

## A snapshot of mantle metasomatism recorded by clinopyroxene inclusions in diamonds

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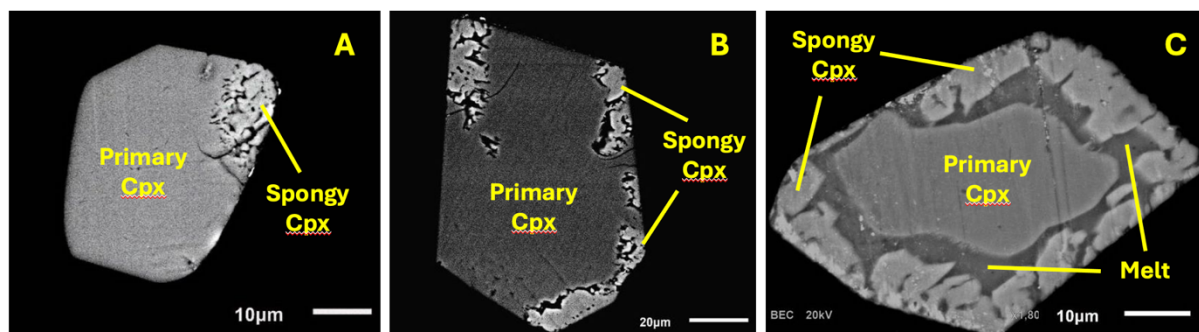
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### Introduction

Most mantle xenoliths brought to the surface by kimberlites record episodes of metasomatic events, manifested either by the formation of new minerals or through changes in trace element concentrations of primary minerals. The metasomatic agent is usually inferred to be either a low-degree melt or a fluid capable of carrying a significant amount of incompatible elements. In-situ characterisation of such agents is challenging due to their mobility and reactivity.

One way of characterising metasomatic agents is by analysing inclusions in diamonds. Such included material is protected by the diamond, which prevents later alteration and/or subsequent metasomatic overprinting. Thus, diamond inclusions may be used to successfully characterise the types of fluids and melts present in the deep mantle. In this study, we analysed five diamonds with eclogitic clinopyroxene inclusions from the Cullinan (Premier) mine in South Africa and the Rassolnaya placer (Ural Mountains) in Russia to investigate the compositions of low-degree melts produced by melting of clinopyroxene.



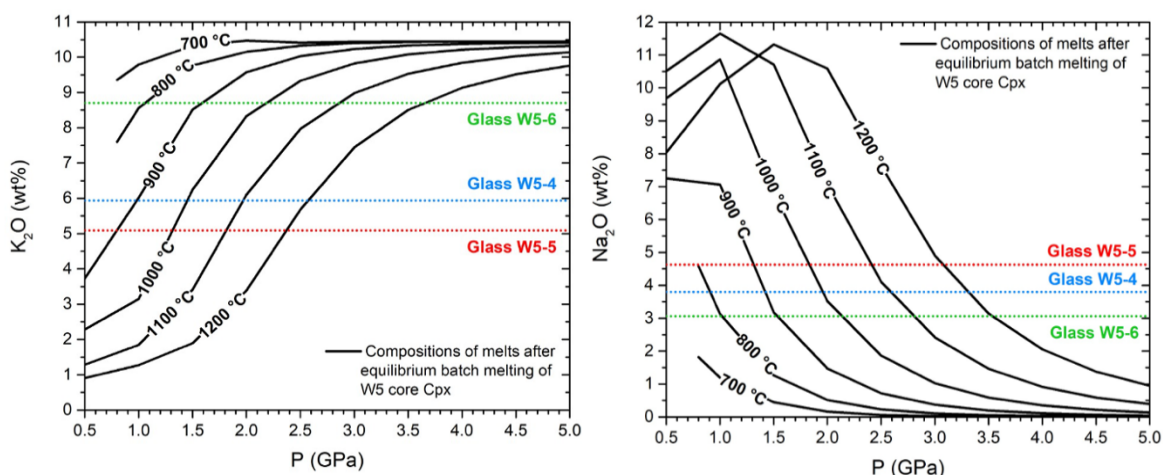
**Figure 1:** Back-scattered electron (BSE) images of selected clinopyroxene (Cpx) inclusions in diamonds from this study. A. Cln-268 (Cullinan), B. U-345 (Rassolnaya), C. U-530 (Rassolnaya).

