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Review

Evolution of Montviel alkaline-carbonatite complex by coupled fractional crystallization, fluid mixing and metasomatism — Part II: Trace element and Sm–Nd isotope geochemistry of metasomatic rocks: implications for REE-Nb mineralization

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ABSTRACT

Magmatic volatiles are critically important in the petrogenesis of igneous rocks but their inherent transience hampers the identification of their role in magmatic and metasomatic processes. For example, while the role of magmatic volatiles in porphyry copper systems is relatively well understood, the behavior of volatiles and metasomatic fluids in mantle and crustal magmatic-hydrothermal systems remains a work in progress. Alkaline-carbonatite complexes usually originate from the mantle and typically host REE deposits which are thought to be almost always of a hydrothermal origin. The question thus arises as to the origin of the REE and fluids and if the alkaline and carbonatite magmas are accompanied by fluids from the mantle up and through the crust. This study presents the results of whole rock trace elements and Sm–Nd isotopes analyses of clinopyroxenites, melteigites, ijolites, melanosyenites, leucosyenites, granites, silicocarbonatites, magnesiocarbonatites and polygenic breccias from the 1894 Ma Paleoproterozoic alkaline-carbonatite complex of Montviel, Abitibi, Canada. The metasomatic rocks range in REE concentrations from 100 ppm to 3.54 wt.% and show ϵ_{Nd} values ranging from +6.8 to -7.2. Based on these results it is demonstrated that volatile-saturated magmas at Montviel were injected through 4 distinct mantle pulses which evolved by fractional crystallization, mixing of depleted mantle and crustal fluids and metasomatism.

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1. Introduction

Magmatic volatiles are critically important in the petrogenesis of igneous rocks but their inherent transience hampers the identification of their role in magmatic and mineralization processes (e.g., Bowen, 1928; Hamilton et al., 1964; Hedenquist and Lowenstern, 1994; de Moor et al., 2013; Black et al., 2014; Plail et al., 2014). The role of magmatic volatiles in porphyry copper systems, for example, is relatively well understood (e.g., Sillitoe, 1973, 2010), but understanding the behavior of volatiles and metasomatic fluids in mantle and crustal magmatic-hydrothermal systems remains a work in progress (Harlov and Austrheim, 2013).

Alkaline and carbonatite complexes usually originate from the mantle and are commonly emplaced during continental rifting, collisional orogenesis or post-collisional extensional settings, possibly associated with mantle delamination (e.g., Chakhmouradian and Zaitsev, 2012). These complexes typically host REE deposits which are almost always magmatic-hydrothermal (Mariano, 1989; Giere, 1996). The question thus arises as to the origin of the REE and the fluids and if the alkaline and carbonatite magmas are accompanied by fluids from the mantle and up through the crust. The Montviel complex, Abitibi, Canada, represents an ideal setting to study the role of fluids in the petrogenesis of alkaline complexes and the metallogenesis of REE deposits because of the presence of a very diverse range of lithologies, each of the lithologies were metasomatized, and the complex was extensively drilled for core samples which were readily available for this study. Montviel alkaline complex is associated with a carbonatite-hosted magmatichydrothermal REE-Nb deposit (Nadeau et al., 2015).

This study presents the results of whole rock trace elements and Sm-Nd isotope analyses of metasomatized clinopyroxenites, melteigites, ijolites, melanosyenites, leucosyenites, granites, silicocarbonatites, magnesiocarbonatites, calciocarbonatites, ferrocarbonatites and polygenic breccias from Montviel. These results are discussed with emphasis on the role of fluids in the petrogenesis of the rocks and on the source of magmas and volatile phases. The petrography of these lithologies, a mineral paragenesis as well as the trace element and Sm-Nd isotope composition of metasomatic biotite and aegirine-augite are presented in a companion paper titled: "Evolution of Montviel Alkaline-Carbonatite Complex by Coupled Fractional Crystallization, Fluid Mixing and Metasomatism - Part I: Petrography and Geochemistry of Metasomatic Aegirine-augite and Biotite; Implications for REE-Nb mineralization". A model is proposed for the evolution of the alkaline complex through 4 distinct mantle pulses and their evolution by fractional crystallization, mixing of mantle and crustal fluids and metasomatism.

2. Geologic context

The Paleoproterozoic Montviel alkaline complex intruded foliated Archean tonalites in the northeastern part of the Sub-Province of Abitibi at 1894 \pm 4 Ma based on U–Pb on zircons from ijolites (David et al., 2006). A chronological sequence of the lithological units was established based on field and drill core cross-cutting relationships (Goutier, 2006; Nadeau et al., 2015). The alkaline complex thus consist of injections of clinopyroxenites, clinopyroxene-nepheline-sodalite rocks (melteigitesijolites), clinopyroxene-K feldspar rocks (melanosyenites), quartzsaturated rocks (leucosyenites-granites), intermediate rocks between carbonatites and ultramafites (silicocarbonatites), carbonatites enriched in Mg (rare magnesiocarbonatites), Ca(calciocarbonatites), and Fe (ferrocarbonatites), late intermixed carbonatites, and polygenic breccias (Fig. 1). Silicocarbonatites, which have 10–50% carbonates, were subdivided into lamprophyric and kimberlitic silicocarbonatites based on their appearance and affinity. All of these rocks were hydrothermally altered (metasomatized).

