote with later pyrrhotite, sphalerite and chalcopyrite. C) Pyrrhotite mantled by galena, which is cut by sphalerite containing blebs of chalcopyrite. D) Pyrrhotite containing some late blebs of sphalerite, which has replaced pyrite and cuts garnet. Scale bar is 0.1 mm.



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Figure 4-6. Paragenetic sequence of silicate, sulphide and oxide mineral crystallization at El Mochito.

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Early Late

<u>Silicates</u>

Garnet (Gr>50)	
Garnet (Ad>50)	-
Pyroxene	
Epidote	

Sulphides and Oxides

Magnetite	
Pyrrhotite	•
Pyrite	• •
Sphalerite	\rightarrow
Galena	
Chalcopyrite	

movement through the system.

FLUID INCLUSION MICROTHERMOMETRY

Methodology

Doubly polished thin sections ranging in thickness from 30 to $80\mu m$ were prepared of samples containing garnet, pyroxene, and sphalerite. Fluid inclusions were examined petrographically and analyzed microthermometrically on both a Fluid Inc.modified U.S.G.S. gas-flow freezing/heating stage and an Olympus BH-2 stage fitted with infra-red (IR)-enhanced oculars and objectives and an IR imaging system. The stage was calibrated to $\pm 0.1^{\circ}$ C for freezing runs and $\pm 2^{\circ}$ C for heating runs, using synthetic fluid inclusion standards (CO₂: -56.6°C ice melting; H₂O: 0.0°C ice melting; H₂O: 374°C critical homogenization of H₂O liquid and vapour).

Petrography

Fluid inclusions were observed in sphalerite, pyroxene, and garnet and classified as primary (P), secondary (S), or pseudosecondary (PS) following the criteria of Roedder (1984). Large, isolated inclusions in the cores of the host crystal, discrete 3-D clusters of inclusions or inclusions along growth zones were classified as primary (Figure 4-7). Inclusions clearly located along fractures, within fracture planes, or zones of alteration, were labeled either as pseudosecondary or secondary, depending on the distribution of the fractures. Where fractures clearly crosscut the mineral, associated fluid inclusions were labeled as secondary, whereas fluid inclusions located along families of fractures that all terminate within the crystal were classified as pseudosecondary. Wherever possible, fluid inclusion assemblages were identified, based on the criteria of Goldstein (2003) and analyzed. Although abundant primary inclusions were noted to occur along growth zones in both grossularitic and andraditic garnet, they were frequently too small to observe any phase changes and most primary, garnet-hosted inclusions analyzed were in the cores of the grossularitic garnet. Abundant primary inclusions were observed in pyroxene, typically along cleavage planes, and in the lighter coloured sphalerite types.

Figure 4-7. Photomicrographs of L-V fluid inclusions in A) grossularitic garnet, B) pyroxene C) low Fe sphalerite, and D) medium Fe sphalerite. Scale bar is 0.1 mm.



The majority of fluid inclusions were the L-V type. Eight LVS inclusions were observed in grossularitic garnet, and two in sphalerite. Primary fluid inclusions in grossularitic garnet range in diameter from 2 to 100 μ m with most being ~8 μ m, whereas primary inclusions in pyroxene and sphalerite average from 4 to 18 μ m in diameter, respectively. The volume proportion of the vapor is, on average, 20%, 35%, 30% and 40% of the inclusion volume of primary inclusions in grossularitic garnet, pyroxene, low-Fe, and medium-Fe sphalerite, respectively.

Pseudosecondary fluid inclusions in andraditic garnet and low-Fe sphalerite range in diameter from 4 to 24μ m, and 4 to 18μ m, and contain 25% and 20% vapour, respectively. Secondary inclusions in grossularitic garnet, andraditic garnet, pyroxene and low-Fe sphalerite range in diameter from 8 to 30μ m, 4 to 14μ m, 4 to 18μ m, and 6 to 18μ m and the volume of the vapour phase occupies, on average, 30%, 15%, 25% and 25%, respectively. The LVS inclusions hosted in grossularitic garnet range in diameter from 25 to 100μ m and the vapour phase occupies approximately 25%. One of the LVS inclusions in sphalerite contained an opaque solid and the other a clear, slightly rounded, isotropic crystal. Both inclusions ranged in diameter from 80 to 100μ m and the vapour phase occupied approximately 50% of the inclusion volume.

LVS Inclusions-Composition of Solid Phases

The solids in grossularitic garnet-hosted inclusions appear square or cubic, occupy similar volumes in each inclusion and therefore appear to be daughter crystals rather than trapped solids (Figure 4-8). Their identity as either halite or sylvite is supported by the absence of viable Raman signals (Rankin and Shepherd, 1998). Analyses of decrepitate mounds from grossularitic garnet-hosted LV fluid inclusions (Figure 4-9A,B) indicate that Na and K are the dominant cations (Table 4-1), and that the proportion of Na exceeds that of K. This suggests that the daughter mineral is probably halite. Due to the nature of the substrate, the quantities of Ca and Fe in the decrepitated mounds could not be evaluated with confidence.

The nature of the two sphalerite-hosted LVS inclusions is difficult to assess, however, both occur close to or on healed fractures and have consequently been labeled

Figure 4-8. LVS inclusions in grossularitic garnet (A-D) and low Fe sphalerite (E,F). The solids in grossularitic garnet are considered to be daughter crystals of halite, whereas the solids in sphalerite are either daughter phases or trapped solids of halite (E) and chalcopyrite (F). Scale bar is 0.1 mm.




Figure 4-9. Decrepitate mounds in grossularitic garnet (A,B) and sphalerite (C,D). The mounds consist mainly of NaCl, although one in garnet may have contained an elevated Ca concentration. Scale bar is 10 microns.

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/t.%.											
Sample	Ca	Na	К	Mg	Mn	Fe	Al	Si	Zn	S	CI

Table 4-1. Compositions of decrepitate mounds on garnet and sphalerite. Values are in wt.%.

Grossular	itic garnet											
2650-24	46.8	3.2	0.0	0.0	3.0	1.2	1.2	8.4	0.0	34.6	1.6	
2650-24	55.0	5.7	0.8	0.8	0.8	1.2	0.0	0.1	2.9	16.8	15.8	
2650-24	38.1	2.2	0.7	4.1	3.3	11.3	7.0	18.5	0.0	12.1	1.1	
2650-24	53.3	0.0	0.8	0.0	0.0	0.6	0.8	1.1	0.0	42.1	0.4	
2650-24	12.3	10.5	2.3	8.2	0.6	0.0	1.3	24.4	0.0	0.0	0.0	
2650-24	10.4	6.8	9.3	1.5	2.4	0.8	18.7	6.1	0.0	3.7	19.3	
2450-10	4.3	41.5	19.0	0.8	0.0	0.9	0.0	3.7	0.0	2.2	25.5	
Low-F	e sphalerite											
2450-8	13.5	23.1	17.6	5.0	0.1	2.5	1.2	0.0	8.9	10.6	17.5	

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as secondary (Fig. 4-8). The opaque solid was identified from Raman analyses as chalcopyrite, whereas the other solid did not produce a Raman response. Whether the transparent phase is a daughter crystal or a trapped solid remains unknown; the opaque phase is considered to be a trapped solid as the sphalerite host contains abundant, late, chalcopyrite inclusions and LA-ICP-MS analyses of sphalerite-hosted inclusions did not detect Cu (see below). The opaque-bearing fluid inclusion is of particular interest due to its secondary nature yet higher trapping temperature when compared to primary low-Fe sphalerite-hosted inclusions.

Microthermometry and Cryogenic Measurements

Temperatures of freezing, first melting, and last melting were measured for fluid inclusions in garnet, pyroxene, and low and medium-Fe sphalerite (Table 4-2). Several inclusions were cooled to temperatures below -100°C without appearing to freeze. The onset of melting was interpreted from the occurrence of a mosaic texture within the inclusions, and reflects the best estimate of the eutectic temperature (T_e) of the corresponding aqueous system. First melt temperatures of primary inclusions ranged from -50.4 to -45.2°C for grossularitic garnet, -55.4 to -46.9°C for low-Fe sphalerite, -39.6 to -31.2 for pyroxene and -31.4 to -27.1 for medium Fe sphalerite. These temperatures are close to the eutectic temperatures for the systems H₂O-NaCl-CaCl₂-MgCl₂ (-57°C), H₂O-NaCl-CaCl₂ (-52°C), H₂O-CaCl₂ (-49.5°C), H₂O-NaCl-FeCl₂ (-37°C), H₂O-FeCl₂ (-35°C), H₂O-MgCl₂ (-33.6°C), H₂O-NaCl-KCl (-23°C) and H₂O-NaCl (-21.2°C), respectively (Dubois and Marignac, 1997; Bodnar, 1993; Davis et al., 1990; Oakes et al., 1990; Chou, 1985; Borisenko, 1977). The majority, however, fall within the range of the eutectics for the H₂O-NaCl-CaCl₂, H₂O-CaCl₂, H₂O-NaCl-FeCl₂, H₂O-FeCl₂, and H₂O-MgCl₂ systems. The presence of CaCl₂ in skarn-forming systems is well documented (Kwak, 1986), and this is commonly one of the principal salt species in skarn-forming fluids (Baker et al., 2003; Crespo et al., 2002; Cepedal et al., 2000; Koděra et al., 1998; Lang et al., 1998; Jamtveit and Andersen, 1993; Theodore and Hammarstrom, 1991; Kwak and Tan, 1981). These inclusions also display anomalous behaviour in that they do not show typical freezing characteristics, such as contraction of the vapour bubble. They had to be cooled rapidly to at least -120°C, and then the

Table 4-2. Microthermometric data for garnet, pyroxene, and sphalerite-hosted fluid inclusions. Grossularitic garnet, pyroxene and sphalerite-hosted inclusions are primary while andraditic garnet inclusions are pseudosecondary. All results of fluid inclusion microthermometry are listed in Appendix 4.

Sample	Chip	T _{m(ice)} (°C)	"Transition" (°C)	Frz-ap	NaCl	T _h (°C)	T₁(°C)	T _e (°C) Hydrohalite	Halite	CaCl ₂
•	-			-	wt.%				(°C)	dissolution (°C)	wt.%
	Gross	ularitic Ga	rnet								
2550-21^	A,B,D,F	-11.4		-55.0	14.3	340.7	427.1				
2550-21 [•]	Α		-85.1		18.1	378.5	465.4	-50.4		235.3	24.5
2550-21°	Α		-78.9		22.1	384.4	465.8	-49.6	-43.7	322.0	23.2
2550-21 [°]	В		-77.8		17.5	370.7	456.8	-54.0		235.9	24.8
2550-21°	В		-80.1		14.1	311.7	389	-49.8		204.4	25.5
2550-21°	В		-76.6		12.1	297.2	372.2	-50.2		164.6	25.8
2550-21°	В		-79.1		15.4	293.4	365.9	-49.6		216.9	25.5
2550-21°	С		-70.1		14.1	344.8	444.2	-40.7		173.6	23.5
2550-21°	D		-79.2		16.4	262.2	334.4	-49.9		220.7	25.2
2650-26*	1,2,3	-10.8		-56.9	14.6	324.5	406.5				
NM-4 ^A	C,D	-9.4		-50.7	13.0	351.7	437.5				
<u>Average</u>		-10.6	-77.9	-55.7	14.4	329.6	412.0	-49.7	-37.8	202.7	25.1
	Andı	aditic Gar	net								
2650-26*	1.3	-2.9		-49.2	4.8	368.1	495.1				
<u>Average</u>		-2.9		-49.2	4.8	368. I	495.1				
		Pyroxene									
2450-6^	2,3,4,6	-2.5		-50.6	4.1	355.3	48 0.9				
2650-26 ^A	4,6	-4.3		-57.8	6.8	354.8	473.7				
2550-3^	В	-2.3		-38.3	3.9	360.0	476.2				
NM98-4 ^A	D	-2.0		-45.9	3.4	372.3	501.8				
6198-153	^ A 👘	-7.7	-70.6		11.2	377.7	505	-34.8			
6198-153	^ A,B,C,D	-6.1		-51.5	8.8	377.1	503.2				
NM4A	Α	-8.1		-54.0	11.8	348.8	456.8				
6566-383	С	-10.8		-58.6	14.8	359.8	468.8				
<u>Average</u>		-4.4	-70.6	-50.2	6.8	363.9	486.7	-34.8			
	Low-	Fe Sphale	rite								
2450-6 ^A	2.5.6	-14.0		-48.8	17.7	302.0	376.0				
2450-10 ^A	1.2	-13.3		-58.9	17.1	303.5	376.4				
2550-19^	B.C.D	-9.6		-51.2	13.4	326.5	404.0				
5382-898	B.C.DF	-16.8		-68.1	14.6	344.7	425.5	-53	-31.5		11.0
5382-898	B,C,D,F	-11.2		-53.8	15.1	339.9	423.3				
6695-371	F	-8.8		-47.3	1.1	345.7	421.7		-41.8		11.3
6695-371	^ F,H	-6.8		-48.6	10.2	343.2	419.2				
6566-383	A,D,F	-10.7		-53.8	6.9	363.5	439.5		-41.1		12.1
6001-435	Α	-4.5		-38.4	7.2	362.1	472.9				
NM-4 ^A	B,C	-6.1		-40.1	9.4	338.0	417.9				
<u>Average</u>		-10.6		-52.4	14.3	332.7	411.7	-52.7	-33.3		
	Mediu	m-Fe Spha	lerite								
2450-10 ^A	1,3	-1.0		-57.36	1.8	354.7	470.0				
2650-24 ^A	2	-1.9		-43.7	3.2	342.7	449.1	-33.2			
5382-898	^ D,F	-1.7		-43.7	2.8	354.9	472.5				
6566-383	^F	-4.1		-43.7	6.6	359.0	448.5	-32.3			
6695-371	F,C	-3.6		-39.9	5.8	357.3	459.2				
4516-65	A,B	-6.2		-42.9	9.4	364.3	470.3				
Average		-3.1		-43.8	4.9	358.3	465.0	-32.6			

^{*}LVS inclusion, all others LV. ^Aaverage values.

temperature increased slowly, to about -80°C, at which point a "transition" occurred and bright patches were noted in the inclusion. This type of transition has been attributed previously to either the metastable eutectic of the H₂O-NaCl-CaCl₂ system (Samson and Walker, 2000; Vanko et al., 1998; Davis et al., 1990; Oakes et al., 1990), the presence of other salt species such as MgCl₂ and FeCl₂ (Baldassaro, 1998; Dubois and Marignac, 1997; Davis et al., 1990), or a solid state transformation and crystal growth from a glassy solid (Angell, 2002). In the present case, evidence of large scale melting near -50°C and -35°C suggests that the changes noted at -80°C probably reflect metastable melting in the H₂O-NaCl-CaCl₂ and H₂O-NaCl-FeCl₂ systems, respectively (Samson and Walker, 2000; Baldassaro, 1998).

In several inclusions, an intermediate phase was observed to disappear before final ice melting. This phase is interpreted to be hydrohalite and melted at an average temperature of -40.6°C in grossularitic garnet (n=3), and -33.3°C in low-Fe sphalerite (n=10). Final ice melting temperatures ranged from -17.8 to -5.0°C, -10.8 to -0.8°C, -16.2 to -4.5°C and -7.9 to -0.3°C for primary inclusions in grossularitic garnet, pyroxene, and low-Fe and high-Fe sphalerite, respectively. Pseudosecondary inclusions in andraditic garnet had final ice melting temperatures that ranged from -2.9 to -0.6°C.

Final ice-melting temperatures were converted to salinity using either the equation of Bodnar (1993) for inclusions that did not show evidence of high proportions of CaCl₂ or the equation of Oakes et al. (1990) and the phase diagram of Williams-Jones and Samson (1990) for inclusions that appeared to contain appreciable CaCl₂ as a dissolved salt component. Based on the halite dissolution temperature, which ranged from 165 to 322°C, and the melting temperature of intermediate phases, the proportions of NaCl and CaCl₂ range from 12.1 to 22.1 wt%, and from 23.2 to 25.8 wt%, respectively, in the LVS inclusions. These inclusions behaved in a manner similar to high salinity inclusions not containing solid phases, in that they had to be cooled to -120°C then slowly heated up before any noticeable change occurred, usually at approximately -80°C.

The temperatures of phase changes during cooling and heating indicate that there are three general salinity ranges (Figure 4-10), one from 5-15 wt. % NaCl eq., associated with inclusions in andraditic garnet, medium-Fe sphalerite and pyroxene, another near 10-30 wt. % NaCl eq., associated with inclusions in grossularitic garnet and low-Fe

Figure 4-10. Histogram of fluid salinity for inclusions hosted by grossularitic garnet, andraditic garnet, pyroxene, low Fe sphalerite, and medium Fe sphalerite. Those inclusions with salinities in the 45 wt. % NaCl equivalent range contained daughter crystals, the remainder were L-V inclusions. The overlap of data for paragenetically exclusive phases shows the relationship between grossularitic garnet and low Fe sphalerite, and between andraditic garnet, pyroxene and medium-Fe sphalerite.



Frequency



sphalerite, and a third ranging from 40 to 50 wt. % NaCl eq., which is associated with LVS grossularitic garnet-hosted inclusions.

Homogenization Temperatures

Liquid-vapour fluid inclusions in grossularitic garnet, andraditic garnet, pyroxene, low-Fe sphalerite, and medium-Fe sphalerite homogenized by vapour disappearance at average temperatures of 333, 364, 333, 358, and 375°C, respectively. The LVS inclusions in grossularitic garnet show similar average homogenization temperatures (330°C) to the LV inclusions hosted by grossularitic garnet with halite dissolution occurring from 165 to 322°C. The distribution of homogenization temperatures demonstrates that the majority of inclusions homogenized between 300 and 400°C (Figure 4-11A). Homogenization temperatures (T_h) were pressure-corrected (T_t) since no evidence for boiling was observed during microthermometric analyses. A maximum pressure of 1 kb was estimated based on a stratigraphic reconstruction of lithologies at El Mochito indicating a cover of 1.5 to 3 Km at the time of formation of the deposit (Dilles, 1982; Williams and McBirney, 1969). Pressure corrections were performed using either FLINCOR (Brown, 1989) or the FLUIDS 1 software package (Bakker, 2003), and indicate that trapping temperatures were 50 to 150°C greater than the measured homogenization temperatures. The pressure-corrected temperatures clearly show two temperature modes, one near 400°C for primary inclusions in grossularitic garnet and low-Fe sphalerite, and another closer to 500°C for primary inclusions in pyroxene and medium-Fe sphalerite and pseudosecondary inclusions in andraditic garnet (Figure 4-11B).

