Contrib Mineral Petrol (1987) 97:433–437

Contributions to Mineralogy and Petrology

Nd and Sr isotope systematics of the Oka complex, Quebec, and their bearing on the evolution of the sub-continental upper mantle

Jianping Wen*, Keith Bell and John Blenkinsop

Ottawa-Carleton Centre for Geoscience Studies, Department of Geology, Carleton University, Ottawa, Ontario K1S 5B6, Canada

Abstract. A detailed isotopic study of minerals and whole rocks from the Cretaceous Oka complex, Quebec, Canada, shows a very small variation in initial Nd and Sr isotopic compositions. Assuming an age of 109 Ma for the complex, apatite, calcite, garnet, melilite, monticellite, olivine and pyroxene and whole rocks yield a range for initial $^{87}Sr/^{86}Sr$ of 0.70323–0.70333; and for initial $^{143}Nd/^{144}Nd$ of 0.51271–0.51284 ($\varepsilon_{Sr}(T) = -14.8$ to -16.2; $\varepsilon_{Nd}(T) = +4.1$ to $+6.6$). The negative ε_{Sr} and positive ε_{Nd} indicate derivation of the Nd and Sr from a source with a time-integrated depletion in the large-ion lithophile (LIL) elements. This agrees with data from other Canadian carbonatites and confirms that a large part of the Canadian Shield is underlain by a source region depleted in the LIL elements. The new data from Oka suggest that the depleted source may have remained coupled to the continental crust until recent time.

Introduction

Carbonatites (magmatic rocks containing > 50% carbonate minerals) have proven useful in monitoring some geochemical characteristics of the sub-continental upper mantle. Because of their high abundances of Sr and the rare-earth elements, any effects of crustal contamination are minimized. A study of initial $^{87}Sr/^{86}Sr$ ratios from carbonatites and associated alkalic rocks of different ages intruded into the Superior and Grenville Provinces of the Canadian Shield (Bell et al. 1982) showed that the initial ratios define an approximately linear relationship when plotted as a function of age. The linear pattern implies that the source region of the Sr in the carbonatites has behaved as a closed system with respect to exchange of Rb and Sr over about 2500 Ma, the range in age from the oldest to the youngest complex. The Rb/Sr ratio of the source region was determined to be about 0.02, significantly less than the value for bulk Earth of 0.03 (DePaolo and Wasserburg 1976), implying that the source region is depleted in the large-ion lithophile (LIL) elements. The time of intersection between the Sr evolution line for bulk Earth and the carbonatite line, about 2900 Ma, was interpreted by Bell et al. (1982) as the mean age of differentiation of the LIL-depleted reservoir from bulk Earth-type material. The Superior crust was suggested as representing the complementary enriched reservoir.

More recent work (Bell and Blenkinsop 1985, 1986, 1987) has shown that an approximately linear relationship also exists between initial $^{143}Nd/^{144}Nd$ ratios and age for the same complexes, implying closed system behaviour of the source region for Sm and Nd. The calculated Sm/Nd ratio is about 0.36, significantly higher than the bulk Earth value of about 0.32, again suggesting a source region depleted in the LIL elements. The intersection of the carbonatite line and the development line for bulk Earth is also about 2900 Ma, but the two ages are not independent because the bulk Earth estimates for Rb–Sr are derived from the Sm–Nd estimates using the mantle array (DePaolo and Wasserburg 1976). The agreement of the intersection ages simply indicates that the fractionation of both the Sm–Nd and Rb–Sr ratios from bulk Earth values occurred at the same time, i.e., roughly 2900 Ma ago.

As a continuation of this work, we here report on the Sr and Nd isotopic systematics of one of the youngest carbonatites in Canada, the Oka complex, near Montreal, Quebec (Fig. 1). Some initial results from Oka have been previously published (Bell et al. 1982; Wen et al. 1985), and a detailed study of the Pb and Sr isotopic compositions has been made (Grünenfelder et al. 1986).

