Scandium Geochemistry of the Oka Carbonatite Complex, Oka, Quebec

G. Nelson Eby

Department of Biological and Physical Sciences, Lowell State College, Lowell, Massachusetts 01854

Abstract

Scandium abundances were determined by X-ray fluorescence for rocks (14 samples) and minerals (84 samples) from the Oka carbonatite complex, Oka, Quebec. Whole-rock data indicate a general trend of scandium enrichment in the order: urtites < ijolites < okaites < sövites < alnöites. The ore minerals (niocalite, perovskite, and pyrochlore) and apatite are the principal carriers of scandium; ferromagnesian minerals contain less scandium and show the order of scandium uptake: biotite < pyroxene < garnet. The scandium content of the calcites is quite variable. Monticellite, melilite, nepheline, albite, the zeolites, and the feldspathoids contain negligible amounts of scandium. Scandium and REE concentrations vary sympathetically for the ore minerals, calcites, and apatites but not for any of the other minerals. Partitioning coefficients for various coexisting phases indicate that, in general, equilibrium was not attained by the Oka rocks. The silicate rocks of the complex crystallized from a differentiating alkali peridotite magma, and the sövites formed from a volatile-rich phase. The selective partitioning of scandium, possibly in the form of complex ions, into the volatile-rich phase may account for the concentration of scandium in the sövites.

Introduction

Scandium is a widely dispersed element in the lithosphere but rarely occurs as a major element in discrete mineral phases. Scandium is a member of the same periodic group as yttrium and lanthanum, and therefore certain chemical similarities exist between these elements. However, because of its significantly smaller ionic radius, the geochemical behavior of scandium is generally quite different from that of yttrium or the lanthanides. In igneous rocks, the lanthanides are concentrated in intermediate and felsic varieties, whereas scandium is concentrated in mafic and ultramafic varieties. Scandium concentration usually shows negative correlation with silica content and positive correlation with total iron. Thus it is generally concentrated in ferromagnesian minerals and certain accessory minerals such as apatite and pyrochlore.

The occurrence of scandium in various geologic environments has been discussed by numerous investigators (*e.g.,* Goldschmidt and Peters, 1931; Oftedal, 1943; Rankama and Sahama, 1950; Goldschmidt, 1954; Vlasov, 1966). Norman and Haskin (1968) have investigated the distribution of scandium and the lanthanides in various rocks. Tilling *et al* (1969) have studied the distribution of scan-

dium in coexisting biotites and hornblendes in igneous rocks. An excellent summary of the geochemistry of scandium is given by Frondel (1970). Although much information now exists concerning the distribution of scandium in various geologic environments, little is known about the distribution of scandium in the rocks and minerals of a carbonatite complex (Heinrich, 1966, p. 242). This paper presents the results of a detailed study of the distribution of scandium in various rocks and minerals of the Oka carbonatite complex, Oka, Quebec.

Geologic Setting

The Oka carbonatite complex is located approximately 25 miles west of Montreal, Canada, and represents the westernmost extent of the "Monteregian Petrographic Province." This province, consisting of closely related alkaline rocks, extends from Oka along a gently curved eastward trend to Mount Megantic (130 miles east of Montreal). The silica content of the rocks increases eastward. The emplacement of the alkaline rocks is believed to have been controlled by a deep-seated fault system (Gold, 1967, p. 291). Breccia pipes, diatremes, and other features indicative of explosive activity are common in the Oka area but are absent elsewhere in the

province. Rubidium-strontium age data indicate the collective age of the Monteregian province to be 110 ± 20 million years (Fairbairn *et al*, 1963).

