THE ECONOMIC GEOLOGY OF SCANDIUM, THE RUNT OF THE RARE EARTH ELEMENT LITTER

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Abstract

Scandium is currently in high demand because of a number of technological advances in the aerospace and automotive sectors of the global economy. In this paper, we review the properties of scandium, the geology of the major economic and potentially economic scandium deposits and the processes that may concentrate scandium to exploitable levels. We also show that, although scandium is classified as a rare earth element (REE), it behaves very differently from the rest of its family. The reason for this is that it has an ionic radius very similar to that of iron and magnesium and consequently concentrates easily in major ferromagnesian rock-forming minerals, notably clinopyroxene. Unlike the other REE, it is therefore a compatible element. In many scandium deposits, clinopyroxene is the main ore mineral, although in some deposits, scandium is hosted by minerals that also concentrate the other REE. As is the case for these other REE, the main source of scandium is the mantle and the conveyors of scandium are alkaline igneous rocks (and carbonatites) including Alaskan-type ultramafic rocks. The main magmatic processes involved in scandium concentration are partial melting and fractional crystallization. We model the fractional crystallization of clinopyroxene to predict the scandium content of Alaskan-type ultramafic rocks, and use this information in conjunction with a simple model of fluid-assisted partial melting to explain the genesis of scandium-rich pegmatites. In addition to magmatic processes, aqueous fluids may play an important or even essential role in scandium ore formation. The lack of reliable high temperature thermodynamic data for the aqueous scandium species precludes modeling their transport in hydrothermal fluids. However, the availability of ambient temperature data allowed us to model scandium concentration by rainwater in laterite developed above an Alaskan-type ultramafic complex. This review is no more than an introduction to the economic geology of scandium and the processes that appear to be responsible for the genesis of scandium ores, but one, which we hope will provide a guide to future in-depth studies of scandium deposits and strategies for their successful exploration and exploitation.

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Introduction

Recent advances in material science, and a combination of low density and high melting point, have created a high demand for scandium as a doping agent to produce the high tensile strength aluminum alloys that are required by the automotive and aerospace industries. Indeed, proportionately, scandium provides the greatest strengthening of any element alloyed with aluminum. A high demand for scandium is also developing because of its use in solid oxide fuel cells to improve conductivity and lower the operating temperature, thereby extending cell life. This increased demand has created a strong need to find new resources of scandium. In principle, as scandium is classified as a rare earth element by the International Union of Pure and Applied Chemists (many geologists do not consider it to be a REE), the exploration rush after 2008 and the discovery of many new REE deposits should have resulted in new resources of scandium. This was not the case. Although all the other REE are present in these deposits, albeit in variable proportions, the concentrations of scandium are commonly insignificant.

The most obvious reason for the difference in the behavior of scandium from the other REE is that its ionic radius (75 pm, six-fold coordination; Shannon, 1976) is 13.5 percent smaller than that of the next smallest REE, the heavy rare earth element, lutetium (86 pm, six-fold coordination). Thus, despite having the same charge as the other REE (3+), scandium is unlikely to fit easily into sites of minerals that are typically occupied by Lu and other heavy REE (HREE). In contrast, yttrium, which lies just below scandium in the periodic table, has an ionic radius that is almost identical to the radius of holmium. Not surprisingly, therefore, yttrium behaves like the other HREE.

In this paper, we examine the chemical characteristics of scandium, review its mineralogy and incorporation in common rock-forming minerals, briefly describe the most important scandium deposits, and discuss its behavior in magmas and aqueous fluids. Using this background, we then proceed to a discussion of the processes that potentially concentrate scandium to economic levels in nature.

Discovery of scandium

The first indication that scandium might exist was the observation by Mendeleev in 1869 (Vickery, 1960; Horovitz, 1975) that there was a gap in the periodic table between elements with an atomic mass of 40 (Ca) and 48 (Ti). He predicted an unidentified element, *ekaboron,* that was discovered

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ten years later by the Swedish chemist Lars Nilson (Nilson, 1879) during spectral analysis of the minerals, euxenite [$(Y,Ca,Ce,U,Th)(Ti,Nb,Ta)_2O_6$] and gadolinite [$(Ce,La,Nd,Y)_2FeBe_2Si_2O_{10}$]. Scandium was subsequently isolated and shown to be a soft metal with a silvery appearance. The name, scandium, comes from the Latin name for Scandinavia.

Properties of scandium

Scandium is a transition metal with the atomic number 21, which places it in Group 3 (IIIB) of the Periodic Table, and has an atomic mass of 44.96. It has the electronic configuration $[Ar]3d^14s^2$ and, in nature, occurs exclusively as ^{45}Sc (13 radioisotopes of scandium have been identified, all with half-lives of < 100 days) and in the 3+ oxidation state. In minerals, scandium occurs dominantly in octahedral coordination with an ionic radius 75 pm. This is also the dominant coordination for the other REE, however, their ionic radii range from 103 pm for La to 86 pm for Lu. Thus, unlike the other REE, scandium is a compatible element because of its similarity in size to Mg^{2+}(72 pm) and Fe^{2+} (78 pm), which allows it to substitute easily into major rock-forming minerals, such as pyroxene and amphibole. Scandium reacts with water to form hydrogen gas and is therefore a useful buffer in experimental hydrothermal geochemistry. Its oxides are among the most basic of all the trivalent elements and are readily hydrolyzed. The essential physical properties of scandium are a melting point of 1,538°C, a boiling point of 2,836°C, and a density of 2.99 g/cm^3. Scandium has an electronegativity of 1.36.

Mineralogy

There are only twelve terrestrial minerals known to contain scandium as an essential component (Table 1). Among these minerals, thortveitite is the most important. Indeed, thortveitite is the principal source of scandium in a number of deposits that have been exploited or considered for exploitation. Thortveitite is a greyish-green to black, monoclinic soro-silicate with a vitreous luster, and was first reported from a granitic pegmatite, later referred to as Landsverk 3, in the Iveland-Evje district north of Kristiansand in Norway. The mineral was discovered in 1903, and identified in 1911 by Jakob Shetelig as a new mineral, the first to contain scandium as a major cation (Schetelig, 1922). Between the mid-1950's and early 1960s, 10s of kilograms of thortveitite from the Iveland-Evje pegmatite field were sold to the Dupont Corporation for the extraction of scandium. The price paid for the thortveitite was ~$2,400 per kilogram (~$19,630 today), which was over twice the price of gold at that time (Ronald Werner, pers. comm.). The next most important scandium mineral is bazzite, the type locality for which is the Baveno granite in the Piedmont region of northern Italy (Gramaccioli et al., 2004; Pezzotta et al., 2005). This granite is also the type locality for three other scandium minerals, namely, cascandite, jervisite and scandiobaddingtonite (Table 1), and contains appreciable thortveitite. These minerals occur either in miarolitic cavities within NYF (Niobium-Yttrium-Fluorine) pegmatites or in pegmatitic pods and granophyric facies within K-rich alkaline granite (Pezzotta et al., 2005). They are commonly accompanied by other REE minerals, notably gadolinite-(Y), and fluorite. Although the Baveno granites and their pegmatites have been quarried for ornamental stone for centuries, they have not been exploited for scandium despite the abundance of scandium minerals. The only other potentially important scandium mineral is kolbeckite, which is also found mainly in pegmatites but, unlike bazzite, is a secondary mineral. Kolbeckite forms during weathering as a result of the breakdown of Ti-Nb-W minerals, which supply the scandium, and minerals like apatite and monazite, which supply the phosphate (Dill et al., 2006).

In addition to scandium minerals *sensu stricto*, significant proportions of scandium may be present in a number of HFSE minerals, notably those of Nb, Ta, Ti, W and Sn. For example, columbite [$(Fe,Mn)Nb_2O_6$], tantalite [$(Fe,Mn)Ta_2O_6$] and ixiolite [$(Ta,Nb,Sn,Mn,Fe)_4O_8$] commonly have Sc concentrations up to 2 wt.% (Wise et al., 1998). There is also a variety of ixiolite referred to as scandium ixiolite, which, in the Tørdal pegmatite in Norway, contains up to 12 wt.% Sc (Bergstøl and Juve, 1988). Microlite [$(Na,Ca)_2Ta_2O_6(O,OH,F)$] and pyrochlore [$(Na,Ca)_2Nb_2O_6(O,OH,F)$] in this pegmatite contain up to 4 wt.% Sc. Titanium minerals known to have high concentrations of scandium include ilmenite and ilmenorutile. For example, in the Iveland-Evje district (Norway), the scandium content of ilmenite in the scandium-bearing pegmatites ranges up to 1000 ppm (Neumann, 1961). Ilmenorutile in these pegmatites may contain up to 2000 ppm Sc (Neumann, 1961). Because of the similar ionic radii of Zr and Sc (72 and 75 pm, respectively), one might expect zirconium minerals to have high concentrations of scandium. However, this is generally not the case, although it should be noted that baddeleyite is the principal scandium ore mineral at Kovdor (see below), and can contain in excess of 650 ppm Sc (Kalashnikov et al., 2016). Zirconolite [$(Ca,Ce)Zr(Ti,Fe,Nb)_2O_7$] in this deposit contains 208 ppm Sc, on average (Kalashnikov et al., 2016). In many scandium-rich pegmatites, zircon is conspicuous for its very low concentrations of scandium. For example, in the Tørdal pegmatites of southern Norway, the zircon contains ~13 ppm Sc (Bergstøl and Juve, 1988). However, Kempe and Wolf (Kempe and

Wolf, 2006) reported that zircon from lode-type, granite-hosted tin-tungsten deposits in the eastern Erzgebirge of Germany contains between 600 and 10,000 ppm Sc. Significantly, wolframite in these deposits contains approximately 1,000 ppm Sc, on average, and cassiterite 2,500 ppm Sc, on average (Kempe and Wolf, 2006).

Although most common rock-forming minerals contain negligible scandium, a number of the ferromagnesian silicate minerals are known to accommodate low but significant concentrations of this metal (Schock, 1975; Samson and Chassé, 2016). Furthermore, because of the high abundance of these minerals, the scandium content may be sufficient to yield an economically exploitable resource. The reason that these minerals can accommodate significant scandium is that the ionic radius of Sc^{3+} (75 pm), as noted earlier, is very similar to that of Mg^{2+} (72 pm) and Fe^{2+} (78 pm). Among them, clinopyroxene is the most important and, as will be discussed below, it is the main source of scandium in the Bayan Obo deposit, China, and the Zhovti Vody deposit in the Ukraine. In these deposits, the clinopyroxene typically contains between 200 and 400 ppm Sc. Locally, scandium concentrations in the clinopyroxene are in excess of 1 wt.%. The associated amphibole also contains appreciable scandium, although the concentrations are lower than those of the clinopyroxene.