Geology

The Oka complex (Fig. 2), one of the most westerly intrusions of the Monteregian Igneous Province (Gold 1972; Gold et al. 1986), intruded Grenville(?) gneisses and anorthosites at least 109 Ma ago (Wen 1985). A recent summary of the geology is given in Gold et al. (1986). Two intersecting ring structures give the complex the form of a distorted figure eight. Carbonate rocks, mostly sövites, underlie about fifty percent of the complex; the remaining rocks consist of melilitites, pyroxenites, nepheline-bearing rocks, glimmerites, and late lamprophyres and intrusive breccias. Okaite, an example of one of the many unusual silicate rocks, consists of melilite and nepheline, with minor or accessory amounts of hauyne, perovskite, apatite, biotite, magnetite, and calcite. The complex has been mined for the Nb contained in pyrochlore.

Several lines of investigation confirm that the Oka complex is Cretaceous in age. Fairbairn et al. (1963) were the first to show this, and later work by Shafiqullah et al. (1970), using K–Ar data from several intrusive units, yielded mica dates with a mean of 116±4 Ma and a K–Ar isochron date of 120 Ma. Confirmed during this latter study were small, but significant, amounts of excess argon. A Rb–Sr isochron on biotite has yielded a date of 109±2 Ma (Wen 1985). Apatite fission track dates suggest that igneous activity in the Monteregian Province extended over a considerable period of time, from 130 to 108 Ma ago (Eby 1984; Gold et al. 1986).

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* *Present address:* Department of Geological Sciences, University of California at Santa Barbara, Santa Barbara, California 93106, USA

Offprint requests to: K. Bell

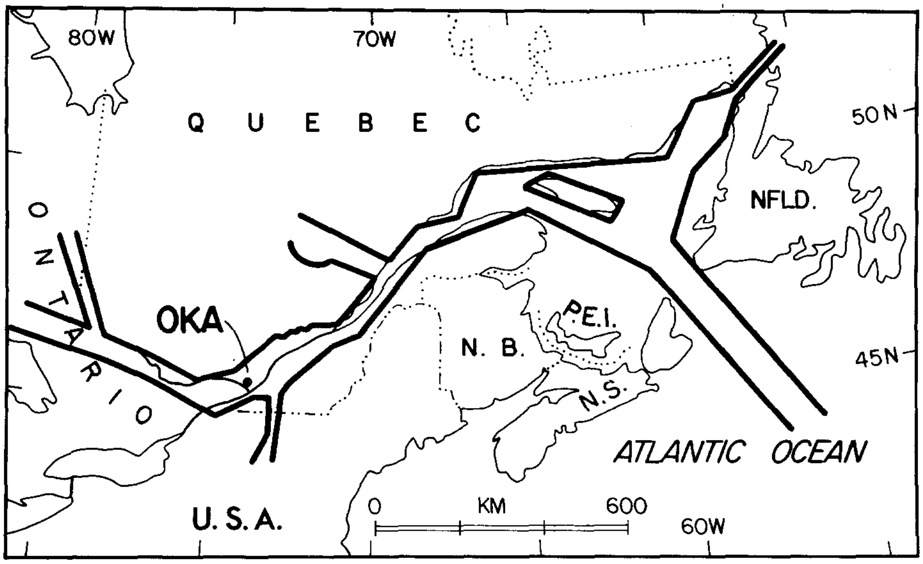

Fig. 1. Location map for the Oka complex. Also shown are the major rift systems of eastern Canada. *N.B.* New Brunswick; *P.E.I.* Prince Edward Island; *N.S.* Nova Scotia; *NFLD.* Newfoundland