The geology and geochemistry of the Oka carbonatite complex have been summarized by Gold (1967, 1969). The rocks of the complex are intruded into a Precambrian inlier composed of quartzo-feldspathic gneiss, granulites, anorthosite, and gabbro. The intersection of two structural trends, the northwest-trending Beauharnois arch and eastward-trending faults associated with the Ottawa-Bonnechère graben, probably controlled the emplacement of the complex. The complex consists of two ring-like structures which intersect near LaTrappe. A suite of alkalic rocks, including okaites, ijolites, and urtites, is intruded into the complex as arcuate dikes and tabular bodies. An irregular zone of fenitization is developed around the complex. Calcite-rich rocks (sövites) were intruded at various stages and have a rather diverse minor mineral content. Late stage alnöites and lamprophyre dikes are found in the area.

Gold (1966, p. 124) considers the Oka rocks to be differentiates from an alkali peridotite magma. The magma chamber is inferred to have had a cylindrical shape with volatiles being trapped at the top (yielding the carbonate rocks) and kimberlitic rock types being developed near the base. Watkinson and Wyllie (1971), on the basis of experimental studies, suggested that the various Oka rocks could be produced by the fractional crystallization of a carbonated nepheline-rich melt. The crystallization sequence is envisaged as being ijolite series → nepheline okaite → okaite → carbonatite. The sodium-rich, aqueous vapor-phase observed in the experimental runs might correspond to the fenitizing agent.

Experimental Procedure

Samples were collected from both outcrops and drill cores. Sample size usually ranged between several hundred grams and several kilograms. The samples were broken into chips and agitated in an ultrasonic cleaner for 20 minutes. The chips were then pulverized and the resulting material was split to yield a whole-rock sample. Mineral separates were prepared from the remaining material using heavy liquid and magnetic separation procedures. The silicate and oxide minerals were further purified by leaching for 5 minutes in 2N HCl (to remove apatite and calcite impurities). The apatites were leached for 5 minutes in 10 percent acetic acid (to remove cal-

cite). The purity of these separates was visually estimated to be greater than 98 percent. Because minute silicate inclusions occur in the calcites, the calcite separates were dissolved in 10 percent acetic acid and the resulting solution was filtered to remove the insoluble material. A weight correction was applied for the amount of insoluble material in the calcite separates.

The analytical procedure has previously been described in detail (Eby, 1972). In brief, the method involves the dissolution of a sample in an appropriate acid media, separation of scandium by a strong acid, cation-exchange procedure, and determination of concentration by X-ray fluorescence spectrometry. Ion-exchange paper is used as the ion collector and support for the X-ray portion of the procedure. A General Electric XRD-6VS spectrometer, with a PET analyzing crystal and a Cr target, was used for the determination of concentrations. The $K\alpha$ line of scandium was used as the analytical line. Replicate analyses of some of the U.S.G.S. standard rocks and rock and mineral samples from the Oka complex indicate a precision of ±10 percent to ±30 percent at the ppm level. Scandium abundances determined for G-2 (3.4 ppm), GSP-1 (6.2 ppm), AGV-1 (11.4 ppm), and BCR-1 (37.5 ppm) are within 10 to 20 percent of most values reported by other investigators for these rock standards (Flanagan, 1969).

Results and Discussion

Whole-rock Concentrations

Data for whole-rock samples (Tables 1 and 2) indicate a regular increase in scandium content in the following order: juvite and urtite < ijolites < okaites < sövites < alnöites. The apatite-pyroxene rock (Table 2, no. 14) represents a special case and contains a pyroxene which is unusually high in scandium (127.1 ppm). The biotite rock (Table 2, no. 15) has the lowest scandium concentration of all the rock samples analyzed, reflecting the low scandium content of the biotite (0.6 ppm) which composes approximately 70 percent of the rock. The position of these two rocks in the sequence of events at Oka is not clear.

