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HENRYMEYERITE IN THE METASOMATIZED UPPER MANTLE OF EASTERN ANTARCTICA

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Abstract

A mineralogical study of lherzolitic and harzburgitic xenoliths of eastern Antarctica shows that the upper mantle of this region has been affected by very strong carbonate metasomatism. We describe for the first time henrymeyerite $(Ba_{0.97}Ca_{0.03}K_{0.03}Na_{0.11})_{\Sigma 1.14}$ $(Fe_{0.92}Mg_{0.17}Al_{0.02})_{\Sigma 1.11}$ $(Ti_{6.66}Si_{0.25})_{\Sigma 6.91}$ O_{16} in mantle material. It was found in fine-grained zones containing second-generation clinopyroxene, spinel, olivine, S-bearing chlorapatite, high-Ba, high-Ti phlogopite, calcite, dolomite, Fe-rich magnesite and a mineral of the clinohumite group.

Keywords: henrymeyerite, mantle metasomatism, xenoliths, eastern Antarctica.

Sommaire

D'après une étude minéralogique de xénolithes lherzolitiques et harzburgitiques provenant de la partie orientale de l'Antarctique, le manteau supérieur de cette région aurait été affecté par une très importante métasomatose carbonatée. Nous décrivons pour la première fois la henrymeyerite, $(Ba_{0.97}Ca_{0.03}K_{0.03}Na_{0.11})_{\Sigma 1.14}$ $(Fe_{0.92}Mg_{0.17}Al_{0.02})_{\Sigma 1.11}$ $(Ti_{6.66}Si_{0.25})_{\Sigma 6.91}$ O_{16}, dans un matériau mantellique. Nous l'avons trouvé dans des zones à granulométrie fine contenant un clinopyroxène de seconde génération, spinelle, olivine, chlorapatite contenant du soufre, phlogopite riche en Ba et en Ti, calcite, dolomite, magnésite riche en Fe, et un minéral monoclinique du groupe de la humite.

(Traduit par la Rédaction)

Mots-clés: henrymeyerite, métasomatose du manteau, xénolithes, Antarctique oriental.

Introduction

In the last decades, mantle metasomatism has been considered to be a significant process of mantle enrichment in incompatible elements. Studies of xenoliths of upper-mantle peridotite and tectonically emplaced mantle peridotites have led several authors (*e.g.*, Kurat *et al.* 1980, 1993, Exley *et al.* 1982, Dautria *et al.* 1992, Ionov *et al.* 1993, 1994, Kogarko *et al.* 1995, 2001, Rudnick *et al.* 1993, Yaxley *et al.* 1991, 1998) to conclude that silicate and carbonate melts or $H_2O–CO_2$ fluids could be very active metasomatizing agents that cryptically (trace elements) or patently (new minerals) change the composition of upper mantle rocks or form veins. Carbonate metasomatism is generally attributed to infiltration of ephemeral melts or $H_2O–CO_2$-rich fluids strongly enriched in rare lithophile elements and LREE. The interaction of such melts or fluids with peridotite wallrocks results in the formation of minerals such as apatite, carbonates, amphibole, phlogopite, sulfides, second-generation clinopyroxenes, olivine, spinels (*e.g.*, Kurat *et al.* 1980, 1993, Ionov *et al.* 1993, 1994, Kogarko *et al.* 1995, 2001, Yaxley *et al.* 1991, 1998, Kurat & Dobosi 2000, Dobosi & Kurat 2002). This process gives rise to high abundances of incompatible trace-elements in wallrocks. In the last

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decades, many new concentrators of incompatible lithophile elements (LREE, P, Ti, alkalis, Sr, Ba, Zr, U, Th) such as wadeite, priderite, jeppeite, lindsleyite–mathiasite, Cr–Ca–Zr–Nb-bearing armalcolite, zirconolite, Nb–Cr-bearing rutile (*e.g.*, Haggerty 1987, Zaccarini *et al.* 2004), were documented in metasomatized mantle materials.

Most of these minerals are enriched in Ti and Ba. Dawson (1999) also noted the widespread distribution of these minerals at the Labait volcano, Tanzania, in Ti- and Ba-containing metasomatized mantle-derived xenoliths. He described harmotome, hydrosilicates rich in Ba, perovskite and high-Ti phlogopite containing up to 1.38 wt% BaO.

