Mantle melting versus mantle metasomatism – “The chicken or the egg” dilemma

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A B S T R A C T
Most eclogitic mantle xenoliths brought to the surface exhibit a certain degree of enrichment with incompatible elements, usually attributed to the effect of mantle metasomatism by a putative metasomatic fluid. The metasomatic overprint is represented mainly by enrichments in Na, K, Ba, Ti and LREE and the original source of this fluid remains unknown. In this paper, we present a detailed petrological study of a typical eclogitic mantle xenolith from the Roberts Victor kimberlite mine in South Africa. We find that its textural and mineralogical features present strong evidence for incipient melting. The melting assemblage we observe did not necessarily require introduction of additional components, that is: in-situ melting alone could produce highly incompatible element enriched melt without involvement of a hypothetical and speculative “metasomatic event”. Due to the higher abundance in incompatible elements and lower solidus temperature than peridotites, mantle eclogites, some of which represent previously subducted oceanic crust, are much more plausible sources of mantle metasomatism, but on the other hand, they can be considered as highly metasomatised themselves. This brings us to the “chicken or egg” dilemma – was the secondary mineral assemblage in mantle lithologies a result or a source of mantle metasomatism?

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1. Introduction

Studies of metasomatism date back to Goldschmidt (1922), who defined it as “a process of alteration which involves enrichment of the rock by new substances brought in from the outside”. The importance of mantle metasomatism has been widely acknowledged since there are hardly any investigations of either mantle xenoliths or conclusions about the potential sources being either subducted slabs, or mantle plumes. The two main types of metasomatic alteration, observed in most lithospheric mantle xenoliths, are “modal” (petrographically visible due to replacement textures and development of secondary, usually hydrous phases) and “cryptic” (with enrichment in trace and rare earth elements (REE), but without petrographic evidence of metasomatism, i.e. no secondary minerals are formed) (Dawson, 1984). These metasomatic overprints are usually so complex that they are considered to have been caused by multiple metasomatic events (e.g. Heaman et al., 2006; Huang et al., 2014; Misra et al., 2004).

Interestingly, although all recovered mantle xenoliths are interpreted to have been metasomatised by an external agent, there are few reports in the literature on the source of the agent itself, i.e. which lithology partially melted, dehydrated or decarbonated to produce a melt or a fluid capable of metasomatising the surrounding mantle? This represents a classic “chicken or the egg” dilemma: how do we recognise a mantle rock, which was a source of metasomatising melt/ fluid, and why was this particular rock not a subject of prior alteration?

To address these questions, we undertook a detailed petrological study of primary and secondary phases of an eclogite xenolith from the Roberts Victor kimberlite pipe (South Africa). We evaluate the possible role of incipient eclogite melting in producing in-situ secondary mineral assemblages. Additionally, we suggest that altered oceanic...
crust has sufficient alkali- and volatile components to account for mineralogical and geochemical features of incipient melting in eclogites without addition of any metasomatic fluid or melt.

2. Sample selection and methods

2.1. SS2 eclogite xenolith

SS2 is a diamond-free eclogite xenolith, about 20 × 15 × 7 cm in size, from the Roberts Victor kimberlite pipe (South Africa) (Fig. 1). The xenolith is a typical example of eclogite xenoliths from this pipe. It is bimodal, with roughly equal proportions of coarse-grained omphacitic clinopyroxene and pyrope-almandine garnet (Table 1, Fig. 1a), which are interpreted as primary phases. The P-T (pressure-temperature) conditions of garnet and clinopyroxene equilibration are estimated to be between 1165 and 1205 °C (Ellis and Green, 1979) and between 1105 and 1150 °C (Krogh, 1988) for pressures between 5 and 6 GPa. This is in a good agreement with the P-T values for Roberts Victor eclogites reported by Huang et al. (2012).

The classification of eclogite xenoliths from Roberts Victor into two distinctive groups was initially proposed by MacGregor and Carter (1970) and followed by subsequent studies (e.g. Gréau et al., 2011; Huang et al., 2012; McCandless and Gurney, 1989; Schulze et al., 2000). According to McGregor and Carter’s classification, Type I eclogites contain coarse-grained subhedral to rounded garnet that is surrounded by anhedral clinopyroxene. Unlike in the Type II eclogites, the Type I garnet and clinopyroxene do not show an interlocking texture and contain large amounts of a secondary mineral assemblage that surrounds every grain. Clinopyroxene from Type I is more altered than in Type II with each grain being surrounded and cross cut by zones of secondary or spongy clinopyroxene. Type I eclogites also contain abundant inclusions of phlogopite, sulfide and rutile, observed in the SS2 xenolith. Huang et al. (2012) also pointed out that Type I eclogites are more metasomatically altered than Type II and are richer in LREE (light REE) and LILE (large-ion lithophile elements). The chemical classification proposed by McCandless and Gurney (1989) aimed to distinguish between the Type I and Type II eclogites using the alkali contents of garnet and clinopyroxene (Fig. 2a). Type I eclogites could be defined by ≥0.09 wt% Na2O in garnet or ≥0.07 wt% K2O in clinopyroxene. We also find that the concentration of TiO2 in both garnet and clinopyroxene could potentially be a valid discriminator (Fig. 2b). Thus, based on its textural and compositional characteristics, the SS2 xenolith, described in this study, can be classified as a Type I eclogite (Gréau et al., 2013; McCandless and Gurney, 1989; MacGregor and Carter, 1970).