Variations in scandium content with rock type can be ascribed to variations in mineralogy and partly to a real increase in the scandium concentration of the residual fluid from which the rocks were crystallized. The effect of mineralogy is evident by higher scandium contents in rocks which contain significant

TABLE 1. Scandium Concentrations (Parts per Million) for Sövites

	1	2	3	4	5	6	7	8	9	10
Whole-rock	21.9	12.3	10.3	--	--	--	--	--	--	--
Calcite	1.3	<0.6	2.7	3.7	1.8	2.2	3.0	1.9	3.8	--
Apatite	--	58.6	64.0	25.8	58.8	68.3	34.4	91.1	39.1	46.4
Biotite	--	--	--	--	--	--	9.3	--	--	--
Pyroxene	--	--	39.7	--	11.1	--	19.8	10.0	--	--
Pyrochlore	--	--	--	103.6	--	--	69.5	--	--	--
Perovskite	--	50.2	--	--	--	--	--	--	--	--
Niocalite	28.5	--	--	--	--	--	--	--	--	--
Melilite	5.9	--	--	--	--	--	--	--	--	--
Monticellite	--	2.1	--	--	--	--	--	--	--	--

TABLE 1 (CONTINUATION)

	11	12	13	14	15	16	17	18	19	20	21	22	23
Calcite	4.4	4.9	5.1	4.5	8.7	4.8	4.8	4.9	4.2	2.4	2.8	2.8	10.4

1. niocalite-melilite sövite (BOK-6); 2. monticellite sövite (BOK-7); 3. soda pyroxene sövite (OL-1); 4. coarse-grained sövite (OL-7); 5. soda pyroxene sövite (A-16-6); 6. apatite-pyrochlore sövite (AB-60-1); 7. soda pyroxene sövite (G-13-8); 8. soda pyroxene sövite (S-34-2); 9. coarse-grained sövite (S-34-15); 10. monticellite sövite (S-43-4); 11. soda pyroxene sövite (P-18); 12. biotite sövite (P-19); 13. apatite sövite (P-20); 14. biotite sövite (P-21); 15. biotite-pyrochlore sövite (P-25); 16. sövite (P-26); 17. biotite sövite (P-27); 18. apatite sövite (P-28); 19. pyrochlore sövite (P-29); 20. soda pyroxene sövite (P-30); 21. sövite (P-31); 22. biotite sövite (P-33); 23. biotite sövite (P-35).

amounts of apatite, pyrochlore, perovskite, and/or niocalite, all of which are relatively rich in scandium. It is also noted that there is a crude correlation between the scandium content of the whole-rock samples and the scandium content of the individual minerals.

The increase in scandium concentration follows the crystallization sequence envisaged for the Oka complex. The early-crystallized rocks, such as the urtites and ijolites, are low in scandium while later-crystallized rocks, such as the sövites and alnöites, are relatively rich in scandium. This trend suggests a selective enrichment of scandium in the residual fluid.

The scandium contents of the sövites (10.3 ppm–21.9 ppm) are significantly higher than those of the limestones (0.4 ppm–1.6 ppm) and marbles (0.47 ppm–0.97 ppm) analyzed by Norman and Haskin (1968). Their single carbonatite analyses (44 ppm) is somewhat higher than that found for the sövites. The scandium content of the alnöites falls within the range reported for basic and ultrabasic rocks.

Mineral Concentrations

The range of scandium concentrations (Tables 1 and 2) varies considerably for each mineral. Several general trends, however, may be noted. The niobium ore minerals (perovskite, pyrochlore, and niocalite)

