Ages and sources of mantle eclogites: ID-TIMS U-Pb-Sr isotope systematics of clinopyroxene

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Background and motivation

Mantle eclogites form an integral, in cases dominant, part of most kimberlite-borne xenolith suites. They have been variously interpreted as representing the metamorphosed equivalents of underplated high-pressure melts or of subducted oceanic crust (Jacob 2004). However, it has proven notoriously difficult to extract meaningful age information from the radiogenic isotope systematics of mantle eclogites. In addition, clinopyroxene (cpx), a major carrier of incompatible lithophile elements, including the parent elements of most commonly used radioactive decay systems, is frequently altered. This can preclude separation of enough pristine material for accurate and precise analysis by common mass spectrometric techniques and hinders efforts to unravel the origins and evolution of mantle eclogites and to link their formation to regional or global tectonothermal events.

The advent of highly sensitive inductively coupled plasma mass spectrometers (ICPMS) combined with laser ablation (LA) devices has in recent years led to radical advances in *in situ* dating techniques, among them the acquisition of Pb isotopic compositions of cpx in eclogites (Schmidberger et al. 2007). Such data have yielded valuable model Pb isotope age constraints, but their interpretation is difficult as it is sensitive to both the choice of model Pb evolution curve and the assumption that cpx is essentially U-free. A survey of the literature, however, indicates that eclogitic cpx contains median U and Pb concentrations of 0.01 and 0.5 ppm, respectively, with U/Pb of 0.02, which can generate measurable amounts of radiogenic Pb over the typically billion-year histories of mantle eclogites. In order to further test the veracity of *in situ* cpx Pb and Sr isotope measurements, we determined the U-Pb, Pb-Pb and Sr isotope compositions of cpx from three African eclogite suites by both LA-ICPMS and isotope dilution thermal ionisation mass spectrometry (ID-TIMS).

Samples and Methods

The samples form part of three well-characterised mantle eclogite suites. Two suites from southern African kimberlites (Lace and Orapa) have major- and trace-element relationships indicative of oceanic crustal protoliths (Aulbach and Viljoen 2015; unpubl. data). Some of the Lace eclogites formed in the Archaean, given highly unradiogenic Pb in two samples (Aulbach and Viljoen 2015), but multiple formation and/or modification ages from Proterozoic to Archaean are indicated for Orapa, based on Re-Os dating of sulphide inclusions in eclogitic diamonds (Shirey et al. 2008). Eclogites from Koidu (West African Craton) comprise two distinct suites, with low-Mg eclogites (ca. 3.4 Ga Re-Os whole rock age array) interpreted as subducted oceanic crust and high-Mg eclogites as continental cumulates that foundered into the underlying lithospheric mantle (Barth et al. 2001, 2002).

In situ Pb isotope compositions were determined by LA-ICPMS using a NuPlasma 1 multi-collector ICPMS coupled to a 213 nm New Wave Nd:YAG laser system in the Canadian Center for Isotopic Microanalysis (CCIM), University of Alberta, following the procedure previously described for cpx in mantle eclogites (Schmidberger et al., 2007). *In situ* Sr isotope ratios were acquired in static collection mode with Faraday cups at Goethe-University Frankfurt, using the RESOlution (Resonetics) 193nm ArF Excimer Laser (CompexPro 102, Coherent) linked to a Thermo Finnigan Neptune multi-collector ICPMS, following methods outlined in Aulbach et al. (2016). Optically clean cpx separates (typically 1-2 mg) were leached 24h in ~6M HCl and another 24h in Millipore or MQ H_2O. Dry samples were weighed and spiked with a mixed ^{205}Pb-^{235}U spike, followed by column chromatography to produce

purified Sr, Pb and U fractions. All ID-TIMS analyses were conducted at CCIM. The isotopic compositions of U and Pb were measured using a VG354 (Daly photomultiplier detector mode) and Thermo Triton Plus (single SEM) TIMS. Purified Sr fractions were run on a Sector 54 TIMS operating in static multi-Faraday detector mode.

Preliminary Results and Discussion

We have obtained ID-TIMS (solution) and LA-ICPMS (*in situ*) Pb isotopic data for most eclogite cpx samples (total of 25 xenoliths). For most xenoliths (n=21), at least two multi-grain (n~10 grains) cpx fractions were analysed by ID-TIMS to evaluate repeatablilty; for the majority of these (14/21) the Pb isotopic compositions agree within analytical uncertainty. Those that have variable Pb isotopic compositions outside analytical uncertainty reflect a multi-component Pb record within a single cpx population. ID-TIMS results for acid-leached eclogitic cpx in this study indicate a moderate range in uranium (0.004-0.369 ppm) and model Th (0.006-5.845 ppm) contents. We have evaluated the effect of an HCl acid-leaching treatment on the Pb isotopic composition of two eclogitic cpx samples. In one case the unleached cpx has U and Th contents and $^{238}U/^{204}Pb$ values that are a factor of 10 higher than leached cpx, indicating the presence of labile U and Th. In contrast, the effect of leaching on cpx Pb contents and Pb isotopic ratios is negligible (<1% change in compositions). Leached eclogitic cpx typically have relatively low $^{238}U/^{204}Pb$ values (<40; n=41/46), however for ancient xenoliths this corresponds to a significant correction for in-growth of radiogenic Pb in Pb-Pb dating studies. In some cases, variable U concentrations at relatively homogeneous Th and Pb contents of multiple leached aliquots suggests that some labile U can remain after the HCl-leaching treatment.