Although no ice melting or homogenization temperatures could be obtained for inclusions in the darkest, most Fe-enriched sphalerite, they were observed to decrepitate between 525 and 550°C during microthermometric runs using the IR-enhanced system.

Figure 4-11. Histograms of homogenization (A) and pressure-corrected trapping temperatures (B) for fluid inclusions hosted in grossularitic garnet, andraditic garnet, pyroxene, low Fe sphalerite, and medium Fe sphalerite. As with the salinity data, there is a coincidence of mineralogic associations, and fluid inclusions hosted by grossularitic garnet have homogenization temperatures similar to inclusions in low-Fe sphalerite, whereas homogenization temperatures for inclusions in pyroxene, medium-Fe sphalerite and andraditic garnet are similar.







GAS CHROMATOGRAPHY ANALYSES

Gas Compositions and log f_{O_2} Conditions

Gas chromatographic analyses of 0.5 to 1g samples of garnet, pyroxene and sphalerite were performed using an on-line HP 5890 series II gas chromatograph equipped with thermal conductivity (TCD) and photo-ionization (PID) detectors, using the method described by Bray and Spooner (1992) and refined by Salvi and Williams-Jones (2003, 1997). There was no evidence from fluid inclusion microthermometry to suggest the presence of carbonic or other non-condensible gases; however, minor concentrations of CO₂, CH₄ and N₂ were detected during gas chromatographic analyses of sphalerite, pyroxene, and garnet. The measured amounts of gases are given in Table 4-3, and the results of 23 analyses indicate that the dominant gas species was H_2O (avg. $X_{H_2O}=0.996$) followed by CO₂ (avg. $X_{CO_2}=0.0023$), with lesser amounts of CH₄ (avg. $X_{CH_4} = 0.0008$) and N₂ (avg. $X_{N_2} = 0.0006$). The medium and high-Fe sphalerite varieties and andraditic garnet contain the highest quantities of CO₂, followed by grossularitic garnet, pyroxene and low Fe sphalerite, with average X_{CO_2} values of 0.0031, 0.0025, 0.0029, 0.0018, 0.0016, and 0.001, respectively. No heavy hydrocarbons were detected during gas chromatographic analyses although Vázquez et al. (1998) and Graney and Kesler (1995) detected trace quantities of C₂H₆. The CO₂/CH₄ ratio was used to calculate the log f_{0_2} of the skarn-forming and mineralizing fluid from the equilibrium constant for the reaction:

$$CO_2 + 2H_2O = CH_4 + 2O_2$$
 (1)

The log K value for the above reaction was calculated at the temperatures and pressure of mineral formation using the computer software Hch (Shvarov and Bastrakov, 1999), and the SUPCRT database (Shock, 1998; Johnson et al., 1992), assuming a water activity of unity. Values of log f_{O_2} were within ±0.4 log units for duplicate analyses, which compares well with analyses of Salvi and Williams-Jones (1997) who noted that reproducibility was ±15% using the same equipment. The log f_{O_2} values ranged from

Table 4-3. Composition of gases in fluid inclusions hosted by garnet, pyroxene and sphalerite. Amounts expressed in nmoles, log K values from Shvarov and Bastrakov (1999).

Sample	H ₂ O	CO ₂	CH₄	N ₂	X _{H2O}	X _{CO2}	X _{CH4}	X _{N2}	loga _{CO2}	loga _{CH4}	log K	log f 02
Grossularitic	Garnet											
2450-10	3297	6.37	1.52	0.85	0.99736	0.002	0.000	0.000	0.37	-0.1	-60.1	-29.8
5578-350	2176	0.13	0.5	0.4	1.00	0.000	0.000	0.000	-1.13	-0.5	-60.1	-30.4
3795-247	4056	0.65	0.86	0.77	0.99944	0.000	0.000	0.000	-0.71	-0.5	-60.1	-30.1
Andraditic Garnet												
2290-7	382	2.02	0.29	0.04	0.99388	0.005	0.001	0.000	0.87	0.0	-51.0	-25.1
SV2650-26	225	0.83	0.86	0.94	0.98846	0.004	0.004	0.004	0.71	0.8	-51.0	-25.5
SV2500-W	817	7.12	0.38	0.13	0.99074	0.009	0.000	0.000	1.08	-0.2	-51.0	-24.9
6643-1700	3598	1.25	0.95	1.05	0.9991	0.000	0.000	0.000	-0.31	-0.4	-51.0	-25.4
Pyroxene												
2550-3	1632	5.81	0.19	0.21	0.99621	0.004	0.000	0.000	0.69	-0.77	-52.5	-25.5
4365-526	165	0.64	0.91	0.74	0.98633	0.004	0.005	0.004	0.51	-0.67	-52.5	-25.6
NM98-4	1865	0.19	1.48	0.6	0.99878	0.000	0.001	0.000	0.73	0.91	-52.5	-26.3
SV2500-W	1448	3.35	0.21	0.14	0.99745	0.002	0.000	0.000	-0.85	0.07	-52.5	-26.7
2636-148	2255	1.08	0.36	0.16	0.99929	0.000	0.000	0.000	-0.17	-0.62	-52.5	-26.0
SJ1410-1	1398	0.98	0.64	0.28	0.99864	0.001	0.000	0.000	-0.01	-0.16	-52.5	-26.1
Low-Fe Sph	ulerite (S	SI)										
SV2500-W	3969	0.41	0.19	2.12	0.99932	0.000	0.000	0.001	-0.90	-1.14	-60.4	-30.1
2450-6	2392	3.15	0.52	1.14	0.99799	0.001	0.000	0.000	0.20	-0.47	-60.4	-29.9
5382-898	2538	7.12	0.33	0.23	0.99698	0.003	0.000	0.000	0.53	-0.70	-60.4	-29.6
6622-1067	1250	0.19	0.75	0.36	0.99896	0.000	0.001	0.000	-0.73	-0.04	-60.4	-30.6
Medium-Fe	Sphaleri	te (S2)										
2290-7	1533	5.82	0.33	0.13	0.99592	0.004	0.000	0.000	0.72	-0.49	-54.7	-26.7
5615-89	1676	7.49	1.76	0.15	0.99442	0.004	0.001	0.000	0.79	0.20	-54.7	-27.1
5230-172	952	3.58	0.32	0.27	0.99564	0.004	0.000	0.000	0.72	-0.30	-54.7	-26.8
High-Fe Sph	alerite (S 3)										
2450-10	118	0.68	0.18	0.13	0.99167	0.006	0.001	0.001	0.90	0.3	-51.0	-25.2
4520-24	1639	0.37	0.7	0.51	0.99904	0.000	0.000	0.000	-0.50	-0.2	-51.0	-25.6
5203-138	712	0.97	0.22	0.16	0.99811	0.001	0.000	0.000	0.28	-0.3	-51.0	-25.2
Averages												
	H ₂ O	CO ₂	CH₄	N,	X _{H20}	X _{CO2}	Хсна	X _{N2}	logacoz	loga _{CH4}		log f or
Garnet (Gr)	3176	2.38	0.96	0.67	0.999	0.001	0.000	0.000	-0.49	-0.37		-30.1
Garnet (Ad)	2537	2.81	0.62	0.54	0.998	0.004	0.001	0.001	0.59	0.06		-25.2
Px	1461	2.01	0.63	0.36	0.996	0.002	0.001	0.001	0.15	-0.21		-26.0
S1	2537	2.72	0.45	0.96	0.998	0.001	0.000	0.000	-0.22	-0.59		-30.0
S2	1387	5.63	0.80	0.18	0.995	0.004	0.001	0.000	0.74	-0.20		-26.9
S3	823	0.67	0.37	0.27	0.996	0.002	0.001	0.001	0.23	-0.06		-25.3
ALL	1743	2.62	0.63	0.50	0.996	0.002	0.001	0.001	0.16	-0.23		-27.1

-24.9 to -30.6 with a total average value of -27.1. The most reduced fluids were extracted from inclusions in grossular-rich garnet (-30.1) and low-Fe sphalerite (-30.0), and the most oxidized from and radite-rich garnet (-25.2), pyroxene (-26.0), medium-Fe sphalerite (-26.9) and high-Fe sphalerite (-25.3). The log f_{O_2} values for and raditic garnet, grossularitic garnet and sphalerite were also calculated based on the CO₂/CH₄ ratios measured by Graney and Kesler, (1995) and Vázquez et al., (1998). These ratios give log f_{O_2} values of -25.7, -30.0 and -27.8 to -28.2 for and raditic garnet, grossularitic garnet and sphalerite.

LA-ICP-MS ANALYSES OF FLUID INCLUSIONS

As a complement to the micothermometric study, the composition of skarn and ore-forming fluids was further evaluated by LA-ICP-MS analyses of fluid inclusions hosted in grossularitic garnet, pyroxene and low and medium Fe sphalerite varieties. Recent developments in LA-ICP-MS techniques permit the effective quantification of the composition of hydrothermal fluids especially the concentrations of ore metals through the analyses of fluid inclusions (Audétat and Pettke, 2003; Gagnon et al., 2002; Günther et al., 1998; Taylor et al., 1997; Shepherd and Chenery, 1995). However, except for the recent PIXE analyses by Baker et al., (2004), microanalytical techniques of this type have not been applied to fluid inclusions in skarn systems. The current study is the first to report the trace element compositions of fluids hosted by garnet, pyroxene and sphalerite in a mineralized skarn and thus provides a direct quantitative assessment of the composition of skarn and ore-forming fluids. All LA-ICP-MS analyses were performed at the Great Lakes Institute for Environmental Research (GLIER) at the University of Windsor using a Continuum[®] Surelite[®] I-20 O-switched, 266 nm Nd:YAG pulsed laser and ThermoElemental[®] X-7 quadrupole ICP-MS. Detailed descriptions of the operating system at GLIER, and LA-ICP-MS systems in general, can be found in Gagnon et al., (2003), Van Achterbergh et al., (2001), Shepherd et al., (1998) and Shepherd and Chenery (1995). Comparison of the ratio of Na in the synthetic glass calibration standard (NIST 610) to an internal standard, i.e., the wt. % Na obtained during fluid inclusion

microthermometry, allowed for the quantitative evaluation of the fluid inclusion compositions (Heinrich et al., 2002; Günther et al., 1998). The concentration of Na calculated from the wt. % NaCl eq., of each inclusion was subsequently corrected based on the LA-ICP-MS results, following the method of Audétat et al. (1998). All inclusions in garnet, pyroxene and sphalerite were opened using a traversing technique (Gagnon et al., 2003) rather than straight drilling or stepwise opening (Günther et al., 1998). During a traversed opening, a laser beam of approximately the same size as the inclusion is focused at a distance away from the targeted fluid inclusion, and the beam is traversed across the sample until it is located immediately above the inclusion. Thereafter, the laser beam can drill in to the inclusion. This method allows for the determination of host mineral composition from the pre-inclusion signal, which is particularly useful for minerals with complex compositions that could mask the inclusion signal, and allows a host correction to be performed (Gagnon et al., 2003). Data correction and quantification were done following the method outlined by Gagnon et al. (2003) using the spectral analysis software Peakfit[®], and the precision was determined to be $\pm 30\%$.

The results of LA-ICP-MS analyses indicate that the most abundant cations in the skarn and mineralizing fluids were Na, K, Ca, and Fe (Table 4-4). The compositional similarity of fluid inclusions in grossularitic garnet and low-Fe sphalerite is particularly obvious when comparing the average and median cation concentrations. These concentrations of the major cations also demonstrate that pyroxene and medium-Fe sphalerite-hosted fluid inclusions are compositionally comparable. In grossularitic garnet, the apparent order of abundance of these cations is Na>K>Fe>Ca, in pyroxene it is Na>K>Ca and in both sphalerite varieties it is Ca>Na>K. We suspect that the proportions of Ca and Fe were underestimated in the silicate-hosted inclusions due to swamping of the inclusion signal by the host and similarly that Fe was underestimated in sphalerite because of a significant FeS component. Inclusions in grossularitic garnet containing daughter crystals have similar compositions to the L-V inclusions.

The most abundant trace elements in the skarn and ore-forming solutions were Zn, Pb, Rb, and As. In grossularitic garnet, the relative order of abundance is Zn>Pb>Rb>Sr, while in pyroxene it is Rb>Sr>Ba>As, in low-Fe sphalerite As>Pb>Rb>Zn and in medium-Fe sphalerite Ag>Pb>Rb>Zn. As for the silicates, it is

Table 4-4. Results of LA-ICP-MS analyses of primary fluid inclusions hosted by garnet, pyroxene and sphalerite. All LA-ICP-MS results are listed in Appendix 5. Values are in ppm.

· · ·	Na	Mg	К	Ca	Mn	Fe	Zn	As	Rb	Sr	Ag	Sb	Ba	Pb
Grossulari	tic Garne	et .		•										
SV2550-21B,D ^A	39462	0.0	12814	30	0.3	3.0	2912	120	628	308	9	62.6	355	1804
SV2550-21B*	46118	0.0	4080	0.0	0.2	0.2	2895	0.0	2291	2364	2.2	125	382	2321
SV2550-21B	57712	0.0	3851	7	0.3	0.0	0.0	3.4	0.0	0.0	16	15	0.0	1343
SV2550-21B*	20948	0.0	18922	2908	2.0	2.0	3919	0.0	394	342	44	159	850	875
SV2550-21C*	20698	0.0	33434	31	1.5	2.6	597	253	1433	75	0.0	439	1104	676
SV2550-21D*	17817	0.0	38239	20	0.1	1.5	1.1	0.0	2838	52	0.2	26	30	8404
SV2550-21E,F ^A	35482	0.5	22039	1320	4.2	45	1687	74	619	354	14	65	245	1078
NM-4C,D ^A	48205	0.5	3706	26	1.9	4674	385	20	140	46	1.0	144	30	0.0
<u>Average</u>	38671	0.35	15945	732	2.6	1279	1391	59	639	309	10	103	240	1160
<u>Median</u>	42720	0.01	14721	29	0.47	3.1	373	0.0	341	79	0.4	47	<i>82</i>	706
Pyroxena	2													
6198-153B	1503	0.6	25623	0.5	12	0.1	0.0	0.0	344	340	0.0	0.0	159	0.0
6198-153D	22762	89	8884	859	28	432	0.6	4.3	81	41	2.0	0.0	0.0	0.0
SV2550-3BA	7826	2	2469	3644	60	737	0.2	0.0	103	78	0.0	0.0	5.8	0.1
<u>Average</u>	9549	19	8383	2358	44	529	0.2	0.9	147	123	0.4	0.0	35	0.1
<u>Median</u>	11341	1.0	4484	430	39	324	0.0	0.0	81	41	0.0	0.0	0.0	0.0
Low-Fe Sphaler	ite (SI)													
NM4-B	28308	4724	11118	830173	0.0	0.2	292	891	109	219	0.0	43	109	0.0
6566-383A ^A	13174	0.0	11975	1565	24.8	8	239	822	824	75	0.0	98.1	94	0.0
5382-898B ^A	15542	0.1	7681	37192	0.0	3943	407	10566	71.9	15	0.0	23.5	64.2	1036
SV2550-19B	9223	0.0	994	20842	0.0	0.1	0.0	0.0	47	13	0.0	0.0	21	0.0
SV2550-3A ^A	14992	0.0	3615	12450	0.1	2.0	0.0	2774	47	0.0	7.1	179	0.0	0.0
6566-383F ^A	16611	0.0	4405	9037	59	0.1	2.5	168	182	82	1.4	0.0	49	0.0
6001-435A	21714	0.0	6593	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	13	0.0	0.0
5382-898F	14684	0.0	39	59191	0.0	0.0	12	35	82	29	26	18	129	0.0
<u>Average</u>	15717	249	7182	64199	11	1455	216	4424	237	44	2.3	52	62	382
<u>Median</u>	14684	0.00	1433	14211	0.0	0.1	42	172	68	10	0.0	18	21	0.0
Medium-Fe Sj	ohalerite	(S2)												
4516-65B	1325	0.0	670	30632	0.0	1.4	0.0	41	1.8	0.0	0.0	1.6	1.1	0.0
6695-371F ^A	1545	6	76	18814	0.0	0.0	15	1.3	17	10	57	2.7	4.2	25
<u>Average</u>	9853	30	1953	25393	1.3	162	35	539	56	17	22	12	28	51
<u>Median</u>	905	0.0	97	20416	0.0	0.0	11	2.0	13	1.6	1.8	2.0	3.6	0.0

*LVS inclusion, all others LV. ^Aaverage values.

difficult to obtain quantitative analyses for the main ore metals due to their presence in the host mineral. Inclusions hosted by grossularitic garnet and low-Fe sphalerite also contain the highest quantities of elements such as Sr, Ba, and Rb, suggesting a strong host influence on their fluid compositions. Due to the paucity of inclusions in andradite and their small size, none were analyzed.

Fluid inclusions in grossularitic garnet, pyroxene, and low and medium-Fe sphalerite have median Zn values of 373, 0.03, 42, and 11 ppm, respectively. Their median Pb values are 706, 0.03, 0.001, and 0.0003 ppm, respectively and the concentration of ore metals correlates positively with salinity (Figure 4-12). Although the majority of ore is associated with pyroxene skarn, there is little Zn and Pb in the pyroxene-hosted inclusions. Based on paragenetic relationships, ore deposition occurred after pyroxene formation, and thus although the pyroxene and medium-Fe sphaleritehosted inclusions have comparable compositions and homogenization temperatures, they precipitated at different stages in the evolution of the hydrothermal system. These data also suggest that metal solubility was high yet undersaturated with respect to sphalerite and galena, in the fluids precipitating the silicates. The solubility of metals appears highest when conditions were the most reducing, i.e., during the formation of grossularitic garnet and low-Fe sphalerite, and low during the formation of pyroxene and medium-Fe sphalerite when conditions were more oxidizing. This is actually opposite to what would be expected for chloride complexed metals and suggests that f_{O_2} did not control metal solubility in the mineralizing fluids.