TABLE 2. Scandium Concentrations (Parts per Million) for Silicate Rock Types

	Urtites		Ijolites					Melteigite	Juvite	Okaites		Alnöites			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Whole-rock	--	3.3	--	5.3	--	5.4	7.2	--	2.8	7.6	8.7	18.5	48.2	96.9	1.6
Calcite	--	--	1.6	<0.6	--	1.8	1.8	--	--	--	<2.5	<1.1	--	3.0	1.1
Apatite	--	--	55.6	40.6	--	26.7	45.1	--	--	--	63.3	--	31.7	19.9
Biotite	--	--	--	--	--	--	--	2.2	--	--	--	--	41.7	--	0.6
Garnet	12.2	--	6.4	3.1	5.5	--	5.7	--	--	--	--	--	--	--	--
Pyroxene	--	--	2.1	0.9	<0.9	6.2	2.1	29.6	--	--	--	--	79.1	127.1	--
Perovskite	--	--	--	--	--	--	--	--	--	67.2	96.6	--	--	--	--
Melilite	--	--	--	--	--	--	--	--	--	1.1	1.5	--	--	--	--
Nepheline	--	0.4	--	--	--	--	--	--	--	--	--	--	--	--	--
Albite	--	--	--	--	--	--	--	--	<0.3	--	--	--	--	--	--
Alter. Prod.	--	--	--	<0.3	--	<0.5	0.7	--	--	0.5	--	--	--	3.0	--

1. altered urtite (A-16-11); 2. fine-grained urtite (A-18-2); 3. altered melanite ijolite (OL-5); 4. altered melanite ijolite (OL-6); 5. altered melanite ijolite (OL-8); 6. altered calcitic ijolite (A-14-1); 7. altered ijolite (A-14-5); 8. altered melteigite (A-16-10); 9. juvite (OL-4); 10. nepheline okaite (BOK-3); 11. okaite (OL-2); 12. alnöite (OK-12); 13. alnoite (A-14-10); 14. pyroxene-apatite rock (A-16-4); 15. biotite rock (A-18-4).

as well as apatite are the major scandium-containing phases. Ferromagnesian minerals concentrate scandium to a certain extent but less so than the nonferromagnesian niobium ore minerals and apatite. This is an unexpected result since scandium is generally believed to follow iron and magnesium. As will be demonstrated later, the abundance of scandium quite closely follows the total abundance of the REE in the calcites and apatites. Monticellite, melilite, and calcite all contain relatively small amounts of scandium, whereas the nephelines, albites, and their alteration products contain even less.

Calcite. The chemistry and crystallography of the Oka calcites have been investigated by Quon (1965), Quon and Heinrich (1966), and Pouliot (1970). These authors concluded that there is a wide variation in minor element content of the calcites within a single carbonatite complex and that there are no systematic variations by province. Pouliot found that only Mg, Fe, and Mn exhibit

FIG. 1. Scandium content of calcites versus total rare-earth content (data of this paper and of Eby, 1971).

correlation with each other, whereas no correlation exists between the concentrations of Sr and Ba and the other elements.

The scandium values for the calcites are also quite variable, ranging from less than 0.6 ppm to 10.4 ppm. In general, the calcites from the sövites are enriched in scandium with respect to the calcites from the other rock types. Calcite samples 11–23 (Table 1) are the same samples studied by Pouliot (1970, Table 1). This enabled a direct comparison of scandium concentration with those concentrations obtained by Pouliot for Sr, Mn, Mg, Fe, and Ba. There was no apparent correlation between any of these elements and scandium. A positive correlation is observed between the total REE content of the calcites and their scandium content (Fig. 1).

Possible contamination of the calcite separates with dolomite is presumed to be minimal; calcite samples 11–23, Table 1, are the identical concentrates used by Pouliot (1970) in his study of the Oka calcites. Pouliot obtained powder patterns of all his calcite concentrates using a Guinier de Wolfe multiple powder camera and did not report dolomite in any of his concentrates. The other calcite concentrates were prepared using a procedure similar to that of Pouliot (1970).

Modal analyses of the rock samples used in this study did not, in general, reveal dolomite to be an important constituent. The heavy liquid separation was performed so that the specific gravity of the separated carbonates was between 2.68 and 2.75. This presumably excluded dolomite grains and most of the calcite grains which might contain included dolomite. The dissolution of the calcite was done in cold dilute acetic acid so that any dolomite which might be present would not readily go into solution. The success of the separation procedure is probably best indicated by the fact that, in the majority of the sample dissolutions, less than 1 percent insoluble residue was found. Thus dolomite should be a minor constituent in any of the calcite analyses, certainly less than 2 percent.