Scandium deposits

China

Bayan Obo

Approximately 90% of global scandium production (15 tons) comes from the Bayan Obo deposit in China, where scandium is recovered as a by-product of the mining of the other REE and iron (Duyvesteyn and Putnam, 2014). The scandium resource has been estimated at 140,000 tons (Ma, 2012), and is hosted mostly by aegirine, although a small but significant proportion is present in bastnäsite-(Ce), monazite-(Ce) and fluorite (Chao et al., 1992; Fan et al., 2016). These minerals are all interpreted to have formed as a result of the interaction of hydrothermal fluids with dolomitic rocks (H8-dolomite), at a temperature of approximately 450 ºC in the case of aegirine (Smith and Henderson, 2000). The occurrence of aegirine as a scandium ore mineral at Bayan Obo (and at Zhovti Vody) distinguishes scandium from the other REE, which are concentrated to exploitable levels exclusively in minerals, such as bastnäsite-(Ce), monazite-(Ce), and xenotime (Y), which contain the REE as major components.

Rare earth mineralization at Bayan Obo occurred in multiple hydrothermal stages (Smith et al., 2016). However, the main stage of REE mineralization was associated with the development of massive and banded aegirine-monazite-bastnäsite-fluorite ores (Fan et al., 2016; Lai et al., 2016; Smith et al., 2016; Yang et al., 2017). In the latter, aegirine-rich layers host the bulk of the scandium and alternate with monazite-bastnäsite-fluorite-rich layers (Fig. 1). The scandium content of the aegirine is approximately 210 ppm, on average (Zhao, 1987), although Shimazaki et al. (2008) reported scandium concentrations as high as 1.18 wt.% in aegirine associated with biotite in a sample of banded bastnäsite-(Ce) ore. According to Zhao (1987), the highest concentrations of scandium are in the massive aegirine Nb-REE ores (169 ppm); the banded ores contain 155 ppm Sc on average. Current scandium exploitation is based largely on the extraction of this metal from the mine tailings through a combination of roasting (typically with sodium hydroxide) to decompose them and sulfuric or hydrochloric acid leaching at temperatures on the order of 300 ºC and 100 ºC, respectively (Li et al., 2013). The tailings contain 200 ppm Sc on average (Li et al., 2013).

Russia (Soviet Union)

Zhovti Vody

After China, Russia is the next most important scandium producing country. Indeed, the former Soviet Union had the only primary producer of scandium in the World, namely the Zhovti Vody deposit in the Ukraine. This deposit supplied scandium for the AlMgLiSc alloys used in the manufacture of MIG fighter jets during the Cold War (Duyvesteyn and Putnam, 2014). After the end of the Cold War, a US-Russian consortium continued to produce a 2% Sc-Al alloy from the ores until 1997, and mining activity continued until 2003. The deposit comprised a resource of 7.4 Mt, grading 105 ppm Sc that also included substantial reserves of iron and uranium (Mikhaylov, 2010).

Like Bayan Obo, the Zhovti Vody deposit contains aegirine as its main scandium-bearing mineral. The aegirine (and associated riebeckite) is of metasomatic origin, and largely replaced amphibole in magnetite amphibolites (Tarkhanov et al., 1992). Approximately 70 % of the scandium is hosted

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by aegirine; the riebeckite hosts 14 % of the scandium (Tarkhanov et al., 1992). Aegirine also occurs as veins and as a breccia cement. Two types of scandium ores were recognized on the basis of grade. The lower grade ores (50-100 ppm Sc) are accompanied by uranium (150-600 ppm U) and elevated concentrations of other REE (800-1500 ppm REE_2O_3), whereas the high grade ores (100-200 ppm Sc) have lower concentrations of other REE (500-750 ppm REE_2O_3), but high concentrations of vanadium (Tarkhanov et al., 1992).

Kovdor

The most important and largest producer of scandium in Russia is the Kovdor baddeleyite-magnetite-apatite deposit, which contains a scandium reserve of 420 tons; the grade of the ore is 800 ppm Sc (Kalashnikov et al., 2016). The orebody is in the form of a pipe-like intrusion that cuts foidolite and diopsidised peridotite. It is zoned inwards from a forsterite-dominant, forsterite-apatite phoscorite (outer zone) into an intermediate zone of calcite-poor, magnetite-rich phoscorite and a core of calcite-rich phoscorite and phoscorite-related carbonatite (Liferovich et al., 1998; Kalashnikov et al., 2016). There are also crosscutting veins of calcite and, locally, veins of dolomite carbonatite (Fig. 2a). Although there are five scandium-bearing minerals, baddeleyite (Fig. 2b), pyrochlore, zirconolite, juonniite and ilmenite in the deposit, virtually all the scandium reserve is in baddeleyite (Liferovich et al., 1998; Kalashnikov et al., 2016). The concentration of scandium in this mineral ranges from 275 ppm in the outer zone to 305 ppm in the intermediate zone and 700 ppm in the core (Kalashnikov et al., 2016). The highest concentration, however, is in the calcite carbonatite veins (960 ppm). Although the baddeleyite is clearly of magmatic origin, the process of scandium enrichment is not known. It would appear, however, that it involved the substitution of Sc^{3+} and Nb^{5+} for Zr^{4+} according to the reaction: $2\ Zr^{4+} = Nb^{5+} + Sc^{3+}$ (Kalashnikov et al., 2016).

Tomtor

The other major source of scandium in Russia is Tomtor, one of the World's largest carbonatites. It has elevated concentrations of the REE, including scandium, however, it was the development of a complex weathering crust that raised the concentration of scandium to exploitable levels. The weathered crust ranges from 4 to 20 meters in thickness, and comprises an upper limonitic leached zone and a lower zone of cementation of limonite and francolite, a carbonate-rich fluorapatite [$Ca_5(PO_4)_3F$]. The following REE-bearing minerals have been observed in this weathered crust:

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monazite-(Ce), xenotime-(Y), pyrochlore and crandallite [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$]. Of these minerals, only crandallite is clearly secondary; the other minerals likely represent a residue from the carbonatite. Appreciable scandium is restricted to xenotime-(Y), which contains from 1.1 to 1.7 wt.% Sc (Lapin et al., 2016). A resource of approximately 100 Mt of ore grading 390 ppm Sc has been delineated (Lapin et al., 2016).

Kumir

Finally, a potentially important scandium deposit in Russia is Kumir (Altai, Russia). Although this deposit has not been mined, it contains a relatively large resource. The scandium mineralization is developed along the contact between alaskite (leucocratic porphyritic granite) and clastic sedimentary rocks comprising siltstone and sandstone (Gusev et al., 2009). Several mineralized zones have been identified, ranging up to 1.9 km in length and 250 m in width. Each of these zones contains an endo-subzone and an exo-subzone, the proportions of which vary significantly. The endo-zones comprise so-called ‘white’ ore consisting of albitite with rare veinlets of tourmaline, fluorite and sulfide, whereas the exo-zones (‘black’ ore) consist mainly of fluorite and biotite, with minor proportions of iron oxides, feldspars, micas and thortveitite. Scandium is hosted almost exclusively in tourmaline in the endo-zone, and occurs dominantly as thortveitite in the exo-zone. A total resource of 3.6 tons of scandium has been identified; scandium concentrations in the ores range between 50 and 2400 g/t. Approximately 64 % of the resource is contained in thortveitite and 27 % in tourmaline, with the remainder distributed amongst micas, feldspars and Fe oxides. Although the deposit is clearly metasomatic and it seems likely that the fluids were derived from the alaskites, the origin of the scandium is unknown. Noting the presence of diabase in the area, Gusev et al. (2009) has speculated that these mafic rocks may have supplied the scandium.

Other countries

Thortveitite-bearing pegmatites

Although scandium has not been produced in appreciable quantities outside China and Russia, there are a number of deposits elsewhere with significant potential. Historically, the most important deposits were thortveitite-bearing NYF pegmatites. These deposits are best known from the Iveland-Evje district in Norway, where they were exploited for scandium from the early 20th century to the 1960s (Fig. 3). Despite being small, these NYF pegmatites were attractive because of the high concentrations of scandium in thortveitite (up to 35 wt.% Sc). The thortveitite

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pegmatites of the Iveland-Evje district are classified as rare element pegmatites (Ercit, 2005), and were emplaced in amphibolites, including a large layered mafic-ultramafic complex (the Iveland-Gautestad complex). Only a small proportion of the pegmatites in the district are thortveitite-bearing, and most of them are hosted by the Iveland-Gautestad complex (Fig. 3b). The pegmatites are typically 5 to 10 m wide and zoned. They comprise a narrow aplitic border, a megacrystic wall-zone composed of quartz, plagioclase and biotite, an intermediate K-feldspar-plagioclase zone and a quartz core. The thortveitite is concentrated dominantly in the wall and intermediate zones where it is associated with plagioclase, K-feldspar and/or biotite. Although the genesis of the thortveitite-bearing pegmatites has been strongly debated, recent papers (Pedersen and Konnerup-Madsen, 2000; Müller et al., 2015) have concluded that they resulted from partial melting of the Iveland-Gautestad complex. Much less attention has been given to the origin of the scandium. However, Goldschmidt (1934) noted that scandium is not an element typically associated with acidic rocks, whereas it is an important component of basic rocks. This, and the fact that the Iveland-Evje pegmatites are hosted by amphibolites, led him to the conclusion that the scandium was extracted from the amphibolites by the pegmatitic magma. This view was subsequently challenged by Neumann (1961), who, without providing an alternative hypothesis, noted that the scandium content of amphibolite adjacent to thortveitite-bearing pegmatites is no different from that of amphibolite adjacent to barren pegmatite.

Thortveitite-bearing pegmatites also have been reported from a number of other localities, notably the Befanamo and Berere districts in Madagascar. Unfortunately very little is known about the occurrences of thortveitite-bearing pegmatites in Madagascar. They have been described as abyssal-type pegmatites by Ercit (2005). One of them, the Befanamo pegmatite, produced 38 kg of thortveitite until mining stopped in 1955 (Murdock, 1963). Perhaps the most significant feature of the Madagascar locality is that, as in Norway, the pegmatites are all hosted by amphibolite (Ercit, 2005).

In North America, the only occurrence of thortveitite-bearing pegmatite is from Ravali county (Montana). There, the thortveitite occurs as micron to mm size crystals in fluorite-bearing granitic pegmatites and their host metagabbro, which are located within the Crystal Mounting fluorite deposit (Foord et al., 1993). The deposit was evaluated as a potential scandium resource in 1984 but never brought into production (Foord et al., 1993). The pegmatites are distributed over an area

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of 1 km^2 in several tabular fluorite bodies formerly exposed over areas ranging from 100 m^2 to about 10,000 m^2 and extending to a depth of less than 200 m below the surface. The thortveitite is associated with clinopyroxene, amphibole, biotite, magnetite and the REE minerals, fergusonite (Y), xenotime-(Y) and allanite-(Ce). In the metagabbro thortveitite accompanies edenite, hornblende, magnetite and biotite. The diopside and edenite contain up to 3.1 wt.% and 1.1 wt.% Sc, respectively. Although the origin of the scandium is unknown, it seems likely, by analogy with the Iveland-Evje pegmatite and Madagascar localities, that the source was the metagabbro.