DISCUSSION

Temperature and Composition of Skarn and Ore Forming Fluids

Microthermometric and gas chromatographic analyses of fluid inclusions in garnet, pyroxene and sphalerite demonstrate that fluids trapped by grossularitic garnet and low-Fe sphalerite were relatively reduced, of lower temperature and had higher salinity than those trapped by pyroxene, andraditic garnet, and medium-Fe sphalerite (Figure 4-13). An apparent mixing trend is also evident, progressing from a lower

Figure 4-12. Plots of Zn, Pb, and Ag versus salinity based on quantitative LA-ICP-MS analyses of primary fluid inclusions in grossularitic garnet, pyroxene, low-Fe and medium-Fe sphalerite. The overall positive trend indicating an increase in Zn, Pb and Ag with increasing salinity suggests that the metals were transported as chloride complexes.



Figure 4-13. Trapping temperature versus salinity for all garnet, pyroxene and sphalerite-hosted fluid inclusions. The mineralogic associations are clearly defined by the circled areas showing that grossularitic garnet and low-Fe sphalerite precipitated from higher salinity and lower temperature fluids than andraditic garnet, pyroxene and medium Fe sphalerite-hosted fluid inclusions. A probable mixing trend from lower temperature, higher salinity to higher temperature, lower salinity is marked with an arrow.



NaCl (wt% equiv.)



temperature NaCl (+CaCl₂) brine to a higher temperature fluid (+FeCl₂) with lower salinity. All fluids were H₂O rich and contained minor CO₂, CH₄ and N₂.

Previous microthermometric studies at El Mochito (Vázquez et al., 1998; Schultz et al., 1985), reported homogenization temperatures ranging from 287 to 554°C for sphalerite (n=7), 185 to 374°C for calcite (n=10) and 350°C for pyroxene (n=1) and boiling was evident from the calcite-hosted inclusions. However, this boiling event did not coincide with skarn or ore deposition since the sampled calcite was part of the retrograde assemblage and no evidence of boiling was noted during the current study. These studies also estimated that salinities were low to moderate with maximum values of ~12 wt. % NaCl equivalent; however, they were neither attributed to a particular fluid inclusion population nor a specific mineral host. While the results of the current study indicate a similar homogenization temperature for pyroxene-hosted inclusions were slightly higher, ranging from 340 to 406°C, and microthermometry results of garnet-hosted inclusions and fluid salinities have also been included, which were not noted previously. Our study also differs in the detection and identification of daughter crystals and trapped solids.

Several fluid inclusions hosted in pyroxene from the Port Royal and North Manto orebodies have higher homogenization temperatures and salinities than pyroxene-hosted fluid inclusions analysed from the Salva Vida and Nacional orebodies. As the source of hydrothermal fluids is interpreted to lie to the northeast of the deposit (Ault and Williams-Jones, in press) and these higher temperatures and salinities could therefore reflect the fact that the orebodies were closer to the potential heat and fluid source.

Variation in $\delta^{34}S_{H_{2}S}$ Values-Implications for Water: Rock Interaction

The $\delta^{34}S_{H_2S}$ values for fluids in equilibrium with El Mochito sulphides were calculated using the sphalerite $\delta^{34}S$ values reported previously (Ault and Williams-Jones, in press), average trapping temperatures of fluid inclusions in sphalerite, and the fractionation factors of Ohmoto and Rye, (1979). At these temperatures (412 to 502°C) and the log f_{O_2} values estimated from gas chromatographic analyses of sphalerite (-25.3

to -30.0), H₂S was the dominant sulfur species during ore deposition and $\delta^{34}S_{H_2S} \approx \delta^{34}S_{\Sigma S}$ $\approx \delta^{34}S_{fluid}$. The $\delta^{34}S_{H_2S}$ values for fluids depositing high-Fe sphalerite were calculated using the highest pressure-corrected homogenization temperature obtained for sphalerite (502°C) since the latter appears to have precipitated from a higher temperature fluid than the other, lower-Fe sphalerite varieties. The $\delta^{34}S_{H_2S}$ values for the fluid that deposited galena and pyrrhotite were the same, within 1 decimal place, for the range of temperatures quoted above. Calculated values of $\delta^{34}S_{H_2S}$ for fluids in equilibrium with sphalerite, galena, and pyrrhotite range from -3.7 to +5.4 per mil with a mean of +0.7 per mil (Table 4-5, Figure 4-14). The average value of $\delta^{34}S_{H_2S}$ and by inference the $\delta^{34}S_{\Sigma S}$ for fluid depositing the low and medium-Fe sphalerite varieties was ~0‰. By contrast, the $\delta^{34}S_{H_2S}$ for the fluid depositing high-Fe sphalerite was slightly higher (+3‰), indicating either that there was a contribution of sulfur from another source or that there were changes in the physico-chemical parameters of the ore-forming fluid.

The δ^{34} S values for sphalerite display an overall decrease from northeast to southwest along the Salva Vida-Nacional trend (Ault and Williams-Jones, in press). At the average δ^{34} S_{sulphide} value of 0.1 per mil and the median metal content of 11 ppm Zn for fluids associated with the most abundant sphalerite type, the medium-Fe variety, an increase in pH by 1 log unit can lead to a decrease in sulphide δ^{34} S values by as much as 5 per mil as shown by the star on Figure 4-15. The intersection of the solubility contour for the median Zn value associated with medium-Fe sphalerite with the average δ^{34} S_{sulphide} contour is at a pH of 8.2 and a log f_{O_2} of -24.2 at 465°C. The observed decrease of δ^{34} S values southwest along the Salva Vida-Nacional trend appears to be consistent with the progressive decrease in fluid:rock ratio that would have accompanied interaction of the host rock with magmatic fluids originating in the northeast. In such a rock-dominated setting, the higher pH conditions could have promoted precipitation of sphalerite with lower δ^{34} S values.

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Table 4-5. Sulphur isotope compositions of fluids in equilibrium with sphalerite, galena and pyrrhotite from El Mochito. Calculations were based on the fractionation factors of Ohmoto and Rye, (1979) and pressure-corrected sphalerite-hosted fluid inclusion homogenization temperatures.

Sample	Mineral	δ ³⁴ S (CDT) %	δ ³⁴ S _{H2S} ‰
4526-128	sphalerite (S1)	-2.4	-2.6
2450-8	sphalerite (S1)	-1.2	-1.4
5382-898	sphalerite (S1)	1.3	1.1
6673-419	sphalerite (S1)	3.0	2.8
6622-1067	sphalerite (S1)	-0.4	-0.6
6001-425	sphalerite (S2)	1.6	1.4
5615-89	sphalerite (S2)	-1.8	-2.0
2550-19	sphalerite (S2)	0.4	-3.4
2450-6	sphalerite (S2)	-3.2	0.0
4512-27	sphalerite (S2)	0.2	0.2
5197-92	sphalerite (S3)	3.9	3.8
4360-102	sphalerite (S3)	0.5	0.4
3795-135	sphalerite (S3)	3.1	2.9
1868-105	sphalerite (S3)	5.6	5.4
Avg. sphalerite		0.8	0.6
Avg. SI		0.1	-0.2
Avg. S2		-0.6	-0.7
Avg. S3		3.3	3.1
2450-3	galena	2.0	3.4
5197-92	galena	0.3	1.7
2650-D	galena	0.5	1.9
4526-128	galena	1.1	2.5
2550-19	galena	0.3	1.7
4360-102	galena	-0.6	0.8
5382-898	galena	0.8	2.2
5615-89	galena	-0.6	0.8
Avg. galena		0.5	1.9
4557-26	pyrrhotite	-2.5	-2.7
5203-138	pyrrhotite	-3.5	-3.7
Avg. pyrrhotite		-3.0	-3.2
Avg. sulphides		0.4	0.7

Figure 4-14. Histogram of $\delta^{34}S_{H_2S}$ values for fluids in equilibrium with sphalerite, galena and pyrrhotite. The mean value of +0.7‰ indicates that the sulfur was dominantly magmatic in origin.



Figure 4-15. Log f_{O_2} -pH diagram indicating the conditions of medium-Fe sphalerite formation and how changes in pH affect mineral δ^{34} S values. Sulphur isotopic contours were constructed using the method of Ohmoto (1972) at the temperatures of medium-Fe sphalerite formation. The total sulphur content of the fluid was estimated at 0.1*m* based on the presence of pyrite, pyrrhotite and magnetite, which are associated with the lower temperature variety of sphalerite. Log *K* values for reactions defining predominance fields of sulphur species and stability fields of Fe-sulphide and oxide minerals were calculated using the program Hch (Shvarov and Bastrakov, 1999) with the updated SUPCRT database (Johnson et al., 1991; Shock, 1998). Log f_{O_2} -pH conditions were constrained by the average amount of Zn in medium-Fe sphalerite (assuming ZnCl₂^o to be the dominant Zn complex; Ruaya and Seward, 1986) and the average δ^{34} S sulphide value of 0.1‰, as shown by the location of the star. At these conditions, a decrease in pH by 1 log unit can result in a decrease in sulphide δ^{34} S by as much as 5‰.



Evolution of Hydrothermal Fluids and Formation of Skarn and Ore at El Mochito

Based on the microthermometric data, two end member fluids are evident; an H_2O -NaCl-CaCl₂ brine associated with grossularitic garnet and low-Fe sphalerite and a lower salinity H_2O -NaCl-FeCl₂ fluid associated with pyroxene, medium-Fe sphalerite and andraditic garnet. The results of the microthermometric and gas chromatographic analyses are similar to those for other of other Zn-Pb skarn deposits. The latter have interpreted to reflect magmatic-hydrothermal fluids of varying temperature and salinity, typically 200-500°C and 1 to 60 wt% NaCl eq., with low to negligible X_{CO_2} (Zhao et al., 2003; Bowman, 1998; Jamtveit and Anderson, 1993; Meinert, 1992; Newberry et al., 1991; Megaw et al., 1988; Kwak, 1986; Erwood et al., 1979; Sawkins, 1964). These studies also indicate that magmatic fluids usually dominate during the earliest stages of skarn formation and meteoric waters become progressively more important during the later, retrograde stages, and ore mineralization.

Although an overprint of previous skarn assemblages by Fe-bearing minerals is also common (Kwak et al., 1986; Einaudi et al., 1981), this typically occurs at lower temperature and salinity. Precipitation of Fe minerals (e.g., hedenbergite, andradite, magnetite, and Fe-sulphides) is frequently interpreted to result from dilution of saline orthomagmatic fluids by meteoric water, which sharply decreases the stability of dissolved species like $FeCl_2^{\circ}$ and in turn the solubility of Fe-minerals (Kwak et al., 1986). At El Mochito, however, while the Fe-overprint appears to have coincided with the influx of lower salinity fluids, these fluids had temperatures up to 100°C higher than those responsible for the initial stage of skarn formation. Moreover, fluid inclusion temperatures and stable isotope data also indicate that the hydrothermal fluids had a substantial magmatic component while Pb isotope data indicate that the lead was derived from a nearby magmatic source (Ault and Williams-Jones, in press).

There are several scenarios that can be invoked to explain the contrasting salinities of the two fluids involved in skarn formation and ore deposition at El Mochito, these include: 1) the presence of conjugate magmatic fluids, one a high density brine and the other of low density vapour condensate; 2) mixing of a low salinity vapour condensate and high salinity formational water; 3) mixing of a high salinity magmatic fluid brine and low salinity meteoric fluid; and 4) mixing of a lower salinity magmatic fluid

and high salinity formational water. Formation of the skarn and ore does not appear to have resulted from fluid boiling judging by the lack of vapour-rich inclusions, which precludes scenario 1. Since a vapour condensate would have a lower density than brine it would travel more easily along any flow paths (Hedenquist, 1995), and phases precipitated from such a fluid should be paragenetically earlier. At El Mochito, the earliest silicate phase (grossularitic garnet) precipitated from fluids with the lowest temperatures yet the highest salinities, further eliminating scenario 1 as well as scenario 2. Most skarn systems show an increasing influence of low salinity and low temperature meteoric fluids over time (Einaudi et al., 1981), and while this may be the case at El Mochito for the paragenetically latest gangue phases, the low salinity fluids were much hotter than the brine fluids, eliminating scenario 3.

Accordingly, we propose a model in which two end member fluids, circulating formational waters and orthomagmatic fluids, mix progressively at depth to form the fluids preserved as inclusions in the silicates and sphalerite (Figure 4-16). In this model, block faulting during the Tertiary formed both the Mochito graben and the Honduras Depression. Emplacement of the intrusive source during the mid Miocene, associated with the Padre Miguel ignimbrite, initiated circulation of formational waters sourced in the Yojoa Group carbonates, forming a hydrothermal cell. The formational fluid is likely to have had a high salinity, e.g. >30 wt% NaCl equivalent, since the Yojoa Group carbonates formed in a relatively restricted, evaporative backreef to patchreef environment (Mills et al., 1967). This fluid was likely a typical basinal brine enriched in Cl, Na, and Ca with initial temperatures ranging from 100 to 200°C (Viets et al., 1996). The formational waters were heated by proximity to the igneous source and eventually formed grossularitic garnet skarn at the deposit. With time, a relatively Fe-rich aqueous fluid of lower wt. % NaCl equivalent (<10 wt. %) was exsolved from the magma and mixed with the formational waters thereby increasing the temperature of the latter but decreasing its salinity.

At shallow depths (~2 km) the earliest fluids to exsolve from a crystallizing magma tend to immediately separate into immiscible brine and vapour (Bodnar, 1995; Bodnar et al., 1985; Burnham, 1979). However, at higher pressure, fluid exsolution occurs in the one phase field, resulting in a relatively low salinity liquid (Baker et al,

Figure 4-16. Model of skarn and ore-formation at the El Mochito deposit. Block faulting during the Tertiary formed both the Mochito graben and the Honduras Depression. Emplacement of the intrusive source at depths >3 km during the mid Miocene (?), associated with the Padre Miguel ignimbrite, initiated circulation of highly saline formational waters. A relatively Fe-rich aqueous fluid of lower wt. % NaCl equivalent was later exsolved from the magma and mixed with the formational waters. Formation of skarn and ore occurred as the mixed fluids flowed along the faults bounding the Mochito Graben, reacting and eventually equilibrating with the Átima limestone.





Atima Fn. (+ Mochito Shale)

Todos Santos Fn.

basement (Cacaguapa schist?)

2004; Baker and Lang, 2003; Hedenquist et al., 1998; Shinohara and Hedenquist, 1997; Fournier, 1987). Skarn and ore formation at El Mochito are interpreted to have occurred at depths between 1.5 to 3 km, and fluid exsolution from the parental magma would obviously have taken place at a greater depth, as no fluid source has been discovered below or at depth near the deposit. At these conditions, the first exsolved aqueous phase would have been a fluid of low to moderate salinity, e.g. ~5 wt. % (Bodnar, 1995; Burnham, 1979). This phase may also have been relatively enriched in Fe due to the scavenging of Fe from coexisting crystallized Fe-rich phases (Koděra et al., 1998) and, if in equilibrium with magnetite, may have had Fe concentrations similar to those of either NaCl or KCl (Whitney et al., 1985; Kilinc, 1969). The abundance of iron in skarn environments is frequently explained by the high concentration of iron in chloride solutions equilibrated with granitic magmas (Whitney et al., 1985). Dilution of magmatic fluids by Cl-poor solutions, such as meteoric waters, causes a decrease in iron concentration leading to deposition of Fe-bearing phases (Whitney et al., 1985). By contrast, mixing with a Cl-rich solution could result in an increase of Fe in solution as a result of increased complexation of iron by chloride. We therefore conclude that at El Mochito, basinal fluids of high wt. % NaCl equivalent interacted with a magmatic fluid and with progressive mixing the fluids were heated and dissolved Fe from the magmatic Such a mixing scenario is clearly demonstrated by the plot of trapping source. temperature versus salinity, which shows that the highest temperatures are coincident with the deposition of Fe phases (Fig. 4-13B). Formation of skarn and ore occurred as these mixed fluids flowed along the NE-SW trending faults bounding the Mochito Graben, reacting and eventually equilibrating with the Átima limestone.

A somewhat similar scenario invoking early, heated formational waters was used to explain the occurrence of highly saline fluid inclusions in the cores of grossularitic garnet at the Funtana Raminosa ore district in Italy (Protano et al., 1996). In their model, Protano et al., (1996) concluded that the earliest saline fluids, which were associated with nucleation of grossularitic garnet, were heated formational waters but that the thermal peak for the system was reached later, most likely during the formation of the andraditic rims. Bowman et al., (1987) and Dilles and Einaudi (1992) noted that main stage alteration and ore-formation at the Bingham and Ann-Mason deposits were the result of

the interaction of magmatic and saline formational fluids. However, our model differs substantially from theirs and those for the majority of skarns, as we believe that the subsequent stages of skarn formation at El Mochito were accompanied by an increasing input of orthomagmatic fluids, whereas other studies have concluded that the later stages of skarn and ore formation are typically accompanied by an influx of meteoric waters. Venneman et al., (1993) demonstrated that zoned garnet crystals at El Mochito display isotopic depletion by as much as 4.0 per mil from core to rim and attributed this decrease to mixing between magmatic and meteoric fluids. However, this decrease could also have resulted from an increase in temperature of a fluid with constant δ^{18} O (Venneman et al., 1993). Vázquez et al., (1998) identified a mixing trend for El Mochito between what they interpreted to be an early, magmatic fluid of high δ^{18} O with a meteoric fluid of low δ^{18} O, based on the stable isotope composition of fluid inclusion waters in garnet and sphalerite, respectively. However, their study indicates that the garnet-hosted fluid inclusions have lower δ^{18} O values compared to the fluids extracted from the sphaleritehosted inclusions. Although they did not distinguish among sphalerite varieties, they most probably sampled the medium-Fe sphalerite variety due to its greater overall abundance compared to the other sub-types; they noted that sphalerite-hosted inclusions were difficult to see due to the dark colour and internal reflectance of the mineral. Since sphalerite clearly post-dates garnet, the earliest fluids were in fact isotopically lighter than the later fluids. Given that basinal fluids typically display negative $\delta^{18}O_{H_2O}$ values compared to magmatic fluids (Faure, 1986), we interpret the shift from early, lower $\delta^{18}O_{H_2O}$ values to later, higher $\delta^{18}O_{H_2O}$ values to be the result of progressive mixing of early basinal brines with later orthomagmatic fluids. While there may have been mixing with meteoric fluids at some stage, we do not consider this to have played a role in the formation of skarn and ore.