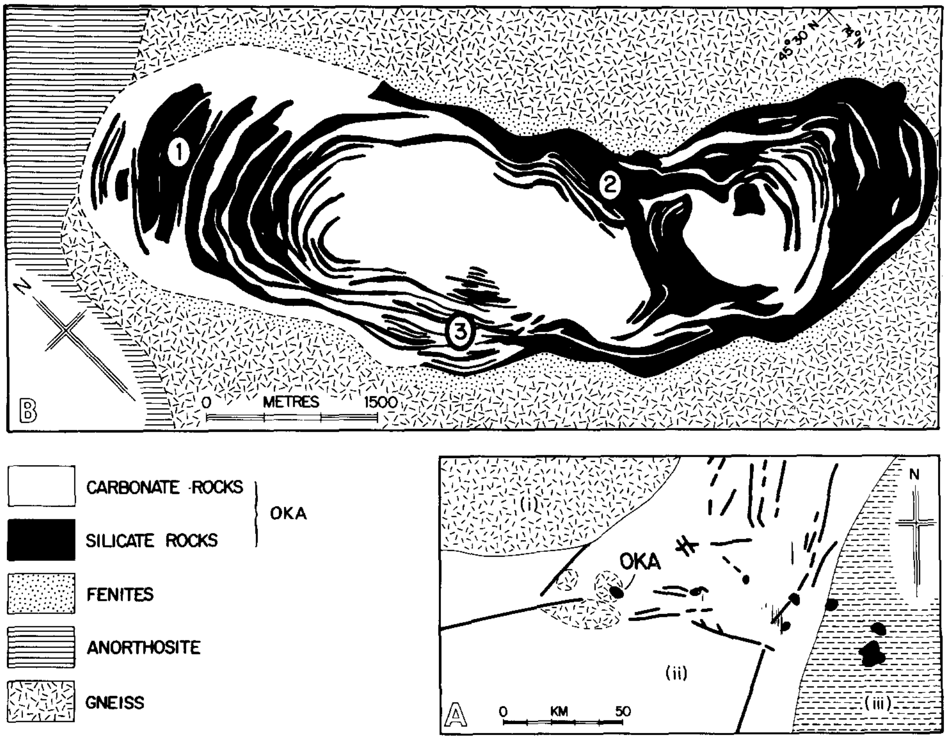

Fig. 2A, B. A Detailed location map: *i* Grenville Province; *ii* St. Lawrence Lowlands; *iii* Appalachian Fold Belt. The other Monteregian intrusions are shown in *black*. **B** Geological map of the Oka complex (after Gold 1972; Gold et al. 1986). Sample locations: *1* Husereau Hill; *2* mine and open pits; *3* Bond Zone

Isotopic tracer studies, in particular C, O, Pb and Sr from the carbonatite, have shown that the Oka complex is remarkably uniform in its isotopic composition. On the basis of well over two hundred analyses Deines (1970) showed that the Oka carbonatite has an average $\delta^{13}C$ value of -5.1, a value typical of many mantle-derived materials; the corresponding $\delta^{18}O$ value is $+7.6$. Although the associated silicate rocks have similar $\delta^{13}C$ values, their $\delta^{18}O$ values are slightly higher. Grünenfelder et al. (1986) have also documented relatively uniform initial Sr isotopic compositions for the Oka complex. The Pb isotopic compositions indicated a low μ source consistent with a LIL-depleted mantle.

Analytical procedures

Samples were collected from a number of localities, including the Husereau Hills, the mine site, and the two nearby open pits. A sample from the Bond Zone was provided by Dr. D.H. Watkinson. Sample localities are shown in Fig. 2. Samples for whole rock analysis were crushed to less than 100 mesh; mineral separates were carried out using a -50 $+80$ mesh split. Minerals were separated using a magnetic separator and heavy liquids. Hand-picking produced a final purity of better than 99%.

Different methods were used to dissolve the samples. Calcites were taken into solution in HCl, while other minerals were dissolved in $HF-HClO_4$. Sövites were first dissolved in HCl, and the residue attacked with $HF-HClO_4$; both solutions were then combined. Other whole rock samples were taken into solution in $HF-HClO_4$. For isotope dilution measurements, the samples were spiked prior to dissolution; a separate aliquot was used for unspiked ratio determinations. Spikes used were ^{87}Rb, ^{84}Sr, ^{145}Nd and ^{149}Sm. Separation of the Rb and Sr was carried out by conventional ion-exchange methods, and separation of the Sm and Nd, by reverse phase chromatography (Richard et al. 1976).

All isotopic analyses were carried out on a Finnigan-MAT 261 multi-collector mass spectrometer. Sr was loaded with phosphoric acid on a Ta single filament; Rb, Sm, and Nd were loaded as chlorides on to the sample filament of a Re double filament assembly. Precision of the ^{143}Nd/^{144}Nd and ^{87}Sr/^{86}Sr ratios quoted is about 0.003% (2 standard deviations of a measurement), estimated on the basis of replicate analyses of rock and chemical standards. The precision of concentration determinations is about 0.5% for Sr, Sm, and Nd, and about 1% for Rb. Blanks in the course of this work were 2 ng for Sr, 0.02 ng for Sm and Nd, and 0.01 ng for Rb. The Eimer and Amend Sr standard gives a ^{87}Sr/^{86}Sr ratio of 0.70802±0.00002; and NBS 987, 0.71023±0.00003. Concentrations of Sm and Nd in BCR-1 (3 determinations) are 6.58 ppm and 28.8 ppm respectively. The ^{143}/Nd/^{144}Nd ratio of BCR-1 is 0.51262±0.00003 (5 analyses).