Laterites

Although, as noted above, thortveitite-bearing pegmatites have produced scandium, it has recently become clear that future production outside China and Russia is most likely to come from laterite deposits. Among these, one of the most important is the Nyngan deposit in New South Wales, Australia, for which a mining lease has just been awarded. This deposit is developed in laterite that formed over the Gilgai igneous complex, an Alaskan-type intrusive suite comprising monzonite, hornblendite, hornblende pyroxenite, magnetite pyroxenite, olivine pyroxenite and dunite (http://www.scandiummining.com). The complex is concentrically zoned from an ultramafic core to rocks of intermediate/felsic composition at the margins. The laterite profile, which reaches 75 m thick, consists from the bottom up of fresh rock, weathered rock, saprolite, limonitic laterite (mainly goethite), and hematitic laterite. Significantly, the highest bedrock concentrations of scandium are in the pyroxenite and magnetite pyroxenite (104-110 ppm), whereas in the olivine pyroxenite and dunite the concentrations decrease to 75 and 55 ppm, respectively (there are no data for the other rock types). The highest grades in the laterite are in limonitic laterite overlying pyroxenite and magnetite pyroxenite. Bulk samples of the limonitic laterite (741 kg) and saprolite (371 kg) yielded Sc concentrations of 347 ppm and 258 ppm, respectively, whereas the hematitic laterite is effectively barren (http://www.scandiummining.com). A measured and indicated resource of 12 Mt grading 261 ppm Sc has been delineated. Although the nature of the scandium mineralization has not been investigated, high scandium recovery (79 %), using an ion exchange method (http://www.scandiummining.com), suggests that the scandium may be present largely as an adsorbed species on the surfaces of the ferric oxy-hydroxide phases that make up the limonitic laterite. Accordingly, we envisage concentration of scandium to have resulted from its primary incorporation as a trace metal in pyroxene and its subsequent liberation to pore water during

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weathering. The high capacity of ferric oxy-hydroxides, e.g., goethite, to adsorb metals likely ensured the enrichment of scandium in the laterites.

In addition to Nyngan, there is a second lateritic scandium deposit in Australia, the Syerston deposit, which is at an advanced stage of exploration. Like the Nyngan deposit, the Syerston laterites are underlain by an igneous complex (the Tout complex) that is concentrically zoned from ultramafic rocks (dunite and clinopyroxenite) in the core to rocks of mafic composition near the margins (www.cleanteq.com/syerston-project). The scandium mineralization is concentrated above the pyroxenite. Accelerated preferential weathering of the ultramafic core led to the development of a 35-40 m thick laterite that thins towards its margins. As at Nyngan, the profile consists from the bottom up of fresh rock, weathered rock, saprolite, limonitic laterite (mainly goethite), and hematitic laterite (Fig. 4). Locally, however, there is also an overlying transported laterite. Scandium grades increase sharply from the saprolite into the overlying limonitic laterite, where they reach a maximum and decrease gradually into the hematitic laterite (Fig. 4b) According to Chassé et al. (2017) the bulk of the scandium (80 vol. %) is adsorbed onto the surface of goethite and the remainder 20 vol. % has substituted for Fe^{3+} in the structure of hematite. The deposit has a measured and indicated resource of 21.7 Mt, grading 429 ppm Sc assuming a cut-off grade of 300 ppm Sc (www.cleanteq.com/syerston-project).

Syenite-hosted deposits

A deposit that is currently being explored for its scandium potential and shows considerable promise is Misery Lake in northern Québec, Canada. The deposit is hosted by a ferrosyenite facies of a Proterozoic syenitic pluton emplaced in A-type granites, and was initially explored for the other rare earth elements, which locally reach concentrations of several weight percent (Petrella et al., 2014). This mineralization occurs largely in the form of LREE-enriched fluorapatite and britholite $(Ce,Ca,Th,La,Nd)_5(SiO_4,PO_4)_3(OH,F)$. In contrast, the scandium is hosted entirely by hedenbergitic clinopyroxene with a relatively consistent concentration of 800 ppm Sc. Scandium grades in several drill holes exceed 150 ppm over many tens of meters and locally reach 300 ppm in cumulate horizons.

Scandium reservoirs

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In order to gain an understanding of how scandium concentrates in nature, it is first necessary to consider the potential sources of this metal. The major reservoirs for any element that concentrates in the crust are the mantle, the oceanic crust, and lower, middle and upper continental crust. The accepted value for the concentration of scandium in the primitive mantle is 16 ppm (Palme and O'Neill, 2014) and in oceanic crust it is between 34 and 48 ppm (Klein, 2003). In the continental crust, scandium concentrations decrease from the lower part (31 ppm) to the upper part (14 ppm) (Rudnick and Gao, 2014).

Mineral-melt and melt-melt partitioning

An important observation that emerged from our review of scandium deposits is that clinopyroxene can be a major host for scandium, both as a primary igneous mineral as well as a product of metasomatic processes. In the case of igneous clinopyroxene, it is therefore likely that scandium has a strong preference for the mineral over the melt. In view of this and the possibility that other major rock-forming minerals may also preferentially concentrate scandium, we have reviewed the available partitioning data for olivine, orthopyroxene, clinopyroxene, plagioclase, amphibole, feldspar and biotite, i.e., most of the main rock-forming minerals. Of these minerals, only orthopyroxene, clinopyroxene, biotite, amphibole and olivine may take up scandium preferentially over the melt, and even for these minerals, the size of the partition coefficient is strongly dependent on the composition of the magma.

Bedard (2005, 2007, 2014) has reviewed the partitioning of scandium between olivine, orthopyroxene and clinopyroxene, and silicate melts. In the case of olivine, the partition coefficient (D) varies as a function of pressure, temperature, forsterite content and melt SiO_2, H_2O, MgO and FeO content. However, the principal control on the D value is the MgO content of the melt; D values increase with decreasing melt MgO content. The same is true for the D values of orthopyroxene and clinopyroxene. It is also worth noting that Li^+ can promote the incorporation of Sc^{3+} in olivine through a coupled substitution involving the replacement of Mg^{2+} (Grant and Wood, 2010). The same may also be true for orthopyroxene and clinopyroxene. Equations enabling the calculation of partition coefficients for olivine, orthopyroxene and clinopyroxene have been formulated by Bedard (2005, 2007, 2014) based on data from natural and experimental systems. In Figure 5 (a-c) we make use of these equations to produce predictive plots of the corresponding mineral-melt partition coefficients for scandium as a function of MgO melt content.

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Also shown on these plots, is a selection of the partition coefficients reported in the literature. As similar plots are not available for amphibole and biotite, we used the partition data for scandium reported in the GERM database (https://earthref.org/KDD/e:21/) and references therein to develop equations for the partitioning of scandium between these minerals and melt. Plots showing these data and lines representing the least squares fits to them are provided in Figure 5 d and e. It is evident from Figure 5 that all of the ferromagnesian minerals referred to above have a wide range of mineral-melt scandium partition coefficients, and that these coefficients decrease with increasing melt MgO content. The highest coefficients are for clinopyroxene and reach ~ 200, and those for amphibole may also reach high values (144). In contrast, the partition coefficients for orthopyroxene and biotite are less than 30 and those for olivine are less than 10. Moreover, the minimum partition coefficients for these three minerals are less than 1; at high MgO content scandium prefers the melt (Figs. 5a, b and e). For clinopyroxene and amphibole, except at extremely high MgO melt content, the minimum partition coefficient is greater than 1, i.e., scandium prefers the mineral (Fig. 5c). In summary, as expected from our review of the economic geology of scandium deposits, clinopyroxene is predicted by the partitioning data to be a major host for scandium.

As discussed earlier, scandium behaves very differently from the other REE and, whereas the latter typically concentrate as REE minerals, scandium can reach ore-forming concentrations in clinopyroxene. The reason for this is that the small ionic radius of scandium permits it to partition very strongly into clinopyroxene over the melt, whereas the other REE, being significantly larger, are much less compatible in clinopyroxene. In Figure 6, we illustrate the clinopyroxene-melt partition coefficients for all of the REE as a function of the ionic radius. Data taken from Olin and Wolff (2010) and Adam and Green (2006) are presented for the partitioning of the REE between clinopyroxene and felsic (high FeO) and mafic (high MgO) melts, respectively. Also shown are D_o values (the partition coefficients for the ideal radius) reported by Olin and Wolff (2010) for the M1 and M2 sites (felsic melts) and curves drawn to help visualize the distribution of the data. As is evident from Figure 6, the distribution of the REE closely represents the form of that predicted by the lattice strain model for clinopyroxene (Wood and Blundy, 1997), and all of the REE, except for Sc, Tm, Yb and Lu in felsic melts and Sc, Yb and Lu in mafic melts, partition preferentially into the M2 site. The partition coefficients for this site are less than 6.5 for felsic melts and less than 1 for mafic melts, respectively. The remaining REE partition into the M1 site and, except for

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Sc, their coefficients range between 3.9 and 6.1 and between 0.39 and 0.49 for felsic and mafic melts, respectively (Fig. 6). The corresponding partition coefficients for Sc are 143 and 2.15, respectively, i.e., they are very close to the maximum predicted partition coefficients for the ideal M1 radius in clinopyroxene for these melts. In summary, the contrast between the ionic radius of scandium and those of the other REE satisfactorily explains why only scandium can concentrate in clinopyroxene.

The only systems for which scandium melt-melt partitioning data are available are carbonate-silicate and fluoride-silicate melts. According to Martin et al. (2013), scandium partitions strongly into the silicate melt of anhydrous carbonate-silicate systems; the partition coefficients, $D_{carb/sil}$, are reported to be in the range of 0.13 to 0.66, with most values being less than 0.25. In hydrous systems, however, the partition coefficients are somewhat higher, generally between 1.1 and 1.9, and thus favor the carbonate phase weakly. In contrast, scandium partitions strongly into fluoride melts with fluoride/silicate partition coefficients generally ranging from 16 in Na-rich systems to 53 in K-rich systems (Shchekina and Gramenitskii, 2008).