The Na-K-Fe metasomatism at Montviel is evident in the replacement of augite by aegirine-augite and aegirine by Na-Fe³⁺-rich fluids. Petrographic textures also suggest that nepheline + analcime and nepheline + cancrinite formed after metasomatic recrystallization of an unidentified precursor. These same fluids provoked the albitization of plagioclase in the syenites and granites and the formation of albite through alteration of nepheline or analcime in the clinopyroxenitemelteigite-ijolite series. The metasomatizing fluid replaced the magmatic biotite with lower temperature biotite and likely recrystallized high temperature potassium feldspars in the syenites to microcline as has been documented in other alkaline complexes (Drüppel et al., 2005; Pirajno, 2013). The role of Fe in the metasomatic fluid is evident from the aegirinization of augite and from the fact that all carbonates with magmatic textures at Montviel are either calcite or dolomite whereas ferroan-dolomite, ankerite, siderite, but also biotite, aegirineaugite and aegirine were hydrothermal or metasomatic. This suggests that ferrocarbonatites were produced from calciocarbonatites by fractional crystallization and Fe-metasomatism.

3. Analytical methods

3.1. Bulk rock analyses

Representative samples of the lithologies at Montviel were crushed and powdered. Fractions of this powder were used for major and trace elements and Sm–Nd isotope analyses. The major and trace elements were analyzed at Actlabs Laboratories, Canada via inductively coupled plasma mass spectrometry (ICP-MS). For rocks with $P_2O_5 > 0.3$ wt.%, Nb, Ta and Zr were neglected as their concentrations could be anomalously low, as reported by the commercial geochemical laboratory (oral communication).

3.2. Thermal ionization mass spectrometry

Sm–Nd isotopes were analyzed at Geotop, UQAM. Sample weighing and chemistry were performed in a class 100 (ISO5) clean room. Powdered samples were weighed (about 0.1 g) and a ¹⁴⁹Sm–¹⁵⁰Nd spike was added to determine Sm and Nd concentrations. The samples were sequentially dissolved and dried in 29 N HF, 29 N HF + 15 N HNO₃, Aqua Regia and 6 N HCl acids. The Sm and Nd fractions were then purified by cation exchange chromatography following the procedure of (Roulleau and Stevenson, 2013). The Sm and Nd isotope concentrations were measured in static collection mode via a double Re filament assembly on a Thermo Scientific Triton Plus thermal ionization mass spectrometer (TIMS). Neodymium was monitored using a JNd1 standard having a value of ¹⁴³Nd/¹⁴⁴Nd = 0.51209 ± 0.00005 and 2 σ errors were 0.000009 in average (n = 19). Typical combined procedure blanks for Nd and Sm were <150 pg.

4. Bulk rock composition

4.1. MORB-normalized LILE-HFSE spidergrams

Bulk rock large ion lithophile elements (LILE; Sr–Ba) and high field strength elements (HFSE; Ta–Nb–La–Zr–Hf–Sm–Ti–Y) concentrations were normalized to MORB (Sun and McDonough, 1989) and plotted on spidergrams (Fig. 2). Clinopyroxenites and silicocarbonatites plot the closest to MORB, with most elements enriched by factors ranging

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Fig. 1. Geological map of Montviel alkaline complex. Modified after Goutier (2006).

from about 1 to 100 (apart from a few Zr–Hf values) and the most incompatible elements (closer to the Ta–Ba join) being more enriched than the less incompatible ones. Mobile Sr and Ba vary between 2–14 and 57–126 times MORB in clinopyroxenites and 6–21 and 42–309 times MORB in silicocarbonatites, respectively. The usually immobile group V elements Nb and Ta are also enriched in these lithologies and vary between 24–87 and 11–106 times MORB in clinopyroxenite and 47–288 and 7–142 times MORB in silicocarbonatites, respectively. The concentration of other incompatible element decrease in order of decreasing incompatibility, from La to Y, with the exception of usually immobile group IV elements Zr and Hf, which appear to be much lower in silicocarbonatites than in clinopyroxenites.

The evolution of these incompatible elements in melteigites, ijolites, melanosyenites, leucosyenites and granites is shown in Fig. 2b. Note that samples with P_2O_5 content greater than 0.3 wt.% yielded unreliable Nb, Zr and Ta concentrations (see methodology). In these cases Hf was used as a proxy for the other HFSE. The trace element profile of the melteigite is similar to those of the clinopyroxenites and silicocarbonatites and the following ijolite, syenite and granite gradually decrease in concentrations of Nb–Ta, Ti–Zr–Hf and La–Sm–Y, except for the melanosyenite which is enriched in Ba–La–Sm–Y as a result of intense pervasive hydrothermal alteration.

This trend of decreasing concentration for all incompatible elements observed in the silicate rocks is different than the one observed in carbonatites. For calciocarbonatites, ferrocarbonatites, mixed carbonatites and the polygenic breccias, while the group V Nb–Ta and the group IV Ti–Zr–Hf are depleted to the point that many are below the limit of detection, the mobile Sr–Ba and the REE are enriched to concentrations reaching several thousand times the depleted mantle values, resulting in a distinctive 'sawtooth' pattern in the spidergrams.

