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# Sodic Cr-diopside compositions record profound pyroxenite/megacrystic (re)fertilization of the central Superior craton lithosphere, Attawapiskat kimberlites, Ontario, Canada

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## Introduction, samples, major- and trace-element analysis

The Victor diamond mine in Ontario, Canada opened in July 2008 and ceased operations in June 2019. Previous researchers documented that Victor diamonds are unusually young ( $\sim$  720 Ma, Aulbach et al. 2018) and grew predominantly in unusually fertile peridotite substrates, specifically garnet lherzolite and garnet wehrlite (Stachel et al. 2018). Our further investigation of this fertile lithosphere accordingly focussed on some 200 clinopyroxene (Cpx) xenocrysts from Victor (in part previously studied by Smit et al. 2014). We adopted high-precision and well-standardized analytical protocols for n=196 major-element analyses by EPMA and n=72 trace-element analyses by LA-SF-ICP-MS at the facilities of the University of Alberta. The analytical protocols are detailed in Hardman et al. (2021).

## **Results and interpretation**

All of the cpx grains were observed to be fresh, with no obvious orthopyroxene, garnet or spinel lamellae, blebs or inclusions. Three EPMA analyses per grain demonstrated effectively no compositional variation and n=61 cpx grains provided valid Nimis and Taylor (2000) pressure-temperature (P-T) estimates that constrain a 39 mW/m<sup>2</sup> model-conductive geotherm. The geotherm is congruent with P-T estimates for n=15 orthopyroxene-bearing garnet pyroxenite and lherzolite xenoliths from the Delta and Victor kimberlites (Smit et al. 2014). In this work we present our data in temperature-composition (T-X) sections where cpx temperatures were projected iteratively to the 39 mW/m<sup>2</sup> geotherm.

The Victor cpx data show Mg-number decreasing step-wise with increasing T (Figure 1). Victor cpx with Mg# > 0.915 resemble cpx in cratonic lherzolites, and with Cr/(Cr+Al)<sub>cpx</sub> in the range 0.55-0.88 at low T (T < 740°C), are interpreted to coexist with Cr-spinel, though not with Cr-pyrope (for which the Cr/(Cr+Al)<sub>cpx</sub> range would be ~ 0.2-0.6). The Victor cpx with Mg# ~ 0.89-0.915 are like cpx in cratonic garnet pyroxenites, and the grains with Mg# < 0.89 are most like cpx megacrysts (though with unusually high Na and Al content). Figure 1 amply illustrates a profound lithosphere-scale progressive dilution of Cr, and progressive enrichment of Al and Na to depth that culminates at 0.30 Na or Al cations per 6-oxygen formula unit (CPFU) at T > 1000°C (equivalent to 4.3 wt% Na<sub>2</sub>O or 7.0 wt% Al<sub>2</sub>O<sub>3</sub>). The Na-Al substitution in the Victor Cr-diopsides occurs as a jadeite (± kosmochlor, aegirine) component, given Si = 1.993±0.009 (1 $\sigma$ ) CPFU for our data. With Si ~ 2.0 CPFU, the Victor cpx stoichiometry effectively precludes Tschermacks-substitution 3+ cations on the T-site, implying that 3+ cations (like Al, Cr) and 3+ trace elements (like V, Sc, Y, REEs) in these pyroxenes occur predominantly in the 6-fold coordinated M1 site.

Figure 2 illustrates several aspects of minor- and trace-element partitioning in peridotitic cpx. The nearcompatible 2+ cations Ni, Mn and Co all show positive log-linear correlations with T, as expected for intermineral partitioning involving magnesian olivine and/or orthopyroxene (Beattie 1993). Low Ti occurs in cpx with Mg# > 0.915 (at low T), and Ti in cpx steadily increases to depth, up to  $T \sim 900 - 1000^{\circ}C$  where ilmenite saturation occurs, upon which Ti steadily decreases with T (in cm-sized megacrystic cpx+ilmenite and olivine+ilmenite assemblages, see Hetman 1996). Most of the trace elements we analyzed are incompatible (i.e. Sc, Sr, Y, Zr, Nb, Hf, Ta, Pb, Th, U and all 14 REEs) and this group shows unusually high concentrations in the (garnet-absent) spinel-facies Cr-diopsides with Mg# > 0.915, though notably lower and comparatively invariant concentrations in pyroxenitic cpx with Mg# ~ 0.89-0.915 in the T interval 620 - 1160°C (Figure 2). We interpret these incompatible trace element data as evidencing "typically" cratonic Zr-Y melt-metasomatism in depleted peridotite, followed by a profound Na-Al-Si pyroxenite±megacrystic (re)fertilization / overprint throughout the deepest 70% of lithospheric section. Partial overprinting resulted in isolated remnants of high-Mg#, low Na-Al cpx ocurring at depth (Figure 1).



**Figure 1:** T-X sections showing major-element composition of n=196 Victor cpx xenocrysts. Nimis-Taylor (2000) temperatures (T-NT00) are projected on a linear 39 mW/m<sup>2</sup> geotherm. CPFU = Cations per 6-oxygen formula unit.



**Figure 2:** T-X sections showing geochemistry of select trace elements for n=72 Victor cpx xenocrysts (determined by LA-SF-ICP-MS). Left-side panel shows n=196 analyses determined by EPMA.

We normalized our Victor cpx REE data to the primitive geochemistry of cpx in high-temperature sheared garnet lherzolite xenolith J4 from Jagersfontein (Stachel et al. 2022). The normalization facilitates recognition of bulk REE uptake in (garnet-absent) spinel-facies low-T cpx, and also of total-REE contents at ~ 45% of primitive values in cpx over the T interval 600 - 1240°C (Figure 3). Such below-primitive REE concentrations likely reflect high modal cpx in the source rocks, consistent with the Mg# 0.89-0.915 characteristics of pyroxenite lithologies. A salient heavy/middle REE fractionation (Yb<sub>J4</sub>/Gd<sub>J4</sub> > 1.8) occurs in megacryst cpx grains with T > 990 °C (Figure 3). We interpret this to result from dissolution/resorption of Cr-pyrope garnet in the megacryst-producing environment.



#### Conclusion

Major- and trace-element characteristics of Cr-diopside xenocrysts from the Victor kimberlite (and the surrounding Attawapiskat kimberlite cluster) bear witness to profound modal-metasomatic pyroxenite/megacrystic refertilization

**Figure 3:** J4-normalized total rare-earth element content (TREE) and heavy/middle REE ratio (Yb/Gd) for n=72 Victor cpx

(or overprinting) throughout ~70% of a previously-depleted lithospheric section. The Na-Al-Si "sodic pyroxenite" metasomatic style is rarely described from cratonic settings, and likely is closely related to early-stage alkaline-magmatic styles of the ca. 1150 Ma Midcontinent Rift. Subsequent slow cooling at ~7.85°C / 100 Ma (Grütter 2009) over some 430 Ma established a steady-state conductive geothermal regime that was permissive for diamond mineralization at ~ 720 Ma (Aulbach et al. 2018).

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