Aqueous geochemistry

As mentioned earlier, scandium occurs exclusively in the 3+ oxidation state in nature, and has a relatively small ionic radius (75 pm). It thus has a high charge to radius ratio (Z/r) and in hard-soft-acid-base (HSAB) terminology is a hard cation (Pearson, 1963). Accordingly, it will tend to form strong aqueous complexes with hard ligands like OH^- and F^-. The data that are available for scandium at ambient temperature confirm this prediction. Scandium forms very strong complexes with both of these ligands. Formation constants (ß) have been determined experimentally for $Sc(OH)^{2+}$, $Sc(OH)_2^+$ and $Sc(OH)_3^0$ at ambient temperature and their values are listed in Table 2. Although formation constants for scandium hydroxide species have not been determined experimentally at higher temperature, theoretical extrapolations of the ambient temperature values have been reported by Shock et al. (1997). The latter data indicate that scandium hydroxide species have similar or slightly greater stability at elevated temperature relative to their stability at 25 °C (Table 2). Significantly, these values are lower than the formation constants for the corresponding Y species (Shock et al., 1997). This is a little surprising given the much smaller radius of the Sc^{3+} ion and thus its greater capacity to bond with hard ligands like OH^- (Pearson, 1963).

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As predicted, scandium also forms very strong complexes with F^- (ScF^{2+}, ScF_2^+ and ScF_3^0); the log ß values for ScF^{2+}, ScF_2^+ and ScF_3^0 at 25 ºC are listed in Table 2. These values are several orders of magnitude higher than the corresponding formation constants for the yttrium fluoride species (Luo and Millero, 2004), and unlike their hydroxy counterparts, the relative stability of the scandium and yttrium species is consistent with hard-soft-acid-base theory (Pearson, 1963). Unfortunately, there are neither experimental data nor theoretical predictions of the stability of scandium fluoride complexes at elevated temperature. However, by analogy with what is known of the behavior of the other REE (Migdisov et al., 2009; Loges et al., 2013), it is reasonable to assume that scandium fluoride complexes will be even more stable at such temperatures.

Another ligand that merits consideration is chloride. Although chloride is a borderline ligand, its concentration in most natural aqueous fluids is orders of magnitude higher than that of OH^- and F^-. As a result, even though it is predicted to form weaker complexes with scandium, the concentrations of these complexes could be sufficient for scandium transport. Unfortunately, there is a little agreement on their stability at ambient temperature, with values for the first formation constant ranging from -0.8 to 1.07 (Wood and Samson, 2006). However, there is agreement that the species are relatively unstable, suggesting that scandium transport by chloride species may be unimportant at ambient temperature. It is nonetheless possible that the stability of scandium chloride complexes is much greater at elevated temperature, as has been shown for the other REE (Migdisov et al., 2009). This remains to be demonstrated experimentally.

Magmatic concentration processes

From the previous discussion, it is evident that magmatic processes have played a major role in the concentration of scandium. In the case of Kovdor, scandium is present in economic concentrations because of its enrichment in a phosphorous-rich basic alkaline magma (phoscorite) as well as carbonatite magma, and its partitioning into baddeleyite. At Bayan Obo, although the scandium is concentrated mainly in clinopyroxene of metasomatic origin, it is likely that the source of the scandium was a carbonatitic magma (Smith et al., 2016 and references therein). Scandium at Tomtor is likewise associated with a carbonatite. In this deposit, however, the scandium mineralization is concentrated in a weathering crust. At Misery Lake, the scandium mineralization is hosted by a syenite in which it occurs exclusively in clinopyroxene. Thus, scandium concentration in the Earth's crust, in large part, is associated with the emplacement of alkaline igneous rocks and carbonatites, and in this respect its behavior is very similar to that of the other REE. Unlike the other REE, however, which are concentrated mainly in REE-dominant minerals (e.g., monazite-(Ce), xenotime-(Y), fluocerite-(Ce)), scandium in alkaline igneous rocks is concentrated mainly in major Fe-bearing rock-forming minerals, notably clinopyroxene, or simple oxides like ilmenite and baddeleyite.

Two processes that can explain the association of alkaline igneous rocks and carbonatites are extreme fractional crystallization of a carbonated nephelinite magma and silicate-carbonate liquid immiscibility. In the case of the former, scandium would partition strongly into the early-forming silicate phases and thus, the residual carbonate magma would contain extremely low concentrations of this element. As discussed previously, scandium would also partition strongly into a silicate melt coexisting immiscibly with carbonate melt, unless the system is hydrous (Martin et al., 2013). Even in the case of hydrous systems, however, scandium does not favor the carbonate melt strongly. Indeed, the partition coefficients range between 1 and 1.9. The manner in which scandium is incorporated in carbonate melts is unknown. What is known is that unlike silicate rocks, which concentrate scandium primarily in clinopyroxene, carbonatites concentrate scandium mainly in early-crystallizing zirconium minerals, such as baddeleyite and zirconolite, and early-crystallizing phosphate minerals, such as juonniite and xenotime-(Y). In the case of the two zirconium minerals, the reason for the uptake of scandium is probably the similarity of the ionic radius of zirconium (72 pm) to that of scandium (75 pm); xenotime-(Y) is a structural analog of zircon that preferentially incorporates the heavy and thus smaller REE.

Another process that may be important in the concentration of scandium in alkaline igneous rocks is fluoride-silicate liquid immiscibility. In contrast to its behavior in silicate-carbonate melt systems scandium, like the other REE, has been shown experimentally to partition very strongly into the fluoride liquid as discussed earlier (Shchekina and Gramenitskii, 2008). Although fluoride-silicate immiscibility has not been shown to concentrate scandium in nature, Vasyukova and Williams-Jones (2014; 2016) have provided compelling evidence that this process played a major role in the concentration of the other REE to economic levels in the Strange Lake pegmatites, Canada. Significantly, despite its low concentration in the fluoride melt, ~23 ppm, the scandium concentration in the silicate melt was below the detection limit of 4 ppm (unpublished data).

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In addition to alkaline igneous rocks and carbonatites, scandium can also reach high concentrations in clinopyroxenites of layered igneous complexes (Webb, 2014). Indeed, the Nyngan and Syerston lateritic deposits described earlier are underlain by Alaskan-type ultramafic complexes ranging in composition from peridotite through pyroxenite to gabbro and monzonite. These complexes are interpreted to be the products of fractional crystallization of magmas originating from the melting of the mantle plumes that generate ocean island basalts (Ishiwatari and Ichiyama, 2004; Pirajno et al., 2008).

In order to predict the probable concentration of scandium in Alaskan-type layered complexes, we have modeled their formation via fractional crystallization using the program PELE (version 7.0; Boudreau, 1999). This program allows the user to establish equilibrium conditions for assemblages involving silicate liquid, minerals and water, based on free energy minimization considerations. The user is able to trace the evolution of a magma undergoing fractional crystallization, including the partitioning of trace elements between minerals and the liquid. The trace element evolution is determined from the initial concentration, which is input by the user, and mineral-melt partition coefficients for each element. The crystallization and melting are modeled by trace element equations using the phase proportions to determine the bulk distribution coefficients (Bedard, 2005, 2007, 2014).

As Alaskan-type layered igneous complexes are believed to be the products of fractional crystallization of magmas similar to those forming continental flood basalts (Ishiwatari and Ichiyama, 2004; Pirajno et al., 2008), we have assumed Columbia River basalt starting compositions. Those selected were for the Tammany Creek/Eden and Goose basaltic suites of Hooper (2000), and represent the most silicic, alkali-rich basalt and the least silicic basalt respectively (Table 3). The starting scandium concentrations were 31 and 41 ppm, respectively. The initial temperature was assumed to be 1250 ºC and the initial pressure 2.5 kbar. Oxygen fugacity was assumed to be buffered by QFM. Olivine was the first mineral to crystallize, and on further cooling was joined by plagioclase, and then clinopyroxene. In order to simulate the formation of the different layered units, we assumed that the fractionation would be controlled by the rate of settling of the major rock-forming minerals under gravity, and this would be determined by the relative differences in their density. Based on their compositions in the simulation, the density of olivine, clinopyroxene and plagioclase was determined to be 4.1, 3.5 and 2.7,

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respectively (orthopyroxene did not saturate in the magma). Accordingly, all the olivine that crystallized was assumed to form a monomineralic layer at the bottom of the magma chamber, which was covered, in turn, by layers of clinopyroxene and plagioclase.

From our earlier discussion, it is evident that scandium concentrates preferentially in clinopyroxene, and thus clinopyroxenite was the target of our modelling. The fractionation of scandium into the clinopyroxenite was calculated at 10 ºC intervals of cooling using the partition coefficient for the corresponding melt composition (MgO content), which was determined from the equation in Figure 5c, and the mass of clinopyroxene that crystallized. As crystallization of olivine also affects the concentration of scandium in the melt, its contribution was similarly calculated (Fig. 5a); plagioclase was assumed not to incorporate scandium. The scandium content of the clinopyroxene layer was thus taken to be the weighted average of the scandium concentration of each batch (10ºC) of clinopyroxene crystallized.

In Figure 7, we show the results of our modeling using the Tammany Creek/Eden starting composition (Table 3). These results indicate that the scandium concentration of the melt was unchanged from its initial value of 31 ppm until the temperature had dropped to 1130 ºC. This marked the onset of olivine crystallization. As the olivine-melt partition coefficient is considerably less than unity for the corresponding MgO content of the melt (3 wt.% MgO), the effect of olivine crystallization was simply to increase the scandium concentration of the residual melt. The same was true for the crystallization of plagioclase, which began at 1100 ºC. The scandium concentration of the melt consequently increased to 41 before clinopyroxene started to crystallize at 1030 ºC (Fig. 7). Over the next 90 ºC decrease in temperature, the scandium concentration of the melt remained relatively constant (41 ppm) due to the compensating effect of the removal of scandium from the melt by the crystallizing clinopyroxene. Below this temperature (940 ºC), however, the progressive increase in the clinopyroxene-melt partition coefficient due to the decreasing MgO content of the melt (Fig. 5c) outweighed the scandium concentrating effect of a decreasing mass of liquid. The scandium content of the first clinopyroxene crystal to form was 139 ppm and rose steadily to a concentration of 530 ppm in the last clinopyroxene to crystallize. Crystallization of clinopyroxene terminated at 900 ºC after 66% crystallization of the magma. At this temperature, the cumulative effect of clinopyroxene crystallization was to produce a layer with an average scandium content of 208 ppm. A similar model using the Goose starting composition yielded an average scandium content of 263 ppm.