Based on the positive correlation between the ore metals and salinity (Fig. 4-12), the metals are interpreted to have been transported as chloride complexes. Ore deposition is therefore considered to have resulted from destabilization of the principal Zn and Pb chloride complexes (Ruaya and Seward, 1986; Seward, 1984) through the following reactions:

$$ZnCl_{2}^{*} + H_{2}S = ZnS + 2Cl + 2H^{+}$$
 (2)

$$PbCl_{3} + H_{2}S = PbS + 3Cl + 2H^{+}$$
 (3)

The preceding reactions demonstrate that fluid neutralization could have caused the precipitation of the ore minerals, however, increasing the activity of sulphur would have had a similar effect. Mixing of reduced formational fluids with the comparatively oxidized magmatic fluids would have served to increase the activity of sulphur in the magmatic fluid via the further reduction of sulphur to H2S, which would also have triggered the precipitation of sphalerite and galena. The metals are considered to have been sourced primarily in the orthomagmatic fluids since modern sedimentary brines rarely contain in excess of 250 ppm Zn and 100 ppm Pb (Hanor, 1996; Land, 1995; Kharaka et al., 1987), and LA-ICP-MS analyses indicate that fluids at El Mochito contain median values of Zn ranging from <1 to 373 ppm and median values of Pb ranging from <1 to 706. These values, and the magmatic Pb and S isotopic signatures, suggest that metals were derived primarily from the magmatic fluid. The temperatures of sphalerite formation ranged from an average temperature of 411°C and 465°C for the low and medium-Fe varieties. The average salinities for the low and medium-Fe sphalerite varieties were 14 wt. % NaCl equivalent and 5 wt. % NaCl equivalent, respectively. Phase relations in the system Zn-Fe-S demonstrate that decreasing temperatures favour the reduction of FeS in sphalerite (Vaughan and Craig, 1997). Based on this observation, we suggest that the proportion of magmatic water was higher during deposition of medium-Fe sphalerite than it was during deposition of low-Fe sphalerite. Since skarn formation is known to be a dynamic process and the deposits form in stages with alteration assemblages overprinting one another in both time and space (Meinert, 1998, 1992; Einaudi et al., 1981) the observed variations in sphalerite composition were probably the result of episodic changes in the proportions of magmatic and formational fluids.

CONCLUSIONS

Fluids associated with skarn and ore formation at the El Mochito Zn-Pb-Ag deposit appear to have consisted of an early, reduced, high temperature, high salinity brine, which was responsible for precipitation of grossularitic garnet, and a later, somewhat oxidized, higher temperature, low salinity Fe-enriched fluid that precipitated andraditic garnet and pyroxene. Sphalerite and other ore minerals post-dated skarn formation. The low-Fe sphalerite appears to have precipitated from heated mixed magmatic and formation waters, whereas the medium-Fe variety precipitated from an orthomagmatic-dominated fluid. Both fluids contained very low quantities of CO2. The values of $\delta^{34}S_{H_2S}$ ranged from -3.7 to 5.4‰, with a mean of +0.7‰, indicating that the source of sulphur was primarily magmatic. The variation in $\delta^{34}S_{H_2S}$ values of the sphalerite suggests a progressive decrease in fluid:rock ratio to the southeast. Metals were transported as chloride complexes in magmatic hydrothermal fluids that contained from <1 to ~400 ppm Zn and <1 to ~700 ppm Pb. These fluids precipitated sphalerite and galena through destabilization of the metal-chloride complexes during fluid mixing. Skarn and ore formation is interpreted to have resulted from mixing between deep circulating formational fluids in a system that initially was dominated by formation waters and later dominated by magmatic fluid.

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<u>Chapter V</u>

Conclusions

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CONCLUSIONS

The El Mochito Zn-Pb-Ag skarn deposit exhibits most of the characteristic features of Zn skarns such as the occurrence of chimney and manto orebodies along structural and lithological contacts, and a Mn- and Fe-rich gangue mineralogy consisting of grossular-andradite series garnet and hedenbergite-diopside pyroxene. The deposit is hosted predominantly by Cretaceous limestone and is interpreted to have formed from magmatic-hydrothermal fluids associated with a nearby ignimbrite unit. Skarn alteration proceeded in a series of steps in which limestone was transformed successively into grossularitic garnet skarn, andraditic garnet skarn, and pyroxene skarn. The mass losses and gains determined from the bulk rock chemistry and mineral stabilities in terms of component activities document an early neutralization of the hydrothermal fluid related to increased interaction with the host carbonate, which formed grossularitic garnet skarn, and increasing fluid:rock ratios, during the formation of andraditic garnet skarn and pyroxene skarn. Ore precipitation post-dated silicate skarn formation and metals are zoned outward from Zn and Fe in the cores of the orebodies to Pb and Ag at the peripheries, reflecting the sequential saturation of sphalerite and galena in the fluid with decreasing temperature.

The δ^{34} S values of sphalerite, galena and pyrrhotite and their equilibrated fluid δ^{34} S_{H₂S} values indicate that sulfur was derived from a magmatic sulfur source. This is also indicated by the Pb isotope ratios of galena, which are most similar to those of the Padre Miguel ignimbrite. Variation in the Pb isotope ratios of the altered limestone and the δ^{34} S values of sphalerite along the Salva Vida-Nacional trend suggest that the source of fluid and metals is to the northeast of the deposit. The variation in δ^{34} S values of the sphalerite is consistent with a progressive decrease in the fluid:rock ratio to the southeast and appears to define the limits of alteration.

Based on microthermometry and gas chromatographic analyses of garnet, pyroxene and sphalerite-hosted fluid inclusions, the fluids associated with skarn and ore formation at El Mochito appear to consist of an early, reduced, high temperature, high salinity brine and a later, slightly oxidized, higher temperature, lower salinity Fe-enriched fluid. Mixing and episodic expulsion of these fluids is evidenced by the overlap of paragenetically unique phases that show similar fluid compositions. LA-ICP-MS analyses of garnet, pyroxene and sphalerite-hosted fluid inclusions indicate that the hydrothermal fluids contained up to 5566 ppm Zn and 8404 ppm Pb, and precipitation of sphalerite and galena appears to have occurred through destabilization of the metal-chloride complexes during fluid mixing.

CONTRIBUTIONS TO KNOWLEDGE

The current study of the El Mochito Zn-Pb-Ag skarn deposit has provided insights into the geochemical processes occurring in skarn systems, particularly those with no visible igneous association. These systems are especially interesting for two reasons; 1) they probably have not been explored to their full potential; and 2) they may be transitional to other deposit types such as massive limestone replacement deposits. Although the results of our study of the mass changes occurring during skarn formation were similar to those of other studies, our study differed in that we showed that skarn formation did not occur from the alteration of a single carbonate parent but rather from an evolving protolith. This suggests that previous studies have either over- or underestimated their mass gains and losses if they have not clearly identified the paragenetic relationships among the different skarn varieties, and employed a single protolith. The identification of zoning in the isotopes of Pb and S has proven useful in the determination of the extent of alteration and direction of fluid flow at the deposit. To our knowledge, the zonation patterns of Pb and S isotopes has not previously been used as such, and could be employed as a potential exploration tool. This is also the first study to quantify the composition of skarn and ore-forming fluids in skarn systems through the use of LA-ICP-MS and one of the first to use this technique on garnet, pyroxene and sphaleritehosted fluid inclusions. The observation that paragenetically distinct phases share a common fluid composition, that the progressive increase in temperature and decrease in salinity may be due to an influx of magmatic rather than meteoric fluids, and the occurrence of a higher temperature yet later Fe-overprint has also not previously been noted.

RECOMMENDATIONS FOR FUTURE WORK

The study of skarn deposits and their calc-silicate mineralogy has been on going for nearly a century. However, the advent of new analytical methods enabling the detailed analyses of trace element compositions of minerals and fluids, in conjunction with the availability of up to date and reliable higher temperature thermodynamic data makes it possible to put a new spin on what may have been considered a well-known and universally accepted story. With this in mind, it would be interesting to see whether alteration and mineralization in skarn systems could be modelled through the use of programs like Hch or CHILLER and complemented by various experimental techniques like the use of a flow-through apparatus or high temperature and pressure experimental cells which could mimic the hydrothermal environment. Although the zonation patterns of Pb and S isotopes appear to be useful as a potential means of determining the direction and limit of hydrothermal alteration, the current study was performed at a local scale and along a well-defined structural trend. If such a zonation trend could be identified over a regional scale it might prove helpful in the exploration for skarn-hosted deposits, particularly where no igneous association is evident. The results of the current study also indicate that the El Mochito deposit and environs have not been explored to their full potential and the area appears to be open to exploration. While other areas in the mine are being expanded and new exploration drifts are being driven, the occurrence of several metal and geophysical anomalies around the deposit and Lago de Yojoa, many rich in Sb, suggest that the ore-forming hydrothermal system was regional and skarn mineralization may be transitional to other styles of mineralization.

APPENDIX I

Sample locations

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Composite plan view of the 2500 level of the El Mochito mine showing sample locations.

	9600N	9700N	N0086	N0066	10000N	10100N	10200N	Salva V
3900E								Ida
4000E	×-12							2200
4100E		37						
4200E		25						
4300E			*					
4400E				2-1-1-2-				
4500E		1			\sum	>		
4600E)¥5	<u>له</u>		
4700E								
4800E								
						-2	SV2500-	
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3500E	-262 9500N	9700N	N0066	10100N	10300N	Salva Vid
						a 2550
3700E		2				
3900F						
4100E			1			
4300E				2		
4500E						
4700E			\} <i>\</i>			
				2550-1	ట	





Salva Vida 2650, dotted lines are fault zones.



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3000E 3100E 3200E 3300E 3400E 3500E	NAC23501	$-\frac{-3}{4}$ $+\frac{-3}{4}$ $+\frac{-3}{4}$ $+\frac{-3}{4}$ $+\frac{-10}{-10}$ $+\frac{-9}{-10}$					Nacional 2300/2310/2350, dotted lines are fault zones.
	9100N	9200N	9300N	9400N	9500N	9600N	

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2600E					
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2700E	67.4 -7.4				
2800E	\sum				
	x -10	\sum			
2900E	ي يوني (
			2		
3000E	Zas				
			NAC24		
3100E			× 50 ×		
			Z	$\widehat{}$	
3200F					
	N0006	9100N	9200N	9300N	9400N

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				1 -
				San Juan 2
5400E				50
5500E	-10	SJ2350-9		
5600E	-'12 -'12	-13 x -14		
5700E				
	N0066	10000N	10100N	

San Juan 2350W, dotted lines are fault zones.





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APPENDIX II

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Electron Microprobe Analyses

<u></u>	6466-207 (14)	5215-303 (4)	5615-564 (4)	SV2650-31	SV2650-26	SV2650-23	SJ2350-7
	2(2	26.00	25.00			()	(4)
S10 ₂	36.2	36.89	35.80	36.64	36.63	37.01	37.07
Al ₂ O ₃	10.8	9.19	11.98	11.15	11.27	13.87	14.09
Cr ₂ O ₃	0.0	0.00	0.00	0.00	0.14	0.00	0.04
TiO2	0.5	0.28	0.29	0.13	0.72	0.11	0.34
Fe ₂ O ₃ *	17.0	18.56	15.05	15.18	14.60	12.37	11.31
MnO	1.3	0.60	4.05	3.13	1.49	1.16	1.44
MgO	0.0	0.03	0.01	0.00	0.07	0.06	0.04
CaO	34.0	34.20	31.95	32.80	34.25	34.24	34.62
Total	99.8	99.76	99.13	99.03	99.16	98.81	98.95
End Member	Composition						
Grossular	57	52	56	56	61	70	71
Andradite	40	46	35	37	35	28	25
Pyrope	0	0	0	0	0	0	0
Almandine	0	0	0	0	0	0	0
Spessartine	3	1	9	7	3	3	3
Uvarovite	0	0	0	0	0	0	0

Electron microprobe analyses of grossularitic garnet. Total number of analyses shown in brackets.

Jeol JXA-8900L electron microprobe analyses using ZAF correction; 15 kV, 30 nA; 20 s peak counts; 5 μ m beam. Typical lower detection limits at 3-sigma are 0.02 wt% for SiO₂, Al₂O₃, MgO, Na₂O and K₂O; 0.03 wt% for CaO; 0.04 wt% for FeO and MnO; and 0.05 wt% for TiO₂. (A) Andradite and pyrope standards were used for major elements. *Total Fe as Fe₂O₃

	5615-75 (9)	6622-1065 (15)	6198-155 (4)	5213-196 (4)	SV2550-19 (6)	NM98-2 (2)	SV2550-21	5213-224 (4)	NAC2350-13	4520-50
SiO ₂	35.55	35.89	34.81	35.61	35.84	34.67	35.90	35.43	36.86	35.02
Al_2O_3	4.20	5.60	3.08	4.47	5.90	2.45	4.37	7.09	7.60	9.70
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	8.60
TiO2	0.08	0.21	0.04	0.01	0.36	0.16	0.31	1.04	0.19	0.01
$M_{\rm P}O$	26.38	24.21	28.18	25.32	23.44	28.51	25.72	20.60	21.11	19.99
MgO	0.07	0.69 0.07	1.23 0.03	1.62 0.07	2.64	1.28	0.52	2.03	1.10	0.99
CaO Total	33.45	33.83	32.93	32.34	31.78	32.95	33.51	0.05 32.09	0.21 33.03	0.02 33.32
End Member	<u>Composition</u>	100.51	100.30	99.45	99.99	100.04	100.44	98.32	100.10	98.99
Andradite	73	65	79	71	63	83	71	55	54	
Grossular	25	33	17	25	31	14	27	33	54	50
Ругоре	0	0	0	0	0	0	27	40	43	48
Almandine	0	0	0	ů 0	0	0	0	0	0	0
Spessartine	2	2	3	1	C C	0	U	0	0	0
Uvarovite	0	0	0	0	0	5 0	1 0	5 0	3 0	2

Electron microprobe analyses of andraditic garnet. Total number of analyses shown in brackets.

Jeol JXA-8900L electron microprobe analyses using ZAF correction; 15 kV, 30 nA; 20 s peak counts; 5 μ m beam. Typical lower detection limits at 3-sigma are 0.02 wt% for SiO₂, Al₂O₃, MgO, Na₂O and K₂O; 0.03 wt% for CaO; 0.04 wt% for FeO and MnO; and 0.05 wt% for TiO₂. (A) Andradite and pyrope standards were used for major elements. *Total Fe as Fe₂O₃

	SV2550-27	SV2650-26	NAC2350-3	NAC2450-6	6198-155	6466-207	NM98-2	NAC2450-11	5615-564
	(7)	(5)	(2)	(3)	(11)	(18)	(3)	(3)	(12)
SiO ₂	50.28	49.01	50.64	48.62	50.19	49.33	48.31	48.58	48.87
Al ₂ O ₃	0.49	0.05	0.09	0.52	0.00	0.01	0.13	0.52	0.01
TiO ₂	0.03	0.01	0.00	0.01	0.16	0.18	0.02	0.01	0.30
FeO*	16.40	17.82	17.70	23.16	20.75	22.44	16.99	21.01	15.65
MnO	1.49	6.74	2.89	1.64	1.40	2.81	11.17	3.44	11.53
MgO	7.45	2.94	5.68	2.56	4.25	2.06	0.71	2.87	0.97
CaO	23.85	23.24	23.71	23.39	23.34	22.96	22.69	23.16	22.64
Na ₂ O	0.06	0.02	0.02	0.05	0.06	0.06	0.03	0.14	0.04
K ₂ O	0.00	0.03	0.02	0.03	0.00	0.01	0.02	0.02	0.01
Total	100.04	99.86	100.74	99.98	100.15	99.86	100.06	99.74	100.02
End-Member	Composition								
Hedenbergite	52.6	59.6	57.6	78.8	69.8	77.49	57.47	70.97	53.87
Diopside	42.6	17.6	32.9	15.6	25.5	12.69	4.27	17.26	5.95
Johannsenite	4.8	22.8	9.5	5.7	4.8	9.83	38.26	11.77	40.18

Electron microprobe analyses of pyroxene. Total number of analyses shown in brackets.

Jeol JXA-8900L electron microprobe analyses using ZAF correction; 15 kV, 30 nA; 20 s peak counts; 5 µm beam. Typical lower detection limits at 3-sigma are 0.02 wt% for SiO₂, Al₂O₃, MgO, Na₂O and K₂O; 0.03 wt% for CaO;

0.04 wt% for FeO and MnO; and 0.05 wt% for TiO2.

A diopside-based standard was used for major elements.

*Total Fe as Fe₂O₃

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	NAC2450-1	NAC2350-3	SV2550-27	SV2650-21	6466-207
	(3)	(4)	(1)	(3)	(3)
SiO ₂	37.58	37.57	37.67	37.74	37.84
TiO ₂	0.15	0.09	0.24	0.03	0.05
Al ₂ O ₃	22.89	22.09	22.50	23.62	22.79
Cr ₂ O ₃	0.01	0.02	0.00	0.00	0.00
Fe ₂ O ₃ *	13.21	13.54	14.00	12.32	13.25
MnO	0.18	0.28	0.01	0.14	0.20
MgO	0.05	0.05	0.05	0.02	0.01
CaO	23.34	23.34	23.18	23.64	23.32
Na ₂ O	0.01	0.00	0.00	0.00	0.02
K ₂ O	0.03	0.01	0.00	0.02	0.01
Total	97.44	97.00	97.63	97.52	97.49

Electron microprobe analyses of epidote. Total number of analyses shown in brackets.

