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Sulfides and chalcophile elements in Roberts Victor eclogites: Unravelling a sulfide-rich metasomatic event

Yoann Gréau [a,b,*], Olivier Alard [a,b], William L. Griffin [a], Jin-Xiang Huang [a,c], Suzanne Y. O'Reilly [a]

[a] ARC Centre of Excellence for Core to Crust Fluid Systems and GEMOC National Key Centre, Dept of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia
[b] Géosciences Montpellier, CNRS UMR-5243, Equipe Manteau et Interfaces, Université Montpellier II, France
[c] State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, China Academy of Sciences, Beijing, China

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ABSTRACT

A suite of eclogite xenoliths from the Roberts Victor kimberlite (South Africa) is remarkable for its high abundances of base metal sulfides (BMS; up to 2 modal %). However, while sulfides are nearly ubiquitous in Type I eclogites (garnet > 0.07% Na_2O), Type II eclogites (garnet < 0.07% Na_2O) systematically lack sulfides. Two different sulfide assemblages are recognised within the Type I xenolith suite. Both populations are polyphase Cu–Ni–Fe sulfides, one characterised by the pyrrhotite (Po) + pentlandite (Pn) + chalcopyrite (Cp) assemblage and the other by the smythite/violarite (Smy/Vi) + (Ni)pyrite (Py) + Cp assemblage. The latter is the most abundant assemblage and reflects the supergene alteration of the "primary" Po + Pn + Cp assemblage. This process overprints the original composition of the sulfides by remobilising elements such as S, Fe, Ni, Se and Te. In the Type I eclogites, BMS occur as inclusions within silicates (garnet and clinopyroxene) and as interstitial grains. No chemical differences were observed between enclosed and interstitial sulfides. However, their relative abundances are correlated, indicating a similar origin. The Po + Pn + Cp assemblage is identical to eclogitic sulfides previously described in some Roberts Victor diamonds. Silicate-enclosed sulfides could appear to be early phases, but they are restricted to the outer parts of the silicate grains, suggesting a late incorporation during partial recrystallisation of silicate phases, induced by fluid-rock percolation-reaction during a metasomatic event. Positive whole-rock correlations between Se and $(La/Sm)^*_N$ and between Cu and $\Sigma LREE^*_N$ indicate a direct link between sulfide content and the enrichment of Mg + incompatible elements in the Type I eclogites, further supporting a metasomatic origin of the sulfide component. Similarly, a negative correlation between $\Sigma LREE^*_N$ and Cu_{cpx} implies that the metasomatic agent was at least partially composed of S-rich fluid (e.g. H_2S, SO_2) that reacted with the rock and leached Cu out of the silicates. The coupling between sulfides and LREE in the Type I eclogites, as well as the absence of sulfides and metasomatic features (e.g. unequilibrated grain boundaries, melt pockets, fluid inclusions, phlogopite) in the Type II eclogites, demonstrate that Type II eclogites did not undergo such a metasomatic event and therefore may represent the less-modified protoliths of Type I eclogites.

1. Introduction

Eclogite xenoliths brought to the surface by the Roberts Victor kimberlite (South Africa) comprise the most extensively studied suite of mantle-derived eclogites in the world (e.g. MacGregor and Carter, 1970; Garlick et al., 1971; Manton and Tatsumoto, 1971; Harte and Gurney, 1975; Ozima and Saito, 1975; Hatton and Gurney, 1977; Kramers, 1979; MacGregor and Manton, 1986; Ongley et al., 1987; Sautter and Harte, 1988; Viljoen et al., 1991; Jacob et al., 2002, 2005; Huang et al., 2010; Gréau et al., 2011). For over forty years, work on their petrology and chemistry has added successive layers of detail, and these data have been used to support widely differing interpretations. The main alternative hypotheses are that mantle eclogites either are rocks produced by magmatic processes in the mantle (e.g. Smyth et al., 1989; Caporuscio and Smyth, 1990; Griffin and O'Reilly, 2007) or are fragments of subducted oceanic slabs (e.g. Anderson, 1982; MacGregor and Manton, 1986; Schulze and Helmstaedt, 1988; Jacob et al., 1994, 2002). These ideas have been debated for 30 years, and the origin of these rocks is still not well understood. Recently, some studies have shown that numerous mantle eclogites have witnessed important metasomatism (Jacob et al., 2009; Smart et al., 2009; Gréau et al., 2011; Huang et al., 2012), which may have overprinted the original microstructural and geochemical characteristics of some of these rocks, blurring away essential features that would be critical to constrain the origin of mantle eclogites. In this regard, even the extensively studied Roberts Victor eclogite suite, from which have been elaborated most of the hypotheses proposed in the literature, has been shown to be intensively microstructurally, chemically and isotopically overprinted (Gréau et al., 2011; Huang et al., 2012).