4.2. Mobile-to-immobile element ratios

Barium, Sr, F and P were normalized to Nb to illustrate their mobility in metasomatic processes with respect to magmatic evolution (Fig. 3). Indeed, at Montviel, Ba–Sr-bearing carbonates, fluorite and fluorapatite were shown to be hydrothermal or metasomatic and related to syn-magmatic, hydrothermal alteration (Nadeau et al., 2015). Silicocarbonatites and mixed carbonatites (which contain silicocarbonatites) have the highest Nb concentrations (300–350 ppm) and clinopyroxenites have intermediate Nb concentrations (150– 200 ppm) (Table 1). Rocks with high Nb concentrations have low Ba/ Nb, Sr/Nb and P/Nb ratios and low to intermediate F/Nb ratios. Evolved silicate rocks such as leucosyenites and granites have very low Nb concentrations (7–21 ppm) and relatively low Ba/Nb, Sr/Nb, F/Nb and P/Nb ratios. In contrast, carbonatites have intermediate to relatively low Nb concentrations but intermediate to relatively high Ba/Nb, Sr/Nb, F/Nb and P/Nb ratios.

4.3. Rare earth element patterns

Chondrite-normalized (Sun and McDonough, 1989) REE patterns for the different lithologies are presented in Fig. 4. Clinopyroxenites and silicocarbonatites have total REE concentrations from 50 to 1500 ppm (Table 1). They are LREE-enriched with (La/Lu)_N ratios of about 4–50 in clinopyroxenites and 25–480 in silicocarbonatites. As was observed

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Fig. 2. Depleted mantle-normalized incompatible element spidergrams for main lithologies from Montviel. (a)clinopyroxenites; (b) other silicate rocks comprise melteigites, ijolites, melano- and leucosyenites and granites; (c) silicocarbonatites; (d) magnesiocarbonatite and calciocarbonatites; (e) ferrocarbonatites; (f) mixed carbonatites and polygenic breccia. Among the incompatible elements, Sr and Ba are mobile, Ta-Nb-Zr-Hf-Ti are incompatible and immobile and REE are generally incompatible and may be mobile. MORB data from Saunders and Tarney (1984) and Sun (1980).

in the spidergrams, the more evolved silicate rocks are gradually depleted in all REE from melteigite to ijolite, syenite and granite, except for the melanosyenite which was intensely pervasively altered, as witnessed by high Ba–Sr content. Total REE contents vary from 575 ppm in the melteigite to about 100 ppm in the granite and leucosyenite. The gradual depletion in REE conserves the negative slope, with (La/Lu)_N varying from about 10–100.

Carbonatites (Fig. 3d–f) are more enriched in REE than all other lithologies. Calciocarbonatites and magnesiocarbonatites have total REE concentrations of 220 ppm to 3.54 wt.%, ferrocarbonatites have total REE concentrations of 3000 ppm to 1.9 wt.%, the fluorocarbonatite (fluorite-rich ferrocarbonatite) has a total REE value of 2500 ppm, mixed carbonatites have total REE contents of 4500 ppm to 3.17 wt.% and the polygenic breccia has a total REE content of 3130 ppm. All carbonatites except the polygenic breccia (which is not truly a carbonatite but is plotted here for convenience) and some ferrocarbonatites have a very pronounced LREE enrichment. The $(La/Lu)_N$ ratio of the magnesiocarbonatites is 4040 because of a very low HREE content. Calciocarbonatites and ferrocarbonatites have similar $(La/Lu)_N$ ratios of 20–450 and 115–390, respectively. However, the calciocarbonatites and ferrocarbonatites have little variation in HREE, i.e. from about 10–100 ppm, but relatively large MREE and LREE variations, from about 100 ppm to 3.0 wt.%. All calciocarbonatites have smaller variations in LREE but relatively larger ones in HREE. Generally,

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Fig. 3. Plot of Nb-normalized Ba (a), Sr (b), F (c) and P (d) against Nb (ppm). Niobium is taken as a proxy for immobile-compatible element whereas Ba, Sr, F and P are mobile in carbonatite.

ferrocarbonatites with less LREE have more HREE, giving them mild negative LREE slopes and positive HREE slopes. The fluorocarbonatite (fluorite-rich ferrocarbonatite) has the least abundant total LREE, with about 1000 ppm of each LREE, and the most HREE, with about 100 ppm of each HREE, giving it the smallest (La/Lu)_N ratio of 20. Mixed carbonatites are similar to ferrocarbonatites and some calciocarbonatites with depleted HREE values (Lu around 10 times chondrites) and enriched LREE values (La of 3300–29,500 times chondrite), making (La/Lu)_N 350–2600. Finally, the polygenic breccias, like the fluorocarbonatite, is enriched in MREE and HREE, and has a mildly negative slope varying from about 1000 times chondrite LREE to 100 times chondrites HREE, giving it a (La/Lu)_N ratio of 10.