In the present work, we describe for the first time henrymeyerite, $BaFe^{2+}Ti_7O_{16}$, in the metasomatized mantle xenoliths from East Antarctica. Henrymeyerite was discovered and investigated in carbonatites from Kovdor massif, Kola Peninsula (Mitchell *et al.* 2000).

GEOLOGICAL SETTING AND PETROGRAPHY

The region where the mantle xenoliths were collected, Oasis Dzetti (Latitude 70°12'–71°08' S, Longitude 67°32'– 69°55' E), is located within the eastern zone of Biver Paleozoic rift system, in the Prince Charles Mountains, eastern Antarctica. This rift extends toward the north–northwest direction for more than 400 km. As the result of rifting during Upper Mesozoic, ultramafic alkaline plugs and dykes were formed. According to K–Ar dating, the age of these rocks is Early Cretaceous (Laiba *et al.* 1987). The ultramafic alkaline plugs are 15 to 200 m across. Olivine melanephelinite and alkaline picrite contain a profusion of mantle xenoliths, in some cases more than 20–25% by volume. The xenoliths are very variable in size and reach 40–50 cm in diameter. The suite of xenoliths is representative of a broad section of the upper mantle, and includes deep-seated garnet lherzolite as well as samples of the shallower mantle, such as spinel lherzolite, harzburgite and dunite. The main rock-forming minerals of the xenoliths are olivine, orthopyroxene, chromian diopside, spinel and garnet. In some samples, we found veinlets of carbonates containing magnesite, dolomite and calcite in metamorphic equilibrium with other minerals (forming grain boundaries with 120° angles). Petrographic investigation showed in general protogranular textures in these xenoliths, according to the classification of Mercier & Nicolas (1975). We found henrymeyerite in carbonatized zones of one xenolith of spinel lherzolite that measures 8 × 6 × 5 cm.

The main rock-forming minerals of that xenolith are coarse-grained olivine, clinopyroxene, orthopyroxene and spinel. They are crossed by numerous veinlets of a fine-grained assemblage, which surrounds and replaces these minerals. These fine-grained zones contain second-generation clinopyroxene, spinel and olivine, S-bearing chlorapatite, high-Ba, high-Ti phlogopite, calcite and dolomite. These xenoliths also contain an assemblage of very late minerals consisting mostly of Fe-rich magnesite, a mineral of the clinohumite group, and a very late mica containing much less Ti and Ba than the earlier mica.

Henrymeyerite was found in close association with the latest minerals, ferroan magnesite, clinohumite and the latest mica (Figs. 1, 2). Calcite, dolomite, chlorapatite also are present locally. Henrymeyerite forms elongate (prismatic) and in some cases skeletal crystals about 25 × 10 μm in size. In some cases, henrymeyerite forms accumulations of closely intergrown very small (1–2 μm) crystals.

Henrymeyerite is dark brown, practically opaque, and in reflected light it is grayish white, and has a high reflectivity.

ANALYTICAL METHODS

Polished thin sections were described and investigated by optical microscopy and scanning electron microscopy. The phases were analyzed with CAMECA SX50 and CAMECA SX100 wavelength-dispersion electron microprobes at the Vernadsky Institute of Geochemistry, Moscow and Institute of Geological Sciences of the University of Vienna, respectively. Operating conditions were: accelerating voltage 15 kV and sample current 20 nA. The standards used were a combination of natural minerals, synthetic compounds and pure metals. Background positions were carefully selected to avoid interferences, particularly for Ba. Standard online procedures of correction as supplied by the EMP manufacturer were applied.

CHEMICAL COMPOSITION

The chemical composition of henrymeyerite and accompanying minerals is given in Table 1. The chemical composition of minerals, measured on different grains, is characterized by relative constancy. The mineral formulae were calculated for 16 atoms of oxygen.