Apatite. Girault (1966, 1967) investigated the occurrence of apatite in the Oka rocks and placed particular emphasis on the abundance and composition of fluid inclusions. In some samples the fluid inclusions composed as much as 1.2 wt percent of the apatite. Girault concluded that the apatites crystallized in the presence of fluid phases at moderate temperatures. Crystallographic data indicate that these apatites can be classed as fluorapatites.
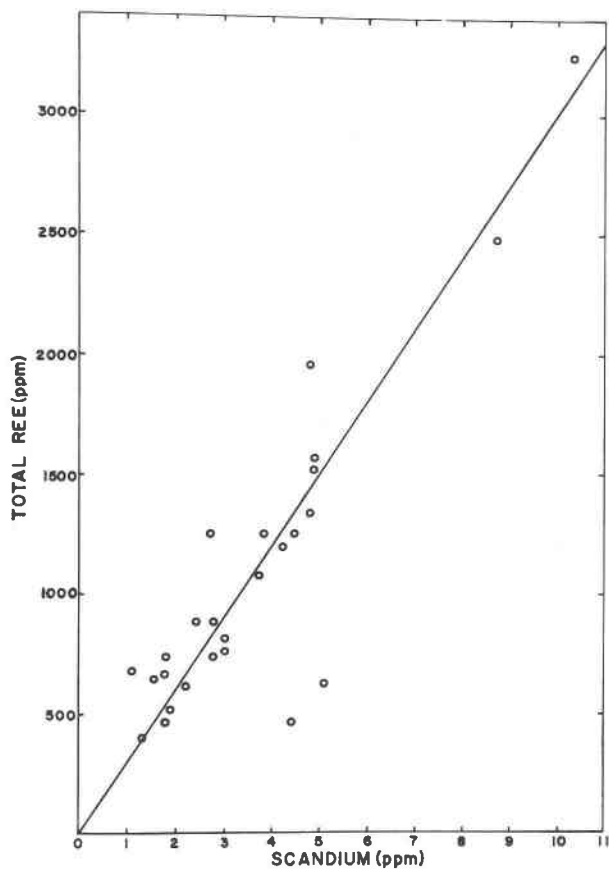
Scandium content of the apatites range from 19.9 ppm to 91.1 ppm. The range in scandium content for apatites from the ijolites (26.7 ppm to 55.6 ppm) is less than that for apatites from the sövites (25.8 ppm to 91.9 ppm). There is no apparent relationship between the scandium content of the apatites in the sövites and the mineralogy of the sövites. There is, however, a definite positive correlation between the total REE concentrations of the apatites and their scandium content (Fig. 2).

The partitioning of scandium between coexisting apatites and calcites is not regular. For the ijolites, the $Sc_{apatite}/Sc_{calcite}$ ratio varies from 7.0 to 34.8; for the sövites, from 10.3 to 47.9; and for the biotite rock, 18.1. These data would tend to indicate that equilibrium was not achieved over very wide areas within the complex.

Ferromagnesian Minerals. Rimsaite (1969) conducted a detailed investigation of the types and chemical zoning of micas from a carbonatite breccia within the Oka complex near LaTrappe. She identified a total of six varieties of mica which were subsequently grouped as three major types based on color. These three types are the green biotites and phlogopites, the brown biotites, and the orange phlogopites. The latter two compose the bulk of the Oka micas. Chemical analyses for these various types of mica have been given by Rimsaite (1969, Table 3).

The biotite samples (predominantly brown, with some green) show a regular increase in scandium content with rock types: biotite rock (0.6 ppm) < altered ijolite (2.2 ppm) < sövites (9.3 ppm) < alnöite (41.7 ppm). This pattern of increase parallels that of the whole-rock scandium and apparently represents crystallization of biotite from a residual fluid which was becoming progressively richer in scandium.