Jeol JXA-8900L electron microprobe analyses using ZAF correction; 15 kV, 30 nA; 20 s peak counts; 5 μ m beam. Typical lower detection limits at 3-sigma are 0.02 wt% for SiO₂, Al₂O₃, MgO, Na₂O and K₂O; 0.03 wt% for CaO; 0.04 wt% for FeO and MnO; and 0.05 wt% for TiO₂.

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Diopside and orthoclase standards were used for major elements.

*Total Fe as Fe₂O₃

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						S1		<u></u>		
2	SV2550-19 (5	5) SJ2350-4 (4)	5215-5 (4)	5615-75 (8)	2450-8 (8)	5615-564 (4)	2450-10 (6)	6001-435 (3)	4526-128 (2)	5382-898 (3)
Zn	62.05	62.54	62.84	65.03	62.94	64.21	62.93	61.02	63.63	65.02
Fe	3.66	3.45	3.20	1.44	3.70	2.09	4.10	4.19	2.62	1 47
Cd	0.54	0.63	0.51	0.79	0.50	0.32	0.55	0.69	0.54	0.47
Mn	0.00	0.00	0.00	0.22	0.00	0.48	0.00	0.00	0.00	0.00
Cu	0.02	0.03	0.02	0.01	0.00	0.01	0.05	0.23	0.04	0.00
S	33.07	33.00	33.04	33.09	33.34	32.93	32.91	33.19	33.12	33.09
Total	99.35	99.65	99.60	100.58	100.42	100.04	100.53	99.33	99.95	100.04
Atomic prop	portions									
Zn	0.95	0.96	0.96	0.99	0.96	0.98	0.96	0.93	0.97	0.99
Fe	0.07	0.06	0.06	0.03	0.07	0.04	0.07	0.08	0.05	0.03
Cd	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.05
Mn	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	1.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	1.03	1.03	1.03	1.03	1.04	1.03	1.03	1.04	1.03	1.03
mol% FeS	6.5	6.1	5.6	2.5	6.4	3.7	7.1	7.4	4.6	2.6
		S1		1			<u>\$2</u>			
							Ne l			
	6673-419 (2)	4360-102 (2)	6466-207 (10)	NAC2450-6 (5)	4502-127 (8)	YO1 (4)	2650-24 (6)	2650-25 (3)	4365-526 (5)	5615-89 (2)
Zn	<u>6673-419 (2)</u> 62.61	4360-102 (2) 61.37	6466-207 (10) 62.18	NAC2450-6 (5) 56.02	4502-127 (8) 58.92	YO1 (4) 55.67	2650-24 (6) 60.06	<u>2650-25 (3)</u> 61.27	4365-526 (5)	<u>5615-89 (2)</u>
Zn Fe	<u>6673-419 (2)</u> 62.61 3.55	<u>4360-102 (2)</u> 61.37 4.78	6466-207 (10) 62.18 3.92	NAC2450-6 (5) 56.02 9.23	4502-127 (8) 58.92 6.71	YO1 (4) 55.67 9.06	2650-24 (6) 60.06 6.59	2650-25 (3) 61.27 5.45	4365-526 (5) 57.39 8.81	5615-89 (2) 59.90 5.91
Zn Fe Cd	6673-419 (2) 62.61 3.55 0.51	4360-102 (2) 61.37 4.78 0.52	6466-207 (10) 62.18 3.92 0.58	NAC2450-6 (5) 56.02 9.23 0.57	4502-127 (8) 58.92 6.71 0.61	YO1 (4) 55.67 9.06 0.75	2650-24 (6) 60.06 6.59 0.56	2650-25 (3) 61.27 5.45 0.57	4365-526 (5) 57.39 8.81 0.57	5615-89 (2) 59.90 5.91 0.86
Zn Fe Cd Mn	6673-419 (2) 62.61 3.55 0.51 0.00	4360-102 (2) 61.37 4.78 0.52 0.00	6466-207 (10) 62.18 3.92 0.58 0.27	NAC2450-6 (5) 56.02 9.23 0.57 0.00	4502-127 (8) 58.92 6.71 0.61 0.00	YO1 (4) 55.67 9.06 0.75 0.00	2650-24 (6) 60.06 6.59 0.56 0.04	2650-25 (3) 61.27 5.45 0.57 0.04	4365-526 (5) 57.39 8.81 0.57 0.04	5615-89 (2) 59.90 5.91 0.86 0.00
Zn Fe Cd Mn Cu	6673-419 (2) 62.61 3.55 0.51 0.00 0.00	4360-102 (2) 61.37 4.78 0.52 0.00 0.03	6466-207 (10) 62.18 3.92 0.58 0.27 0.02	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21	4502-127 (8) 58.92 6.71 0.61 0.00 0.04	YO1 (4) 55.67 9.06 0.75 0.00 0.05	2650-24 (6) 60.06 6.59 0.56 0.04 0.01	2650-25 (3) 61.27 5.45 0.57 0.04 0.01	4365-526 (5) 57.39 8.81 0.57 0.04 0.07	5615-89 (2) 59.90 5.91 0.86 0.00 0.00
Zn Fe Cd Mn Cu S	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23
Zn Fe Cd Mn Cu S <i>Total</i>	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop</i>	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 <i>ortions</i>	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop</i> Zn	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 <i>ortions</i> 0.96	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop.</i> Zn Fe	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 ortions 0.96 0.06	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94 0.09	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95 0.07	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86 0.17	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90 0.12	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85 0.16	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92 0.12	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83 0.94 0.10	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17 0.88 0.16	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89 0.92 0.11
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop</i> Zn Fe Cd	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 <i>ortions</i> 0.96 0.06 0.00	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94 0.09 0.00	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95 0.07 0.01	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86 0.17 0.01	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90 0.12 0.01	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85 0.16 0.01	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92 0.12 0.01	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83 0.94 0.10 0.01	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17 0.88 0.16 0.01	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89 0.92 0.11 0.01
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop</i> Zn Fe Cd Mn	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 <i>ortions</i> 0.96 0.06 0.00 2.00	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94 0.09 0.00 3.00	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95 0.07 0.01 0.00	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86 0.17 0.01 0.00	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90 0.12 0.01 0.00	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85 0.16 0.01 0.00	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92 0.12 0.01 0.00	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83 0.94 0.10 0.01 0.00	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17 0.88 0.16 0.01 0.00	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89 0.92 0.11 0.01 3.00
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop</i> Zn Fe Cd Mn Cu	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 <i>ortions</i> 0.96 0.06 0.00 2.00 0.00	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94 0.09 0.00 3.00 0.00	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95 0.07 0.01 0.00 0.00	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86 0.17 0.01 0.00 0.00	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90 0.12 0.01 0.00 0.00 0.00	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85 0.16 0.01 0.00 0.00	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92 0.12 0.01 0.00 0.00 0.00	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83 0.94 0.10 0.01 0.01 0.00 0.00	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17 0.88 0.16 0.01 0.00 0.00 0.00	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89 0.92 0.11 0.01 3.00 0.00
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop.</i> Zn Fe Cd Mn Cu S	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 ortions 0.96 0.06 0.00 2.00 0.00 1.04	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94 0.09 0.00 3.00 0.00 1.04	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95 0.07 0.01 0.00 0.00 1.03	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86 0.17 0.01 0.00 0.00 1.04	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90 0.12 0.01 0.00 0.00 1.03	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85 0.16 0.01 0.00 0.00 1.04	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92 0.12 0.01 0.00 0.00 1.04	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83 0.94 0.10 0.01 0.00 0.00 1.05	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17 0.88 0.16 0.01 0.00 0.00 1.04	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89 0.92 0.11 0.01 3.00 0.00 1.04
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop.</i> Zn Fe Cd	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 <i>ortions</i> 0.96 0.06 0.00	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94 0.09 0.00	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95 0.07 0.01	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86 0.17 0.01	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90 0.12 0.01	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85 0.16 0.01	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92 0.12 0.01	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83 0.94 0.10	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17 0.88 0.16 0.01	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89 0.92 0.11
Zn Fe Cd Mn Cu S <i>Total</i> <i>Atomic prop</i> Zn Fe Cd Mn Cu S	6673-419 (2) 62.61 3.55 0.51 0.00 0.00 33.24 99.90 <i>ortions</i> 0.96 0.06 0.00 2.00 0.00 1.04	4360-102 (2) 61.37 4.78 0.52 0.00 0.03 33.44 100.14 0.94 0.09 0.00 3.00 0.00 1.04	6466-207 (10) 62.18 3.92 0.58 0.27 0.02 33.05 100.01 0.95 0.07 0.01 0.00 0.00 1.03	NAC2450-6 (5) 56.02 9.23 0.57 0.00 0.21 33.33 99.37 0.86 0.17 0.01 0.00 0.00 1.04	4502-127 (8) 58.92 6.71 0.61 0.00 0.04 33.10 99.38 0.90 0.12 0.01 0.00 0.00 1.03	YO1 (4) 55.67 9.06 0.75 0.00 0.05 33.35 98.88 0.85 0.16 0.01 0.00 0.00 1.04	2650-24 (6) 60.06 6.59 0.56 0.04 0.01 33.33 100.55 0.92 0.12 0.01 0.00 0.00 1.04	2650-25 (3) 61.27 5.45 0.57 0.04 0.01 33.54 100.83 0.94 0.10 0.01 0.00 0.00 1.05	4365-526 (5) 57.39 8.81 0.57 0.04 0.07 33.34 100.17 0.88 0.16 0.01 0.00 0.00 1.04	5615-89 (2) 59.90 5.91 0.86 0.00 0.00 33.23 99.89 0.92 0.11 0.01 3.00 0.00 1.04

Electron microprobe analyses of sphalerite.

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Election	microprob	analyses	n spuarer ne	*•						
			S2					S3		
	6622-1067 (2)	5197-92 (2)	6001-425 (2)	4516-65(5)	4512-27 (2)	5226-176 (7)	2650-23 (9)	NAC2350-9 (2)	NAC2450-3 (4)	SV2A (1)
Zn	60.21	59.04	60.39	57.68	58.16	53.76	54.35	53.73	54.62	49.91
Fe	5.87	6.58	5.60	7.17	7.90	11.84	11.81	11.68	10.58	15.19
Cd	0.67	0.49	0.52	0.54	0.61	0.41	0.51	0.76	0.54	0.56
Mn	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.00	0.00	0.00
Cu	0.05	0.00	0.00	0.05	0.00	0.03	0.03	0.01	0.09	0.01
S	33.42	33.49	33.13	33.53	33.13	33.43	33.72	33.33	33.36	33.62
Total	100.22	99.59	99.62	98.96	99.80	99.49	100.42	99.50	99.19	99.28
Atomic prop	portions									
Zn	0.92	0.90	0.92	0.88	0.89	0.82	0.83	0.82	0.84	0.76
Fe	0.11	0.12	0.10	0.13	0.14	0.21	0.21	0.21	0.19	0.27
Cd	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
Mn	5.00	6.00	7.00	0.00	4.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	1.04	1.04	1.03	1.05	1.03	1.04	1.05	1.04	1.04	1.05
mol% FeS	10.3	11.5	9.8	12.7	13.7	20.5	20.3	20.3	18.5	26.3

Electron microprobe analyses of sphalerite.

	1	S3
	1868-105 (2)	3795-135 (2)
Zn	54.71	55.58
Fe	10.73	10.21
Cd	0.55	0.60
Mn	0.00	0.00
Cu	0.00	0.00
S	33.44	33.74
Total	99.42	100.13
Atomic prop	ortions	
Zn	0.84	0.85
Fe	0.19	0.18
Cd	0.00	0.01
Mn	7.00	8.00
Cu	0.00	0.00
S	1.04	1.05
mol% FeS	18.7	17.7

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····	6466-207 (3)	5226-176 (3)	5615-564 (5)	2650-25 (5)	2450-8 (4)	2650-24 (2)	2550-27 (4)	NM2350-3 (4)	2350-3 (4)	4502-34 (4)
Pb	82.53	86.48	87.08	86.47	83.71	81.93	83.13	85.15	84.26	83.48
Bi	1.82	0.00	0.00	0.00	1.31	2.19	1.40	0.41	1.09	1.36
Ag	1.45	0.07	0.04	0.00	1.05	1.70	1.11	0.47	0.88	1.09
S	13.64	13.31	13.53	13.22	13.52	13.58	13.59	13.26	13.52	13.36
Total	99.44	99.86	100.65	99.69	99.60	99.40	99.23	99.29	99.76	99.29
Atomic proportions										
Pb	0.40	0.42	0.42	0.42	0.40	0.40	0.40	0.41	0.41	0.40
Bi	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.01
Ag	0.01	0.00	0.00	0.00	0.01	0.02	0.01	0.00	0.01	0.01
S	0.43	0.42	0.42	0.41	0.42	0.42	0.42	0.41	0.42	0.42
	5615-75 (4)	5197-92 (2)	1868-105 (2)	5615-89 (2)	SV2550-19 (4 6673-419		4360-102	NAC2450-6 (5)	NAC2350-9 (2)	4256-128(2)
Pb	87.04	86.27	86.13	85.60	86.00	85.84	86.83	83.34	83.62	85.66
Bi	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.99	0.31	0.00
Ag	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.60	0.26	0.00
S	13.34	13.52	13.64	13.49	13.55	13.34	13.33	13.44	12.85	12.98
Total	100.46	99.79	99.77	99.08	99.55	99.18	100.16	98.38	97.04	98.64
Atomic proportions										
Pb	0.42	0.42	0.42	0.41	0.42	0.41	0.42	0.40	0.40	0.41
Bi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
<u>S</u>	0.42	0.42	0.43	0.42	0.42	0.42	0.42	0.42	0.40	0.40
	6001-435 (2)	5382-898 (3)	4502-127 (2)	-						
Pb	87.03	86.23	86.38	-						
Bi	0.00	0.00	0.00							
Ag	0.00	0.00	0.00							
S	13.71	13.45	13.49							
Total	100.74	99.68	99.87							
Atomic proportions										
Pb	0.42	0.42	0.42							
Bi	0.00	0.00	0.00							
Ag	0.00	0.00	0.00							
S	0.43	0.42	0.42							

Electron microprobe analyses of galena.

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	P	yrite		Ch	alcopyrite				
2	2650-25 (2)	2650-23 (6)		2450-10	5226-176 (2)				
Fe	47.06	46.36	Cu	33.66	33.36				
Cu	0.02	0.18	Fe	30.50	31.11				
Zn	0.01	0.69	Zn	0.93	0.98				
S	54.02	53.38	s	34.78	34.86				
Total	101.11	100.62	Total	99.87	100.31				
<u>Atomic p</u>	roportions								
Fe	0.84	0.83	Cu	0.53	0.53				
Cu	0.00	0.00	Fe	0.55	0.56				
Zn	0.00	0.01	Zn	0.01	0.01				
<u>s</u>	1.68	1.67	s	1.08	1.09				

Electron microprobe analyses of pyrite and chalcopyrite.

Jeol JXA-8900L electron microprobe using CITZAF correction; 20 kV, 40 nA; 45 s peak counts, except 20 s for Fe and Mn; 2 µm beam. Typical lower detection limits at 3-sigma are 0.01 wt% for Cd and S; 0.03 wt% for Fe and Mn; 0.04 wt% for Zn; 0.05 wt% for Cu; 0.02 wt% for Ag and S; 0.08 wt% for Bi; and 0.09 wt% for Pb. Sphalerite, galena, pyrite and chalcopyrite-based standard for major elements.

Pyrite: Jeol JXA-8900L electron microprobe using CITZAF correction; 20 kV, 40 nA; 45 s peak counts, except 20 s for Ni and Cu; point beam. Typical lower detection limits at 3s are 0.01 wt% for S, 0.02 wt % for Co and Ni, and 0.03 wt% for Fe, As and Cu. Offline correction for As-Fe interference by linear fit of analysed standard composition.

Chalcopyrite: Jeol JXA-8900L electron microprobe using CITZAF correction; 20 kV, 40nA; 40 s peak counts; point beam; Typical lower detection limits at 3s are 0.01 wt% for S, 0.02 wt % for Cu, and 0.03 wt% for Fe, Zn and Ag. Values in brackets are the number of analyses.

APPENDIX III

Bulk Rock Geochemical Analyses of Rock Samples

	SV2650-26 SV2550-18 N2290-10			SV2650-24 SV2650-25 SJ2350-4 SV25			SV2550-19	SV2550-21	\$12350-2	N2350 5	N2250 12
w1%			_				3.2000 17	012050-21	532550-2	112330-3	N2330-13
SiO ₂	40.72	32.73	35.20	24.97	34.19	21.15	31.83	32.61	27 56	31 31	20.38
Al ₂ O ₃	6.41	3.11	2.16	4.89	2.30	1.02	3.35	6.96	0.77	4 07	29.56
TiO ₂	0.70	0.09	0.12	0.24	0.12	0.07	0.15	0.40	0.07	0.22	0.10
Fe ₂ O ₃	15.98	28.22	25.71	40.74	18.49	23.14	17.26	17.99	9.73	18 16	0.10
MnO	3.30	0.77	2.11	0.74	4.07	0.81	2 87	1 18	1 72	2 71	23.13
MgO	2.55	0.12	0.73	2.18	2.05	13.00	1.06	0.44	4.72	2.71	1.31
CaO	28.96	33.12	31.54	18.50	20.57	19.36	24 55	32 26	13 12	0.00	1.33
Na ₂ O	0.04	0.01	0.03	0.02	0.03	0.01	0.01	0.01	0.13	23.80	21.11
K ₂ O	0.00	0.06	0.01	0.04	0.01	0.02	0.02	0.03	0.21	0.01	0.02
P_2O_5	0.15	0.03	0.02	0.08	0.04	0.08	0.05	0.06	0.02	0.06	0.02
LOI	1.86	2.35	1.49	1.40	3.40	2.67	4.52	2.05	8 34	2 01	5.70
Total	100.67	100.61	99.11	93.80	85.27	81.32	85.68	93.98	67 54	4.71 95 95	J.19 95 74
ppm							00100	20.20	07.54	05.05	03.24
Zn	950	619	3673	65168	87477	182424	103774	56628	257076	103418	155500
РЪ	2911	420	1130	991	36831	20138	30358	3544	3482	27870	2100
Cu	5	6	57	108	399	4299	252	521	64057	474	200
Ag	12	42	23	29	50	270	75	52	252	90	130
Sb	8	8	5	9	23	11	34	6	263	28	8
Ba	4	4	2	6	3	4	5	3	16	3	4
As	44	101	118	53	39	264	75	149	21	27	70
Cd	9	5	35	534	707	1958	726	352	1844	719	1031
Ce	758	10	45	6	11	<3	<3	7	<3	4	4
Со	22	37	<1	25	110	70	75	34	135	20	93
Cr	96	16	16	44	25	<5	23	47	<5	43	30
Ni	16	8	1	13	11	4	5	2	22	4	2
Sc	15	1	3	6	3	3	3	5	2	5	3
V	85	19	21	58	26	21	30	44	6	27	18
Sr	22	19	6	8	17	3	17	17	9	3	20
Th	7	2	1	3	2	2	<0.5	4	<0.2	2	<02
U	2	1	3	1	3	<0.5	0.3	2	<0.5	-	<0.5
Y	16	4	4	8	7	2	6	12	2	7	6
Zr	264	40	33	75	42	34	41	50	92	77	32

Bulk rock geochemical analyses of garnet skarns.