2.2. Analytical methods

Thin sections and an epoxy mount were prepared from SS2 eclogite. Back-scattered electron images were obtained using a Hitachi SU-70 Schottky field emission SEM at University of Tasmania (UTAS) and a Hitachi 4300 field emission SEM at the Centre for Advanced Microscopy, Australian National University (ANU). These were used to characterise textural relationships.

Quantitative major element analyses of minerals were obtained using a Cameca SX100 Electron probe Microanalyzer (EPMA) at the Central Science Laboratory, University of Tasmania (UTAS). The operational conditions were 15 kV accelerating voltage, 10 nA beam current and a 10 μm spot with natural plagioclase, hornblende, olivine and clinopyroxene chosen as primary and secondary standards. Secondary mineral assemblages in veins and melt pockets were analysed with 15 μm defocused beam. Table 1 presents averages of 7–10 spot analyses.
per phase. 179 spot analyses of the secondary assemblages were performed in order to obtain an average SiO₂ content (44 wt% SiO₂) later used as an internal standard for the Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) analysis.

The sample was mounted in epoxy resin for LA-ICPMS analysis of trace elements. We used a Perkin Elmer Nexion quadrupole mass spectrometer coupled to a New Wave Research UP213 Nd:YAG laser at the University of Oxford. A beam diameter of 50 μm was employed for garnet, clinopyroxene and spongy clinopyroxene. Clinopyroxene analyses were repeated with a 100 μm beam diameter during a different LA-ICPMS session and the results of two sessions agreed within the uncertainty. Secondary mineral assemblages located on the grain boundaries and in small veins cross-cutting the xenolith were analysed using a 100 μm beam diameter.

The following masses were counted: ⁴⁷Ti, ⁸⁵Rb, ⁸⁸Sr, ⁹⁰Sr, ⁹²Zr, ⁹³Nb, ¹³⁸Ba, ¹⁴⁰La, ¹⁴⁰Ce, ¹⁴²Nd, ¹⁵²Sm, ¹⁵³Eu, ¹⁵⁸Gd, ¹⁶⁵Dy, ¹⁶⁹Ho, ¹⁶⁵Er, ¹⁷⁷Lu, ¹⁹⁰Hf, ¹⁹⁷Ta, ²³⁵Th, ²³⁸U, with yields calibrated on NIST 610 glass standard as the primary standard. BCR-2G and NIST 612 glasses were chosen as secondary standards. No > 8–9 unknowns were run between each set of standards. The internal reference element for all analysed phases was Si, previously measured by EPMA. The data for garnet were filtered to exclude contributions from multiple garnet-hosted melt inclusions. 44 wt% SiO₂ was chosen as the abundance of the internal reference element for the secondary assemblage with ~17% uncertainty (1σ) due to the high heterogeneity of the material represented by quenched phases. To minimise the uncertainty, 37 replicate analyses of the secondary assemblage were performed. Background was counted for the first 20 s, followed by a 40 s period of ablation. The background was minimised by a 60-second wash-out period between each analysis. The GLITTER (www.es.mq.edu.au/geom/glimmer) software package was employed for the data reduction.

3. Results

3.1. Textural observations

Grains of primary garnet and clinopyroxene in SS2 are rarely in direct contact, but are rimmed by a fine-grained secondary assemblage (Fig. 1c). The main minerals within the secondary assemblage are amphibole, phlogopite, calcite, spinel, secondary clinopyroxene, zeolites and minor phases, such as rutile, apatite, sulfides and barite (Figs. 1, 3, 4, 5). Additionally, veins filled with the same secondary assemblage (Figs. 3b, 4d) cut across primary mineral grains. Zeolites (analcime and natrolite) compose rounded and irregularly shaped pools that were likely to have been formerly occupied by melt (Figs. 3a-d, 4a-c). Euhedral calcite crystals have grown from the walls inside these pools (Fig. 3a, c, d).

Apart from the intergranular phase assemblage, both primary garnet and clinopyroxene contain secondary minerals included in the coarse, primary crystals. In garnet, these are usually rounded pockets (up to 300 μm) containing an assemblage similar to that observed in the cross-cutting veins and along the grain boundaries (Fig. 1d).