The Oka garnets have been chemically classified as titanium-rich andradites (melanites). Nickel (1960) and Gold (1966) report chemical analyses for several of these garnets. With one exception, the concentration of scandium in the garnets varies between 3.1 ppm and 6.4 ppm.

The pyroxenes of the urtite–melteigite series and of the sövites have been identified as sodic augites. The pyroxenes of the alnöites are titanaugites. Gold (1966) lists several chemical analyses for these two types of pyroxenes. Scandium contents of the pyroxenes range from 0.7 ppm for a sample from an ijolite to 127.1 ppm for the pyroxene from the
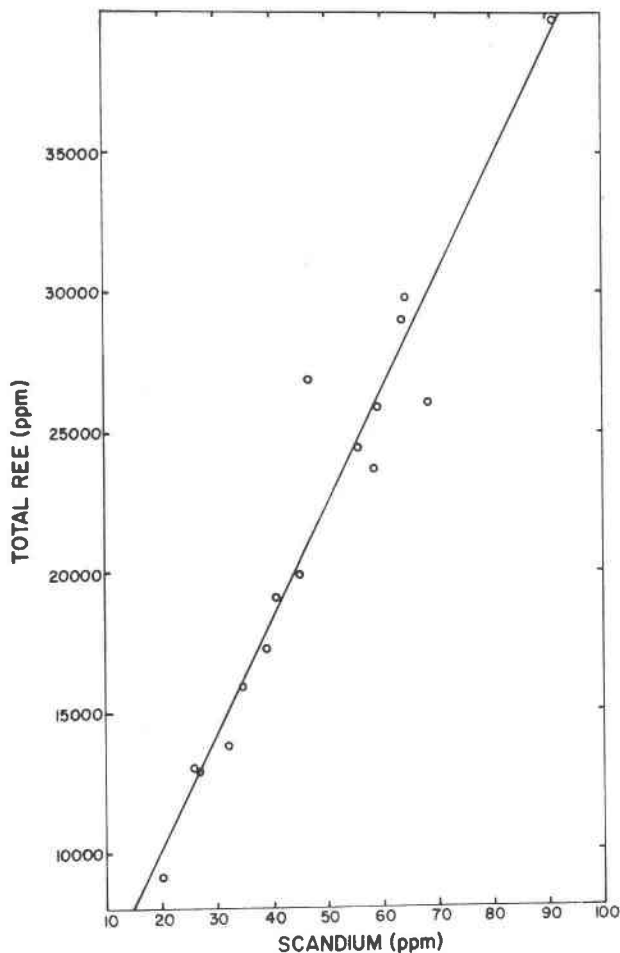

FIG. 2. Scandium content of apatites versus total rare-earth content (data of this paper and of Eby, 1971).

apatite-pyroxene rock. Again, a general trend of scandium enrichment in the pyroxenes is noted in the order ijolites < sövites < alnöites.

The partitioning of scandium between coexisting pairs of these mafic minerals is of some interest. For the garnet–pyroxene pairs, the ratio $Sc_{garnet}/Sc_{pyroxene}$ varies from 2.7 to 3.4. For the pyroxene–biotite pairs, the ratio $Sc_{pyroxene}/Sc_{biotite}$ is 1.9 for an alnöite, 2.1 for a soda pyroxene sövite, and 14.3 for a melteigite. These partitioning data indicate that the uptake of scandium will be in the order biotite < pyroxene < garnet. The low scandium content of the garnets may be a function of the absolute concentration of scandium in the residual fluid when the garnet-containing rocks were crystallized.

For the calcite–pyroxene pairs, the $Sc_{pyroxene}/Sc_{calcite}$ ratio varies from 5.3 to 14.3 for the sövites and from 1.2 to 3.5 for the ijolites. For the apatite–

pyroxene pairs, the $Sc_{apatite}/Sc_{pyroxene}$ ratio for the sövites varies from 1.6 to 9.1 while the ratio for the ijolites varies from 4.3 to 45.1. These data, therefore, suggest a trend of relative enrichment of scandium in the pyroxenes, with respect to both apatite and calcite, when proceeding from the ijolites to the sövites.