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	NM98-2	NM98-3	NM98-4	SV2550-27	N2450-5	NAC2450-0	5 N2450-9	5215-265	5190-129	N2350-3B	N2450-10	4516-64
wt%												
SiO ₂	40.64	58.68	44.02	35.7	38.23	31.93	39.22	38.39	34.73	38.01	23.10	27.17
Al_2O_3	5.95	0.34	0.48	5.25	2.57	7.84	5.06	5.01	15.54	11.52	4.24	4.48
TiO ₂	0.361	0.096	0.037	0.166	0.35	0.37	0.32	0.29	0.71	1.14	0.35	0.32
Fe ₂ O ₃	10.65	13.11	17.83	19.59	20.29	16.82	19.08	16.22	12.65	18.20	30.22	24.11
MnO	9.85	4.91	6.73	0.94	2.32	1.44	2.30	3.75	0.45	0.81	1.14	0.95
MgO	1.13	1.52	2.89	4.4	1.98	1.15	2.08	2.85	3.16	7.18	1.14	2.21
CaO	28.04	16.52	19.62	16.63	20.64	17.94	21.01	18.80	21.55	17.56	16.94	13.30
Na ₂ O	0.02	0.03	0.05	0.02	0.06	0.03	0.05	0.03	0.06	0.05	0.01	0.02
K ₂ O	0.02	0.04	0.01	0.1	0.04	0.04	0.07	0.06	0.11	0.19	0.03	0.07
P_2O_5	0.05	0.02	0.02	0.04	0.7	0.12	0.09	0.07	0.14	0.27	0.01	0.16
LOI	2.02	4.15	1.5	4.84	3.59	3.95	2.98	4.60	6.92	3.79	6.16	5.65
TOTAL	98.73	99.42	93.19	87.68	90.77	81.63	92.26	90.09	96.01	98.72	83.34	78.43
ppm												
Zn	5568	9599	1581	103000	77900	128000	70000	89320	39735	12200	166592	215277
Pb	8681	6558	18134	695	18189	8520	1909	9767	89	47	93	411
Cu	14	4	65	333	412	2240	1699	169	263	697	146	381
Ag	15	11	42	17	51	181	83	101	7	13	28	35
Sb	32	22	45	101	46	79	66	175	91	68	51	149
Ba	6	5	5	25	3	4	10	83	<50	6	26	17
As	19	6	3	35	54	31	39	83	4	6	26	17
Cd	43	94	160	5729	650	1046	554	48	21	30	133	95
Ce	2	1	0	3	16	31	28	585	465	135	1767	585
Со	12	11	17	10	14	37	43	23	38	41	2	13
Cr	66	22	12	35	56	50	45	32	5	19	46	341
Ni	2	2	2	1	10	16	6	42	91	172	35	52
Sc	8	2	1	5	5	11	6	10	14	39	6	11
v	45	10	18	45	44	73	78	6	17	13	4	5
Sr	8	27	11	88	68	184	97	38	106	115	43	35
Th	4	1	1	2	3	4	3	118	1 99	207	51	97
U	2	1	1	6	2	4	2	3	7	11	2	4
Y	12	1	2	9	7	17	13	3	3	7	0	0
Zr	145	52	12	58	129	113	74	9	19	11	8	10

Bulk rock geochemical analyses of pyroxene skarns.

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	SV2600-1	5 5230-456	5213-248	N2350-3A	N2450-1	N2450-2	N2450-7	N2450-11	N2350-1	N2450.8
wt%				112550 511	112+30-1	112450-2	112450-7	112450-11	142550-1	112430-0
SiO ₂	39.81	37.47	41.30	39.67	40.56	40.26	42 74	39 79	27 35	41.83
Al ₂ O ₂	15.53	17.49	12.06	14.20	11.17	14.46	8 4 5	7 79	9.04	11.09
TiO ₂	0.70	0.82	0.61	0.92	0.51	0.63	0.37	0.37	0.49	0.49
Fe_2O_3	13.81	13.13	12.61	13.42	16.79	16.55	17.34	21.09	11.81	15 46
MnO	0.59	0.75	0.71	0.99	1 14	0.82	1.75	2.05	1.16	1 33
MgO	2.56	1.96	4.63	2.61	3.43	1.79	3.20	3.95	2.43	2.67
CaO	22.89	22.87	22.38	22.92	22.49	23.28	22.38	20.22	26.06	19.76
Na ₂ O	0.05	0.04	0.04	0.04	0.06	0.09	0.05	0.06	0.04	0.04
K ₂ O	0.04	0.10	0.01	0.10	0.16	0.14	0.03	0.06	1.05	0.05
P ₂ O ₅	0.18	0.16	0.15	0.18	0.08	0.05	0.09	0.01	0.12	0.13
LOI	3.63	3.52	4.66	3.61	4.41	2.89	4.43	5.51	19.02	4.22
TOTAL	99.79	98.31	99.16	98.66	100.80	100.96	100.83	100.90	98.57	97.07
ppm.										
Zn	186	90	218	468	1550	1650	190	5390	109	22058
Pb	115	25	18	26	98	613	12	14	197	469
Cu	2	8	4	2	85	1705	7	110	5	11
Ag	4	0.9	0.6	<0.4	5	44	<5	<5	2	8
Sb	804	262	77	100	182	245	133	148	<0.4	242
Ba	3	10	<1	15	13	7	24	33	45	16
As	169	58	17	38.2	50	48.6	48	39	49	54
Cd	1	3	2	4	10	11	1	49	14	246
Ce	46	35	64	82	31	22	44	30	1.4	39
Co	84	27	2	2	12	16	20	13	44	23
Cr	106	105	77	136	75	93	51	49	12	70
Ni	24	13	10	2	14	9	19	6	60	14
Sc	23	21	19	18	14	17	9	9	5	14
V	111	132	104	147	83	97	57	52	9	97
Sr	240	410	195	370	237	298	175	190	113	212
Th	12	10	8	11	7	8	4	4	273	7
U	6	5	14	7	3	3	3	3	6	4
Y	17	25	25	28	18	16	19	15	2	21
Zr	184	251	182	278	142	175	111	110	18	110

Bulk rock geochemical analyses of epidote skarns.

APPENDIX IV

Results of Fluid Inclusion Microthermometry

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Mx	Sample	Chip	T _{m(ice)} (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	Т _ь (°С)	T _t (°C)	T _e (℃)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCl
Gr	2550-21	Α	-5.0		-42.8	7.9	337.0	409.0					
Gr	2550-21	Α					340.9	412.9					
Gr	2550-21	Α		-85.1		42.6	378.5	465.4	-50.4		235.3	24.5	18.1
Gr	2550-21	Α		-78.9		45.3	384.4	465.8	-49.6	-43.7	322.0	23.2	22.1
Gr	2550-21	Α		-78.9			375.6	447.6	-49.8	-40.2			
Gr	2550-21	В	-17.8		-67.2	20.8	394.1	472.6					
Gr	2550-21	В					322.9	394.9					
Gr	2550-21	В		-77.8		42.3	370.7	456.8	-54.0		235.9	24.8	17.5
Gr	2550-21	В					347.2	419.2					
Gr	2550-21	в		-76.0			285.2	357.2	-50.3	-37.8			
Gr	2550-21	В		-78.2			307.9	379.9	-51.7				
Gr	2550-21	В		-77.6			363.9	435.9	-52.1				
Gr	2550-21	В		-83.0			358.3	430.3	-53.2				
Gr	2550-21	В		-80.1		39.6	311.7	389	-49.8	· .	204.4	25.5	14.1
Gr	2550-21	В		-76.6		37.9	297.2	372.2	-50.2		164.6	25.8	12.1
Gr	2550-21	В		-79.1		40.9	293.4	365.9	-49.6		216.9	25.5	15.4
Gr	2550-21	С		-70.1		37.6	344.8	444.2	-40.7		173.6	23.5	14.1
Gr	2550-21	D					284.3	410.3					
Gr	2550-21	D		-79.2		41.6	262.2	334.4	-49.9		220.7	25.2	16.4
Gr	2550-21	Ε		-79.1			319.9	391.9	-49.6				
Gr	2550-21	F					347.6	474.6					
Gr	2550-21	F					351.2	423.2					
Gr	2650-26	1	-13.7		-61.8	17.5	325.6	397.6					
Gr	2650-26	1	-8.4		-53.1	12.2	351.8	441.5					
Gr	2650-26	1	-9.1		-52.4	13.0	347.2	442.9					
Gr	2650-26	1	-9.2		-53.7	13.1	346	418					
Gr	2650-26	1	-8.4		-54.2	12.2	356.2	428.2					
Gr	2650-26	1	-7.6		-44.5	11.2	352.7	424.7					
Gr	2650-26	1	-9.2		-53.3	13.1	355.8	444.6					
Gr	2650-26	1					354.4	426.4					
Gr	2650-26	1					354.9	426.9					
Gr	2650-26	1					352.1	424.1					

Results of fluid inclusion microthermometry on primary inclusions. *LVS. All homogenize to liquid.

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Mx	Sample	Chip	$T_{m(ice)}$ (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	Т _ь (°С)	T _t (°C)	T _€ (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCi
Gr	2650-26	1	-8.6		-56.1	12.4	273.3	345					
Gr	2650-26	1	-9.2		-57.5	13.1	268.3	336.9					
Gr	2650-26	1	-8.9		-63.8	12.7	282.1	354.3	-45.2				
Gr	2650-26	1	-8.9		-52.6	12.7	326.9	409.2					
Gr	2650-26	3	-11.2		-58.9	15.2	301.2	427.2					
Gr	2650-26	3	-11.4		-59.2	15.4	310.3	436.3					
Gr	2650-26	3	-15.6		-62.2	19.1							
Gr	2650-26	3	-12.1		-61.8	16.1	304.8	378.3					
Gr	2650-26	3	-16.1		-65.3	19.5	324.9	397.5					
Gr	2650-26	3	-15.3		-62.8	18.9	298.8	368.2					
Gr	2650-26	3	-14.9		-63.1	18.6	285.8	357.8					
Gr	NM-4	С	-6 .7		-45.7	10.1	356.8	452.4					
Gr	NM-4	С	-8.3		-48	12.0	324.1	406.7					
Gr	NM-4	С	-6.3		-49.9	9.6	352.2	424.2					
Gr	NM-4	С	-8.0		-47.3	11.7	351.1	441.5					
Gr	NM-4	С	-8.2		-48.5	11.9	348.0	474.0					
Gr	NM-4	D	-14.0		-57.5	17.8	369.3	451.5					
Gr	NM-4	D	-12.8		-56.2	16.7	354.9	426.9					
Gr	NM-4	D	-13.7		-56.7	17.5	351.6	431.4					
Gr	NM-4	D	-6.3		-46.9	9.6	356.9	428.9					
	<u>Average</u>		-10.5	-78.6	-55.3	20.0	333.7	415.2	-49.7	-40.6	221.7	24.8	
Рх	2450-6	2					349.3	477.6					
Px	2450-6	2	-1.9		-43.5	3.2	344.8	473.1					
Px	2450-6	2					358.2	486.5					
Px	2450-6	2	-1.7		-55.7	2.9	342.6	470.9					
Px	2450-6	2					358.2	486.5					
Px	2450-6	2					352.3	480.6					
Px	2450-6	2					363.7	492					
Px	2450-6	3					348.3	476.6					
Px	2450-6	3					357.4	485.7					
Px	2450-6	3	-1.2		-34.8	2.1	368.3	496.6					
Px	2450-6	3	-1.7		-55.2	2.9	363.2	491.5					
Рх	2450-6	3	-2.7		-51.5	4.5	356.8	485.1					

Mx	Sample	Chip	$T_{m(ice)}$ (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	T _h (°C)	T _t (°C)	T _e (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCl
Px	2450-6	3	-3.4		-51.8	5.6	353.9	482.2					
Px	2450-6	3	-3.1		-48.9	5.1	351.8	461.7					
Px	2450-6	4	-2.6		-53.5	4.3	366.6	490.2					
Px	2450-6	4	-1.6		-54.6	2.7	344.5	462.3					
Px	2450-6	4	-3.4		-52.7	5.6	356.3	465.3					
Px	2450-6	4	-4.2		-54.6	6.7							
Px	2450-6	4					364.3	492.6					
Px	2650-26	4	-4.2		-52.5	6.7	356.3	484.6					
Px	2650-26	4	-3.8		-60.1	6.2	356.4	484.7					
Px	2650-26	4	-4.0		-57.9	6.4	378.7	528.5					
Px	2650-26	4					353.5	481.8					
Px	2450-6	6					351.1	479.4					
Px	2650-26	6	-4.5		-60.9	7.2	358.5	461.3					
Px	2650-26	6	-3.7		-61.3	6.0	371.3	499.6					
Px	2650-26	6	-4.5			7.2	357.6	483.6					
Px	2650-26	6	-4.3			6.9	346.3	445.9					
Px	SV2550-3	В	-2.2		-37.3	3.7	360.2	477.2					
Px	SV2550-3	В	-1.9		-37.5	3.2	360.1	477.2					
Px	SV2550-3	В	-2.3		-38.2	3.9	359.0	487.3					
Px	SV2550-3	В	-2.4		-35.1	4.0	361.2	483.1					
Px	SV2550-3	В	-2.6		-40	4.3	359.3	454.2					
Px	SV2550-3	В	-2.6		-41.8	4.3	359.9	478.4					
Px	NM98-4	D	-2.3		-47.7	3.9	372.2	505.7					
Px	NM98-4	D	-2.7		-42.4	4.5	376.0	504.3					
Px	NM98-4	D	-1.8		-43.2	3.1	376.4	505.4					
Px	NM98-4	D	-1.4		-52.6	2.4	376.3	505.3					
Рх	NM98-4	D	-2.3		-38.8	3.9	367.6	496.6					
Рх	NM98-4	D	-1.7		-50.6	2.9	365.1	493.4					
Px	6198-153	a	-0.8			1.4	339.8	447.2					
Рх	6198-153	а		-72.9			392.5	524.5	-34.3				
Рх	6198-153	а					405.7	537.7					
Px	6198-153	a					393.4	525.4					
Px	6198-153	a					392.8	524.8					
Рх	6198-153	a					385.9	517.9					

Mx	Sample	Chip	T _{m(ice)} (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	T _h (°C)	Т, (°С)	Т _с (°С)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCl
Px	6198-153	a				· · · · · ·	394.1	526.1				···· ···	
Px	6198-153	a					390.1	522.1					
Px	6198-153	a					388.2	520.2					
Px	6198-153	b					345.2	477.2					
Px	6198-153	b		-74.2			390.8	522.8	-39.1				
Px	6198-153	b		-69.8			388.8	520.8	-35.3				
Px	6198-153	b		-68.8			368.6	500.6	-38.7				
Px	6198-153	b		-70.5			348.3	480.3	-39.6				
Px	6198-153	b		-72.6			389.2	521.2	-31.3				
Px	6198-153	c	-7.6		-48.7	11.2	355.4	446.5					
Px	6198-153	d	-5.4	-69.8		8.4	382.5	505.5	-32.2				
Px	6198-153	d	-6.2	-76.6		9.5	363.3	460.1	-31.2				
Px	6198-153	đ	-9.6	-67.7	-58.3	13.5	386.2	518.2	-34.3				
Px	6198-153	d	-9.4	-65.8	-56.3	13.3	367.2	499.2	-34.8				
Px	6198-153	d		-68.5			364.2	496.2	-34.9				
Px	6198-153	d		-70.3			378.2	510.2	-31.6				
Px	6198-153	d	-9.8		-54.3	13.7	357.7	489.7					
Px	NM4A	а	-8.0		-53.6	11.7	349.9	438.9					
Px	NM4A	а	-7.9		-54.4	11.6	352.1	441.8					
Px	NM4A	а	-8		-53.5	11.7	349.9	481.9					
Px	NM4A	а	-7.2		-53	10.7	349.8	440.7					
Рх	NM4A	а	-7.6		-54.7	11.2	347.4	479.4					
Px	NM4A	а	-8.1		-52.9	11.8	349.9	438.8					
Px	NM4A	а					349.5	481.5					
Px	NM4A	а					340.0	472					
Рх	NM4A	а	-9.9		-55.6	13.8	350.8	436.4					
Px	6566-383	c	-10.8		-58.6	14.8	362.8	448.7					
Px	6566-383	c					356.8	488.8					
	<u>Average</u>		-4.4	-70.6	-50.2	6.8	363.9	486.7		-34.8			
S 1	2450-6	2	-13.1		-55.8	17.0	302.8	374.9					
S 1	2450-6	5	-12.7		-33.9	16.6	310.9	384.8					
S 1	2450-6	6	-12.9		-57.6	18.1	309.6	383.0	-49.3	-29.3		13.7	4.4
<u>S1</u>	2450-6	6	-16.2		-56.8	19.6	292.2	368.2					