Primary clinopyroxene contains bands and patches of secondary “spongy” clinopyroxene and alkali-rich phases (Figs. 1b, 5a). The “spongy” clinopyroxene is the dominant secondary mineral assemblage formed around and within the primary clinopyroxene. The “spongy” clinopyroxene is surrounded by large cavities, Na- and K-rich glass-like material and/or a small amount of K-feldspar. Because of the small size, it is impossible to determine whether the glass is fully recrystallised into the feldspar or some of it is still preserved. Sometimes, a Ba-, Sr- and S-rich phase occurs in small veins together with the K-feldspar. Unlike the secondary assemblage present in cross cutting veins and melt pockets within the primary phases, the “spongy” clinopyroxene assemblage does not contain zeolites. Carbonate-rich and two sulfur-rich assemblages (sulfate, present as small, 10–20 μm wide veins of barite, and Fe-rich sulfide with minor Ni

| Table 1 | Major element composition of the primary phases and melt inclusions. |
|--------|---------------------------------------------------------------|
| Cpx primary | Cpx spongy | Cpx | Plagioclase | Amphibole | Phlogopite | Calcite | K-Feldspar | Bulk secondary* |
| SiO₂ | 54.59 | 52.48 | 52.48 | 53.83 | 54.05 | 52.48 | 54.59 | 52.48 | 52.48 | 52.48 | 52.48 | 52.48 | 52.48 |
| TiO₂ | 0.38 | 0.17 | 0.19 | 0.20 | 0.19 | 0.17 | 0.18 | 0.20 | 0.19 | 0.17 | 0.19 | 0.17 | 0.19 |
| Al₂O₃ | 6.77 | 7.28 | 7.28 | 6.77 | 6.77 | 6.77 | 6.77 | 6.77 | 6.77 | 6.77 | 6.77 | 6.77 | 6.77 |
| FeO | 6.23 | 6.97 | 6.97 | 6.23 | 6.23 | 6.23 | 6.23 | 6.23 | 6.23 | 6.23 | 6.23 | 6.23 | 6.23 |
| MgO | 4.04 | 4.15 | 4.15 | 4.04 | 4.04 | 4.04 | 4.04 | 4.04 | 4.04 | 4.04 | 4.04 | 4.04 | 4.04 |
| CaO | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 | 14.29 |
| Na₂O | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 | 20.37 |
| P₂O₅ | 0.12 | 0.13 | 0.13 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| H₂O | 0.19 | 0.20 | 0.20 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 |
| Total | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 | 98.99 |

*179 spot analyses of the secondary assemblage were performed according to stoichiometry.
and Cu) are observed along with the secondary silicate phases in veins and inclusions and along grain boundaries between primary garnet and clinopyroxene (Figs. 3b, 4a,c,e). The sulfide assemblage forms pools of different size (from few microns to a thousand microns) and of uneven shape. These pools are usually severely altered, with hematite and chlorite veinlets cutting through (Fig. 4e). Additionally, some of the barite can be found in the form of euhedral crystals. Anhedral barite is located within the veins of the secondary mineral assemblage as well as substituting and rimming Fe-sulfide and rutile (Figs. 3b, 4c). Rutile contains exsolution lamellae of ilmenite (Figs. 4b, 5b).

3.2. Major element compositions of primary and secondary phases

Major element compositions for all analysed phases are presented in Table 1. Garnet compositions are similar to the one reported for Type I eclogites by Huang et al. (2012). It is predominantly pyrope-almandine and contains 17.2 wt% FeO, 22.9 wt% Al₂O₃, 14.7 wt% MgO and 4.22 wt% CaO. Primary clinopyroxene is omphacitic in composition and contains 4.22 wt% Na₂O, 6.77 wt% Al₂O₃, 6.23 wt% FeO, 12.08 wt% MgO and 14.3 wt% CaO. The “spongy” clinopyroxene is diopsidic, with 1.87 wt% Na₂O, 17.6 wt% CaO and 4.22 wt% Al₂O₃ in comparison to the primary

![Figure 2](image1.png)

**Fig. 2.** Major element compositions of garnet and clinopyroxene from SS2. (a) Na₂O in garnet plotted against K₂O in clinopyroxene, previously used by McCandless and Gurney (1989) to discern between the Type I and Type II eclogites. (b) TiO₂ in garnet and clinopyroxene, which shows a similar pattern to panel (a). Grey symbols are garnets and clinopyroxenes from Huang et al. (2012, 2014).

![Figure 3](image2.png)

**Fig. 3.** (a) Optical image of euhedral calcite crystals growing into the melt pool, currently filled with zeolite aggregates. (b) Veinlet with melting products on a boundary between two primary garnet crystals. (c) A blown-up area of panel (b) with calcite crystals growing into the melt pool. (d) Zoned calcite crystals with darker parts more enriched in Sr (up to 1.1 wt% SrO). All panels, except (a) are back-scattered images.
omphacitic clinopyroxene, which has much higher concentrations of Na and Al, and lower amounts of Ca (Table 1).

Sulfide, present both within the secondary mineral assemblage and as inclusions in primary phases, is usually of pure FeS composition with small amounts of Ni and/or Cu. Barite has elevated Sr contents (up to 6 wt% SrO).

Compositional zoning is a common feature for the minerals present within the secondary assemblage. Although almost every single mineral is zoned to a certain extent, the most commonly observed are zoned calcite, which usually has elevated Sr-contents (up to 1.1 wt% SrO) on the rims and phlogopite (with variable Na (0.2–1.6 wt% Na2O) and Ba (up to 1.5 wt% BaO) contents. Compositional variations in calcite crystals are evident in the back-scattered electron images in Fig. 3d. In Table 1 average compositions of grains are reported.