* Corresponding author at: ARC Centre of Excellence for Core to Crust Fluid Systems and GEMOC National Key Centre, Dept of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia.
E-mail address: yoann.greau@mq.edu.au (Y. Gréau).

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However, these studies have also identified specimens apparently free of such overprinting and which would be better candidates to (re-)evaluate the nature of mantle eclogites. A complete understanding of Earth's evolution requires that we constrain the origins of all the components of the heterogeneous lithospheric mantle, and mantle-derived eclogites are one of these significant components.

Although eclogite xenoliths were one of the first mantle lithologies in which the sulfide component was carefully described (Czamanske and Desborough, 1968; Desborough and Czamanske, 1973; Frick, 1973; Tsai et al., 1979) our chemical knowledge of the chemistry of the sulfide phases in eclogites remains limited. This early interest probably reflected the high abundance of sulfide in some xenoliths and the significant size of some sulfide grains (>500 μm). Since then sulfide minerals have been systematically described in peridotites from many geological contexts but eclogite xenoliths have not benefited from the same level of interest. In the last decades progress has been made in understanding the significance of sulfide phases in Earth's mantle, and in using sulfide chemistry to constrain petrological processes (e.g. Dromgoole and Pasteris, 1986; Lorand, 1989a, 1989b, 1989c; Szabo and Bodnar, 1995; Guo et al., 1999). It is now clear that the sulfides are sensitive to mantle processes such as melting and metasomatism (Alard et al., 2000; Lorand and Gregoire, 2006; Lorand et al., 2008; Lorand and Alard, 2010; Alard et al., 2011), but also to crustal contamination (Lorand and Alard, 2010, 2011).

Here we document the mineralogical and geochemical features of base metal sulfides (BMS) in the Roberts Victor eclogites and present new whole-rock data for sulfide-hosted elements such as S, Se, Te, Cu and Ni (chalcophile elements). Although this study is focused primarily on the origin and the petrogenesis of the BMS assemblage in the Roberts Victor xenolith suite, the data also bring important information on the history of these eclogites, and shed some light on the origin of the diamonds they contain.

2. Geological setting and samples

The Group II kimberlite pipe in the Roberts Victor mine (South Africa: 25° 34′E, 28° 27′S) is one of many kimberlite intrusions in the Kaapvaal craton. Rb–Sr dating of mica indicates an eruption age of 128 ± 15 Ma (Smith et al., 1985). This kimberlite has been extensively studied, not only because of its diamond yield but also because between 80 and 98% of the abundant, large xenoliths that it carries are eclogites (MacGregor and Carter, 1970; Hatton, 1978).

We have studied 29 eclogite xenoliths collected in 2006 at the Roberts Victor mine and 9 more samples from an older GEMOC collection. The sample suite includes 28 Type I eclogites, and 10 Type II eclogites, as defined by McCandless and Gurney (1989). Using the Na_2O contents in garnet and the K_2O contents in clinopyroxene, McCandless and Gurney recognised that the two Roberts Victor eclogite groups defined by MacGregor and Carter (1970) on the basis of their microstructures, were also two chemically distinct groups of eclogites. In this chemical scheme, eclogites that have Na_2O contents in garnet > 0.07 wt.% and/or K_2O contents in clinopyroxene > 0.08 wt.% belong to Type I,

Table 1
Sulfide abundances and assemblages of Roberts Victor eclogites.

