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ALKALI-CARBONATE FLUIDS IN THE LITHOSPHERIC MANTLE

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INTRODUCTION

The mantle xenoliths entrained by kimberlite and alkali basalts magmas commonly show chemical and textural evidence of metasomatism by mantle fluids. The compositions of these fluids span a broad range, including basaltic and alkali-rich basaltic melts, carbonate-rich melts, hydrous and CO₂-rich fluids, kimberlitic and lamproitic melts (Menzies and Hawkesworth, 1987; Pearson et al., 2003 and references therein). A more direct approach to the compositions of mantle fluids is provided by the fluid inclusions in diamonds. The fluids trapped in diamonds are described as mixtures of three major end members: carbonatitic (and high-Mg carbonatitic), hydro-silicate and saline (e.g. Klein Ben-David et al., 2007 and 2009). The carbonatitic (or carbonate) fluids hosted by diamonds are often very enriched in alkali elements (e.g. Kaminsky et al., 2009). The alkali enrichment of mantle carbonate fluids is also inferred from trace element studies on silicate minerals in mantle xenoliths affected by carbonate metasomatism (e.g. Yaxley et al., 1991). Furthermore, experimental petrologists have demonstrated that alkali-rich carbonate fluids are generated by low-degree melting of carbonated peridotites and eclogites (Wallace and Green, 1988; Dasgupta et al., 2005). Therefore, although there are numerous, but indirect lines of evidence in support of the percolation of alkali-rich carbonate fluids through

the mantle, so far the inclusions in diamonds have remained the only direct proof to the occurrence of these fluids in the Earth mantle.

In this study we describe the primary and secondary inclusions trapped in ilmenite grains of a new sample of polymict breccia, collected at the Bultfontein Dumps (Kimberley, South Africa). The primary inclusions host a multi-phase assemblage enriched in magnesite, dolomite, phlogopite, kalsilite and alkali-rich carbonates, with minor Fe-Ti oxides, phosphates, halides, sulfates and sulfides. This assemblage is interpreted to crystallize from an alkali-carbonate melt trapped during the precipitation of ilmenite at mantle depth. The secondary inclusions are likely related to the percolation of kimberlite fluids and host a fluid enriched in CO₂, Na, K, Cl, S and P. This inferred composition is similar to the residual fluid that crystallized the groundmass of the Udachnaya-East Kimberlite (Kamenetsky et al., 2004).

SAMPLE DESCRIPTION

Polymict breccias are rare mantle xenoliths sampled by kimberlite magmas. These rocks are mechanical mixtures of minerals and rock clasts of diverse origin, cemented by variable amounts of metasomatic ilmenite, rutile, phlogopite, olivine and sulfides (Lawless et al., 1979). Because of extreme chemical heterogeneity, polymict



breccias are interpreted as fragments of aborted kimberlite magmas frozen at depth (Lawless et al., 1979; Pokhilenko, 2009).

The currently studied polymict breccia (DU-1) was sampled by B. Wyatt at the Bultfontein Dumps, which comprises waste material from mining of the Bultfontein kimberlite. The sample is characterized by veins enriched in xenogenic material and large (up to 5 cm) blebs of metasomatic ilmenite, emplaced in a spinel harzburgite wall rock. Thermometric calculations applied to the minerals of the harzburgite yield equilibrium temperatures of 670-760°C, which correspond to pressure of 25-27 k bar on a 41 mW/m². The inclusions investigated in this study reside in the ilmenite blebs.

ANALYTICAL METHODS

Preliminary investigation and elemental mapping of the inclusions hosted by DU-1 ilmenite were performed on carbon coated thin sections at the University of Melbourne using a Philips (FEI) XL30 ESEM TMP equipped with an OXFORD INCA energy-dispersive x-ray spectrometer (EDS). A beam voltage of 15 kV was employed during the acquisition of x-rays for elemental maps and semi-quantitative chemical analyses. For a more detailed study several ilmenite grains were hand-picked, and the largest were mounted on an epoxy. After polishing without using water and carbon-coating the epoxy mount, the ilmenite grains were inspected at the Central Science Laboratory, University of Tasmania with a Hitachi SU-70 field emission scanning electron microscope (FESEM) equipped with an OXFORD INCA-XMax80 EDS. We have performed standardless chemical analyses and acquired x-ray elemental maps in order to recognize the different minerals in the inclusions employing a beam voltage of 10 kV.

EXTENDED ABSTRACT MINERALOGY OF INCLUSIONS

Primary inclusions are multiphase and enriched in carbonates. They are located in the cores of ilmenite blebs, at distance from fractures and sub-grain boundaries. The size of these inclusions ranges between 2 and 20 µm, and their shape is irregular with crenulated and sinuous boundaries. The common occurrence of voids suggest that a volatile-rich fluid phase was present, but then escaped after opening of the inclusions during sample preparation. The primary inclusions host abundant solid phases that, according to their compositions, have been grouped in:

- a) carbonates. Magnesite and dolomite are the most abundant constituents of the inclusions, and alkali-rich carbonates are common. The alkali-rich carbonates include Na-K-Ca carbonate (gregoryite), Na-rich carbonate (nahcolite and/or natrite), Na-Ca carbonate (shortite and/or nyerereite), and Na-Mg carbonate (eitelite);
- b) silicates. Phlogopite and kalsilite frequently occur, whereas olivine is more rare;
- c) Fe-Ti oxides. Priderite and freudenbergite (K-rich and Na-rich Fe³⁺-bearing titanates) are common constituents of these inclusions and they often mantle the cavity walls. Rutile, pleonaste spinel and members of the magnetite-magnesioferrite series are not abundant;
- d) phosphates. Apatite, strontian apatite and bradleyite [Na₃Mg(PO₄)(CO₃)] are frequent in the carbonate-rich inclusions;
- e) halides. Small grains of halite and sylvite are common;
- f) sulfates and sulfides. Minor constituents of these inclusions are the alkali-rich phases celestine [SrSO₄], kogarkoite [Na₃(SO₄)F], apthitalite [(K,Na)₃Na(SO₄)₂] and djerfisherite [K₆Na(Fe,Cu,Ni)₂₅S₂₆Cl], and the sulfides pentlandite and pyrrhotite.