4.4. Sm-Nd isotope data

Sm–Nd isotope data for bulk rock samples are presented in Table 2 and in Fig. 5. On the ¹⁴³Nd/¹⁴⁴Nd vs ¹⁴⁷Sm/¹⁴⁴Nd plot it is evident that the measured isotope ratios do not produce an isochron but are bracketed between two fitted isochrones; a 1.894 Ga isochron representing the U–Pb age of the complex (David et al., 2006) and an arbitrary 1.0 Ga isochron that closes the bracket. Both isochrons were drawn using an initial ¹⁴³Nd/¹⁴⁴Nd ratio of 0.5105 to represent the depleted mantle at 1.9 Ga. This suggests the Sm–Nd system experienced opensystem behavior. Initial ε_{Nd} values based on the U–Pb age of 1.894 Ga vary between enriched values of -7.2 to depleted values of +6.8(Fig. 5b–c). A plot of the ε_{Nd} values and the Nd concentrations of the samples yield an exponential correlation (Fig. 5b) or a linear array when plotted against 1/Nd (Fig. 5c), except for one polygenic breccia data point which has a moderate Nd concentration and a low ε_{Nd} value. The linear correlation extends from a high Nd – high ε_{Nd} endmember to a low Nd – low ϵ_{Nd} endmember. Mixed carbonatite, magnesiocarbonatite and ferrocarbonatites cluster tightly around ϵ_{Nd} values of +3.7 to +5.3 and Nd concentrations of 540 to 1110 ppm (2970 to 6730 ppm total REE (TREE)). Both the early lamprophyric and the late kimberlitic silicocarbonatites also cluster close to the mixed carbonatites, magnesiocarbonatites and ferrocarbonatites at ε_{Nd} values of +6.4 to +6.8, but with lower Nd concentrations of 195 to 255 ppm (1150 to 1520 ppm TREE). The leucosyenite and granite samples plot at low Nd concentrations of 19 and 20 ppm, respectively, and low but significantly different ε_{Nd} values of -7.2 and -2.3, respectively. The clinopyroxenite and the ijolite plot between the extreme endmembers of +6.8 and -7.2, at ε_{Nd} values of +2.8 and +2.1, respectively, with Nd concentrations of 70 and 90 ppm (275 and 420 ppm TREE), respectively. The calciocarbonatite also plots closer to the negative ε_{Nd} end-member at -3.7 and 34 ppm Nd (220 ppm TREE). The polygenic breccia plots away from the linear array at an $\varepsilon_{\rm Nd}$ value of -3.8 and Nd = 490 ppm (3130 ppm TREE).

5. Discussion

Cross-cutting relationships in outcrops and drill cores are the most important piece of evidence for the relative chronology of the evolution of the alkaline complex from clinopyroxenite to more evolved silicate rocks, silicocarbonatites and carbonatites (Goutier, 2006; Nadeau et al., 2015) and the petrographic observations of mineralogical and textural relationships presented here and in the companion paper demonstrate that metasomatism was omnipresent throughout the evolution of the magmatic-hydrothermal system. The trace element and isotopic geochemistry of the metasomatic rocks (this research) and minerals (companion paper) documents distinct metasomatic fluids in silicate

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Table 1

Bulk rock major and trace element concentrations. Total Fe is reported as Fe₂O₃*. LOI means 'lost on ignition' and can be used to calculate H₂O when compared to CO₂. No value means the result was below the limit of detection, except for sample LP12.UMPO4 which had Nb over the limit of detection of 1000 ppm. Total REE includes lanthanides and Y.

Lithology	Sample	Be	Sc	Со	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb	Мо	Ag	Sn	Sb	Cs	Ba
Detection limit		1	1	1	10	30	1	1	1	2	2	2	4	1	2	0.5	1	0.5	0.5	3
Clinopyroxenite	MV12.UM01	7	19	55	460	160	27	3		153	794	52				10.3	3		2.5	846
Clinopyroxenite	MV12.IJ02	4	64	44	330	280	27	2		253	319	12	790	217		10.6	5	1.5	3.4	1512
Clinopyroxenite	MV13.SERP1	24	28	81.3	288.5	104	6.7		1.1	76	1873.9	21	58.1	141.2	6.9	0.2	2	1.6	0.7	617
Clinopyroxenite	MV12.UM02	8	18	23	60	160	18	2		46	932	19			2	6.4	5	1.5		688
Melteigite	MV12.IJ01	7	20	50	340	220	25	2		89	1752	32			3	7.7	4	1.4	1.6	917
Ijolite	MV12.SY02	5	4	12		90	20	1		54	943	18				4.9	3	1.2	3.4	1974
Melanosyenite	MV12.UMM01B	6	8	21	30	110	20	2	5	112	2607	22				4.8	2	1.3	2.7	3276
Leucosyenite	MV12.SY04	3	4	5		40	22			139	494	11	86	21		3.5	1	1.2	0.9	639
Granite	MV12.GR01	4					20			217	171	3	120	7		3.9	1	1.1	1.7	704
Silicocarbonatite (Gl Bx)	LP12.SICB01	3	8	25	30	320	13	2		259	2835	24				3.1	3	1.1	4.1	3249
Silicocarbonatite (lamp-like)	M12.HREE02A	10	15	65	90	110	22		6	113	1866	41				4.3	3	1.4	1.3	2894
Silicocarbonatite (kimb-like)	M12.KI01	7	15	44	130	40	24	1		147	771	33				6.4	4	1.1	3.1	500
Silicocarbonatite (kimb-like)	MV13.DYK1	4	20	67	80	120	19	2		76	1461	24				3	3		1.2	3791
Silicocarbonatite (kimb-like)	MV13.DYK2	4	13	64	60	190	17	2		82	1275	6	193	340		1.8	2		3.2	3708
Magnesioocarbonatite	LP12.FECB01B		14	7		410	25	3	9	6	10,170	7		212	4	2.9		1		14,050
Calciocarbonatite	M12.CACB01A						1				15,020	43		3		2.8		1		18,140
Calciocarbonatite	MV12.RAMP2		2	4	10	1470	24	3	14		38,000	616		14		2.9		1.1		3040
Calciocarbonatite	MV12.HREE05	2	9	3	30	90	152	31	76		57,650	1159	9	33	1160	6.1	1	2		228,800
Ferrocarbonatite	MV12.CAFECB02		2	11		650	11	3	7		2123	204	5	19	3	4		0.9		2295
Ferrocarbonatite	MV13.FECL1		5			600	12	2		3	4842	22		142						55,110
Ferrocarbonatite	MV13.FECL2		5	18		2070	26	4	10	19	6364	29			73				0.7	93,130
Ferrocarbonatite	MV13.FECBAL		2	10		680	19	6	13		6001	21		51						39,720
Ferrocarbonatite	MV13.FECP	2	16	12		1660	73	12	30	7	14,820	42			5					37,800
Ferrocarbonatite	LP12.UMPO4A2	1	15	4	20		13	3	8	4	8942	286				1.5	3			2408
Mixed carbonatites	MV12.LATE2		1	14		2110	22	5	13	21	7877	98	4	30	24	3.1	1	0.9	1	52,900
Mixed carbonatites	MV13.CACMIX		15	34		80	118	21	50	32	30,380	96	9	296	249	1.4			1	60,610
Polygenic breccia	MV12.MBX02B	6	14	27	50	150	21	3	10	86	2731	770			13	4	3	1	2.6	805