Results

The Rb−Sr and Sm−Nd concentrations and initial ratios for both minerals and whole rocks are given in Tables 1 and 2. The concentrations of Sr, Sm and Nd in almost all samples are very high. Strontium contents range from 750 to nearly 20000 ppm; Sm, 8 to 1080 ppm; and Nd,

Table 1. Rb−Sr data for Oka samples

Sample number	Rock type or mineral	Rb (ppm)	Sr (ppm)	^{87}Sr/^{86}Sr (initial)	ε_{Sr}(T)
Mineral analyses					
OC 203	Calcite	0.213	19140	0.70333	−14.8
OC 320	Calcite	0.154	11100	0.70324	−16.1
68-14	Calcite	1.24	19210	0.70328	−15.5
OC 203	Apatite	0.490	7620	0.70333	−14.8
OC 320	Apatite	0.707	6340	0.70323	−16.2
68-14	Apatite	1.48	7620	0.70331	−15.1
OC 315	Diopside	4.43	1661	0.70327	−15.6
OC 318	Diopside	25.5	754	0.70328	−15.5
OC 203	Melilite	2.82	9600	0.70333	−14.8
OC 320	Monticellite	10.4	2230	0.70324	−16.1
68-14	Andradite (yellow)	4.63	2360	0.70333	−14.8
68-14	Andradite (red)	4.63	997	0.70332	−14.9
Whole-rock analyses					
OC 200	Carbonatite	7.15	13960	0.70330	−15.2
OC 202	Ijolite	23.4	3010	0.70333	−14.8
OC 203	Okaite	21.5	10850	0.70333	−14.8
OC 305	Carbonatite	18.1	10460	0.70325	−15.9
OC 306	Zeolite-biotite-perovskite	100	5920	0.70323	−16.2
OC 308	Zeolite-biotite-calcite-hauyne	57.9	5520	0.70327	−15.6
OC 310	Carbonatite	11.9	12300	0.70328	−15.5
OC 313	Calcite-zeolite-perovskite-biotite	37.7	9130	0.70328	−15.5
OC 315	Carbonatite	15.9	10540	0.70328	−15.5
OC 318	Carbonatite	42.1	4320	0.70326	−15.8
OC 319	Carbonatite	0[a]	7250[a]	0.70328	−15.5
OC 320	Carbonatite	0[a]	7180[a]	0.70327	−15.6
68-14	Andradite-calcite	23.2	6450	0.70332	−14.9

[a] Rb and Sr concentrations were measured by X-ray fluorescence

Table 2. Sm−Nd data for Oka samples

Sample number	Rock type or mineral	Sm (ppm)	Nd (ppm)	Sm/Nd (weight)	^{143}Nd/^{144}Nd (initial)	ε_{Nd}(T)
Mineral analyses						
68-14	Calcite	7.84	99.0	0.0792	0.51273	+4.5
OC 203	Apatite	1079	7310	0.148	0.51275	+4.9
OC 320	Apatite	541	4510	0.120	0.51281	+6.1
OC 318	Diopside	40.9	233	0.176	0.51275	+4.9
OC 203	Melilite	19.0	184	0.103	0.51276	+5.1
68-14	Andradite (yellow)	79.7	524	0.152	0.51271	+4.1
68-14	Andradite (red)	169	806	0.210	0.51271	+4.1
Whole-rock analyses						
OC 203	Okaite	73.9	697	0.106	0.51276	+5.1
OC 320	Carbonatite	58.1	478	0.122	0.51284	+6.6
68-14	Andradite-calcite	65.9	528	0.125	0.51279	+5.7