The values reported above for the scandium concentrations of the modeled pyroxenites are significantly higher than those reported for clinopyroxenites in layered igneous complexes. For example, the scandium concentration of pyroxenite in the Gilgai complex was analyzed to be 110 ppm and that of an olivine clinopyroxenite at Sulawesi, to be 90 ppm (Maulana et al., 2015). It should be noted, however, that clinopyroxenite typically contains appreciable concentrations of other minerals, e.g., olivine and orthopyroxene. Indeed, in the examples cited above the proportion of clinopyroxene is roughly 50%, thus our calculations based on the Tammany Creek/Eden- and Goose-basalt-derived pyroxenites would predict scandium concentrations of 104 and 131 ppm, respectively, i.e., values that are quite similar to those observed in nature. It should also be noted that our model proceeded to an advanced stage of crystallization (66 %), in which the silica content of the residual melt was that of a typical granite (72 wt% SiO_2). If, however, the model had been terminated after 50 % crystallization (61 wt% SiO_2; andesite), the scandium concentration in the pyroxenite layer would have been 155 ppm using the Tammany Creek starting composition. This would correspond to 78 ppm for a pyroxenite containing 50 % other minerals.

The final igneous environment, in which scandium is known to be concentrated to economic levels is that of granitic pegmatites, exemplified by some of the pegmatites in the Iveland-Evje pegmatite district of southern Norway. There, as discussed earlier, the scandium is concentrated in the mineral thortveitite. Both the barren and fertile pegmatites are hosted dominantly by amphibolites, including a mafic-ultramafic layered complex (the Iveland-Gautestad complex). Significantly, however, the thortveitite-bearing pegmatites are restricted to the Iveland-Gautestad complex. Although the genesis of the pegmatites has been a matter of considerable debate, the most recent paper on the subject has concluded that they are the products of very low degrees of partial melting of the complex (Müller et al., 2015). This hypothesis suggests an attractive explanation for how scandium may have concentrated in these pegmatites. As discussed above, the clinopyroxenites of Alaskan-type layered igneous complexes are commonly enriched in scandium. We therefore speculate that scandium in the thortveitite-bearing pegmatites originated through partial melting of pyroxenitic members of the Iveland-Gautestad complex. In order to estimate the concentration of scandium in the pegmatitic magma, it is first necessary to estimate the degree of partial melting, which, according to the experimental study of Kushiro et al. (1996), can be done assuming that at the onset of melting all potassium present in the ultramafic source is released to the magma. The degree of partial melting can therefore be estimated simply by knowing the potassium content of the source and that of the magma. In the present case, this would be the K content of the clinopyroxenite of the Iveland-Gautestad complex (source) and the pegmatite (magma). Unfortunately, we are not aware of compositional data for pyroxenite in the Iveland-Gautestad complex, but Pedersen and Konnerup-Madsen (2000) have reported that the ultramafic rocks of the complex contain 0.23 wt.% K_2O. The only compositional data that we have found for a pegmatite in the Iveland-Gautestad complex is that for the Solas pegmatite (Snook, 2013). This pegmatite contains 2.32 wt.% K_2O. Accordingly, we predict that the Iveland-Evje pegmatites were the product of approximately 10 % partial melting. As melting of the complex was probably induced by metamorphic fluids, it is reasonable to propose that scandium present in the clinopyroxenite would have been released by these fluids to the pegmatitic melt as the residual clinopyroxenite was converted to amphibolite. Assuming that the clinopyroxenite of this complex contained 100 ppm Sc (see above), it therefore follows that the pegmatite magma contained 1000 ppm Sc, which we further assume would have been sufficient to saturate it with thortveitite. Given that endmember thortveitite contains approximately 35 wt.% Sc, this would correspond to 2.9 kg of thortveitite per ton of pegmatite. Although we do not have information on the concentration of scandium in the pegmatites that were mined in the Iveland-Evje district, a rough estimate can be made from the mining data reported by Neumann (1961). According to these data, the amounts of thortveitite extracted from the pegmatites ranged from a maximum of 20 kg in the Steane pegmatite to 0.5 kg in the Slobrekka pegmatite. Considering that the production was from small quarries, which likely yielded no more than a few tons to a few tens of tons of ore, our estimate of a thousand ppm Sc in the pegmatite magma seems reasonable. In summary, our calculation shows that thortveitite-bearing pegmatites can result from low degrees of the partial melting of clinopyroxenite, yielding pegmatitic magmas containing approximately 1000 ppm Sc.

Aqueous mobilization of scandium

Although it is evident that magmatic processes are important in the concentration of scandium to economic levels, there is compelling evidence that hydrothermal processes can also play a major role in this concentration. Indeed, in the Bayan Obo deposit, which was described earlier, the

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scandium is present almost exclusively in aegirine of metasomatic origin. This is important, because the Bayan Obo deposit produces ~90 % of the World's scandium. In this deposit, aegirine replaced dolomite and magnetite metasomatically. The origin of the dolomite is controversial, with some researchers proposing that it is sedimentary, albeit diagenetically altered (dolomitization), and other researchers proposing that it is a carbonatite (Smith et al., 2016 and references therein). Irrespective of which of these hypotheses is correct, there is little doubt that the aegirine is hydrothermal as shown by the fact that it contains fluid inclusions and may be present both as a replacement mineral and in veins. In principle, it should be possible to gain insights into the hydrothermal concentration of scandium from a consideration of the aqueous scandium speciation. The presence of abundant fluorite in the Bayan Obo deposit and the relatively high salinity of the fluid (5-15 wt.% NaCl, Smith and Henderson, 2000) suggest that both fluoride and chloride might be important ligands for scandium speciation. The former is supported by the fact that Sc^{3+} is a hard cation and F^- is a hard anion (see earlier discussion of aqueous geochemistry), and the latter by the very high chloride activity (chloride is a borderline anion). It is likewise possible, that hydroxide could be an important ligand given that it is also a hard anion. Unfortunately, there are no experimental data for species involving any of these ligands at elevated temperature and the theoretical predictions for reactions involving hydroxide species yield percentage level concentrations of scandium in the fluid, which is clearly unreasonable. Thus, any quantitative evaluation of the hydrothermal transport of scandium at Bayan Obo or any other deposit must await experimental determination of the stability of scandium species involving fluoride, chloride and hydroxide.

As discussed earlier, scandium is concentrated to potentially economic levels during the development of laterites over ultramafic rocks. In the case of the Nyngan laterite deposit, which is being developed for production, there is strong evidence that scandium was mobilized from pyroxenite into the laterite. The laterite profile starts with a hematitic laterite at the top followed downwards by limonitic laterite, saprolite, weathered rock and fresh rock. Scandium concentration reaches a maximum in the limonitic laterite (http://www.scandiummining.com). By analogy with laterites elsewhere (Freyssinet et al., 2005; Butt and Cluzel, 2013), it is envisaged that the laterite formed by the downward percolation of surface water, which leached elements from the upper layers leaving behind the iron-rich hematitic and limonitic horizons, and that further downward movement of these waters led to concentration of metals, e.g., nickel, in the saprolite. Although

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many metals, including Ni, are mobilized down to the saprolite horizon, scandium is an important exception in that it underwent more limited mobility, i.e., it was concentrated in the overlying limonitic horizon by adsorbing onto goethite. Nonetheless, it seems evident, as discussed earlier, that scandium was released to these waters during the breakdown of clinopyroxene and transported over a distance of many meters.

In order to model the mobility of scandium, we have evaluated the solubility of scandium hydroxide solid using the available thermodynamic data for this phase and aqueous scandium hydroxide species. This places a maximum limit on the concentration of scandium in downward percolating water. The solubility of the solid is given by the sum of the scandium concentrations produced by the following reactions:

$Sc(OH)_{3s}=Sc^{3+}+ 3OH^-$ (1)

$Sc(OH)_{3s}=ScOH^{2+}+2OH^-$ (2)

$Sc(OH)_{3s}=Sc(OH)_2^{+}+OH^-$ (3)

$Sc(OH)_{3s}=Sc(OH)_3$ (4)

The thermodynamic data for these reactions are presented in Table 4. From the stoichiometry of the reactions, it can be seen that the solubility of scandium hydroxide, at constant temperature, is governed entirely by the activity of OH^-, in other words, pH.

A number of studies of laterites over ultramafic rocks have shown that the pH of the waters ranges from about 5 to 5.5 at the surface, through 6.5 in the limonitic laterite to about 7 at the depth of the saprolite (van der Ent et al., 2013). We have therefore assumed that the initial pH of our mobilizing fluid was 5. Based on Reactions 1 to 4 and the thermodynamic data referred to above, the maximum possible initial concentration of scandium in solution was 1084 ppb.

In Figure 8, we have modeled the effect of increasing pH on the solubility of scandium. As is evident from this figure, the solubility of scandium decreases sharply through the hematitic laterite to a value of 13 ppb in the limonitic laterite, corresponding to a pH of 6.5. Given that scandium was concentrated by adsorption and reached a maximum concentration in the limonitic laterite, it follows that the downward-percolating water was undersaturated in respect to scandium

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hydroxide, i.e., it had an initial Sc concentration of less than 13 ppb. With further increase in pH, the scandium concentration approaches a constant value of ~7 ppb in the saprolite (Fig. 8). Although 13 ppb may seem insufficient to produce a laterite containing several hundred ppm Sc (the grades of the Nyngan and Syerston deposits are 261 and 429 ppm, respectively), the calculation described below shows that such deposits can be produced from waters with such a low scandium concentration in a relatively short time.

Laterites form in hot, humid environments (with dry periods) reflecting annual rainfall in excess of a meter (de Oliveira and Campos, 1991; Freyssinet et al., 2005). In order to determine the time taken for a limonitic laterite to accumulate 350 ppm Sc (a concentration intermediate between that of the average concentration of scandium in the Nyngan and Syerston deposits), we assumed an annual rainfall of 1 m, a bulk density of the laterite of 1 g/ml (Georgiou and Papangelakis, 1998) and an initial Sc concentration of 10 ppb (this concentration is the mean of the saturation concentration in the limonitic laterite and saprolite). In our model, the rainwater reacts with pyroxenite exposed at a topographic high, where it acquires its scandium, and percolates through a 35-40 m thick column of laterite developed at lower elevation, eventually depositing the scandium in a 10 m thick limonitic horizon (the average thickness of the Syerston limonitic laterite). According to our model, it would take 350,000 years to produce a limonitic laterite deposit containing 350 ppm Sc. This is considerably less than the roughly one million years required to produce a 10 to 50 m thick laterite (Golightly, 1981; Elias, 2002). In summary, although our model is based on simple solubility and precipitation rather than adsorption, it provides clear evidence that the modeled concentration of scandium in the waters forming Sc-bearing laterites, albeit very low, is sufficient to produce an economic deposit in a geologically reasonable period of time.