rocks and carbonatites, and Sm–Nd isotope systematics of metasomatic rocks presented here demonstrate that the system was open and evolved byfractional crystallization and mixing of fluids from depleted and enriched sources. Based on the above results and as discussed below, it is suggested that the metasomatic fluid was a mix of the magmatic system's own volatile phase originating from the depleted mantle, and external fluids from the overlying crust. The petrogenesis of the alkaline complex was inextricably accompanied by metasomatism and thus evolved by a combination of fractional crystallization, fluid mixing and metasomatism. Here, a 'fluid' refers to a low density, low viscosity phase, distinct from silicate and carbonatite melts, and composed of volatile species (H₂O, CO₂, H₂S, HCl, etc.), metals (Na⁺, K⁺, Fe^{2+ or 3+}, REE³⁺, etc.) and ligands (e.g., Cl⁻, HS⁻, CO₃²⁻, etc.). This fluid may be in a supercritical state, at the liquid or at vapor state.

5.1. Metasomatism of crystallizing mantle magmas

The clinopyroxenites represent the first magmas injected at Montviel, although the presence of olivine pseudomorphs in some rocks suggests that the original compositions may have been more primitive. Based on the trace element concentrations of clinopyroxenites, these ultramafic magmas were enriched in immobile Nb (140–220 ppm), Ta (2–17 ppm) and Hf (2–23 ppm) (Fig. 2; Table 1). However, highly variable concentrations of REE (150–1100 ppm) and the existence of hydrothermal REE-bearing minerals such as cordylite-(Ce), kukharenkoite-(Ce) and synchysite-(Ce) (Nadeau et al., 2015) suggest that these REE were mobile and thus subsequently enriched in clinopyroxenites by metasomatic processes.

Clinopyroxenites and silicocarbonatites have higher Nb and lower Ba/Nb, Sr/Nb, F/Nb and P/Nb. Silicate rocks evolved towards low Nb leucosyenite and granites by fractional crystallization, for example of perovskite, pyrochlore, zirkelite, ilmenite, titanite and possibly biotite. Quartz-saturated leucosyenites and granites show limited Ba–Sr–F–P metasomatism. Carbonatites also evolved towards low Nb by fractional crystallization, but acquired high Ba/Nb, Sr/Nb, F/Nb and moderate P/Nb by metasomatism.

Given that the REE were enriched in these rocks by metasomatic processes (Nadeau et al., 2015), a 143 Nd/ 144 Nd₀ = 0.510330 (ϵ_{Nd} value of +2.8) for bulk clinopyroxenites and 143 Nd/ 144 Nd₀ = 0.510296 (ϵ_{Nd} value of +2.1) on ijolites (Table 2; Fig. 5) suggests that the fluids which metasomatized the crystallizing ultramafic to mafic magmas originated from a source with ¹⁴³Nd/¹⁴⁴Nd ratios higher than that of the chondritic uniform reservoir (CHUR), which had 143 Nd/ 144 Nd₀ = 0.509135 at 1894 Ma based on an a present day 147 Sm/ 144 Nd = 0.1967 (Faure, 1977). The open system behavior of the fluiddominated isotopic system suggest that the high ¹⁴³Nd/¹⁴⁴Nd fluid mixed with external fluids and variations of ε_{Nd} values from +2.8 to +2.1 as well as ε_{Nd} values of biotite and aegirine-augite (see companion paper) show these external fluids had relatively lower ¹⁴³Nd/¹⁴⁴Nd₀ ratios. It is likely that the high and low ¹⁴³Nd/¹⁴⁴Nd fluid sources were the depleted mantle and the enriched crust, respectively (Bell and Blenkinsop, 1989).