The secondary fluid inclusions are arranged along healed fractures and sub-grain boundaries. They host daughter crystals of halite, sylvite, Na-rich carbonate, phosphates and alkali-sulfates.

DISCUSSION

The primary inclusions in DU-1 ilmenite are enriched in carbonates and alkali-rich minerals, and likely represent a fluid that was trapped during ilmenite crystallization. The irregular shape and crenulated boundaries of the inclusions, and the common formation of priderite and freudenbergite along the cavity walls indicate that the trapped fluid interacted with the ilmenite host.

The dominance of magnesite and dolomite, and the frequent occurrence of kalsilite, phlogopite, halides and alkali-rich carbonates, phosphates and sulfates in the carbonate-rich inclusions suggest that the trapped fluid was enriched in CO₂, Mg, Ca, K, Na, P and to a lesser extent S, F and Cl, whereas Si was relatively scarce. The chemical features of the trapped fluid extrapolated by the mineralogical content of the carbonate-rich inclusions evidence that an alkali-carbonate melt was present during the crystallization of ilmenite blebs in DU-1 xenolith.

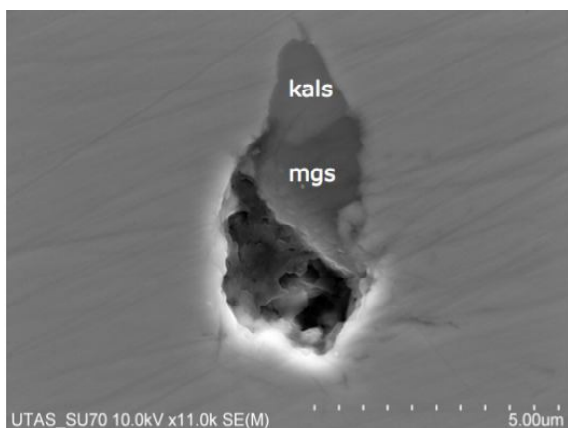


Figure 1. Secondary-electron image of primary inclusion in DU-1 ilmenite enriched in magnesite (mgs) and kalsilite (kal).

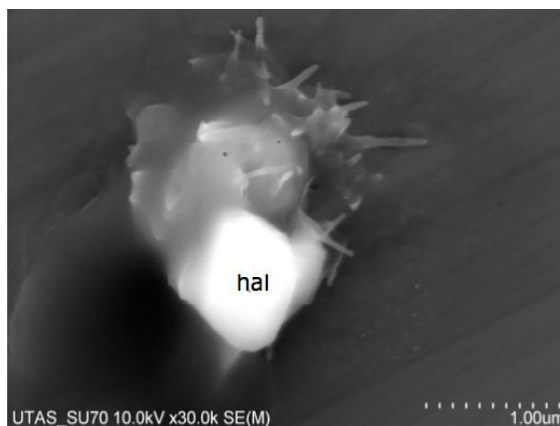


Figure 2. Secondary-electron image of secondary decrepitated inclusion in DU-1 ilmenite; hal = halite.

Previous researchers have proposed that the metasomatic minerals in polymict breccias are likely to have crystallized from precursor kimberlite (or proto-kimberlite) magmas (Lawless et al., 1979; Pokhilenko, 2009). As ilmenite is part of the metasomatic assemblage of polymict breccias, the alkali-carbonate melt trapped in DU-1 ilmenite might derive from the (proto-)kimberlite magma.

The fluid in secondary inclusions has affinities with the alkali-carbonate melt of the primary inclusions (i.e. enrichment in CO₂, Na, K, Cl, S, P), but differs in the absence of silicates, magnesite and dolomite. Although we cannot estimate the exact composition of this alkali and halogen-rich carbonate fluid, we recognize its broad similarity to the residual fluid that crystallized the groundmass of the Udachnaya-East

EXTENDED ABSTRACT

Kimberlite (Kamenetsky et al., 2004). Hence, we interpret the alkali-halogen carbonate fluid that fills the secondary inclusions of DU-1 ilmenite as the differentiated product of the kimberlite magma.



CONCLUSIONS

Our SEM investigation of primary and secondary inclusions in ilmenite grains from polymict breccia DU-1 has enlightened the occurrence of two different types of carbonate fluids, which were trapped during distinct stages of the xenolith evolution. An alkali-carbonate melt occurred at mantle depth (25-27 kbar) during the formation of the polymict breccia. This is the first report of an alkali-carbonate melt in the shallow lithospheric mantle. An alkali and halogen-rich carbonate fluid permeated the xenolith after it was consolidated, probably during transport of the xenolith toward the surface within the turbulent kimberlite melt. Both the fluids are likely related to primitive or pre-cursor kimberlite melts.

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