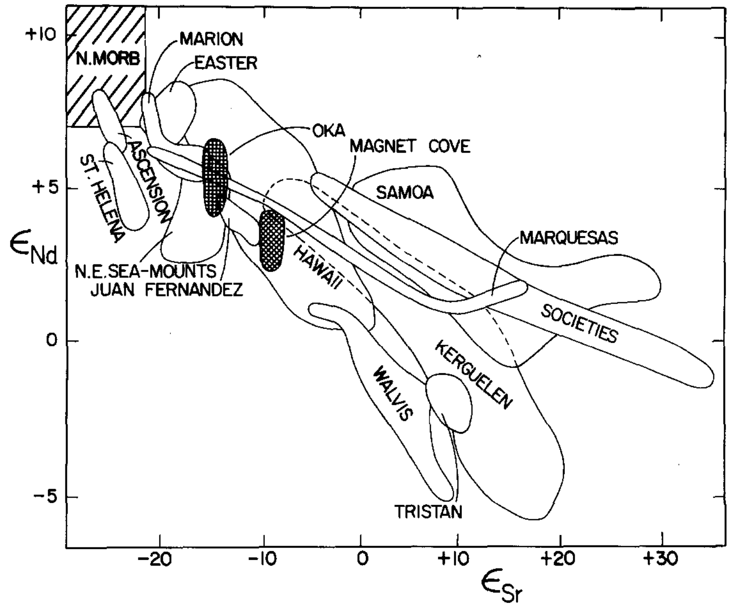

Fig. 3. $\varepsilon_{Sr}(T)-\varepsilon_{Nd}(T)$ anti-correlation diagram. Fields for oceanic basalts from White and Hofmann (1982) and Hart et al. (1986). *N-MORB* normal mid-ocean ridge basalts

100 to 7400 ppm. Apatites and calcites in particular are very high in Sr, Sm, and Nd; the apatite from the okaite OC 203 has the highest Sm and Nd concentrations. In most minerals the Rb content is less than 5 ppm.

The Rb/Sr ratio for most samples was so low that only minor corrections (less than 0.00005) for radiogenic ^{87}Sr had to be applied to the measured $^{87}Sr/^{86}Sr$ ratios. For the Sm–Nd data, a correction for radiogenic ^{143}Nd was required, but this was at most 0.00009, and introduced no significant uncertainty into the results. The age used for the correction was 109 Ma, the value obtained from a Rb–Sr isochron on biotites (Wen 1985; Wen et al. 1985).

The initial isotopic ratios show only small variations. The initial $^{87}Sr/^{86}Sr$ ratios range from 0.70323 to 0.70333, while the initial $^{143}Nd/^{144}Nd$ ratios show a slightly larger spread, 0.51271 to 0.51284. The calcite OC 320 in particular has a higher $^{143}Nd/^{144}Nd$ and lower $^{87}Sr/^{86}Sr$ initial ratio than the other samples. The variations are slightly but significantly larger than the estimated precision of the isotopic analyses. The initial ratios are also given in the tables in the $\varepsilon(T)$ notation of DePaolo and Wasserburg (1976), with T being taken as 109 Ma. Values for the Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of bulk Earth used are 0.0827 and 0.7045 respectively. The ε_{Nd} values are all positive, while the ε_{Sr} values are all negative.

The Sm/Nd ratios for three whole rocks, including both okaite and carbonatite, are extremely uniform, averaging 0.11. The two andradites, identified on the basis of microprobe analyses, have Sm/Nd ratios that are low for garnets. Apatite and calcite inclusions in the garnets, observed in thin section, are probably responsible for the lower ratios.

Discussion

From the data shown in Tables 1 and 2 it is evident that the Oka complex had fairly uniform Sr and Nd isotopic ratios at the time of its formation. Furthermore, there is little sign of isotopic disequilibrium among the mineral phases. No major differences between the initial ratios for either the Sr or Nd in the carbonate and silicate minerals are observed.