3.3. Trace element compositions of primary and secondary phases

Normalised trace element diagrams for garnet and primary clinopyroxene are very similar to those reported by Huang et al. (2012) (Fig. 6) for other Type I eclogite xenoliths from the Roberts Victor pipe. The trace element compositions of spongy clinopyroxene with the included small alkali-rich pockets (recrystallised into feldspars)
Kamenetsky, 1999). Feldspar and amphibole are less abundant, while the presence of a large number of new phases (e.g. Aulbach et al., 2007; Carpenter et al., 2002; Ionov et al., 1994; Schiano and Clocchiatti, 1994; Schiano et al., 1994) – reaction of the xenolith with a host magma (Shaw and Dingwell, 2008) – breakdown of metasomatic minerals that were formed during previous melting and crystallisation events (Yaxley and Kamenetsky, 1999; Yaxley et al., 1997) – decompression-induced incongruent melting prior to xenolith entrainment in the host magmas (Su et al., 2011) – decompression-induced incongruent melting after the entrainment by the host magmas (Misra et al., 2004).

Even though there is no agreement on the exact mechanism of the formation of the spongy clinopyroxene (and other reaction phases), it is obvious that these textures are common in both peridotitic and eclogitic xenoliths and that the presence of melt and its interaction with the primary phases are necessary precursors for their formation.

The composition of the glass-like material associated with the spongy clinopyroxene can be indicative of the primary phases composition. For instance, glass from peridotitic affinities is usually more Mg-rich and with a higher Na2O/K2O ratio than the eclogitic (e.g. Ionov et al., 1994; Yaxley and Kamenetsky, 1999). In SS2 xenolith, glass is recrystallised mainly into the K-feldspar, which contains 14.42 wt% K2O and only 1.14 wt% Na2O. Potassium-rich glass was also reported by Misra et al. (2004) associated with the spongy clinopyroxene in the Udachnaya pipe eclogites (up to 6.32 wt% K2O and up to 0.86 wt% Na2O) and by Liu et al. (2009) for the world’s largest diamondiferous eclogite xenolith (UD-111/02), from the Udachnaya kimberlite.

The higher K/Na ratio for the eclogitic secondary mineral assemblage could be characteristic of the primary phlogopite or any other K-bearing phases now absent due to their complete melting. The former presence of primary phlogopite is also consistent with the elevated Ba-contents of the secondary mineral assemblage. However, as discussed below, the presence of primary phlogopite is not necessary, because the abundance of potassium in the bulk secondary assemblage is 0.35 ± 0.31 wt% K2O. Even if the highest value of ~0.7 wt% K2O is assumed, fairly low degrees of partial melting of the primary mineral assemblage alone could well account for it.

4.2. Textural evidence for incipient melting

The nature of sub-cratonic mantle metasomatism, as well as the origin of the kimberlite magmas, remain debatable (e.g. Le Roex et al., 2003; Ringwood et al., 1992; Tappe et al., 2013; Tappe et al., 2017). A large number of studies of eclogite xenoliths entrapped in kimberlite reveal significant modification of the primary mineral assemblage and the appearance of a large number of new phases (e.g. Aulbach et al., 2007; Fung and Haggerty, 1995; Huang et al., 2014; Pyle and Haggerty, 2008).
1998; Sobolev et al., 1999; Spetsius and Taylor, 2002). Given the high concentrations of incompatible elements (both LILE and high-field-strength elements) found in these secondary minerals, the traditional approach is to attribute crystallisation of the secondary mineral assemblage to modal and cryptic metasomatism prior to the kimberlite magma percolation, to in-situ partial melting due to infiltration of metasomatic fluids and/or to interaction with the kimberlitic magma itself (e.g. Misra et al., 2004; Spetsius and Taylor, 2002). All of these scenarios are plausible; however, none of them explain the nature and origin of the metasomatic fluids, which are evidently abundant in K, Na, Cl, Ca, Ti, Ba, CO2, H2O, LREE and other highly incompatible components. Moreover, formation of kimberlitic magmas requires large amounts of these components to be present in the mantle source.

The textures and both primary and secondary mineral assemblages observed in the SS2 xenolith are similar to those reported previously in metasomatically altered eclogite xenoliths (Huang et al., 2014; Misra et al., 2004; Pyle and Haggerty, 1994; Pyle and Haggerty, 1998; Sobolev et al., 1999; Spetsius and Taylor, 2002). On the other hand, we interpret the textural and mineralogical features of this sample as strong evidence for incipient melting. The melting assemblage surrounds absolutely every grain within the primary assemblage. Even in such cases, when one primary mineral is present as a small inclusion in another primary mineral, a small rim with melting products around the inclusion is observed (Fig. 5).

In addition to the silicate-rich melt, it is likely that there existed an immiscible sulfur-rich liquid (Fig. 4a,e). Depending on the P-T-fO2 conditions and the composition of the silicate, sulfur reaches saturation in silicate melts at ~1000–2000 ppm (e.g. Fortin et al., 2015; Li and Ripley, 2009; Smythe et al., 2016). Even the higher end of this range does not seem to be enough to incorporate all sulfur in the silicate melt. Since at mantle P-T conditions sulfides are usually present in a liquid form (Zhang and Hirschmann, 2016), sulfur segregates into separate, immiscible sulfide liquid, making sulfides quite common in eclogite xenoliths, although still present in fairly low abundances (<2 vol%) (Gréau et al., 2013; Howarth et al., 2015). Under highly oxidised conditions, possibly even sulfate liquids are formed (Giuliani et al., 2013).