Gold (1966) reports an analysis for a monticellite from a monticellite sövite. The scandium content of a monticellite from a compositionally similar rock is quite low (2.1 ppm), which is consistent with previous observations (Frondel, 1970) that olivine is virtually devoid of scandium.

Melilites. Gold (1966) reports the composition of the various melilites found in the Oka rocks. The melilites are all soda-rich varieties. Watkinson (1972) found that the melilites from the jacupirangite–okaite–carbonatite series of the Oka complex were essentially unzoned and that the melilites from the carbonatite showed a slight enrichment in sodium. The two melilite samples from the okaites have scandium concentrations of 1.1 ppm and 1.5 ppm while the melilite sample from a sövite has a scandium content of 5.9 ppm. This probably reflects an increase in scandium in the residual fluid during the crystallization of the sövites.

Conclusions

In most igneous rocks, scandium is concentrated mainly in the pyroxenes, dark micas, and garnets (plus certain accessory minerals) and is virtually absent from olivine, plagioclase, and nepheline. Alteration products, both feldspathoids and zeolite minerals, also have extremely low scandium concentrations. In contrast, for the carbonatitic rocks of the Oka complex, the accessory minerals (apatite, perovskite, pyrochlore, and niocalite) are the major hosts for scandium. For the calcites, apatites, and ore minerals the scandium content is correlated positively with the total REE content.

The wide variability of the partition coefficients for various coexisting phases indicates the absence of wide-range equilibrium for the various rocks of the Oka complex. This is not a surprising result since the emplacement of the Oka rocks was a multistage event, and the discrimination of these various events is extremely difficult. In addition, the large amount of volatiles and the probability of gas-streaming, would likely result in a disequilibrium situation for the crystallization of the original magma. Deines (1970) investigated the carbon and oxygen isotopic composition of the carbonate phases (mainly calcite and

dolomite) in both the carbonate and silicate rocks of the Oka complex. He concluded that the δC^{13} frequency distribution could be produced by a Rayleigh-fractionation that started with a slightly inhomogeneous isotopic reservoir. The variations in δO^{18} were too great to be accounted for by a simple Rayleigh-fractionation but might be explained by isotopic exchange with, or incorporation of, the intruded gneisses. The isotope data, therefore, provide additional evidence for disequilibrium in the original magma.

The concentration of scandium in the accessory minerals, which were probably formed from a volatile-rich phase, suggests that a complexing mechanism may have been important in controlling the distribution of scandium. Scandium may have been selectively partitioned into the volatile-rich phase as a soluble carbonate and/or fluoride complex. The phosphate ion acts as a precipitant for scandium (Beck, 1951; Vickery, 1953), and this may account for the concentration of scandium in the apatites. Concentration of scandium in the niobium ore minerals may be due to the favorable ionic size of the sites which contain niobium and/or titanium. A coupled substitution with other elements is required in order to maintain charge neutrality. The sympathetic variation between REE and Sc abundances for the volatile-rich phases (calcite, apatite, and the ore minerals) may lend support to the mechanism of selective partitioning of these elements into the vapor-rich phase. For the silicate minerals, which presumably formed from a "normal" liquid, there is no correlation between REE and Sc abundances. This is the relationship (lack of correlation) which has usually been observed.

The distribution of scandium among the various rock types agrees reasonably well with the proposed origin of the Oka complex. Early crystallization of olivine (virtually Sc-free) from an alkali peridotite magma would result in the concentration of scandium in the residual melt. Selective partitioning of scandium into the volatile-rich phase could account for the concentration of scandium in the sövites, and the late stage alnöites (possibly recharged) can be derived from a residual fluid which has been enriched in scandium.

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