Conclusions

Although, as pointed out in the introduction to this paper, scandium is a rare earth element, we have demonstrated that it behaves very differently from the other rare earth elements. Scandium is the runt of the litter! Its unusual behavior stems from the fact that it has an ionic radius that is considerably smaller than that of any other REE. Indeed, the ionic radius of scandium is very similar to that of Mg^{2+} and Fe^{2+}. As a result, whereas the other REE are incompatible elements, scandium is compatible in that it is able to concentrate in major ferromagnesian rock-forming

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minerals, notably clinopyroxene. Not surprisingly, therefore, clinopyroxene is the principal ore mineral in a significant proportion of scandium deposits. However, in some deposits scandium reaches economic concentrations in other minerals, e.g., baddeleyite (Kovdor), xenotime (Tomtor) and goethite (Nyngan and Syerston). Historically, scandium has also been exploited from pegmatites, which are interpreted to be the product of small degrees of metamorphic fluid-induced partial melting of clinopyroxenite that concentrated this now incompatible element to levels sufficient to saturate the magma in thortveitite. In keeping with its classification as a REE, scandium is hosted mainly in alkaline intrusions and carbonatites, or rocks which have been affected by fluids that have interacted with such rocks or their magmas. The overarching conclusion of the study is that scandium has a mantle source, and can be concentrated to economic levels by magmatic and/or fluid-mediated processes in a variety of rock types at temperatures ranging from magmatic to ambient.

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Figure captions

Figure 1

a – A photograph of an outcrop of banded ore from the main pit of the Bayan Obo REE-Fe ore deposit, China. b – A photomicrograph in transmitted light of banded ore from Bayan Obo showing alternating layers rich in aegirine and rich in fluorite; monazite-(Ce) is present in both layers. In (a) and (b) the abbreviation Aeg refers to aegirine, Fl refers to fluorite, Bas refers to bastnäsite-(Ce) and Mz refers to monazite-(Ce). Dr. Xiaochun Li kindly provided the photograph shown in (a).

Figure 2

a - An exposure in the Kovdor open pit showing baddeleyite-bearing phoscorite (dark) cut by dykes of juonniite-bearing ($CaMgSc(PO_4)_2(OH)\cdot 4H_2O$) dolomite carbonatite (light). b – A backscattered electron image showing baddeleyite crystals within phoscorite. The abbreviations are: Bd – baddeleyite, Cc – calcite, Fo – forsterite and Mt – magnetite. The images presented here were kindly supplied by Dr Andrey Kalashnikov. The person in (a) is Professor Anatoly Zaitsev.

Figure 3

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a – A photograph of the Landsverk brothers taken in the early 1960s showing them mining for thortveitite. This mineral was first discovered in 1903 in a pegmatite, later named Landsverk 3 after the brothers shown in this photograph. It was subsequently identified (1911) by Jakob Shetelig as the new mineral, thortveitite, the first to contain scandium as a major cation. The photograph was graciously provided by Ronald Werner (Evje and Hornnes Geomuseum, Fennefoss, Norway). b – The adit into the Kåbuland pegmatite, which was also mined for thortveitite; several kilograms of thortveitite were recently recovered from the mine, which had long been flooded. Part of the pegmatite as well as the host Iveland Gautestad amphibolites can be seen in the photograph. The photograph was supplied by Ronald Werner (copyright to the Evje and Hornnes municipality). c – A photograph of a mass of thortveitite crystals weighing approximately 1 kg. The picture was taken by Kjell Gunnufsen and made available to us by Ronald Werner.

Figure 4

a – A cross-section through the Syerston lateritic scandium deposit showing the distribution of saprolite and the different laterite facies as well as the locations of a selection of drill holes. b – An idealized drill-log showing the saprolite and laterite facies and the distribution of scandium concentrations (sampled at 50 cm intervals) as a function of depth for a representative hole. The figure was prepared from modified versions of diagrams supplied to the authors by Dr. Mathieu Chassé.

Figure 5

Plots showing mineral/melt partition coefficients (D) as a function of the MgO content of the melt for (a) olivine, (b) orthopyroxene, (c) clinopyroxene, (d) amphibole and (e) biotite. The dashed lines in (a), (b) and (c) represent the equations (shown on the diagram) reported by Bedard (2005, 2007, 2014) for the corresponding minerals. Those in (d) and (e) represent least squares fits to the data shown on the diagrams.

Figure 6

Clinopyroxene-melt partition coefficients for the REE as a function of ionic radius in low and high MgO melts. The data for the low MgO melts (Fe-rich high silica rhyolites) are from Olin and Wolff

(2010) and those for the high MgO melts are from Adam and Green (2006). The D_0 values for the M1 and M2 sites (low MgO melt) are from Olin and Wolff (2010). The dashed curves are designed to help visualization of the distribution of the partition coefficients and do not represent fits to the data. Inspection of these curves, however, reveals that they are very similar in shape to those predicted by the lattice strain model for clinopyroxene-melt partitioning (Wood and Blundy, 1997).

Figure 7

Results of the modeling of the fractional crystallization of ocean island basalt (OIB) designed to predict the concentration of scandium in a clinopyroxenite cumulate. The model was performed using the program PELE (version 7.0; Boudreau, 1999) and a starting composition corresponding to that of the Tammany Creek/Eden member of the Columbia River basalts (Hooper, 2000). The initial temperature was 1250 ºC, the pressure was 2.5 kbar, oxygen fugacity was set to the QFM buffer and the model was conducted in 10 ºC decrements. The figure illustrates changes in the percent crystallization, the mass of clinopyroxene crystallized, and the concentration of scandium in the melt, in the clinopyroxene, and cumulatively in the pyroxenite.

Figure 8

A plot of scandium concentration in pure water as a function of pH. The plot was designed to simulate the effect of the percolation of meteoric water into laterite. It was assumed that the scandium was dissolved as hydroxy species in equilibrium with solid scandium hydroxide. It was further assumed that the initial pH was 5.0, that the pH climbed to 6.5 in the limonitic laterite and exceeded 7 in the saprolite. The calculations were conducted for 25 ºC, and the data were taken from Baes and Mesmer (1976) ($Sc(OH)_{3s}$) and Wood and Samson (2006) (aqueous species). See main text for further detail.

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Table 1 Terrestrial minerals containing scandium as an essential component.

	Name	Formula[1]	Wt. % Sc	Type locality	Common host
1	Thortveitite	$Sc_2Si_2O_7$	34.84	Iveland, Norway	Granitic pegmatite
2	Pretulite	$ScPO_4$	32.13	Fischbacher Alpen, Austria	Quartz veins
3	Kolbeckite	$ScPO_4 \cdot 2H_2O$	25.55	Schmiedeberg, Germay	Phosphate deposits
4	Jervisite	$NaScSi_2O_6$	19.02	Baveno, Italy	Granitic pegmatite
5	Eringaite	$Ca_3Sc_2(SiO_4)_3$	18.52	Wiluy River, Russia	Rodingite
6	Bazzite	$Be_3Sc_2Si_6O_{18}$	15.68	Lake Maggiore, Italy	Granitic pegmatite
7	Heftetjernite	$ScTaO_4$	15.51	Tørdal, Norway	Granitic pegmatite
8	Juonniite	$CaMgSc(PO_4)(OH) \cdot 4(H_2O)$	15.32	Kovdor, Russia	Carbonatite
9	Cascandite	$CaScSi_3O_8(OH)$	14.3	Baveno, Italy	Granitic pegmatite
10	Scandiobabingtonite	$Ca_2(Fe^{2+},Mn)ScSi_5O_{14}(OH)$	7.28	Novara, Italy	Granitic pegmatite
11	Kristiansenite	$Ca_2ScSn(Si_2O_7)(Si_2O_6OH)$	5.25	Tørdal, Norway	Granitic pegmatite
12	Oftedalite	$(Sc,Ca)_2KBe_3Si_{12}O_{30}$	4.44	Tørdal, Norway	Granitic pegmatite

[1] – in some cases the Sc site contains additional elements, e.g., Y in thortveitite.

Table 2 Formation constants of aqueous scandium species.

T ºC	Complex	log ß	Source
25	$Sc(OH)^{2+}$	10.0	Baes and Mesmer (1976), Wood and Samson (2006)
25	$Sc(OH)_2^+$	18.3	Baes and Mesmer (1976), Wood and Samson (2006)
25	$Sc(OH)_3^0$	25.9	Baes and Mesmer (1976), Wood and Samson (2006)
25	ScF^{2+}	7.0	Wood and Samson (2006)
25	ScF_2^+	12.8	Wood and Samson (2006)
25	ScF_3^0	17.1	Wood and Samson (2006)
100	$Sc(OH)^{2+}$	9.8	Shock et al. (1997)
200	$Sc(OH)^{2+}$	10.2	Shock et al. (1997)
300	$Sc(OH)^{2+}$	11.3	Shock et al. (1997)
100	$Sc(OH)_2^+$	18.3	Shock et al. (1997)
200	$Sc(OH)_2^+$	18.8	Shock et al. (1997)
300	$Sc(OH)_2^+$	20.6	Shock et al. (1997)
100	$Sc(OH)_3^0$	26.0	Shock et al. (1997)
200	$Sc(OH)_3^0$	26.7	Shock et al. (1997)
300	$Sc(OH)_3^0$	29.1	Shock et al. (1997)

Table 3 Compositions of the basalts used in the modeling of fractional crystallization designed to simulate the concentration of scandium in Alaskan-type layered igneous complexes (clinopyroxenites), and the values of the parameters used in the models.

Wt. %	**Tammany Creek/Eden basalt**[1]	**Goose basalt**[2]
SiO_2	53.50	47.99
TiO_2	2.87	3.78
Al_2O_3	13.62	11.70
FeO	12.87	17.24
MnO	0.19	0.28
MgO	3.11	4.23
CaO	7.58	8.91
Na_2O	2.90	2.71
K_2O	2.12	1.31
P_2O_5	1.24	1.85
Sc (ppm)	31	41
Model parameters		
	Tammany Creek/Eden basalt	**Goose basalt**
Initial temperature, °C	1250	1250
Final temperature, °C	900	940
Cooling interval, °C	10	10
Pressure, kbar	2.5	2.5
Oxygen buffer	QFM	QFM
Initial Sc concentration in melt (ppm)	31	41

[1] – Average of four analyses

[2] - Average of ten analyses

Table 4 Reactions and their stability constants used in calculating the solubility of scandium hydroxide solid as a function of pH. See text for further detail.

