Physicochemical properties of mantle eclogite, and mass transfer in ancient subduction zones

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Kimberlite-borne xenolithic ("mantle") eclogite has been studied for many decades. A broad consensus now exists that most such samples represent the metamorphic products of recycled crustal material of basaltic to picritic composition. Protoliths comprise both extrusive and intrusive sections, possibly of spreading ridge origin. Given their mostly Archaean ages, geodynamic implications, such as the construction of thick cratonic roots during collisional tectonics, the production of TTG-like continental crust from partial melting in subduction zones and even the onset of a plate tectonic regime, have long been discussed. If we accept an origin as mid-ocean ridge basalt and gabbro, such samples can also provide insights into the convecting mantle source from which their igneous protoliths were derived. Such applications are contingent on a good grasp of each individual sample's multistage petrogenesis, comprising differentiation processes in the ocean floor, seafloor weathering *en route* to the trench, dehydration and partial melting in palaeo-subduction zones and interaction with fluids produced in other parts of the slab, and during their later extended residence in the cratonic lithosphere. This is possible availing of a wide array of elemental and isotopic tracers, in combination with constraints from high-pressure experiments and thermodynamic modelling. Excluding samples with strongly differentiated or cumulate progenitors and those showing signs of intense metasomatic overprint, proxies for composition (*e.g.*, $^{87}Sr/^{86}Sr$), temperature (*e.g.*, Ti, Sm) and oxygen fugacity (*e.g.*, $V \pm Fe^{3+}/\Sigma Fe$) of the palaeo-convecting mantle can be found that are relatively insensitive to fractionation of olivine during emplacement, alteration under anoxic ancient deep ocean waters, and melt loss on subduction. Such novel applications suggest that the ancient convecting mantle was more reduced by ~1 log unit and warmer by ~100–150 °C than the modern one, and indicates the existence of depleted convecting mantle regions by 3 Ga ago.

Intriguingly, age dating of mantle eclogitic materials (xenoliths and inclusions in diamond) occurring on multiple cratons (Kaapvaal, Zimbabwe, Congo-Kasai, Siberia, North Atlantic) reveal a clustering of ages around 2.9–2.7 Ga ago, possibly indicative of the amalgamation of the first supercontinent (Fig. 1a). In contrast, rarer Palaeoproterozoic ages (Slave, East European), which overlap those of orogenic eclogites from localities around the world, may reflect assembly of the Nuna/Columbia supercontinent at ~2.1–1.9 Ga. Therefore, mantle eclogite can also provide insights into processes occurring during the recycling and closure of palaeo-ocean basins. A first-order observation afforded by the relatively recent development of an eclogite oxybarometer is that mantle eclogite, even that with stable isotope evidence for interaction with seawater, has lower oxygen fugacity than either modern or ancient oceanic crust (Fig. 1b). Such low values are not permissive of the stabilisation of either carbonate or sulphate. While this explains why cratonic eclogite is a fertile diamond source that is frequently sulphide-bearing, it also indicates that this lithology has little oxidising power to contribute to palaeo-arcs, with implications for the metallogeny in such settings. Signatures interpreted as evidence for interaction with other slab lithologies include the presence of unsupported radiogenic Sr (sediment), higher Ni contents in interstitial than in occluded sulphide minerals (?serpentinite), and stepped REE patterns that are strongly reminiscent of those detected in

Phanerozoic orogenic eclogites affected by interaction with copious amounts of fluids plausibly liberated during dehydration of oceanic mantle.

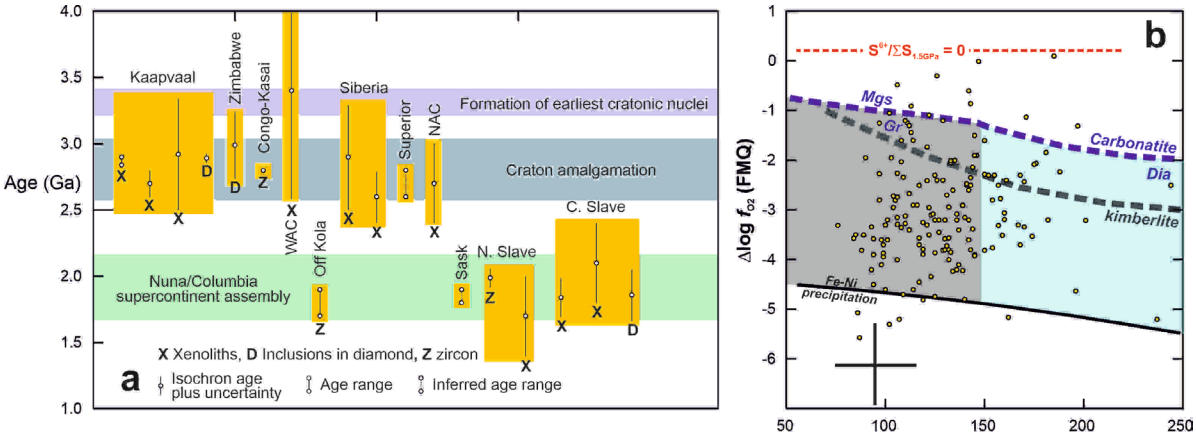

Figure 1a - Summary of age constraints for the formation of cratonic eclogite sources sampled by xenoliths (X) and diamonds (D), using bulk rocks, mineral separates or zircons (Z) (Aulbach, unpublished database). b - Oxygen fugacity estimates for eclogite and pyroxenite xenoliths relative to the fayalite-magnetite-quartz buffer (expressed as $\Delta \log f O_2$ (FMQ)) as a function of depth (Aulbach, unpublished database). Also shown are, for conditions along a conductive geotherm corresponding to a surface heatflow of 40 mW/m^2, the stability of carbonatite vs. diamond and graphite and of carbonated silicate melt with 10 mol% CO_2 (~kimberlite), and the Fe-Ni precipitation curve (~metal saturation) from Stagno et al. (2013). Sulphur is entirely reduced below the red stippled line (based on Matjuschkin et al., 2016).

Much remains to be learned from these priceless rocks. For example, “novel” stable isotope systems, such as Mg or Zn, may be employed to probe for interaction of ancient oceanic crust with carbonate-bearing slab lithologies. Multiple S isotope data not only can detect the presence of sulphate-derived S, but also put a rough time stamp on the S source (pre- vs. post-atmospheric oxygenation around 2.4 Ga ago). In combination with Fe isotopes, this might allow tracing redox interactions in ancient subduction zones. Lithium and B isotopes may constrain the role of serpentinite- and sediment-derived fluids. Few such data exist currently, but could help to constrain ancient volatile cycles. Compositional and isotopic data from mantle eclogite that has not been mantle-metasomatised are also helpful to understand the chemical structure of the modern convecting mantle as sampled by ocean island basalts derived from sources affected by contamination with ancient oceanic crust. Finally, mineralogical and chemical differences exist between mantle eclogite and its orogenic counterpart, which may reflect the secular evolution of the terrestrial crust-mantle-atmosphere system, but also different subduction-exhumation dynamics for orogenic vs. mantle eclogite, the details of which remain to be unraveled.

Matjuschkin, V., Blundy, J.D., Brooker, R.A., 2016. The effect of pressure on sulphur speciation in mid- to deep-crustal arc magmas and implications for the formation of porphyry copper deposits. *Contributions to Mineralogy and Petrology* 171, 66.

Stagno, V., Ojwang, D.O., McCammon, C.A., Frost, D.J., 2013. The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature* 493, 84-88.