Because of fractional crystallizationand fluid mixing, the fluid accompanying the melteigites was in disequilibrium with the clinopyroxenites and that accompanying the ijolites was in disequilibrium with the melteigites. Multiple injections of ijolites as indicated by cross-cutting relationships in drill cores thus produced large amounts of mantle magmatic fluids which mixed with surrounding crustal fluids and metasomatized the crystallizing clinopyroxenites, melteigites and ijolites. Evidence that the silicate rocks were not altered by subsequent carbonatite fluids lies in their different chemical and isotopic compositions: Clinopyroxenites have relatively smooth MORB-normalized incompatible element spidergrams and mild negative slopes of chondrite-normalized REE patterns whereas carbonatites have strong positive Sr-Ba-REE anomalies (Figs. 2, 4). The altered clinopyroxenites and ijolites have ϵ_{Nd} values ranging from $+\,2.8$ to $+\,2.1,$ the altered silicocarbonatites have $\epsilon_{\text{Nd}}=+6.8$ and +6.4 , and altered carbonatites have $\varepsilon_{Nd} = +5.3$ to +3.7 (except the unaltered calciocarbonatite with ϵ Nd = -3.7), i.e., dramatically different Nd-isotope ratios.

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La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Hf	Та	W	Tl	Pb	Bi
0.1	0.1	0.05	0.1	0.1	0.05	0.1	0.1	0.1	0.1	0.1	0.05	0.1	0.04	0.2	0.1	1	0.1	5	0.4
179	444	59.4	247	44.5	11.3	29.3	3.6	15.2	2.3	5.1	0.57	2.9	0.38	20.1			0.1		
32.8	108	16.8	71.8	12.9	3.31	8.1	1.1	4.6	0.6	1.3	0.16	1	0.15	23.3	17	6	0.3		
18.7	49.1	6.97	30.3	6.85	2.08	6.1	0.86	4.17	0.76	2.14	0.44	3.25	0.53	1.6	1.7	18	0.4	13	0.2
53.3	114	14.5	57.5	10.3	2.82	7.8	1	4.9	0.9	2	0.3	2.1	0.34	5		7	0.1		
115	233	28.5	110	19.2	5.18	14	1.8	8.6	1.4	3.1	0.39	2.2	0.29	9.2		7	0.1	11	
74.4	174	22.8	87.3	14.7	3.69	9.7	1.1	5.2	0.8	2	0.28	2	0.35	2.6		6			
199	407	51	189	26.7	6	13.4	1.3	5.5	0.8	1.7	0.22	1.3	0.18	3		8	0.3	11	
16.5	34.5	4.59	18.7	3.4	0.82	2.1	0.3	2	0.4	1.1	0.16	1	0.15	2.1	0.2	14	0.4		
28.5	51.8	5.88	20.5	2.9	0.68	1.5	0.2	0.7	0.1	0.3		0.2	0.04	3.6	0.2	7	0.8	32	
165	387	54.8	216	25.5	5.42	11.3	1.2	6.3	1	2.2	0.25	1.4	0.19	0.7		5	0.3	18	
283	500	55	195	30.1	7.75	18.2	2.3	10.5	1.7	3.9	0.43	2.2	0.26	3		7	1.1	11	
75.7	175	23	92	17.2	4.84	13.4	1.9	8.7	1.4	3.4	0.44	2.6	0.35	8.2		9	0.4		
393	706	75.7	255	32.4	7.58	16.5	1.6	6.8	0.9	1.9	0.24	1.4	0.2	7.8			0.7	7	
315	597	66.8	240	30.3	6.27	11	0.6	2.1	0.2	0.5	0.07	0.5	0.07	4.2	22.8		0.4		
2260	3260	291	828	62.3	9.42	12.5	0.8	2.1	0.2	0.4		0.3	0.06	0.2	0.8	5		13	
32.1	66.3	8.37	33.8	8.9	2.97	9.1	1.6	8.3	1.4	3.4	0.37	1.8	0.19			5			
1500	2530	255	859	149	47.4	141	26.1	147	24.8	52.9	4.91	18.7	1.71	0.9		6		486	2.4
7570	14,800	1810	7070	1190	307	826	104	428	50.7	67.6	4.91	19.5	1.79	3.1		6	1.7	301	30.3
461	972	132	633	196	61.2	175	24	87	9.2	12.5	0.99	4.4	0.43	0.6		4	0.5	964	19.5
866	1620	171	540	51.1	10.9	19.4	1.5	6.2	0.8	2	0.27	1.7	0.24					46	
1180	2890	344	1160	103	19.9	35.4	2.5	9.2	1.2	2.7	0.39	2.8	0.56	0.3			0.2	44	6
369	1680	333	1690	230	35.8	45.4	2.1	5.9	0.7	1.4	0.16	0.9	0.13					15	
4120	9590	1070	3650	310	53.6	81.9	4.1	13.9	2.3	7.2	1.21	10.2	2.06	0.3				67	1.1
311	782	123	605	126	34.1	83.6	12.1	62.5	11	27.7	3.15	15.1	1.71	3.3		3		64	
779	1630	228	1110	334	74.2	146	10.9	37.2	4.4	6.1	0.56	2.6	0.24	0.3	0.2	14	0.2	85	1.9
7000	15,600	1770	6220	634	116	191	12.6	36.2	3.2	5.2	0.47	2.3	0.29	0.6			0.3	80	3.6
298	689	100	489	168	61	196	33.8	180	31.2	71.3	7.78	35.1	3.74	3.2		7	0.2	106	1

5.2. Assimilation of crustal rock and silica saturation

Following the evolution of the clinopyroxenites, melteigites and ijolites a significant fraction of melanosyenites evolved to quartz leucosyenites and granites. The leucosyenite and the granite yielded ε_{Nd} values of -7.2 and -2.3 respectively, suggesting enriched to extremely enriched sources for the evolved rocks, consistent with their relatively high SiO₂ contents of 58.9 and 73.4 wt.%, and low MgO contents of 1.6 and 0.1 wt.%, respectively (Table 1). Because of their moderate to low degree of alteration (Fig. 3), the low ¹⁴³Nd/¹⁴⁴Nd₀ signatures of leucosyenites and granites are attributed to assimilation of crustal rock by the evolving magmas, which is consistent with the existence of a thermal divide between silica-undersaturated and silica-saturated magmas and the low trace element content of leucosyenites and granites (Bowen, 1928; Landoll and Foland, 1996).