	Reaction	log K	Source
1	$Sc(OH)_{3s} = Sc^{3+} + 3OH^-$	-32.7	Baes and Mesmer (1976)
2	$Sc^{3+}+OH^- = ScOH^{++}$	10	Table 2
3	$Sc^{3+}+2OH^- = Sc(OH)^{2+}$	18.3	Table 2
4	$Sc^{3+}+3OH^- = Sc(OH)_3$	25.9	Table 2
5	$Sc(OH)_{3s} = ScOH^+ + 2OH^-$	-23	Reaction (1) + Reaction (2)
6	$Sc(OH)_{3s} = Sc(OH)^{2+} + OH^-$	-14.4	Reaction (1) + Reaction (3)
7	$Sc(OH)_{3s} = Sc(OH)_3$	-6.8	Reaction (1) + Reaction (4)
8	$H_2O = H^+ + OH^-$	-14	

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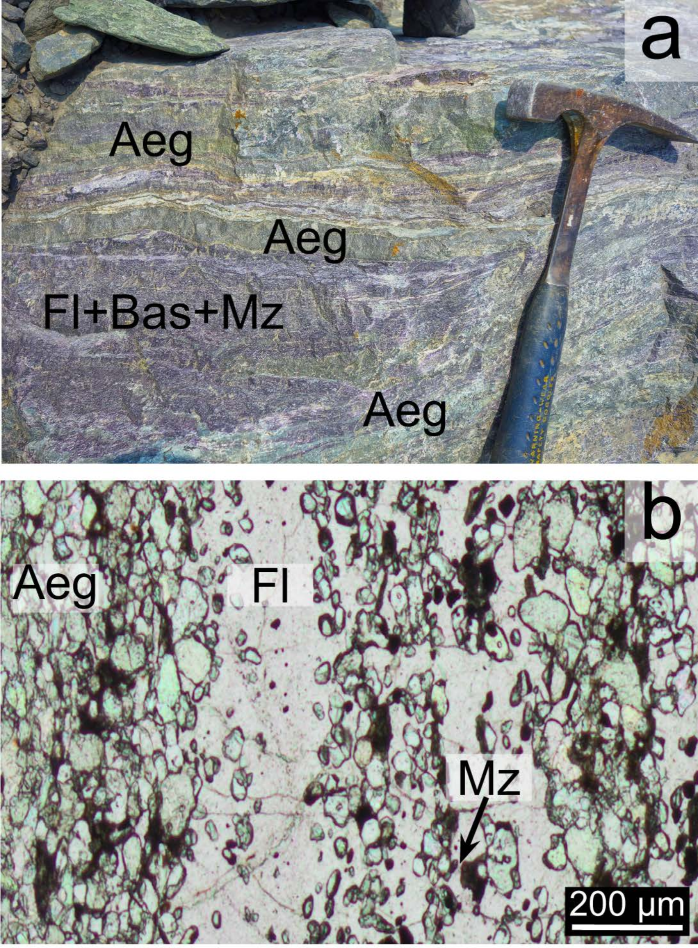
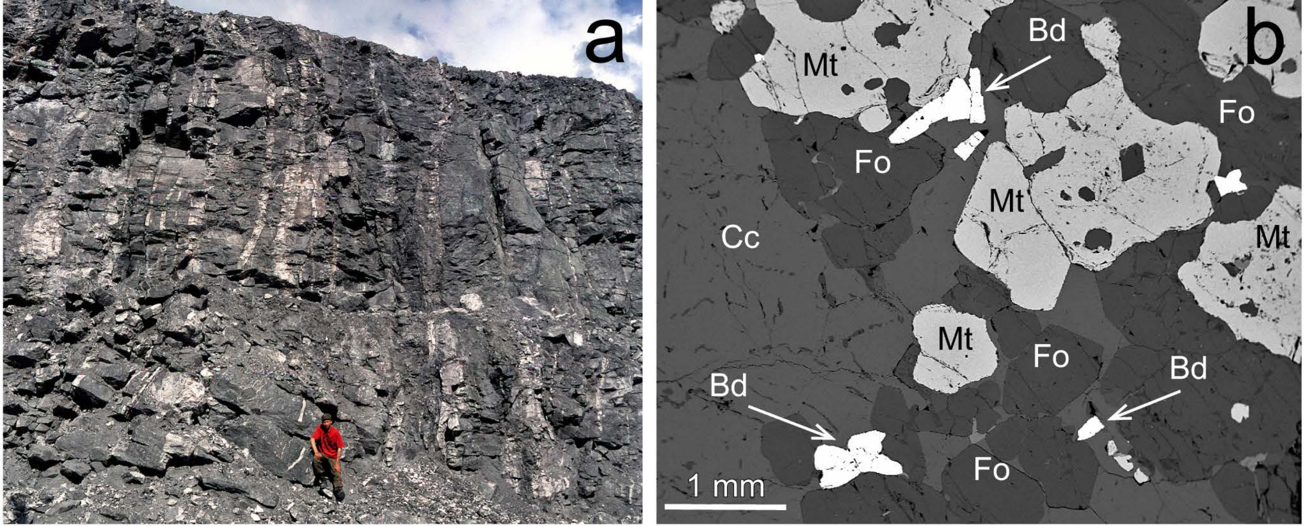
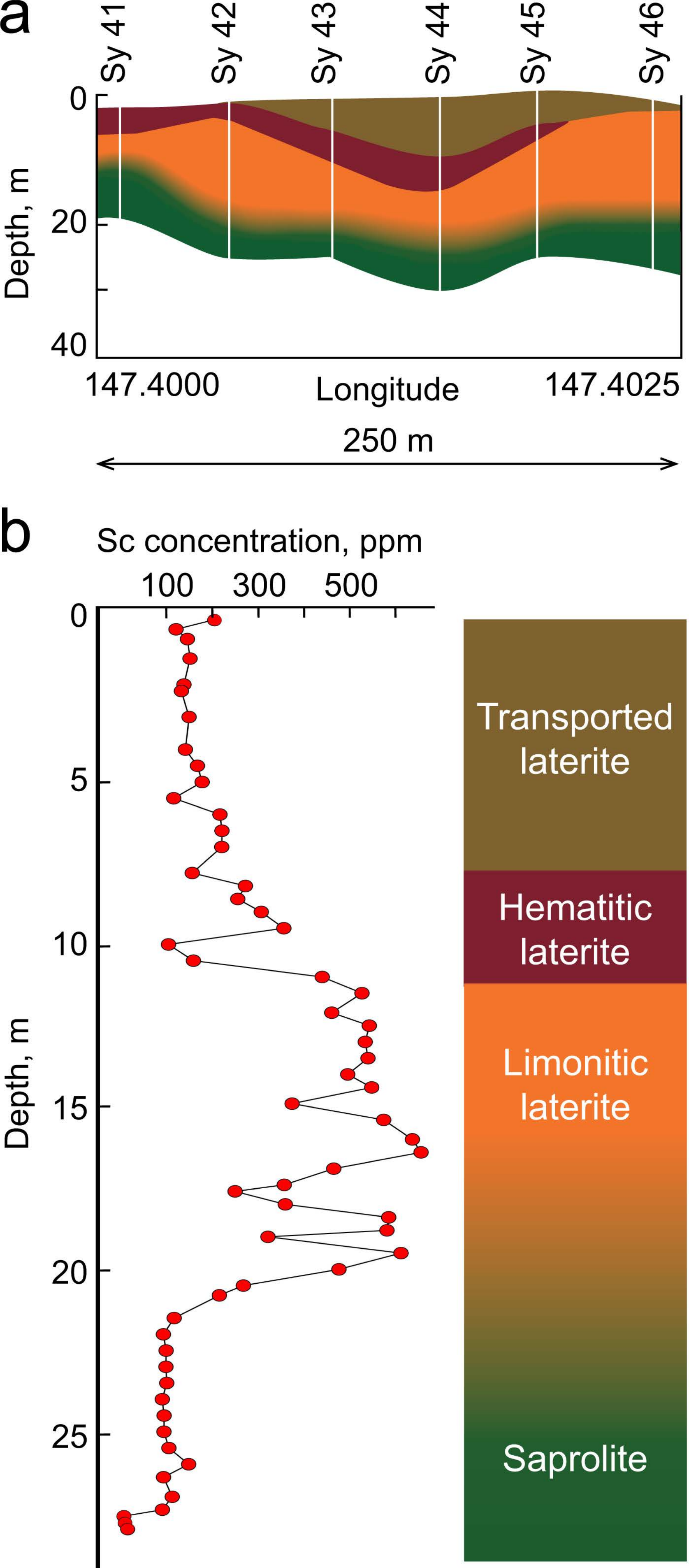
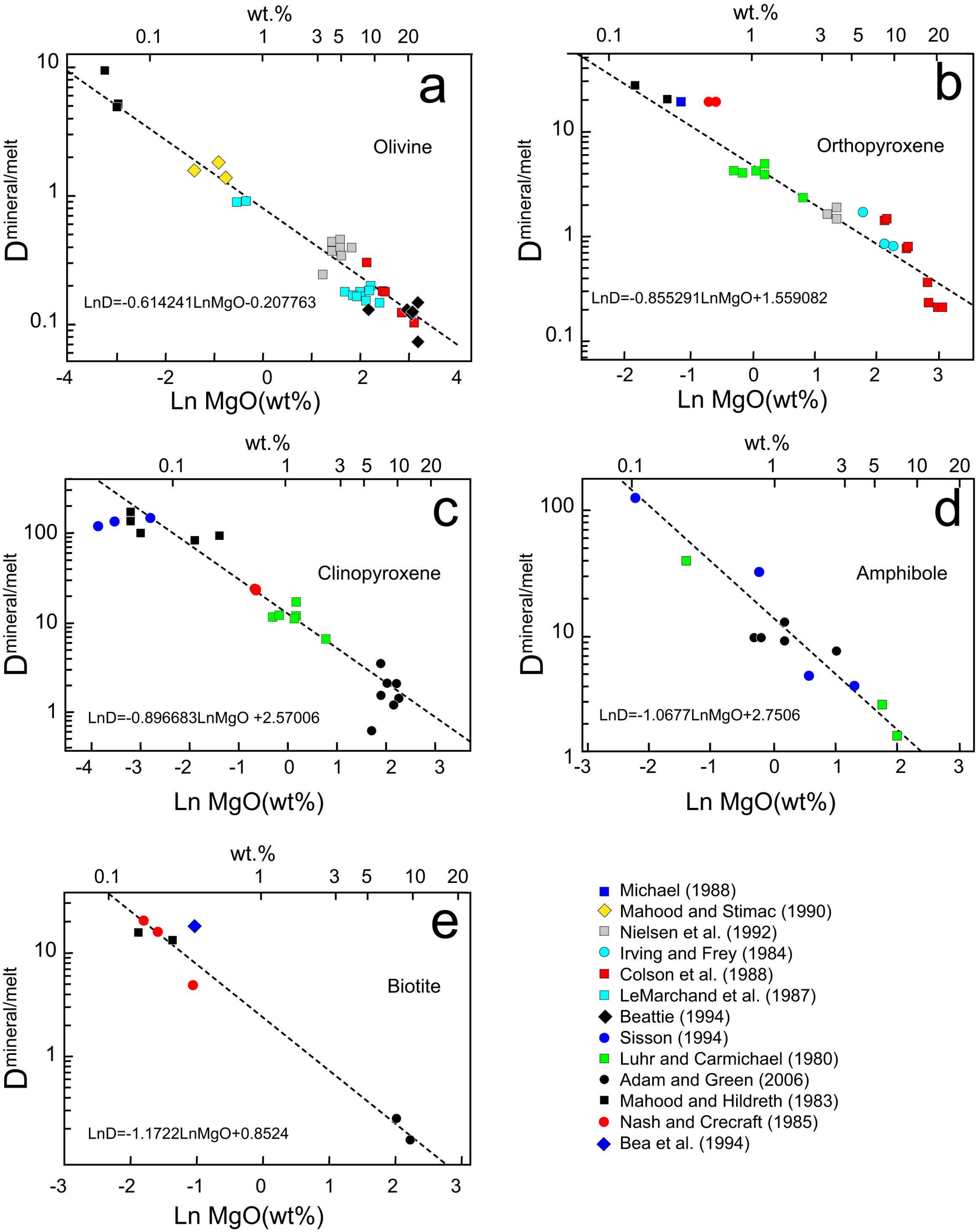
"The Economic Geology of Scandium, the Runt of the Rare Earth Element Litter." Economic Geology 113, no. 4 (Jun 2018): 973-88.
http://dx.doi.org/10.5382/econgeo.2018.4579.