4.3. Compositional evidence for the incipient melting

The second type of evidence for incipient melting is compositional. The secondary mineral assemblages that develop on the grain boundaries, along the veins that cut across the xenoliths and in the melt pockets within the garnet crystals, all consist of the same minerals.

![Fig. 6. Trace element patterns of garnet and primary clinopyroxene in comparison with the garnet and clinopyroxene reported by Huang et al. (2012) from Type I (light grey) and Type II (dark grey) Roberts Victor eclogites. All patterns are normalised to CI chondrites (McDonough and Sun, 1995).](image-url)
which are almost identical in composition. If there were a fluid percolating into the eclogite, it would pass along the veins and fractures, and the crystallised secondary phases would be different to the sites of modification unaffected by the fluid.

Similarly to the spongy clinopyroxene, Ba-rich minerals were found in mantle xenoliths in both peridotitic and eclogitic affinities from different localities worldwide (Almeida et al., 2014; Kogarko et al., 2007; Kogarko et al., 2012; Mitchell and Lewis, 1983; Mogarovskii et al., 2007; Pyle and Haggerty, 1998). These include multiple findings of barite (e.g. Pyle and Haggerty, 1998), Ba-rich Ti-phlogopite (Kogarko et al., 2012; Mogarovskii et al., 2007; Kamenetsky et al., 2014), Ba-rich apatite (Kamenetsky et al., 2014) and a number of rare and unusual minerals, like priderite (Almeida et al., 2014), henrymeyerite (Kogarko et al., 2007) and Ba-rich titanates (Almeida et al., 2014). Priderite is a mineral with a formula close to A13MgO16 where the A-site is occupied mainly by Ba and K, and M-site by Ti, Fe and Cr, while henrymeyerite is a mineral from the priderite group. These minerals occur within the secondary mineral assemblage, rimming younger generations of rutile or ilmenite (Ba-rich titanites), or, as barite, forming cross cutting veins.

Most authors attribute this barium enrichment to be a result of alkaline- or carbonate-rich melt metasomatism (Foley et al., 1994; Kogarko et al., 2012) with high-Ba phlogopite suggested to crystallise at the early stages of magmatic crystallisation (Kogarko et al., 2012). Foley et al. (1994) have synthesised priderite experimentally and have confirmed its stability up to diamond-forming pressures of 5 GPa, supporting the finding of this mineral in diamond inclusions (Jaques et al., 1989).

An alternative explanation for the Ba-enrichment may come from the nature of the eclogitic xenoliths. The observed enrichment in K, Ba and other incompatible elements is inherited and reflects the initial composition of the oceanic crust that has been converted into eclogite. Due to hydrothermal alteration, the upper part of the oceanic crust contains up to a few wt% of volatiles and significant amounts of P (up to 0.17 wt% P2O5), Na (up to 3.3 wt% Na2O and K (up to 7.3 wt% K2O) and other incompatible elements (Alt and Teagle, 2003). Ba-enrichment (up to 143 ppm in altered tholeiitic basalts; Alt and Teagle, 2003) derives from the seawater component. The original composition of the altered oceanic crust in terms of minor components is highly uncertain; and their concentrations can vary over an order of magnitude, which probably causes variation in the melting products within the kimberlite xenoliths worldwide. Most of the highly incompatible elements, like LILE, are located in minute phases along grain boundaries. This has been revealed by comparing the bulk-rock compositions to the compositions of the constituent minerals (e.g. Condie et al., 2004; Suzuki, 1987; Yamamoto et al., 2009).

But even if potassium is present only at typical MORB-concentrations, this would be enough to cause the pattern of so-called K-rich metasomatism. According to experimental data, at 3.5–5 GPa potassium is almost completely incompatible and even 0.5 wt% H2O and 0.4 wt% K2O in the starting composition at low degrees of melting (~ 4–7%) produced hydrous, felsic melt with up to 10 wt% K2O (Kiseeva et al., 2012). Thomson et al. (2016) reported 2.8 wt% Na2O and 0.29 wt% K2O at 3 GPa for low degrees melt (~ 10%) of a carbonated eclogite that contains 2.48 wt% Na2O and 0.06 wt% K2O in the starting mixture. To our knowledge, there are no measurements of Ba in experimental melts produced by melting of altered oceanic crust at high pressures, however, given its highly incompatible character, lower degree (~ 10%) melts will be strongly enriched in Ba.

The fate of incompatible elements (including K, Ba, LREE) and carbon during subduction is still a matter of debate. In their review, Dasgupta and Hirschmann (2010) estimated about half of the subducted carbon is transported into the mantle beyond the sub-arc region. Kelemen and Manning (2015) and Poli (2015) argue that the presence of water (which is ubiquitous in subducted slabs) is drastically depressing the carbonate solidus fluxing CO2-rich aqueous fluids into the wedge and decreasing the amount of subducted carbonate. Regardless of the amount of carbonate that is currently subducted, there is enough evidence for the presence of recycled crustal components in the upper mantle and even the mantle transition zone (e.g. Stachel and Harris, 2009; Tappert et al., 2005). The amount of calcium within the bulk secondary assemblage is fairly low (~ 2 wt% CaO), which implies that the carbonate was probably lost during post-magmatic processes.