5.3. Transition to carbonatites

Lamprophyric and kimberlitic silicocarbonatites are 'true' silicocarbonatites in the sense that they contain 10–50% magmatic carbonate minerals which were co-magmatic with other (silicate, ...) minerals present in the rock. By contrast, glimmerite breccias are not 'true' silicocarbonatites as they appear to have formed by infiltration of carbonatite melt into glimmerites.

Highly metasomatized 'early' lamprophyric and 'late' kimberlitic silicocarbonatites yielded ε_{Nd} values of + 6.4 and + 6.8, respectively, representing extremely depleted values, and Nd concentrations intermediate between silicate rocks and most carbonatites (Fig. 5b). Combined with the similar trace element concentration of silicocarbonatites and clinopyroxenites (Figs. 2–4), this suggests that the fluids in silicocarbonatites did not evolve from fluids in melteigites, ijolites and melanosyenites but were instead related to fluids from clinopyroxenites. Although melteigites and ijolites did crystallize some calcite and dolomite, the silicocarbonatites represent an upsurge of magmatic (calcite and dolomite) and hydrothermal (ankerite) carbonates. Hence, we suggest that clinopyroxenite first evolved to melteigites, ijolites and syenites and were followed by a subsequent pulse of lamprophyric silicocarbonatites, somehow connected to clinopyroxenites and originating from the depleted mantle.

The only sample of calciocarbonatite for which Nd data is available is barren and unaltered and returned a negative ϵ_{Nd} value of -3.7 (Fig. 5; Table 2), suggesting an enriched source region depleted in REE (34 ppm Nd; 220 ppm TREE; sample MV12.CACB01). This confirms that the REE were transported by the metasomatic fluids and not by the calciocarbonatite magma. By contrast, samples of hydrothermalized calciocarbonatites are strongly enriched in REE (up to 7070 ppm Nd and 3.54% REE) and display geochemical signatures similar to that of ferrocarbonatites, magnesiocarbonatites and mixed carbonatites, which have positive ϵ_{Nd} values of +3.7 and +5.3 and up to 6220 ppm Nd and 1.9% REE (Table 1). The REE-bearing metasomatic fluid thus appears to have had an extremely depleted source, most probably from within the depleted mantle.

5.4. Multiple mantle pulses

The apparent mixing trend observed on the ϵ_{Nd} vs Nd (or 1/Nd) plot (Fig. 5b, c) a priori suggests fluid mixing between 'REE-depleted/low $^{143}Nd/^{144}Nd'$ and 'REE-enriched/high $^{143}Nd/^{144}Nd'$ source endmembers. However, this does not agree with the chronologic evolution of the complex as reported by Goutier (2006) and Nadeau et al. (2015), and summarized above, and with the fact that the fluids which altered the clinopyroxenites were not the ones originating from the carbonatites.

The process through which lamprophyric silicocarbonatites evolved to calciocarbonatites is not totally understood because of a lack of samples representing this differentiation process. Nevertheless, crosscutting relations show that the silicocarbonatites were followed by glimmerite breccias, calciocarbonatites, magnesiocarbonatites and

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Fig. 4. Chondrite-normalized REE patterns for: (a) clinopyroxenite, (b) silicocarbonatites, (c) melteigite, ijolite, melanosyenite, leucosyenite and granite, (d) magnesiocarbonatites and calciocarbonatites, (e) ferrocarbonatites, (f) mixed carbonates and polygenic breccia. Chondrite data are from Sun and McDonough (1989).

Table 2					
Bulk rock and	mineral sepa	arate Sm–Nd	isotopic	composi	tions

Lithology	Sample number	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	$2\sigma\text{error}$	$^{143}\text{Nd}/^{144}\text{Nd}_0$	eNd (1.894Ga)
Clinopyroxenite	MV12.IJ02	12.9	71.8	0.111112	0.511715	9.7E-06	0.510330	2.8
Ijolite	MV12.SY02	14.7	87.3	0.098334	0.511521	7.3E-06	0.510296	2.1
Leucosyenite	MV12.SY04	3.4	18.7	0.108491	0.511173	4.1E-06	0.509821	-7.2
Granite	MV12.GR01	2.9	20.5	0.084931	0.511128	4.8E-06	0.510070	-2.3
Calciocarbonatite	MV12.CACB01A	8.9	33.8	0.142883	0.511776	4.0E-06	0.509995	-3.7
Magnesiocarbonatite	LP12.FECB01B	62.3	828	0.045726	0.510964	2.2E-06	0.510394	4.1
Ferrocarbonatite	MV12.CAFECB02	196	633	0.191034	0.512836	7.1E-06	0.510455	5.3
Ferrocarbonatite	MV13.FECL1bis	51.1	540	0.055432	0.511068	4.2E-06	0.510377	3.7
Mixed carbonatites	MV12.LATE2	334	1110	0.178429	0.512652	8.0E-06	0.510428	4.7
Polygenic breccia	MV12.MBX02B	168	489	0.215312	0.512442	7.0E-06	0.509759	-3.8
Silicocarbonatite (lamp-like)	M12.HREE02A	30.1	195	0.094349	0.511688	8.0E-06	0.510513	6.4
Silicocarbonatite (kimb-like)	MV13.DYK1	32.4	255	0.075871	0.511481	7.1E-06	0.510536	6.8