When calculated with total iron as Fe^{2+}, the formula of henrymeyerite from eastern Antarctica is $(Ba_{0.95}Ca_{0.03}K_{0.03}Na_{0.10})_{\Sigma 1.11}$ $(Fe_{0.90}Mg_{0.17})_{\Sigma 1.07}$ $(Ti_{6.65}Nb_{0.03}Si_{0.24}Al_{0.02})_{\Sigma 6.94}$ O_{16}. The low analytical totals obtained for mantle-derived henrymeyerite are likely to be caused by the presence of H_2O in the structure of this mineral, because it is present in close association with hydrous minerals, such as clinohumite and mica. We should point out that more than half of the members of the cryptomelane group contain H_2O (redledgeite, mannardite, manjiroite, cesarolite).

This mineral formula corresponds to the ideal formula of henrymeyerite, $BaFe^{2+}Ti_7O_{16}$, and it closely approaches the formula of henrymeyerite at the type

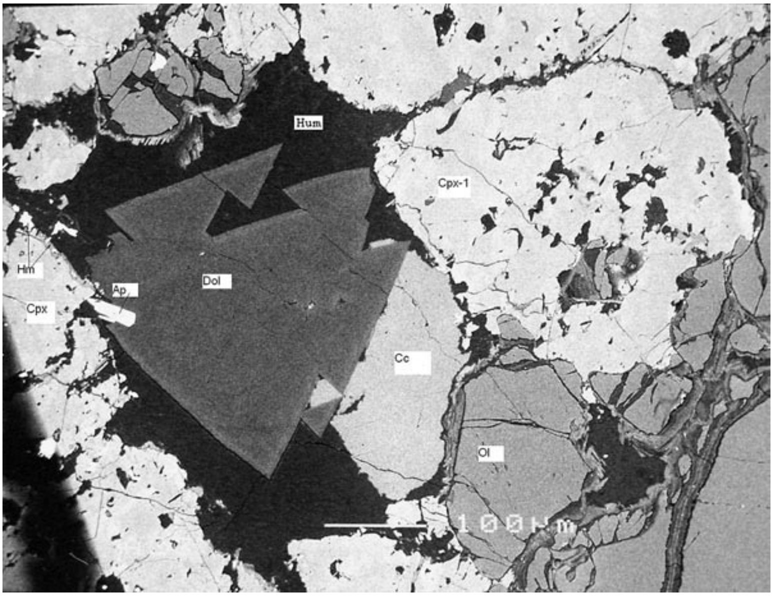

FIG. 1. Back-scattered-electron image of the mineral association containing henrymeyerite. Cpx-1: first-generation clinopyroxene, Cpx: second-generation clinopyroxene, Ol: olivine, Dol: dolomite, CC: calcite, black: magnesite and humite-group mineral, Hm: henrymeyerite, Ap: apatite, Hum: humite-group mineral.

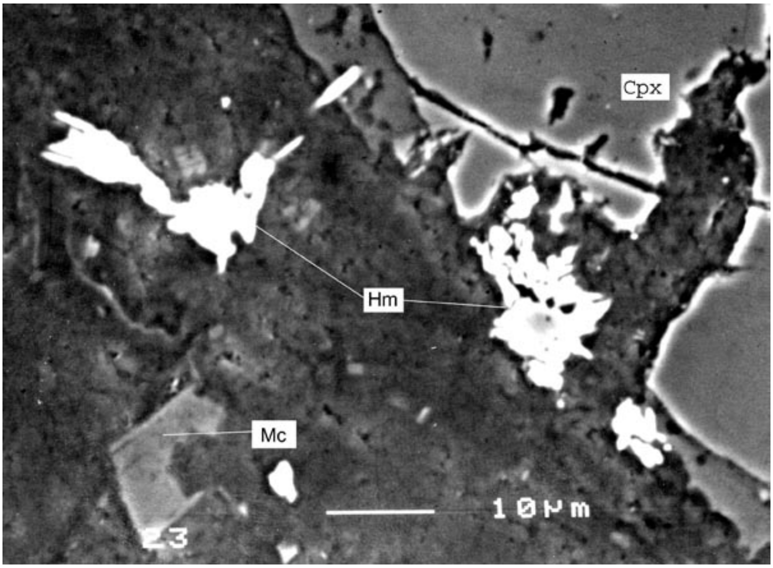

FIG. 2. Back-scattered-electron image of the very late assemblage of minerals including henrymeyerite. Cpx: second-generation clinopyroxene, Hm: henrymeyerite, Mc: late mica, black: background magnesite and humite-group mineral. The grey spot in the core of henrymeyerite on the right side of the photomicrograph is the trace of microprobe beam.