The Na/K ratio of the glass is partly a function of pressure. As mentioned above, potassium is incompatible at low pressures and becomes compatible only with the stability of K-hollandite at pressures ≥ 15 GPa (Grassi and Schmidt, 2011; Kiseeva et al., 2013; Wang and Takahashi, 2000). Since Na becomes compatible in the clinopyroxene from about 2.5–3 GPa, lower pressure melts would be both K- and Na-rich. Incipient melting of primary clinopyroxene at pressures < 2.5 GPa would result in the formation of more diopsidic secondary clinopyroxene and alkali-rich melt.

### Table 2

| Garnet | α (17) | Cpx | α (14) | Cpx spongy + melt | α (13) | Secondary assemblage | α (37) |
|--------|--------|-----|--------|-------------------|--------|----------------------|--------|
| Rb     | b.d.l. | b.d.l. | 7.47 | 1.43 | 39.9 | 15.2 |
| Ba     | b.d.l. | 0.42 | 0.03 | 83.7 | 11.5 | 1161 | 1090 |
| La     | b.d.l. | 1.53 | 0.13 | 3.69 | 0.99 | 9.91 | 3.65 |
| Ce     | 0.12   | 0.02 | 0.35 | 10.4 | 1.98 | 21.0 | 10.2 |
| Nd     | 0.48   | 0.04 | 0.16 | 7.96 | 1.02 | 12.0 | 7.20 |
| Sr     | 0.61   | 0.05 | 2.54 | 193 | 10 | 277 | 123 |
| Sm     | 0.56   | 0.07 | 1.24 | 0.05 | 1.37 | 0.07 | 1.41 | 0.93 |
| Eu     | 0.28   | 0.04 | 0.37 | 0.03 | 0.41 | 0.01 | 0.44 | 0.22 |
| Gd     | 1.38   | 0.16 | 1.02 | 0.04 | 1.12 | 0.11 | 1.39 | 0.63 |
| Tb     | 0.35   | 0.04 | 0.13 | 0.01 | 0.15 | 0.01 | 0.26 | 0.09 |
| Dy     | 3.17   | 0.28 | 0.71 | 0.04 | 0.78 | 0.06 | 1.96 | 0.64 |
| Ho     | 0.86   | 0.05 | 0.13 | 0.01 | 0.13 | 0.01 | 0.52 | 0.18 |
| Er     | 3.12   | 0.17 | 0.30 | 0.03 | 0.33 | 0.04 | 1.79 | 0.61 |
| Yb     | 3.83   | 0.21 | 0.18 | 0.03 | 0.20 | 0.02 | 2.12 | 0.71 |
| Y      | 22.2   | 1.19 | 3.03 | 0.09 | 3.30 | 0.17 | 13.49 | 4.37 |
| Lu     | 0.60   | 0.06 | 0.02 | 0.01 | 0.020 | 0.006 | 0.35 | 0.11 |
| Ti     | 1873   | 154 | 2294 | 206 | 2195 | 62 | 4688 | 3587 |
| Zr     | 20.1   | 5.13 | 21.8 | 0.55 | 25.1 | 1.80 | 51.5 | 23.1 |
| Hf     | 0.43   | 0.14 | 1.26 | 0.10 | 1.29 | 0.06 | 1.56 | 0.99 |
| Nb     | 0.06   | 0.02 | 0.01 | 0.01 | 0.020 | 0.006 | 0.35 | 0.11 |
| Ta     | b.d.l. | b.d.l. | 1.58 | 0.70 | 15.7 | 11.9 | 1.53 | 0.32 |
| Th     | b.d.l. | b.d.l. | 0.07 | 0.03 | 1.22 | 0.91 | 2.07 | 0.91 |
| U      | b.d.l. | b.d.l. | 0.08 | 0.04 | 0.42 | 0.40 | 0.08 | 0.04 |

b.d.l. below detection limit.
This is commensurate with the secondary mineral assemblage found within primary clinopyroxene grains, which consists of Al- and Na-depleted secondary clinopyroxene and alkali-rich melt pools. Additionally, the alkali-rich nature of the melt together with carbonate-rich components could produce carbonate-silicate immiscible liquids (Kiseeva et al., 2012), resulting in melts pools that are enriched in Na and K.

Thus, the melting assemblage we observe now did not necessarily require any introduction of additional components. In-situ melting alone could produce highly incompatible element enriched melt without the need for involvement of a hypothetical “metasomatic event”. Neither compositional nor textural characteristics of the studied xenolith are indicative of whether the melting occurred prior or after the xenolith’s entrainment by the host kimberlite magma. The trigger mechanism for the incipient melting is likely to be either decompression and/or heating. Su et al. (2011) arrived at a similar conclusion, however the authors argued that only the major element pattern may be explained by the incipient melting.