The positive ε_{Nd} and negative ε_{Sr} values shown in Tables 1 and 2 indicate that the Sr and Nd have evolved in a source region with a time-integrated depletion in the LIL elements, a finding consistent with results from other carbonatites (Bell et al. 1982; Bell and Blenkinsop 1985; Grünenfelder et al. 1986; Demaiffe et al. 1986; Nelson et al. 1986). Because the Oka complex is relatively young the data from it can be compared with data from young oceanic volcanics using the anti-correlation plot. Figure 3 shows that the Oka data lie close to that part of the mantle array where the data from ocean island and mid-ocean ridge basalts overlap. From this it appears that the carbonatite source is not as depleted as the one that generated MORB. Also plotted on Fig. 3 are data from the Magnet Cove, Arkansas, carbonatite (Tilton et al. 1987), of Cretaceous age. The average initial $^{143}Nd/^{144}Nd$ ratios from Oka and Magnet Cove are similar, but the initial $^{87}Sr/^{86}Sr$ ratio of 0.70363 for Magnet Cove is significantly higher, a feature attributed by Tilton et al. (1987) to regional heterogeneities in the sub-continental mantle.

That the Canadian sub-continental upper mantle is depleted contrasts markedly with the lithospheric LIL-enrichment found in southern Africa (Allsopp and Eriksson 1986), a feature that suggests fundamental differences in the sub-crustal processes operating beneath Canada and southern Africa. We have yet to analyse any carbonatite from Canada that indicates an enriched mantle source. Ancient enrichment is a feature that appears to be widespred in many mantle xenoliths (e.g., Kramers et al. 1983; Richardson et al. 1985). If the source for the Oka magma is ancient lithosphere it seems unlikely that such a reservoir could escape the effects of the incursion of fluids from below. Either the effects of ancient enrichment have been masked during the formation of the carbonatite magma or only non-metasomatized parts of the reservoir have been sampled.

McKenzie (1985) has recently provided some insights into magma extraction that may have some bearing on this problem. He has shown that a magma with low viscosity can separate rapidly from large source regions under small degrees of partial melting, and under such conditions can be highly enriched in the incompatible elements, yet still retain the isotopic signature of its source region. This proposal provides a means of generating carbonatites or their parental magmas without invoking the mechanism of mantle metasomatism, nor disrupting the closed system character of the source region, a feature that would explain the isotopic data from all of the Canadian carbonatites so far studied. McKenzie's model shows that carbonatite magmas can average the isotopic characteristics over significant volumes of mantle. Although McKenzie is implying that carbonatite magmas are primary the same model also holds for other basic magmas of low viscosity, such as nephelinites, that may be parental to carbonatites. This still, however, does not explain the enriched isotopic signature associated with the Phalaborwa complex of South Africa (Allsopp and Eriksson 1986).

Most carbonatites show light-REE enrichment (Bowden 1985) and this feature is also shown by the data from the Oka complex. The average whole-rock Sm/Nd value of 0.11 from Oka is quite different from that estimated for the depleted mantle source (Bell and Blenkinsop 1986) below the Canadian Shield which has a value of 0.358 ± 0.008, almost ten per cent higher than that of bulk Earth. The light REE enrichment must therefore have occurred either slightly before or during the time of magma generation.

Conclusions

The mantle source from which the Oka magma was produced shows a time-integrated depletion in the LIL elements, a finding that agrees with the Pb results from Oka (Grünenfelder et al. 1986) and studies on other carbonatites (Bell et al. 1982; Bell and Blenkinsop 1985; Demaiffe et al. 1986; Nelson et al. 1986). The Oka data, when combined with data from other Canadian carbonatites of different ages (Bell et al. 1982; Bell and Blenkinsop 1985, 1987), show that parts of the Canadian Shield have been underlain by such a source region since the late Archean and that this source has probably been coupled to the continental crust until at least the Cretaceous. This heterogeneous, depleted source region has now been documented over an area extending from the Big Spruce Complex in the Northwest Territories (Cavell et al. 1986) to northern and central Ontario and parts of Quebec, Canada, (Bell and Blenkinsop 1986) south to Arkansas (Tilton et al. 1987) in the southern United States, an area of over 7×10^6 km^2.

Acknowledgements. This work was supported by Natural Sciences and Engineering Research Council of Canada operating grants A7813 (K.B.) and A7960 (J.B.), and equipment grants E4167 and E5761. J. Wen thanks the Government of the People's Republic of China for support of his graduate work. We also thank D.H. Watkinson for donation of samples, and J.W. Card and J. Stevenson for their assistance.

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Received September 4, 1986 / Accepted July 6, 1987