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Мx	Sample	Chip	$T_{m(ice)}$ (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	T _h (°C)	T _t (°C)	T _e (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCl
S 1	2450-10	1	-12.6		-59.2	16.5	307.3	380.6					
S 1	2450-10	1	-13.9		-58.6	17.7	300.9	371.9					
S 1	2450-10	1	-13.9		-58.6	17.7	300.9	376.9					
S 1	2450-10	1	-12.6		-59.2	16.5	307.3	380.6					
S1	2450-10	2	-13.5			17.3	302.4	374.0					
S 1	2450-10	2	-13.1			17.0	302.4	374.4					
S 1	2550-19	В	-9.6		-51.5	13.1	311.8	389.6		-26.7		10.0	3.1
S 1	2550-19	В	-10.2		-53	14.1	317.2	394.4					
S 1	2550-19	В	-9.9		-44.8	13.8	321.3	400.8					
S 1	2550-19	В	-11.4		-55.3	15.4	349.8	433.0					
S 1	2550-19	В	-8.6		-51.5	16.6	311.8	387.8		-26.7		9.5	7.1
S1	2550-19	В	-9.7		-44.8	13.6	321.3	402.7					
S1	2550-19	В	-11.3			15.3	325.6	401.6					
S1	2550-19	В	-10.5		-38.1	14.5	314.7	401.4					
S1	2550-19	В	-12.7		-56.6	16.6	326.2	402.2					
S1	2550-19	В	-10.7		-50.3	14.7	309.3	385.3					
S1	2550-19	В					306.3	382.3					
S1	2550-19	В	-6.6		-53	10.0	317.2	389.2					
S1	2550-19	В	-8.9		-55.3	12.7	349.8	421.8					
SI	2550-19	В	-6.9		-52.1	10.4	357.1	452.2					
S 1	2550-19	В	-6.5		-56.1	9.9	359.2	431.2					
S1	2550-19	В	-6.2		-50.7	9.5	307.1	379.1					
S1	2550-19	С	-7.3		-32.9	10.9	312.6	388.6					
S 1	2550-19	С	-10.3		-52.2	14.3	320.4	396.4					
S1	2550-19	С	-9.6		-55.7	13.5	318.7	394.7					
S1	2550-19	C	-11.7		-55.8	15.7	327.9	403.9					
S1	2550-19	D	-10.9		-56.8	14.9	328.6	408.2					
S1	2550-19	D	-11.0		-57.2	15.0	339.4	411.4					
S1	5382-898	В	-12.6			16.5	312.2	388.2					
S1	5382-898	В	-4.6		-46.9	8.1	365.2	441.2		-34.8		7.0	1.1
S 1	5382-898	В	-14.3		-68.8	18.0	350.6	426.6	-51.8				
S1	5382-899	В	-16.3		-67 .3	19.6	336.9	412.9	-52.1				
<u>S1</u>	5382-898	В	-11.2		-37.1	15.2							

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Mx	Sample	Chip	$T_{m(ice)}$ (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	Т _ь (°С)	T _t (°C)	T _e (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCl
S1	5382-898	С	-13.9		-63.3	17.7	335.2	411.2	-50.7				
S 1	5382-898	С	-17.5		-63	20.6	343.8	417.4	-55.3				
S1	5382-898	С	-14.8		-60.4	19.6	344.2	420.2	-52.2	-28.3		14.0	5.6
S 1	5382-899	С	-6.2		-48.7	11.2	337.6	432.9		-34.4		9.4	1.8
S1	5382-898	С	-13.4		-55.6	17.3	357.8	433.8					
S1	5382-898	С	-12.4		-57.1	16.3							
S1	5382-898	D	-10.3		-51.8	14.3	332.4	413.8					
S1	5382-898	D	-8.7		-58.2	12.5	337.8	413.8					
S1	5382 -8 98	D	-15.3		-63.8	18.9	329.4	405.4	-55.3				
S1	5382-898	D	-15.2		-62.7	20.1	341.0	437.4	-53.1	-28.6		13.7	6.4
S1	5382-898	D	-14.2		-59.7	18.0	360.6	463.9					
S1	5382-898	D	-16.2		-64.3	19.6	364.1	469.3	-55.1				
S1	5382 -8 98	D	-8.4		-50.7	12.2	333.5	409.5					
S1	5382-898	F	-15.2		-67.7	18.8	324.7	400.7	-58.8				
S1	5382-898	F	-9.7		-55.2	13.6	330.1	406.1					
S1	5382-898	F	-12.4		-63.2	16.3	368.2	478.2					
S1	5382-898	F	-13.9		-55	17.7	337.5	413.5	-49.3				
S1	6695-371	F	-8.8		-47.3	12.6	345.7	421.7	-41.8				
SI	6695-371	F	-6.6		-48.7	10.0	353.8	429.8					
S1	6695-371	F	-6.7		-46.8	10.1							
S1	6695-371	Н	-7 .1		-50.2	10.6	332.6	408.6					
S1	6566-383	D	-15.1		-56.1	18.7	380.4	456.4					
S1	6566-383	F	-10.4		-51.5	14.4	353.1	429.1	-41.6				
S1	6566-383	F	-6.5		-53.8	9.9	357.1	433.1	-40.6				
S1	6001-435	Α	-4.5		-38.4	7.2	362.1	472.9					
S1	NM-4	В	-4.5		-35.5	7.2	311.8	401.4					
S1	NM-4	С	-6.0		-39.8	9.2	347.6	423.6					
S1	NM-4	С	-6.4		-39.7	9.7	343.4	419.4					
SI	NM-4	С	-6.4		-38.8	9.7	345.2	421.2					
S1	NM-4	С					344.4	420.4					
S1	NM-4	С	-6.0		-40.6	9.2	338.2	429.3					
SI	NM-4	С	-6.0		-41.8	9.2	331.6	407.6					
S1	NM-4	С	-5.9		-40.6	9.1	327.2	403.2					

Mx	Sample	Chip	T _{m(ice)} (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	T _h (°C)	T _t (°C)	T _e (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCl
S 1	NM-4	С	-7.1		-42.1	10.6	343.7	434		······································			
S 1	NM-4	С	-6.9		-41.8	10.4	344.5	420.5					
S1	NM-4	С					340.0	416.0					
	<u>Average</u>		-10.5		-52.1	14.3	331.9	411.0	-50.5	-29.8		11.0	4.2
S2	2450-10	1	-1.2		-61.2	2.1	354.3	467.7					
S2	2450-10	1	-0.9		-59.9	1.6	358.8	476.4					
S2	2450-10	1	-1.1		-58.5	1.9	353.6	467.0					
S2	2450-10	1	-1.1		-60.3	1.9	350.5	466.5					
S2	2450-10	3	-0.8		-46.9	1.4	356.5	472.5					
S2	2450-10	1	-0.3		-37.9	0.5	348.6	464.6					
S2	2650-24	2	-1.1		-39	1.9	373.7	501.0					
S2	2650-24	2	-2.7			4.5	367.8	482.5					
S2	2650-24	2	-0.8			1.4	360.1	479.0					
S2	2650-24	2					356.7	472.7					
S2	2650-24	2					354.2	470.2					
S2	2650-24	2	-1.2			2.1	364.8	480.8					
S2	2650-24	2	-1.6			2.7	375.9	501.9					
S2	2650-24	2	-2.3		-48.3	3.9	320.7	414.1	-33.2				
S2	538 2-8 98	D	-2.2		-39	3.7	364.7	480.7					
S2	5382-898	D	-1.1		-38.8	1.9	365.1	486.0					
S2	5382-898	F	-1.7		-53.3	2.9	334.8	450.8					
S2	6566-383	F	-3.3		-40.4	5.4	356.1	462.1	-27.1				
S2	6566-383	F	-3.8		-45.2	6.2	354.6	430.6	-37.4				
S2	6566-383	F	-5.1		-48.8	8.0	368.8	440.8					
S2	6566-383	F	-5.5		-42.1	8.5	360.3	432.3					
S2	6566-383	F					369.5	485.5					
S2	6695-371	F	-3.2		-38.9	5.3	356.1	470.0					
S2	6695-371	F	-2		-33.2	3.4	362.4	477.2					
S2	6695 - 371	F	-3.4		-39.3	5.6							
S2	6695-371	F	-3.2		-38.9	5.3	356.1	449.5					
S2	6695-371	F	-2.0		-33.2	3.4	362.4	455.8					
S2	6695-371	F	-1.9		-40.5	3.2	358.9	474.9					
<u>S2</u>	6695-371	F	-2.8		-37.2	4.6	362.5	478.5					

Mx	Sample	Chip	$T_{m(icc)}$ (°C)	"Transition" (°C)	Frz-ap	wt% NaCl eq.	Т _ь (°С)	T _t (°C)	T _e (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂	wt% NaCl
S2	6695-371	F	-2.6		-37.7	4.3	360.1	476.1					
S2	6695-371	F	-2.6		-38.9	4.3	367.7	483.7					
S2	6695-371	С	-3.5		-39.7	5.7	340.6	416.6					
S2	6695-371	С	-5.1		-42.2	8.0	360.2	436.2					
S2	6695-371	С	-5.2		-43.9	8.1	363.9	467.1					
S2	6695-371	F	-3.2		-36.6	5.3	338.0	443.0					
S2	6695-371	F	-7.9		-49.3	11.6	364.0	457.4					
S2	6695-371	F	-6.6		-48.7	10.0	353.8	447.2					
S2	4516-65	В	-4.2		-50.7	6.7	364.1	480.1					
S2	4516-65	В	-5.3		-48.2	8.3	372.8	494.0					
S2	4516-65	Α	-7.7		-35.2	11.3	367.2	460.6					
S2	4516-65	Α	-7.5		-37.6	11.1	353.0	446.4					
	<u>Average</u>		-3.1		-43.8	4.9	358.3	465.0	-32.6				

Mx	Sample	Chip	T _{m(ice)} (°C)	Frz-ap	wt% NaCl	T _h (°C)	Τ _ι (℃)	Т _е (°С)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂
Ad	2650-26	1	-2.9	-49.2	4.8	368.1	495.1				
Ad	2650-26	1	-2.8	-56.1	4.6	399.4	526.4				
Ad	2650-26	1	-2.4	-53.3	4.0	385.8	512.8				
Ad	2650-26	1	-0.6	-47.7	1.1	378.2	505.2				
Ad	2650-26	1	-1.3	-42.1	2.2						
Ad	2650-26	1				373.8	499.8				
Ad	2650-26	3				342.4	469.4				
	Average				3.4	374.6	501.5				
S 1	5382-898	D	-4.2	-41.0	6.7	290.2	366.2				
S1	5382-898	D	-3.8	-41.0	6.2	311.3	387.3				
S 1	5382-898	В	-5.2	-56.5	8.1	284.5	356.5				
S1	5382-898	В	-4.9	-56.1	7.7	364.0	436				
S1	5382-898	В	-5.4	-54.2	8.4						
S1	6566-383	С				361.9	437.9				
S 1	6566-383	С				365.0	441				
S 1	6566-383	С	-4.1	-38.8	6.6	369.9	479.7				
S1	6566-383	F	-4.8	-42.4	7.6	375.8	451.8				
S1	6566-383	F	-4.5	-45.7	7.2	374.6	450.6				
S 1	6566-383	F	-5.2	-44.2	8.1	384.9	501.3				
S 1	6566-383	F	-5.4	-37.6	8.4	357.7	433.7				
S1	6566-383	F	-4.9	-40.3	7.7						
S 1	6566-383	F	-3.5	-45.9	5.7	361.5	469.4				
S 1	6566-383	F	-3.3	-42.2	5.4	378.3	454.3				
S1	6566-383	F	-3.1	-31.3	5.1						
S 1	6566-383	F	-5.4	-26.2	8.4	331.7	407.7				
S 1	6566-383	F				367.6	443.6				
S 1	6566-383	F				364.1	440.1				
S 1	6695-371	С	-3.5	-39.7	5.7	340.6	416.6				
S1	6695-371	С	-5.1	-42.2	8.0	360.2	436.2				
S 1	6695-371	С	-5.2	-43.9	8.1	363.9	467.1				
S1	6695-371	F	-3.2	-36.6	5.3	338.0	443				
S 1	6566-383	F	-5.2	-45.5	8.1	347.3	423.3		-35.5		
	Average				7.1	352.0	435.4				

Results of fluid inclusion microthermometry on pseudosecondary inclusions. All homogenize to liquid.

Mx	Sample	Chip	T _{m(ice)} (°C)	"Transition" (°C)	Frz-ap	wt% NaCl	T _h (°C)	Τ _ι (°C)	Т _е (°С)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂
G2	2550-21	С	-2.9			4.8	321.7	447.7				
G2	2550-21	В	-1.2		-51.5	2.1	358.2	484.2				
G2	2550-21	С	-3.1		-38.9	5.1	375.6	501.6				
G2	2550-21	D		-75.9			140.0	266.0	-44.2	-31.3		
G2	2550-21	D		-72.2			138.8	264.8	-43.1	-30.0		
G2	2550-21	Α	-4.3		-37.1	6.9	388.3	460.3				
G2	2550-21	F	-4.0		-31.9	6.4	371.7	443.7				
G2	2550-21	в					397.5	469.5				
G2	2550-21	В					360.9	432.9				
G2	2650-26	1					326.4	452.4				
G2	2650-26	1					309.2	435.2				
G2	2650-26	1					301.6	427.6				
G2	2650-26	1					308.6	434.6				
G2	2650-26	1					289.8	415.8				
G2	2650-26	3	-12			16.0	162.2	288.2				
G2	2450-10	1	-2.4		-56.8	4.0	380.6	506.6				
G2	NM-4	D	-11.7		-49.9	15.7	356.5	428.5		-40.6		
	Average					7.6	311.0	421.2				
Ad	2650-26	3	-16.6		-60.1	19.9	221.5	290.1	-53.6			
Ad	2650-26	3	-10.3		-47.7	14.3	200.5	269.1				
Ad	2650-26	1	-8.8		-54.4	12.6	172.9	241.5	-44.8			
Ad	2650-26	3	-10.4		-60.7	14.4	187.4	256.0		-23.6		
Ad	2650-26	3	-15.4		-59.7	19.0	161.3	229.9	-49.3			
Ad	2650-26	3	-16.4		-59.4	19.8	228.6	297.2	-53.8			
Ad	2650-26	3	-17.5		-61.1	20.6	183.2	251.8				
Ad	2650-26	3	-15.6		-62.2	19.2	183.3	309.3				
Ad	2650-26	1	-0.4		-39.8	0.7	320.9	389.5				
Ad	2650-26	1	-4.6		-48.7	7.3	316.1	384.7				
Ad	2650-26	2	-9 .1		-52.2	13.0	338.8	407.4				
Ad	2650-26	2	-8.5		-54.7	12.3	258.1	325.8				

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Results of fluid inclusion microthermometry on secondary inclusions.

All homogenize to liquid.

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Mx	Sample	Chip	T _{m(ice)} (°C)	"Transition" (°C)	Frz-ap	wt% NaCl	Т _ћ (°С)	T _t (°C)	Τ _ε (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂
 Ad	2650-26	3	<u></u>				309.8	378.4				
Ad	2650-26	1	-5.3		-49	8.3	304.9	373.5				
Ad	2650-26	3	-10.4		-58.1	14.4	351.7	477.7				
Ad	2550-21	D	-10.1		-55.7	14.0	120.7	189.3				
Ad	6198-153	A	-8.3			12.0	181.9	250.5	-43.7			
Ad	6198-153	А	-7.3			10.9						
Ad	6198-153	А	-7.9			11.6	177.5	231.5				
Ad	6198-153	Α	-7.3			10.9						
Ad	6198-153	Α	-8.5			12.3	184.4	239.5				
Ad	6198-153	Α	-8.2			11.9	196.5	265.1				
Ad	6198-153	Α	-8.4			12.2	196.2	253				
Ad	6198-153	А	-7.7			11.3	197.3	265.9				
Ad	6198-153	Α	-7.8			11.5	218	278.7				
Ad	6198-153	Α	-8.3			12.0	185	253.6				
	Average					13.0	224.9	296.2				
Px	2450-6	2	-1.8		-44.6	3.1	245.8	318.4				
Px	2450-6	2	-1.9		-42.4	3.2	237.2	307.7				
Px	2450-6	2	-1.2		-31.2	2.1	154.9	221.2				
Px	2450-6	4	-1.1		-38.7	1.9	143.9	199.6				
	Average					2.6	195.5	261.7				
S 1	6001-435	с	-1.8		-34.8	3.1	357.8	433.8				
S1	6001-435	A	-5.3		-31.1	8.3	356.2	432.2				
51	NM-4	С	-4.3		-37.9	6.9	367.9	443.9				
SI	NM-4	с	-4.1		-38.7	6.6	372.1	448.1				
S 1	NM-4	с	-4.3		-38	6.9	371.5	481.3				
S 1	NM-4	с	-4.5		-38.4	7.2	368.1	444.1				
S 1	NM-4	с	-4.0		-39.4	6.4	373.9	486.2				
S 1	NM-4	с	-4.5		-40.3	7.2	341.6	417.6				
S 1	NM-4	С	-4.3		-40	6.9	358.6	434.6				
S 1	NM-4	С	-3.9		-39.6	6.3	314.7	390.7				
S 1	NM-4	с	-4.2		-38.6	6.7	359.2	435.2				
S 1	NM-4	с	-4.5		-41.1	7.2	358.1	434.1				