Sample	Host rock	N sulf	e-Gt	e-cpx	i	Po (mss1)	Pn	Cp	Smy/Vi	Ni–Py	Py	FeOOH
RV07-1	Eclogite-Type I	4	1	1	2	–	+	+	–	++	–	++
RV07-2	Eclogite-Type I	1	–	1	–	–	–	–	–	–	–	+++
RV07-3	Eclogite-Type I	2	1	–	1	–	+	+	–	++	++	+
RV07-5a	Kyanite eclogite-Type I	1	–	–	1	+	+	+	–	–	+	–
RV07-5b	Kyanite eclogite-Type I	1	–	–	1	–	–	+	+	+	+	–
RV07-7	Eclogite-Type I	0	–	–	–	–	–	–	–	–	–	–
RV07-8	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
RV07-9a	Phlogopite eclogite-Type I	14	5	2	7	–	–	++	–	+++	++	++
RV07-9b	Phlogopite eclogite-Type I	23	–	8	15	–		++	++	+++	–	–
RV07-10	Eclogite-Type I	0	–	–	–	–	–	–	–	–	–	+++
RV07-11	Eclogite-Type I	19	1	2	16	+++	+++	+++	+	–	-	–
RV07-12	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
RV07-14	Eclogite-Type I	28	9	5	14		–	++	++	+++	++	–
RV07-16	Eclogite-Type I	10	–	1	9	–	–	–	–	++		+
RV07-17	Eclogite-Type I	14	–	5	9	–	–	++	+++	+++	+++	+
RV07-18	Eclogite-Type I	37	2	17	18	–	–	++	+++	+++	+	–
RV07-19	Eclogite-Type I	0	–	–	–	–	–	–	–	–	–	–
RV07-20	Eclogite-Type I	23	5	18	–	+++	–	++	–	+	–	+++
RV07-23a	Kyanite eclogite-Type I	3	–	–	3	++	–	–	–	–	–	–
RV07-23b	Kyanite eclogite-Type I	2	–	–	2	–	–	–	–	–	+	–
RV07-24	Eclogite-Type I	9	5	–	4	–	–	++	++	+++	++	++
RV07-25	Kyanite eclogite-Type I	0	–	–	–	–	–	–	–	–	–	+
RV07-26	Kyanite eclogite-Type I	9	3	3	3	–	–	+	–	++	++	+
RV07-30	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
RV07-31	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
RV07-33	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
RV07-34	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
RV07-36	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
RV07-37	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
Rva	Kyanite eclogite-Type I	7	5	–	2	+++	+++	+++	+++	+	++	–
RVb	Kyanite eclogite-Type I	37	10	4	23	+++	++	+++	+++	++	++	–
RV5	Kyanite eclogite-Type I	1	–	–	1	–	–	++	++	–	+++	–
RV6	Eclogite-Type I	36	–	–	36	–	++	++	–	+++	+++	–
BD1191	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–
BD3699	Kyanite eclogite-Type I	5	1	–	4	+	–	++	+	+++	+++	–
RV-1G	Eclogite-Type I	117	14	32	71	–	–	++	–	+++	+++	+
RV-2G	Eclogite-Type I	9	–	7	2	–	–	++	+	+++	+++	+
RV73-12	Eclogite-Type II	0	–	–	–	–	–	–	–	–	–	–

N sulf = number of sulfide per thin section, e-Gt = garnet enclosed sulfide, e-Cpx = clinopyroxene enclosed sulfide, I = interstitial sulfide.
Po = pyrrhotite, mss1 = mono-sulfide solution 1, Pn = pentlandite, Cp = chalcopyrite, Smy/V = smythite/violarite, Ni–Py = nickel rich pyrite, Py = Pyrite, FeOOH = iron (oxy)hydroxide.
'–' = absent or not observed, '+' = rare, '++' = present, '+++' = very abundant.