locality, the Kovdor carbonatite complex: $(Ba_{0.96}Na_{0.10}K_{0.01}REE_{0.05})_{\Sigma 1.12}\ Fe_{1.03}\ (Ti_{6.82}Nb_{0.06}Si_{0.04})_{\Sigma 6.92}\ O_{16}$ (Mitchell *et al.* 2000).

Henrymeyerite belongs to the cryptomelane group, which comprises nine mineral species [cryptomelane $K(Mn^{4+},Mn^{2+})_8O_{16}$, priderite $(K,Ba)_x(Ti,Fe^{3+})_8O_{16}$, redledgeite $Ba_x(Ti_{8-2x}Cr^{3+}{}_{2x})O_{16}$, ankangite $Ba(Ti^{4+},V^{3+},Cr^{3+})_8O_{16}$, hollandite $Ba(Mn^{4+},Mn^{2+})_8O_{16}$, coronadite $Pb(Mn^{4+},Mn^{2+})_8O_{16}$, mannardite $[Ba_x(H_2O)_{2-x}](Ti_{8-2x}V^{3+}{}_{2x})O_{16}$, manjiroite $(Na,K)(Mn^{4+},Mn^{2+})_8O_{16}\bullet nH_2O$, and cesarolite $PbH_2Mn_3O_8$.

In 1978, Zhuravleva *et al.* found a new mineral in carbonatites from the Kovdor massif with the chemical formula $(Ba_{0.7}K_{0.1})(Fe_{1.1}Ti_{6.9})O_{16}$, which they called barian priderite. Later, Mitchell *et al.* (2000) described possibly the same mineral, and they called it henrymeyerite. Mitchell *et al.* (2000) suggested that Ba–Fe, Ba–Cr and Ba–V end-members of the cryptomelane group form extensive solid-solutions, with the general formula $Ba_{x+\frac{1}{2}y}[Fe^{2+}{}_x(Fe^{3+},V^{3+},Cr^{3+})_yTi_{8-x-y}]O_{16}$, and the corresponding end-member compositions are redledgeite $Ba_x(Ti_{8-2x}Cr^{3+}{}_{2x})O_{16}$, mannardite $[Ba_x(H_2O)_{2-x}](Ti_{8-2x}V^{3+}{}_{2x})O_{16}$, henrymeyerite $(BaFe^{2+}Ti_7O_{16})$, "Ba–Ti hexatitanite" $BaFe^{3+}{}_2Ti_6O_{16}$, all with tetragonal symmetry.

DISCUSSION

The field of stability of henrymeyerite is not known. There are no experimental data except for the synthesis experiments of Mitchell *et al.* (2000). Henrymeyerite, with the formula $BaFeTi_7O_{16}$, was synthesized at 1300°C by heating a chemical mixture in air for 48 hours. At Kovdor, henrymeyerite is found in a late-stage mineral assemblage associated with a tetra-ferriphlogopite–calcite–dolomite carbonatite cross-cutting metasomatized phoscorite rocks (Mitchell *et al.* 2000). Henrymeyerite has also been reported from a calcite–dolomite carbonatite replacing tetra-ferriphlogopite–magnetite–calcite carbonatite at Seblyavr (Sorokhtina 2000).