### Analytical results

Secondary electron microscopy reveals that all clinopyroxenes exhibit the presence of secondary spongy textures in their rims (Fig. 1). The compositions of primary and spongy clinopyroxenes and associated melt compositions were studied using a JEOL Superprobe JXA-8230 at The Hebrew University of Jerusalem, Israel. Primary cores are chemically homogeneous with compositions within the range: 53.4-55.9 wt% SiO<sub>2</sub>, 7.0-14.9 wt% Al<sub>2</sub>O<sub>3</sub>, 3.2-8.1 wt% Na<sub>2</sub>O, 6.2-13.8 wt% MgO, 0.1-0.3 K<sub>2</sub>O, and 9.15-19.7 wt% CaO. Spongy clinopyroxene located at the rims is highly heterogeneous, even within the same inclusion, and is typically more diopsidic in comparison with the primary clinopyroxene: 51.7-55.1 wt% SiO<sub>2</sub>, 3.1-11.1 wt% Al<sub>2</sub>O<sub>3</sub>, 0.9-4.22 wt% Na<sub>2</sub>O, 8.2-18.3 wt% MgO, and 13.9-23.7 wt% CaO. Potassium is below 0.1 wt% K<sub>2</sub>O. The melt for inclusion U-530 has a composition that is highly silicic and Na-rich: it contains 60-63 wt% SiO<sub>2</sub>, 20-21 wt% Al<sub>2</sub>O<sub>3</sub>, 7.6-8.0 wt% Na<sub>2</sub>O, and 0.7-0.8 wt% K<sub>2</sub>O. This composition is comparable to the melts reported by Taylor et al. (2000) for melt pockets adjacent to spongy clinopyroxene inclusions in diamonds from an eclogite xenolith from Yakutia. Other inclusions contain melt pockets of submicrometer size, making them difficult to measure.

In order to test whether the spongy clinopyroxene and melt reflect closed-system melting of the primary clinopyroxene within the diamond, we applied pMelts modelling (Ghiorso, et al. 2002). We used the primary core clinopyroxene as a starting composition and melted it at a wide range of pressure-temperature (P-T) parameters. Given that we only have one melt composition measured and that the melt compositions reported by Taylor et al. (2000) are very heterogeneous, we chose to use P-T parameters that closely reproduce spongy clinopyroxene compositions. The modelling results applied to five inclusions reported in this study and three inclusions reported by Taylor et al. (2000) suggest that in order to achieve the best analysed vs. modelled match for spongy clinopyroxene, equilibrium pressures for most inclusions should be in the range of 0.5-1 GPa. Temperatures vary between 800 and 1300 °C. Interestingly, calculations for some inclusions indicate that minimum pressures approach atmospheric conditions (close to 0 GPa), implying that high pressures are not necessary for melting.

The melt composition in equilibrium with spongy clinopyroxene modelled by pMelts cannot fully reproduce the measured melt compositions, especially for FeO, MgO and CaO contents which are highly underestimated by pMelts in comparison to the measured values. However, this could be an analytical artifact, because due to the very small sizes of the melt pockets the analyses are likely to be compromised by some measurements that overlap with the adjacent spongy clinopyroxene. This results in artificially high FeO, MgO and CaO contents of the calculated melt.



**Figure 2:** K<sub>2</sub>O and Na<sub>2</sub>O compositions of melts modelled by pMelts for W5 primary clinopyroxene from Taylor et al. (2000). Dashed lines indicate compositions of glass reported by Taylor et al. (2000) for the same inclusion in diamond. Melting degree values (F, in %) decrease progressively from 0.5 to 5.0 GPa for the isotherms as follows: from 69.2 to

6.5 at 1200 °C; from 48.9 to 6.2 at 1100 °C; from 24.6 to 6.1 at 1000 °C; from 15.6 to 6.1 at 900 °C; from 8.3 to 6.0 at 800 °C; from 6.7 to 6.0 at 700 °C.