Importantly, in order to produce a metasomatic melt or fluid in the mantle, a mantle lithology is required to partially melt, and there are only two possible sources that could produce melts in the cratonic mantle – peridotites and eclogites. Once these mantle-derived fluids segregate from their source, they may be out of equilibrium with the wallrock through which they migrate, acting as a flux, reacting with the wall rock, triggering its partial melting and causing so-called “mantle metasomatism”.

5. Conclusions

By using petrological, compositional and experimental evidence, we conclude that the altered oceanic crust represented by an eclogite in the deep mantle is a plausible source of mantle metasomatic fluids and melts. Changes in P-T conditions can cause initiation of melting, and in this case there is no requirement for an external “influence” on the observed “melting assemblage”.

On the other hand, it is still possible that there could be some influence from the external fluids. The proportion of externally and internally derived fluids could be variable and it is impossible to discern between the two of them. However, any externally derived fluid would need a source rock that is likely to be an eclogite and that is taking us back to the “chicken or egg dilemma”.

Fig. 7. Trace element patterns of garnet, primary clinopyroxene, secondary clinopyroxene and secondary mineral assemblage normalised to CI chondrites (McDonough and Sun, 1995).
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References

Almeida, V.V., Janasi, V.D.A., Svisero, D.P., Nannini, F., 2014. Mathiasite-loveingite and priderite in mantle xenoliths from the Alto Paranaiba Igneous Province, Brazil: genesis and constraints on mantle metasomatism. Central European Journal of Geosciences 6 (4), 614–632.

Alt, J.C., Teagle, D.A.H., 2003. Hydrothermal alteration of upper oceanic crust formed at a spreading ridge: mineral, chemical, and isotopic evidence from DSDP Site 801. Chem. Geol. 201 (3–4), 191–211.

Aulbach, S., Pearson, N.J., O'Reilly, S.Y., Doyle, B.J., 2007. Origins of xenolithic eclogites and pyroxenites from the central Slave craton, Canada. J. Petrol. 48 (10), 1843–1873.

Carpenter, R.L., Edgar, A.D., Thibault, Y., 2002. Origin of spongy textures in clinopyroxene and spinel from mantle xenoliths, Hassan Depression, Germany. Mineral. Petrology. 74 (2–4), 149–162.

Condie, K.C., Cox, J.O'Reilly, S.Y., Griffin, W.L., Kerrich, R., 2004. Distribution of high field strength and rare earth elements in mantle and lower crustal xenoliths from the southwestern United States: the role of grain-boundary phases. Geochim. Cosmochim. Acta 68 (19), 3919–3942.

Dauphas, R., Hirschmann, M.M., 2010. The deep carbon cycle and melting in Earth’s interior. Earth Planet. Sci. Lett. 298 (1–2), 1–11.

Dawson, J.B., 1984. In: Kornprobst, J. (Ed.), Contrasting types of upper-mantle metasomatism? in Kimberlites II. The mantle and crust-mantle relationships. Elsevier, pp. 289–294.

Draper, D.S., Green, T.H., 1997. 9-T phase relations of silicate, alkaline, aluminous mantle-xenolith glasses under anhydrous and C-H-O fluid-saturated conditions. J. Petrol. 38 (9), 1187–1234.

Ellis, D.J., Green, D.H., 1979. Experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. Contrib. Mineral. Petrol. 71 (1), 13–22.

Foley, S., Hofer, H., Brey, G., 1994. High-pressure synthesis of priderite and members of the sodalite-mathiasite and hawthorneite-yeniseite groups. Contrib. Mineral. Petrol. 117 (2), 164–174.

Fortin, M.-A., Riddle, J., Desjardins-Langlais, Y., Baker, D.R., 2015. The effect of water on the sulfur concentration at sulfide saturation (SCS) in natural melts. Geochim. Cosmochim. Acta 160, 100–116.

Fung, A.T., Haggerty, S.E., 1995. Petrography and mineral compositions of eclogites from the Koidu kimberlite complex, Sierra-Leone. Journal of Geophysical Research-Solid Earth 100 (B10), 20451–20473.

Giuliani, A., et al., 2014. Mafic xenoliths: a sulfide fluid preserved in a MARID xenolith from the Bulfontein Kimberlite (Kimberley, South Africa). Earth Planet. Sci. Lett. 376, 74–86.

Goldsmith, V.M., 1922. On the metasomatic processes in silicate rocks. Econ. Geol. 17, 105–123.

Grass, D., Schmidt, M., 2011. Melting of carbonated peridotite at 18–13 GPa: generating K-rich carbonates for mantle metasomatism. Contrib. Mineral. Petrol. 162 (1), 169–191.

Gréau, Y., Alard, O., Grif

Huang, J.X., Gréau, Y., Grif

Jaques, A.L., et al., 1989. Composition of crystalline inclusions and C-isotopic composition of diamonds from the Roberts Victor kimberlite, South Africa: evidence from bulk-rock geochemistry. J. Petrol. 44 (12), 2261–2286.