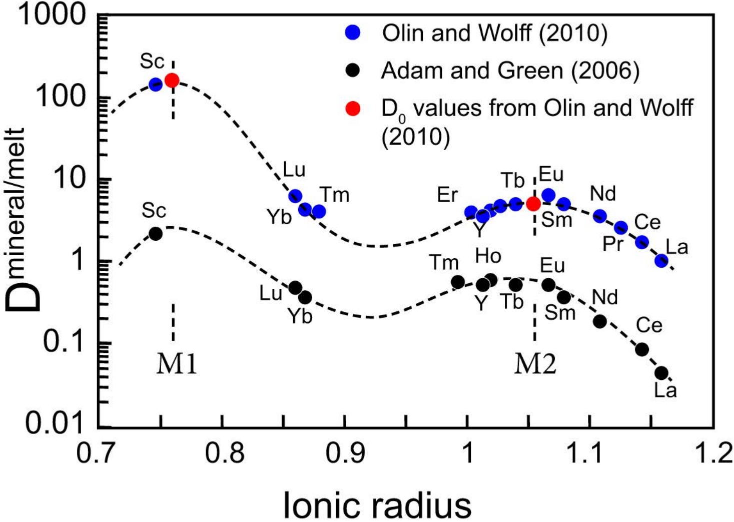

a
Aeg
Aeg
Fl+Bas+Mz
Aeg
b
Aeg
Fl
Mz
200 µm


a
b
Mt
Bd
Fo
Fo
Mt
Cc
Mt
Mt
Fo
Bd
Bd
Fo
1 mm

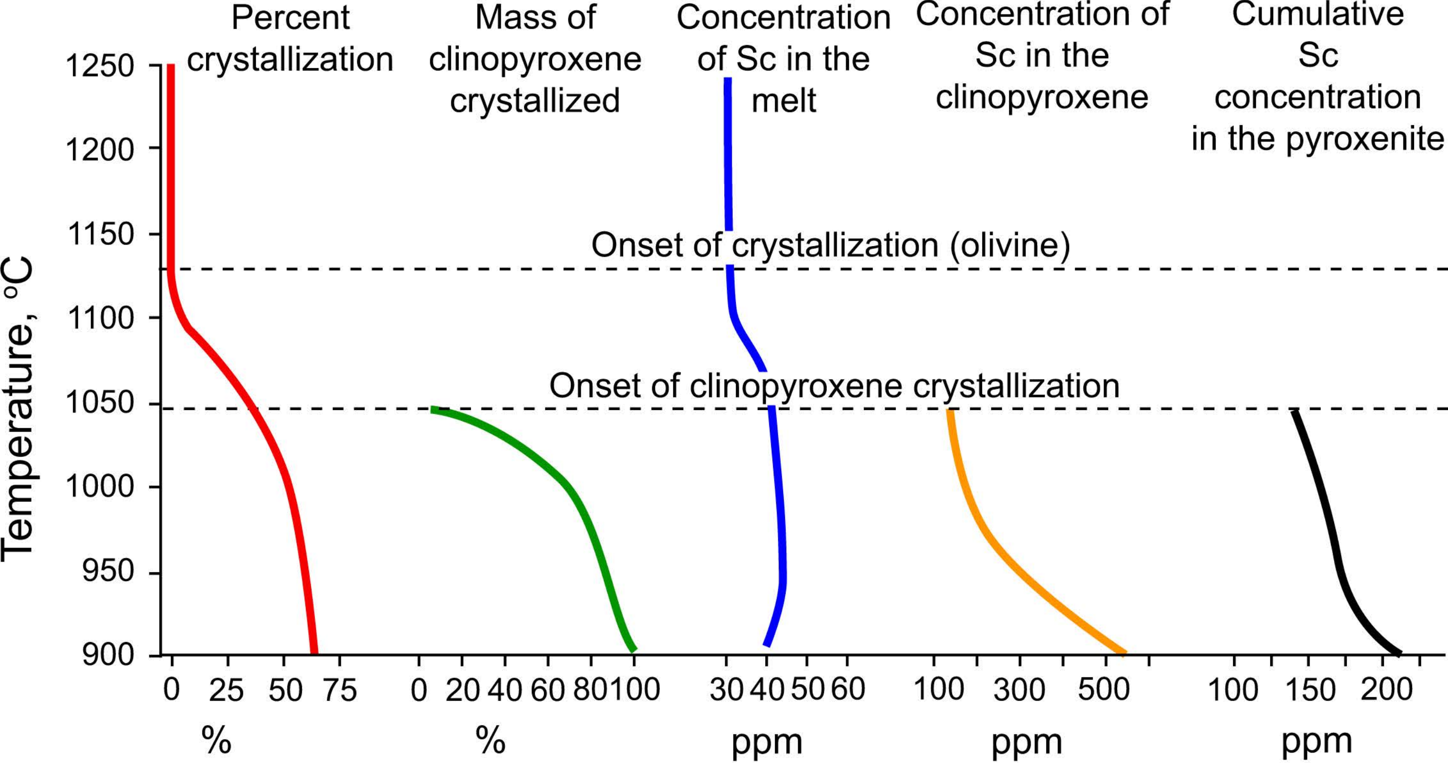

a
b
c

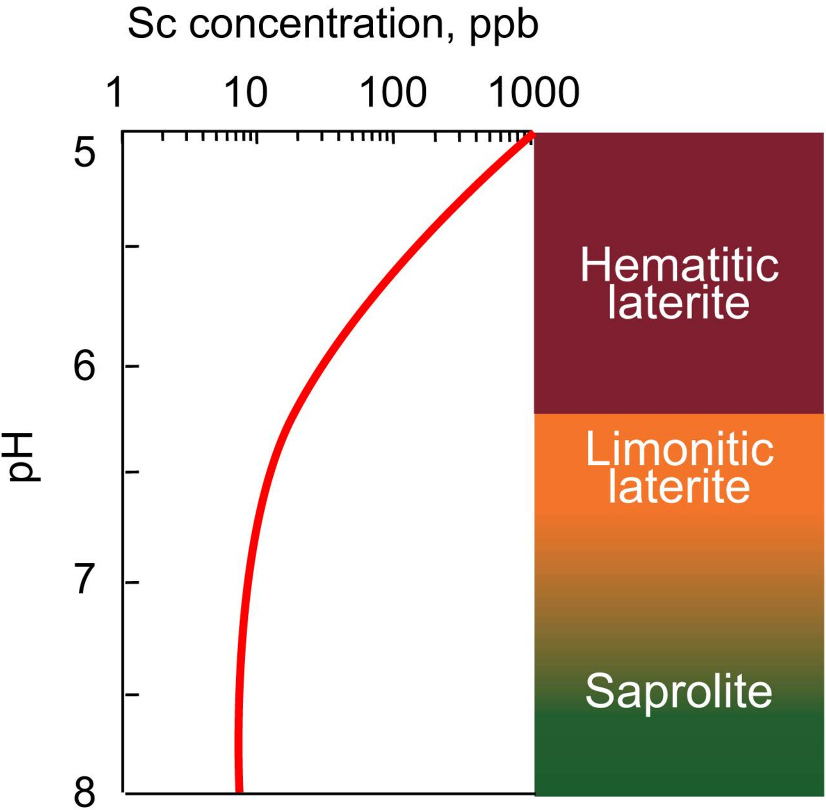

a
Sy 41
Sy 42
Sy 43
Sy 44
Sy 45
Sy 46
0
20
40
Depth, m
147.4000
Longitude
147.4025
250 m
b
Sc concentration, ppm
100
300
500
0
5
10
15
20
25
Depth, m
Transported laterite
Hematitic laterite
Limonitic laterite
Saprolite


wt.%
0.1
1
3
5
10
20
a
Olivine
LnD=-0.614241LnMgO-0.207763
b
Orthopyroxene
LnD=-0.855291LnMgO+1.559082
c
Clinopyroxene
LnD=-0.896683LnMgO +2.57006
d
Amphibole
LnD=-1.0677LnMgO+2.7506
e
Biotite
LnD=-1.1722LnMgO+0.8524
D^mineral/melt
Ln MgO(wt%)
Michael (1988)
Mahood and Stimac (1990)
Nielsen et al. (1992)
Irving and Frey (1984)
Colson et al. (1988)
LeMarchand et al. (1987)
Beattie (1994)
Sisson (1994)
Luhr and Carmichael (1980)
Adam and Green (2006)
Mahood and Hildreth (1983)
Nash and Crecraft (1985)
Bea et al. (1994)



1000
100
10
1
0.1
0.01
D mineral/melt
0.7
0.8
0.9
1
1.1
1.2
Ionic radius
● Olin and Wolff (2010)
● Adam and Green (2006)
● D$_0$ values from Olin and Wolff (2010)
Sc
Lu
Yb
Tm
Er
Y
Tb
Eu
Sm
Nd
Ce
Pr
La
Sc
Lu
Yb
Tm
Ho
Y
Tb
Eu
Sm
Nd
Ce
La
M1
M2


Percent crystallization
Mass of clinopyroxene crystallized
Concentration of Sc in the melt
Concentration of Sc in the clinopyroxene
Cumulative Sc concentration in the pyroxenite
Temperature, °C
1250
1200
1150
1100
1050
1000
950
900
Onset of crystallization (olivine)
Onset of clinopyroxene crystallization
0 25 50 75
%
0 20 40 60 80 100
%
30 40 50 60
ppm
100 300 500
ppm
100 150 200
ppm


Sc concentration, ppb
1
10
100
1000
pH
5
6
7
8
Hematitic laterite
Limonitic laterite
Saprolite