TABLE 1. COMPOSITION OF HENRYMEYERITE AND ASSOCIATED MINERALS IN AN EASTERN ANTARCTIC MANTLE XENOLITH

	1	2	3	4	5	6	7	8
SiO_2 wt.%	1.84	0.37	0.07	0	0	45.24	33.32	35.75
Al_2O_3	0.14	-	0	0	0	8.16	14.40	12.95
TiO_2	66.43	67.78	0	0	0	3.33	11.97	6.60
FeO	8.06	9.2	7.49	0.09	1.7	5.48	7.90	9.58
MgO	0.86	-	38.79	0.12	18.87	12.58	14.62	16.41
MnO	0	-	0.31	0.12	0.29	0.02	0	0.1
CaO	0.19	0.02	5.06	56.61	32.23	24.06	0.11	0.07
NiO	0	-	0	0	0	0.03	0.13	0.06
BaO	18.16	18.25	0.03	0.06	0.01	0	7.75	1.47
Na_2O	0.4	0.4	0.03	0.01	0.06	0.33	0.53	0.59
K_2O	0.2	0.05	0	0	0	0	6.48	12.08
La_2O_3	0	0.5	-	-	-	-	-	
Ce_2O_3	0	0.56	-	-	-	-	-	
Nb_2O_5	0.49	1.0	-	-	-	-	-	
Cr_2O_3	0	-	0	0	0	0.14	0.03	0.56
F	-	-	-	-	0	-	1.07	0
Subotal	96.77	98.13	51.78	57.01	53.16	99.37	98.31	96.22
F=O							0.45	
Total							97.86	

Column headings: 1: henrymeyerite *, 2: henrymeyerite **, 3: Fe-bearing magnesite, 4: calcite, 5: dolomite, 6: second-generation clinopyroxene, 7: kinoshitalite-bearing early mica, 8: late phlogopitic mica. * this work, ** Mitchell *et al.* (2000).

At both localities, henrymeyerite is closely associated with dolomite, fluorapatite, tetra-ferriphlogopite and clinohumite. In the Seblyavr complex, henrymeyerite was also found together with Ba-rich zirconolite and Ba–Nb oxides. In the Kovdor and Seblyavr carbonatites, henrymeyerite is believed to have precipitated from low-temperature hydrothermal fluids bearing Ba, Nd, Ti, P and other rare elements that were leached from rocks emplaced earlier, like phoscorites and dolomite carbonatites. This process took place in the temperature range 160–300°C.

Henrymeyerite in the mantle xenolith from eastern Antarctica is also confined to the late assemblages of minerals. It is only found in veinlets cross-cutting early-generation olivine, orthopyroxene, clinopyroxene and spinel. The metasomatic veinlets contain early and late generations of minerals. The earlier generation includes clinopyroxene, olivine, second-generation spinel, apatite, calcite, Fe-rich dolomite, ferroan magnesite and high-Ba, high-Ti phlogopite. The late minerals include a humite-group mineral, magnesite, sulfur-containing apatite, Ba–Ti-poor mica and henrymeyerite. It is probable that the interaction of primary dolomitic melts or fluids with mantle material according to reactions (1) and (2):

$$\begin{array}{l} \underset{\text{orthopyroxene}}{2\,Mg_2Si_2O_6} + \underset{\text{melt}}{CaMg(CO_3)_2} \\ = \underset{\text{olivine}}{2\,Mg_2SiO_4} + \underset{\text{clinopyroxene}}{CaMgSi_2O_6} + \underset{\text{fluid}}{2CO_2} \end{array} \tag{1}$$

$$\begin{array}{l} \underset{\text{melt}}{3\,CaMg(CO_3)_2} + \underset{\text{clinopyroxene}}{CaMgSi_2O_6} \\ = \underset{\text{melt}}{4\,CaCO_3} + \underset{\text{olivine}}{2\,Mg_2SiO_4} + \underset{\text{fluid}}{CO_2} \end{array} \tag{2}$$

resulted in the transformation to carbonated wehrlite, which led to the formation of second-generation olivine, clinopyroxene and calcite. The influx of incompatible elements with the metasomatizing melt or fluid, such as Sr, Ba, LREE, Ti, K and phosphorus, resulted in the formation of Sr- and LREE-rich apatite and high-Ba, high-Ti phlogopite. Large numbers of CO_2-filled micro-inclusions trapped by the rock-forming minerals show that the principal metasomatic processes in the eastern Antarctic mantle were carbonatization and wehrlite formation.

Usually, the very latest mineral assemblage, which includes clinohumite, magnesite, mica with low Ba and

Ti contents, sulfur-bearing apatite and henrymeyerite, is developed in the central parts of metasomatic veins and vugs. Henrymeyerite probably originates by the decomposition of the earlier high-Ba, high-Ti phlogopite.

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