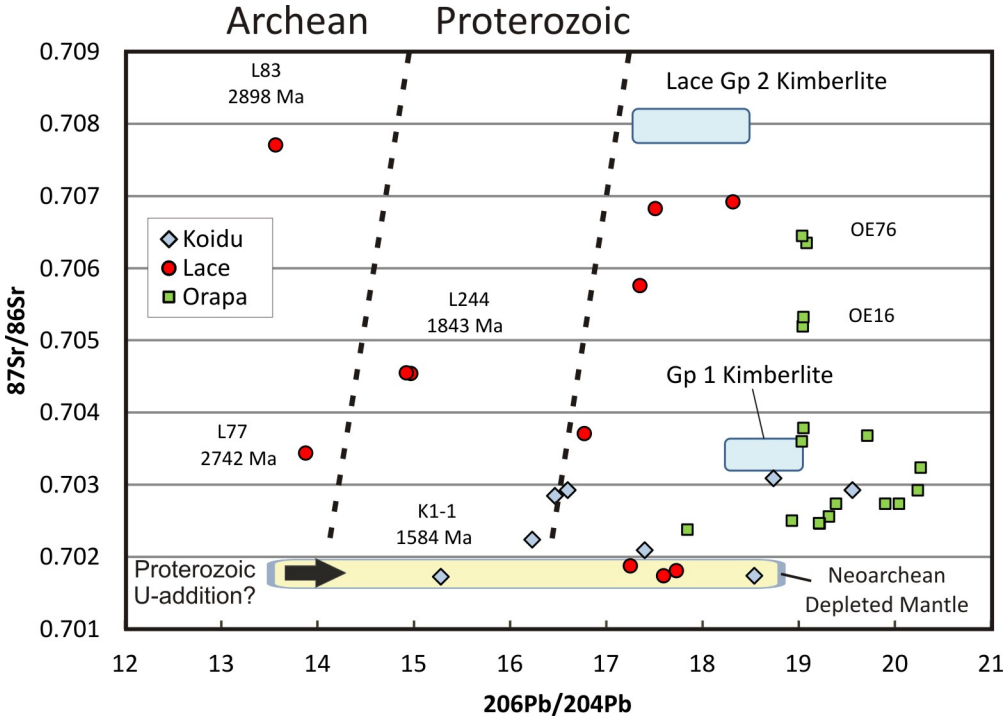

Figure 1. Measured $^{87}Sr/^{86}Sr$ versus $^{206}Pb/^{204}Pb$ obtained by ID-TIMS for cpx in three eclogite xenolith suites.

Preliminary results show that acid-leached eclogitic cpx with low U contents and matching *in situ* and solution Pb isotope ratios can contain a significant component of radiogenic Pb (up to 10%); hence *in situ* Pb-Pb cpx analyses commonly do not reflect their initial Pb isotopic compositions, resulting in underestimated/inaccurate Pb-Pb model ages. The ID-TIMS cpx data for Lace ($^{206}Pb/^{204}Pb$=13.54-18.32), Koidu (16.25-19.56), and Orapa (17.92-20.27) eclogites define crude linear arrays on Pb-Pb plots with Paleoproterozoic secondary isochron dates (2.15, 2.24 and 1.80 Ga, respectively). Two cpx fractions from Lace eclogite L83, which have high Pb contents (~6 ppm), unradiogenic Pb isotopic

compositions ($^{206}Pb/^{204}Pb$=13.57-13.52), the lowest $^{238}U/^{204}Pb$ values (1.0-1.5), and ancient single-stage model Pb dates (2.90-2.84 Ga; minimum estimates for their formation) support an Archaean formation age.

All eclogite suites display a large range in $^{87}Sr/^{86}Sr$ values (Figure 1; total range is 0.7017-0.7077) and there is general agreement for most samples between *in situ* and solution results. Several eclogites, representing examples from each suite, have Neoarchean depleted mantle-like $^{87}Sr/^{86}Sr$ values (0.7017-0.7025), consistent with a subducted oceanic lithosphere protolith. The origin of cpx with radiogenic strontium isotopic compositions is less clear. In some instances there may be cryptic metasomatism caused by the host kimberlite, some Lace eclogites have cpx compositions approaching that of the Lace kimberlite ($^{87}Sr/^{86}Sr$=0.7072-0.7084; Howarth et al. 2011). In others the compositions are more radiogenic than the host kimberlite so likely reflect metasomatic processes influencing the xenoliths prior to entrainment in kimberlite magma. An interesting feature of this study is that Sr and Pb isotopes do not always show coherent behaviour in eclogite cpx; radiogenic Pb (>> Depleted Mantle) is observed in samples with restricted depleted mantle-like $^{87}Sr/^{86}Sr$, perhaps due to heterogeneous contributions from various slab components, as previously suggested (Aulbach et al. 2016). Taken together, two pieces of isotopic evidence indicate that some Lace and Koidu eclogites are Archaean: 1) Unradiogenic Pb as described above and 2) very low $^{87}Sr/^{86}Sr$ in some xenoliths. In this scenario, the secondary isochrons recorded by Lace and Koidu xenoliths are interpreted as Palaeoproterozoic metasomatic overprint events.

Although this must be regarded as work in progress, our preliminary results confirm that the conclusions arrived at based on both the cpx Pb and Sr LA-ICPMS and ID-TIMS isotopic techniques are the same. *In situ* LA-ICPMS Pb-Pb isotope acquisition is a high-throughput method that provides guidance for sample targeting for the more precise yet highly time-intensive solution work. Together with *in situ* Sr isotope determination it further serves as a valuable check on the purity of the separated cpx with respect to kimberlite contamination. Finally, this study highlights that a ID-TIMS U-Pb study of cpx has the potential to provide geologically meaningful minimum formation ages for mantle eclogites, as well as their source compositions and evolution.

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