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Fig. 5. Measured ¹⁴³Nd/¹⁴⁴Nd (a) and ε_{Nd} (b) vs ¹⁴⁷Sm/¹⁴⁴Nd in bulk rocks from Montviel. The 1.894 Ga isochron is from U–Pb on zircon in ijolite (David et al., 2006). The 1.0 Ga isochron and the initial ¹⁴³Nd/¹⁴⁴Nd value are arbitrary.

ferrocarbonatites and almost all of these rocks were pervasively altered, returning ϵ_{Nd} from $+\,5.3$ to $+\,3.7$ and REE from 900 ppm to 3.54 wt.%.

An episode of intermixing dykes, pods and lenses of silicocarbonatites, calciocarbonatites and ferrocarbonatites (termed mixed carbonatites) followed, thus representing a third pulse of volatile-saturated mantle magmas. Some unaltered magmatic calciocarbonatites were observed cross-cutting hydrothermally altered ferrocarbonatites, showing that each pulse had its own fluids, and some were strongly altered and returned up to 3.17 wt.% REE%) and an $\epsilon_{Nd} = +4.7$, again conferring the metasomatic fluid a REE-rich, depleted mantle source.

A dyke of kimberlitic silicocarbonatite crosscuts- and hosts clasts of all lithologies except polygenic breccia. One sample of kimberlitic silicocarbonatite returned an extremely depleted ε_{Nd} value of +6.8 and 255 ppm Nd (1520 ppm REE), very similar to values of the early lamprophyric silicocarbonatite (ε_{Nd} = +6.4, 195 ppm Nd, 1150 ppm REE). The kimberlitic silicocarbonatites contain fresh olivine and metasomatic aegirine-augite and biotite, suggesting a fourth pulse of mantle-derived magmatic-hydrothermal activity (Figs. 5, 6). The brecciated texture of the rock testifies to the highly energetic, possibly explosive emplacement of this unit.

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Fig. 6. 4-step model for the evolution of Montviel alkaline system via assimilation, fractional crystallization and metasomatism. Each step represents a distinct mantle pulse.

The polygenic breccia is the last unit to have been emplaced during the evolution of the alkaline complex. Like the preceding dyke of silicocarbonatite, it hosts olivine and is highly brecciated. A bulk sample of the polygenic breccia yielded an ε_{Nd} value of -3.8 and 3130 ppm REE suggesting that hydrothermal fluids which metasomatized the polygenic breccia originated from the crust. Although the contact between the kimberlite-like silicocarbonatite and the polygenic breccia was not observed, given that they were the 2 last units to be emplaced and that both are polygenic breccias, it is likely and seems logical that the kimberlitic silicocarbonatite magmas triggered the explosion which eventually formed the polygenic breccias, while the source of the fluids phase transited from the depleted mantle to the crust.

6. Conclusions

The present paper demonstrates that the alkaline-carbonatite complex of Montviel, Abitibi, Canada resulted from 4 distinct mantle injections of volatile-saturated magmas which evolved via fractional crystallization, fluid mixing and metasomatism. The emplacement of the Montviel complex began with the injection of volatile-saturated olivine clinopyroxenite magmas derived from the mantle that evolved to silica-undersaturated melteigites, ijolites and melanosyenites through fractional crystallization, mixing of high ε_{Nd} (depleted) and low ε_{Nd} (enriched) fluids, and Na-K-Fe metasomatism. The depleted and enriched fluid sources are inferred to be the depleted mantle and the crust, respectively. The syenitic magmas also evolved by assimilating silica-saturated crustal rocks to produce the quartz-saturated leucosyenites and granites. A second mantle pulse resulted in the injection of fluid-saturated lamprophyric silicocarbonatites and calciocarbonatites with strongly positive ϵ_{Nd} and enriched REE fluid signatures, thus probably originating from the depleted mantle. The fluid mixed with surrounding fluids and eventually metasomatized the crystallizing carbonatites to ferrocarbonatites by recrystallizing calcite and dolomite to ferroan dolomite, ankerite and siderite. A third mantle pulse, distinct but similar to the previous one but of a smaller magnitude, resulted in intermixed dykes, lenses and pods of silicocarbonatites, calciocarbonatites and ferrocarbonatites (termed mixed carbonatites). One metasomatized sample of mixed carbonatites returned an $\varepsilon_{Nd} = +4.7$, suggesting a depleted mantle source for the REE-bearing fluids. The last and fourth mantle pulse resulted in the injection of a dyke of volatile-saturated kimberlitic silicocarbonatite accompanied by fluids from the depleted mantle, a shift of the fluid source from the mantle to the crust, as witnessed by a transition of positive to negative ε_{Nd} values, explosion of the magmatic-hydrothermal system and formation of the polygenic breccia. We suggest that the crustal fluids which penetrated the magmatic system might have caused a phreatomagmatic explosion, remobilizing the light REE and thus preferentially enriching the heavy REE.

Conflict of interest

The authors declare they have no conflicts of interests with the present manuscript.

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