Li, C.S., Ripley, E.M., 2009. Sulfur contents at sulfur saturation in eclogite: implications for natrosilicic and carbonatitic conjugate melts. Geochim. Cosmochim. Acta 73 (4), 985–997.

Mitchell, R.H., Lewis, R.D., 1983. Priderite-bearing xenoliths from the Prairie Creek mica peridotite, Arkansas. Can. Mineral. 21 (Feb), 39–64.

Moharogovskii, V.V., Lutkov, V.S., Lutkova, V.Y., 2007. Barium and strontium in the upper mantle of the Patmos and Tien Shan. Geochim. Int. 45 (7), 685–697.

Pol, S., 2011. Carbon mobilized at shallow depths in subduction zone by carbonatic liquid inclusions. Nat. Geosci. advance online publication.

Pyke, J.M., Haggerty, S.E., 1998. Eclogite and the metasomatism of eclogites from the Jagersfontein Kimberlite: punctuated transport and implications for alkali magmatism. Geochim. Cosmochim. Acta 62 (7), 1207–1231.

Ringwood, A.E., Kesson, S.E., Hibberson, W., Ware, N., 1992. Origin of kimberlites and related magmas. Earth Planet. Sci. Lett. 113 (4), 521–538.

Schiano, P., Clocchiatti, R., 1994. Worldwide occurrence of silica-rich melts in sub-continental and sub-oceanic mantle nodules. Nature 368 (6472), 621–624.

Schiano, P., Clocchiatti, R., Shimizu, N., Weiss, D., Mattielli, N., 1994. Cogenetic silica-rich and carbonate-rich melts trapped in mantle peridotites in Kerguelen ultramafic xenoliths: implications for metasomatism in the oceanic upper mantle. Earth Planet. Sci. Lett. 123 (1–4), 167–178.

Schulze, D.J., Valley, J.W., Spicuzza, M.J., 2000. Coesite eclogites from the Roberts Victor kimberlite, South Africa. Lithos 54 (1–2), 23–32.

Chajap, C.S., 2009. Textural development of amphibolites during breakdown reactions in a synthetic peridoticite. Lithos 110 (1–4), 215–228.

Chajap, C.S., Dingwell, D.B., 2008. Experimental peridotite-melt reaction at one atmosphere: a textural and chemical study. Contrib. Mineral. Petrol. 155 (2), 199–214.

Chajap, S.J., Heidelbach, F., Dingwell, D.B., 2006. The origin of reaction textures in mantle peridotite xenoliths from Sal Island, Cape Verde: the case for “metasomatization” by the host lavas. Contrib. Mineral. Petrol. 151 (6), 681–697.

Smythe, D.J., Wood, B.J., Kiseeva, E.S., 2016. The S content of silicate melts at sulfide saturation: new experiments and a model incorporating the effects of sulfide composition. Am. Mineral. http://dx.doi.org/10.2138/am-2017-5800CCBY.

Sokcu, K., 1987. Grain-boundary exchange of incompatible elements in peridotite xenoliths. Chem. Geol. 65 (1–4), 5–18.

Tappe, S., Pearson, D.G., Kjaergaard, B.A., Nowell, G., Dowall, D., 2013. mantle transition zone input to kimberlite magmatism near a subduction zone: Origin of anamolous Nd-Hf isotope systematics at Lac de Gras, Canada. Earth Planet. Sci. Lett. 377, 235–251.
Tappe, S., Brand, N.B., Stracke, A., van Acken, D., Liu, C.-Z., Strauss, H., Wu, F.-Y., Luguet, A., Mitchell, R.H., 2017. Plates or plumes in the origin of kimberlites: U/Pb perovskite and Sr-Nd-Hf-Os-C-O isotope constraints from the Superior craton (Canada). Chem. Geol. 455, 52–78 (in this issue).

Tappert, R., et al., 2005. Subducting oceanic crust: the source of deep diamonds. Geology 33 (7), 565–568.

Thomson, A.R., Walter, M.J., Kohn, S.C., Brooker, R.A., 2016. Slab melting as a barrier to deep carbon subduction. Nature 529 (7584), 76–79.

Wang, W.Y., Takahashi, E., 2000. Subsolidus and melting experiments of K-doped peridotite KLB-1 to 27 GPa: its geophysical and geochemical implications. J. Geophys. Res. Solid Earth 105 (B2), 2855–2868.

Yamamoto, J., et al., 2009. Intergranular trace elements in mantle xenoliths from Russian Far East: example for mantle metasomatism by hydrous melt. Island Arc 18 (1), 225–241.

Yaxley, G.M., Kamenetsky, V., 1999. In situ origin for glass in mantle xenoliths from southeastern Australia: insights from trace element compositions of glasses and metasomatic phases. Earth Planet. Sci. Lett. 172 (1–2), 97–109.

Yaxley, G.M., Kamenetsky, V., Green, D.H., Falloon, T.J., 1997. Glasses in mantle xenoliths from western Victoria, Australia, and their relevance to mantle processes. Earth Planet. Sci. Lett. 148 (3–4), 433–446.

Zhang, Z., Hirschmann, M.M., 2016. Experimental constraints on mantle sulfide melting up to 8 GPa. Am. Mineral. 101 (1–2), 181–192.