Both measured and modelled melt compositions are highly felsic, resembling K-feldspar or albite, which is in good agreement with the reports of these minerals adjacent to spongy clinopyroxene (e.g. Kiseeva, et al. 2017; Spetsius and Taylor 2002). Formation of either Na- or K-rich melts is a function of both bulk rock composition and the P-T parameters of melting. For peridotitic compositions more Na-rich melts are common (e.g. Ma, et al. 2015), while for the eclogitic paragenesis melts are usually K-rich (Kiseeva et al. 2017; Spetsius and Taylor 2002; Taylor et al. 2000). To see the dependence of the melt composition on P-T parameters, we selected W5, a K-rich primary clinopyroxene inclusion in diamond reported by Taylor et al. (2000), and melted it over the range of 700-1200 °C and 0.5-5 GPa (Fig. 2). Using W5's composition and the compositions of three associated melts (after Taylor et al., 2000), allowed us to compare the modelled with the measured compositions.

pMelts modelling suggests that lower temperatures responsible for the lower degrees of melting (Fig. 1A) are yielding potassium-rich melts, while at higher temperatures the higher proportion of Na-rich primary pyroxene melts, and due to sodium incompatibility at lower pressures, is enriching the melt in Na<sub>2</sub>O (Fig. 1C). This indicates that in K- and Na-bearing systems, spongy clinopyroxene coexisting with K-rich melt or K-feldspar pockets around it has most likely formed due to a low-degree of melting.

Figure 2 shows that K-rich and Na-rich melts can occur due to the primary clinopyroxene melting over a wide range of pressures. In the case of the studied inclusions in diamonds, melting pressures are low, (<1 GPa), degrees of melting are high (up to 40%), and the melting is likely triggered by decompression during the diamond ascent to the surface. In the cratonic mantle; however, primary clinopyroxene melting is likely to be caused by the introduction of a metasomatic agent or an increase in temperature. In that case, even at relatively high pressures (3-5 GPa), low-degree melts of primary K-bearing clinopyroxene can lead to the formation of K-rich melt and subsequently to K-rich silicic metasomatism if this melt is separated from the source (Pyle and Haggerty 1998; Spetsius and Taylor 2002). This suggests that primary eclogitic clinopyroxene is an excellent source of K-rich silicic melts in the cratonic mantle.

## References

- Ghiorso MS, Hirschmann MM, Reiners PW, Kress VC (2002) The pMELTS: A revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. *Geochemistry, Geophysics, Geosystems* 3(5):1-35
- Kiseeva ES, Kamenetsky VS, Yaxley GM, Shee SR (2017) Mantle melting versus mantle metasomatism - "The chicken or the egg" dilemma. *Chemical Geology* 455:120-130
- Ma GSK, Wang K-L, Malpas J, Iizuka Y, Xenophontos C, Turkmani AA, Chan GHN, Usuki T, Chan QHS (2015) Melt pockets and spongy clinopyroxenes in mantle xenoliths from the Plio-Quaternary Al Ghab Volcanic Field, NW Syria: implications for the metasomatic evolution of the lithosphere. In: Khan A, Deschamps F (eds) *The Earth's Heterogeneous Mantle: A Geophysical, Geodynamical, and Geochemical Perspective*, vol. Springer International Publishing, Cham, pp 205-257
- Pyle JM, Haggerty SE (1998) Eclogites and the metasomatism of eclogites from the Jagersfontein Kimberlite: Punctuated transport and implications for alkali magmatism. *Geochimica Et Cosmochimica Acta* 62(7):1207-1231
- Spetsius Z, Taylor L (2002) Partial melting in mantle eclogite xenoliths: connections with diamond paragenesis. *International Geology Review* 44(11):973-987
- Taylor LA, Keller RA, Snyder GA, Wang WY, Carlson WD, Hauri EH, McCandless T, Kim KR, Sobolev NV, Bezborodov SM (2000) Diamonds and their mineral inclusions, and what they tell us: A detailed "pull-apart" of a diamondiferous eclogite. *International Geology Review* 42(11):959-983