Mx	Sample	Chip	T _{m(ice)} (°C) "Transition" (°C)	Frz-ap	wt% NaCl	T _h (°C)	T _t (°C)	Т _е (°С)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂
<u>S1</u>	 NM-4	c .	-4.5	-40.8	7.2	358.0	434.0				
S1	NM-4	c	-4.5	-38.6	7.2	350.5	426.5				
S1	NM-4	c	-3.8	-40.4	6.2	361.1	437.1				
S1	NM-4	c	-3.9	-39.2	6.3	360.6	436.6				
S1	NM-4	C	-2.8	-36.8	4.6	294.3	370.3				
S1	NM-4	C	-3.1	-36.6	5.1	296.6	372.6				
S1	NM-4	c	-3.1	-36.9	5.1	280.0	356.0				
S1	NM-4	С	-3.0	-37.2	5.0	287.1	359.1				
S1	2450-6	2				234.8	306.8				
S1	2450-10	2	-0.9	-34.5	1.6	264.2	340.6				
S1	2450-10	1	-0.3	-37.9	0.5	348.6	420.6				
S1	2450-10	2	-0.9	-34.5	1.6	264.2	340.6				
S1	2550-3	A	-2.2	-38.2	3.7	357.0	429.0				
SI	2550-3	A	-2.1	-40.1	3.5	358.9	430.9				
S1	2550-3	A	-4.0	-46.2	6.4	356.5	428.5				
81	2550-3	A	-1.3	-38.4	2.2	354.9	426.9				
SI	2550-3	A	-3.7	-38.9	6.0	354.7	426.7				
S1	2550-3	А	-2.5	-33.4	4.2	350.9	422.9				
S1	2550-3	А	-2.8	-36.9	4.6	353.3	429.3				
S1	2550-3	A	-3.0	-37.3	5.0	351.3	427.3				
S1	2550-3	А	-1.4	-26.9	2.4	345.5	421.5				
S1	2550-3	А				347.6	423.6				
S1	2550-3	A				354.2	430.2				
S1	2550-3	А				353.8	429.8				
SI	5382-898	в	-0.9	-45.2	1.6	326.9	398.9				
S1	5382-898	в	-1.4	-47.7	2.4	365.9	437.9				
S 1	6566-383	D	-5.5	-40.7	8.5	362.0	474.6				
S1	6566-383	D	-4.8	-40.7	7.6	361.0	437.0				
SI	6566-383	F	-1.3	-44.3	2.2	335.2	411.2				
S1	6566-383	Α	-4.6	-46.3	7.3	349.3	425.3				
S1	6566-383	А	-4.1	-39.2	6.6	358.8	434.8				
S1	6695-371	F	-4.2	-41.1	6.7	226.7	302.7				
<u>81</u>	6695-371	F	-4	-36.6	6.4	222.4	298.4				

My	Sample	Chip	T _{m(ice)} (°C) "Transition" (°C)	Frz-ap	wt% NaCl	T _h (°C)	T _t (℃)	T _€ (°C)	Hydrohalite (°C)	Halite dissol'n (°C)	wt% CaCl ₂
	6605 271	F	-43	-40.8	6.9	220.0	296				
SI 01	6605-371	г F	-3.4	-39.5	5.6	219.0	282.2				
51	6605-371	F	-2.9	-39.8	4.8	215.5	291.5				
81 61	6605-371	F	-3.5	-37.1	5.7	193.2	269.2				
S1 S1	6566-383	c	-6.1	-48.4	9.3	370.2	446.2		-40.2		
S1	5382-898	Ē	-14.2	-38.2	18.0	337.7	413.7		-33.8		
S1	5382-898	E	-11.6	-59	15.6	332.1	408.1				
51	5382-898	c	-14.2	-72.2	18.0	342.3	419.8	-53.9			
\$1	5382-898	c	-15.3	-58.7	18.9	345.8	422.4				
S1	5382-898	С	-15.4	-63.2	19.0	340.1	416.1				
S1	5382-898	C	-13.2	-59.7	17.1	348.3	424.3	-54.9			
S1	5382-898	В	-13.6	-68.5	17.4	338.3	410.3	-55.9			
S1	5382-898	в	-3.4		5.6	360.8	436.8				
S1	5382-898	в	-3.8		6.2	314.2	390.2				
S1	5382-898	в	-7.1	-48.5	10.6						
SI	5382-898	в	-7.0	-47.3	10.5						
SI	5382-898	в	-2.1	-37.8	3.5	300.4	376.4				
S1	5382-898	в	-2.2								
S1	5382-898	в	-4.7	-63.1	7.4	331.2	407.2				
S1	5382-898	в				338.0	414				
S1	5382-898	в	-13.2	-24.6	17.1	404.0	480				
S 1	5382-898	в	-10.7	-24.6	14.7	355.3	431.3				
S 1	5382-898	в	-2.2	-58.9	3.7						
S 1	5382-898	в	-3.9	-60.2	6.3						
S 1	5382-898	в	-7.4	-53.1	11.0						
S 1	5382-898	в	-7.9	-55.0	11.6						
S 1	5382-898	в	-6.8	-53.0	10.2						
S 1	5382-898	в	-3.3	-59.9	5.4						
S 1	5382-898	в	-16.8	-68.1	20.1	353.7	429.7	-55.4			
S 1	5382-898	В	-14.2	-60.4	18.0	362.2	438.2	-46.9			
S 1	5382-898	В	-11.6	-49.7	15.6	328.1	404.1				
S 1	5382-898	D	-9.9	-53.3	13.8	338.5	421.8				
	Average				7.4	330.5	407.3				

APPENDIX V

Results of LA-ICP-MS Analyses of Fluid Inclusions

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*LVS inclusion. Na Mg K Ca Mn Fe Zn As Rb Sr Ag Sb Ba Pb														
	Na	Mg	K	Ca	Mn	Fe	Zn	As	Rb	Sr	Ag	Sb	Ba	РЬ
Grossulari	tic Garnet													
SV2550-21D*	17817	0.0	38239	20	0.1	1.5	1.1	0.0	2838	52	0.2	26	30	8404
SV2550-21D	42753	0.0	13593	59	0.5	3.7	4030	185	597	554	3.0	125	254	2470
SV2550-21C*	20698	0.0	33434	31	1.5	2.6	597	253	1433	75	0.0	439	1104	676
SV2550-21B	36171	0.0	12034	0.0	0.2	2.4	1794	55	659	62	15	0.0	456	1138
SV2550-21B*	46118	0.0	4080	0.0	0.2	0.2	2895	0.0	2291	2364	2.2	125	382	2321
SV2550-21B	57712	0.0	3851	7	0.3	0.0	0.0	3.4	0.0	0.0	16	15	0.0	1343
SV2550-21B*	20948	0.0	18922	2908	2.0	2.0	3919	0.0	394	342	44	159	850	875
NM-4C	4503	0.1	708	6	3.4	32524	0.0	0.0	38	0.4	6.6	0.0	0.0	0.0
NM-4C	46478	0.0	281	27	0.1	0.5	0.0	0.0	254	54	0.0	4.1	33	0.0
NM-4C	46000	0.4	0.3	0.0	9.0	10	0.0	0.0	0.0	31	0.5	105	32	0.0
SV2550-21F	50125	0.0	15848	93	0.5	0.7	4.5	0.0	265	501	22	50	419	890
SV2550-21F	16870	0.0	48670	1494	6.0	11	167	0.0	157	27	0.0	56	79	92
SV2550-21F	42687	0.0	20496	25	0.0	1.9	3228	0.1	271	724	0.0	0.0	59	598
NM-4D	66782	0.0	234	19	0.6	24	113	97.0	18	14	0.0	74	35	0.0
NM-4D	60315	2.8	6697	23	0.4	2	0.0	0.0	112	72	0.0	0.0	22	0.0
NM-4D	57988	0.0	8556	36	0.0	5	454	44.6	250	65	0.1	0.0	86	0.0
NM-4D	55369	0.0	9466	71	0.0	151	2127	0.0	307	83	0.0	824	0.0	0.1
SV2550-21E	19798	0.1	7436	1061	0.2	13	292	0.0	358	147	7	84	139	737
SV2550-21E	32874	0.3	27142	0.0	4.2	42	1764	0.0	1072	541	0.4	21	269	1082
SV2550-21E	27026	0.0	20039	10347	2.8	0.4	2318	0.1	1572	562	0.0	83	1182	3177
SV2550-21E	45465	0.0	17318	112	0.9	11	0.2	329.2	364	0.0	0.0	0.0	20	0.0
SV2550-21E	31177	0.1	27852	106	0.6	9	3020	0.0	324	168	0.9	44	95	750
SV2550-21E	56095	0.1	4997	1068	14	156	0.1	0.0	63	0.0	41	0.0	0.0	591
SV2550-21E	45225	5.0	15864	1530	21	287	6.3	0.0	667	178	68	0	0	0.1
SV2550-21E	25878	0.0	30062	1.4	0.0	1.4	3873	223	1324	635	0.3	66	280	3092
SV2550-21E	32568	0.0	28745	0.0	0.2	2.3	5566	333	995	771	31	382	403	1924
<u>Average</u>	38671	0.3	15945	732	2.6	1279	1391	59	639	309	10	103	240	1160
<u>Median</u>	42720	0.0	14721	29	0.5	3.1	373	0.0	341	79	0.4	47	82	706

Results of LA-ICP-MS analyses of primary garnet, pyroxene and sphalerite-hosted fluid inclusions. Values in ppm.

	Na	Mg	К	Ca	Mn	Fe	Zn	As	Rb	Sr	Ag	Sb	Ba	Pb
Pvro	xene													
6198-153D	22762	89	8884	859	28	432	0.6	4.3	81	41	2.0	0.0	0.0	0.0
6198-153B	1503	0.6	25623	0.5	12	0.1	0.0	0.0	344	340	0.0	0.0	159	0.0
SV2550-3B	27	5	4484	10471	39	1879	0.0	0.0	228	235	0.0	0.1	0.0	0.0
SV2550-3B	11341	0.6	810	430	48	8	0.0	0.0	0.0	0.0	0.0	0.0	17	0.0
SV2550-3B	12111	1.0	2111	31	92	324	0.5	0.0	81	0.0	0.0	0.0	0.0	0.3
<u>Average</u>	9549	19	8383	2358	44	529	0.2	0.9	147	123	0.4	0.0	35	0.1
<u>Median</u>	11726	3.3	3298	644	44	378	0.3	0.0	81	21	0.0	0.0	0.0	0.0
SI Spl	halerite													
NM4-B	28308	4724	11118	830173	0.0	0.2	292	891	109	219	0.0	43	109	0.0
6566-383A	28701	0.0	311	0.0	0.4	31	761	2256	82	4.9	0.0	2.5	31	0.0
6566-383A	4801	0.0	18577	2571	91	0.8	129	0.7	434	0.0	0.0	122	161	0.0
6566-383A	5128	0.0	20502	317	8	0.0	23	113	849	56	0.0	33	55	0.0
6566-383A	14066	0.0	8510	3372	0.5	0.0	42	919	1932	240	0.0	235	128	0.0
5382-898B	13219	0.0	97	62240	0.0	0.0	1894	0.0	3.9	1.2	0.0	1.8	0.0	0.0
5382-898B	26941	0.9	4.9	6400	0.0	27598	5	71244	0.0	0.6	0.0	0.0	0.9	7249
5382-898B	5743	0.0	237	54959	0.0	0.0	49	1012	10	2.7	0.0	35	3.9	0.0
5382-898B	2121	0.0	45917	12687	0.0	1.1	215	1187	0.0	10	0.0	30	0.0	0.0
5382-898B	18283	0.0	1270	41387	0.0	1.2	96	508	61	16	0.0	81	12	0.0
5382-898B	33270	0.0	409	37091	0.0	0.0	280	9	231	71	0.0	0.0	433	0.0
5382-898B	9220	0.0	5832	45581	0.0	0.1	307	0.0	196	0.0	0.0	17	0.0	0.0
SV2550-19B	9223	0.0	994	20842	0.0	0.1	0.0	0.0	47	13	0.0	0.0	21	0.0
SV2550-3A	35	0.0	6119	24900	0.3	4.0	0.0	5138	56	0.0	0.0	288	0.0	0.0
SV2550-3A	29948	0.0	1111	0.0	0.0	0.0	0.0	410	38	0.0	14	70	0.0	0.0
6566-383F	17299	0.0	7376	14211	118	0.1	5	165	296	122	2.7	0.0	71	0.0
6566-383F	15923	0.0	1433	3864	0.0	0.0	0.0	172	68	42	0.0	0.0	28	0.0
6001-435A	21714	0.0	6593	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	13	0.0	0.0
5382-898F	14684	0.0	39	59191	0.0	0.0	12	35	82	29	26	18	129	0.0
Average	15717	249	7182	64199	11	1455	216	4424	237	44	2.3	52	62	382
<u>Average</u> Median	14684	0.0	1433	14211	0.0	0.1	42	172	68	10	0.0	18	21	0.0
S2 Sp	halerite													
4516-65B	1325	0.0	670	30632	0.0	1.4	0.0	41	1.8	0.0	0.0	1.6	1.1	0.0
6695-371F	134	17	41	20645	0.0	0.0	22	0.0	0.0	0.8	167	2.4	0.0	0.0
6695-371F	486	0.0	154	20188	0.0	0.0	17	4.0	23	2.4	3.7	4.7	6	0.0

	Na	Mg	К	Ca	Mn	Fe	Zn	As	Rb	Sr	Ag	Sb	Ba	Pb
6605-371F	4014	0.0	33	15610	0.0	0.0	5	0.0	27	26	0.0	1.1	6	74
Average	9853	30	1953	25393	1.3	162	35	539	56	17	22	12	28	51
<u>Median</u>	905	0.0	97	20416	0.0	0.0	11	2.0	13	1.6	1.8	2.0	3.6	0.0

	Na	Mg	К	Ca	Mn	Fe	Zn	As	Rb	Sr	Ag	Sb	Ba	РЬ
Grossular	itic Garnet											<u> </u>		
SV2550-21A	650	3.6	0.0	11195	73	35596	13	0.4	0.0	1.3	0.0	0.0	0.1	2.3
SV2550-21C	15856	0.0	3016	3.3	0.1	0.1	319	50	150	146	4.0	53	115	479
SV2550-21E	62528	0.3	0.2	367	0.9	11	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.2
NM-4C	4493	56872	0.0	1104	0.5	435	0.0	0.0	19	0.0	0.0	354	0.0	0.1
<u>Average</u> <u>Median</u>	26344 10174	1.3 1.9	1005 0.1	3855 735	25 0.7	11869 223	111 7	17 0.2	50 10	49 0.7	1.3 0.0	18 27	39 0.1	161 1.2
SI Spl	halerite													
5382-898C*	8925	0.0	2498	9407	0.0	0.0	1.7	31	211	74	0.0	0.0	12	0.0
6566-383A	86	0.0	27520	1031	0.2	0.0	0.0	62	3.4	7	0.0	75	11	0.0
6566-383A	2716	4539	16051	1838	5	0.0	803	2591	421	138	0.0	1567	126	0.0
SV2550-3A	2639	0.0	15	28076	0.0	0.1	327	0.0	0.0	0.0	0.0	7	0.2	0.0
SV2550-3A	2202	0.0	168	7066	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.0	1.7	0.0
6566-383F	19029	0.0	14422	0.0	0.0	0.5	0.0	3486	668	12	0.0	232	0.1	0.0
6566-383F	23944	0.0	4539	0.0	0.1	0.3	137	5280	207	9	390	125	17	4411
6566-383F	21785	246	2113	791	6911	0.5	0.1	894	38	8	19	20	9	0.0
6566-383F	29251	0.0	2583	0.0	0.0	0.4	231	0.0	64	0.0	0.0	95	42	0.0
SV2550-19D	0.0	0.0	0.0	0.2	0.0	58974	66	221	129	0.0	0.0	74	0.0	0.0
NM4-C	1236	0.0	0.0	18816	0.0	0.0	36	0.0	0.1	0.0	0.0	0.0	0.0	0.0
NM4-C	259	0.0	0.0	19653	0.0	0.1	133	15	0.0	0.0	0.0	4.9	0.0	0.0
NM4-C	20670	685	5519	0.0	0.0	0.0	255	0.0	72	0.0	4.8	0.0	13	0.0
SV2550-19B	35271	0.0	6202	15535	0.0	0.0	0.0	896	206	53	0.0	0.0	22	0.0
SV2550-19B	27526	0.0	3533	0.0	0.0	0.1	0.0	0.0	52	0.0	0.0	0.0	0.0	0.0
SV2550-19B	2379	0.0	334	15403	0.0	0.2	12942	0.0	78	4.2	0.0	1.2	2559	0.0
5382-898C	21	1460	35081	0.0	0.0	0.0	51	929	65	0.6	3.0	15	6	0.0
5382-898C	9750	0.0	0.0	20906	0.0	0.0	707	179	65	57	0.0	2.5	256	0.0
6001-435A*	215	0.0	75	17603	550	14739	0.0	0.0	0.2	0.7	105	0.2	0.1	0.0
5382-898F	27836	0.0	19254	22499	0.0	0.0	1.8	0.0	183	35	0.0	8	11	0.0
5382-898E	31315	0.0	270	31932	0.0	0.0	6	0.0	195	85	0.0	8	43	573
5382-898E	27050	0.0	5635	28647	0.0	0.0	24	258	217	0.0	0.0	0.0	58	0.0
5382-898E	36839	0.0	6308	27622	0.0	0.0	17	36	269	89	0.0	1.4	72	75

Results of LA-ICP-MS analyses of secondary garnet, pyroxene and sphalerite-hosted fluid inclusions. Values in ppm. *LVS inclusion

	Na	Mg	K	Ca	Mn	Fe	Zn	As	Rb	Sr	Ag	Sb	Ba	РЬ
S1 Sp	halerite													
6566-383F	40956	0.0	21950	0.1	0.0	0.0	0.0	31	3339	57	0.0	25	0.0	0.0
5382-898E	1835	478	0.0	43294	0.0	0.1	8.0	206	0.0	207	0.0	28	0.6	17288
5382-898F	6079	0.0	2004	66220	0.0	0.0	0.0	48	275	13	42	58	73	0.0
5382-898B	26914	5133	205	27116	0.0	0.0	48	0.0	1.7	7	0.0	0.0	25	0.0
5382-898B	10063	1837	129	17454	0.0	0.0	792	0.0	0.0	3.5	0.0	0.0	12	0.0
<u>Average</u>	16202	394	5214	16345	298	2949	631	499	245	26	23	28	129	8 <i>94</i>
<u>Median</u>	<i>9907</i>	0.0	2306	15469	0.0	0.0	20	31	68	7	0.0	6	12	0.0