MANTLE GEOCHRONOLOGY AND THE AGE OF THE SUB-CRATONIC LITHOSPHERE

N.J Pearson[1], W.L. Griffin[1], S.Y. O'Reilly[1] & O. Alard[2]

[1]*GEMOC Key Centre, Department of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia*
[2]*CNRS, Université de Montpellier, 34095 Montpellier Cedex 05, France*

Introduction

High precision *in situ* analysis of trace-element compositions and isotope ratios has revolutionised geochronology and geochemistry over the past decade. Most of the advances are due to the proliferation of laser-ablation microprobe inductively coupled plasma mass spectrometry (ICP-MS) and the rapid development of the multi-collector (MC-) ICP-MS. One of the main benefits of *in situ* analysis is that it allows the isotopic data to be interpreted in a microstructural context and to be integrated with geochemical data from other microanalytical techniques. This approach not only provides age information but helps to constrain the nature of the source rocks and to unravel the processes that have subsequently modified it.

Knowledge of the age, composition and evolution of the sub-continental lithospheric mantle (SCLM) is essential to an understanding of continental dynamics and the long-term stability of cratons. The combination of U-Pb dating of zircons and model ages derived from Hf isotopes has been demonstrated to be a powerful technique for understanding crustal evolution (e.g. Griffin et al., 2004a). Unfortunately the occurrence of zircon in mantle peridotites is rare and it is usually interpreted to be a product of metasomatism (e.g. Konzett et al., 2000; Zheng et al., 2006).

Re-Os Isotopes in Peridotites

Re-Os isotopic analyses of mantle-derived peridotites have contributed much of what is currently known about the age of the SCLM. ^{187}Re is the parent element of ^{187}Os (β-decay, $t^{1/2} = 1.666\ 10^{-11}a^{-1}$) and because it is moderately incompatible it is largely extracted from the mantle into basaltic melts during the formation of mafic crust. In contrast, Os is strongly compatible and it is concentrated in the residual mantle. Since the first application of Re-Os to dating mantle lithosphere formation (Walker et al., 1989) the assumption has been made that the model ages represent the age of primary melt depletion and lithosphere stabilisation.

Most of the initial information on the age of the SCLM has been provided by analysis of the whole-rock Re-Os isotopic system in mantle-derived peridotites, sampled as exposed massifs and xenoliths brought up by volcanic eruption. Model ages from xenoliths from beneath the Siberian, Kaapvaal and Slave cratons indicate that parts of the sub-continental lithospheric mantle are as old as the overlying Archean crust. Nevertheless, the significance of younger ages in the Re-Os dataset for cratonic xenoliths remains unclear. Do the younger ages represent melt extraction events or are they result of disturbance of the Re-Os system during metasomatism? This question has been investigated by applying *in situ* analytical techniques.

Sulfide is the dominant host for Os and the other platinum group elements (PGE) in mantle-derived peridotites, contributing between 80-100% of the whole-rock budget of these elements. *In situ* LAM-ICPMS analysis of PGEs shows that multiple generations of sulfide occur within many peridotites as evidenced by the variations in PGE patterns with micro-structural context (Alard et al., 2000). Inclusions of sulfide in primary silicates are characterised by high Os (20-1000 ppm) but low Pd/Ir (0.001-1), whereas interstitial sulfides and those associated with metasomatic phases typically have low Os (<30 ppm), Ir but high Pd/Ir ratios (up to 1000).

The development of *in situ* analysis techniques for Re-Os isotopes using laser ablation MC-ICP-MS enables the determination of ^{187}Os/^{188}Os in single sulfide grains (Pearson et al., 2002). Analyses of enclosed and interstitial sulfides in peridotite xenoliths show that the two types of sulfide differ significantly in their Re-Os systematics. Enclosed sulfides, such as those occurring in macrocrystic olivine in kimberlites, typically have unradiogenic Os compositions. Interstitial sulfides typically have ^{187}Os/^{188}Os ranging from asthenospheric (0.127) to highly radiogenic values (0.175). Analyses of multiple sulfide grains from single samples of spinel peridotite define mixing trends that may have either positive or negative slopes. In such samples it is clear that the whole-rock Re-Os signature reflects a mixing of several sulfide populations (Alard et al., 2002; Pearson et al., 2002). The observed trends also indicate the mobility of radiogenic Os, but not Re, and the disturbance of the Re-Os isotopic system during metasomatism.

Archean Lithospheric Mantle

In situ Re-Os isotopic analysis of sulfide phases in peridotite xenoliths from kimberlites in the Kaapvaal Craton has been used to determine the history of the SCLM and to establish links with crustal events (Griffin et al., 2004b). Samples from the Western Terrane (Finsch, Kimberley and Jagersfontein) and from the Southeastern Terrane (Northern Lesotho pipes) were included in the study to investigate the stabilization of the craton. Sulfides with the compositional features of both the 'enclosed' and 'interstitial' types of Alard et al. (2000) are present but both types may occur enclosed in primary silicates. This reflects the recrystallization in the SCLM and the presence of multiple generations of sulfides with widely varying Os contents, Re/Os and ^{187}Os/^{188}Os. The oldest sulfide ages are preserved in the most depleted peridotites, typically at shallower levels of the SCLM. Sulfide addition accompanies metasomatism by asthenosphere-derived silcate melts and fluids, and there is an associated decrease in the maximum sulfide T_{RD} model ages. The Re-Os model ages of the whole-rock samples therefore represent mixtures and because the model age of whole-rock sample is younger than the maximum sulfide T_{RD} it is unlikely to date any specific geological event.

The age distribution of sulfides with $^{187}Os/^{188}Os$ <0.08, interpreted as MSS residual from melting (or last affected by metasomatism), show distinct differences between the terranes: Western Terrane, 2.9-3.2 Ga; Southeastern Terrane, 3.0-3.6 Ga. The peaks correlate with the oldest crustal ages in each terrane and indicate that the formation of the SCLM was earlier than, or contemporaneous with, the earliest crustal formation. Each terrane appears to have carried its own SCLM keel at the time of craton assembly. Distinct model-age peaks reflect the timing of the suturing of terranes (2.65, 2.75 Ga), and later rifting/collision of the western margin of the Kalahari Supercraton (1.8-2.2 Ga, ca 1 Ga). The sulfide age data push back the mean age of SCLM stabilization of the Kaapvaal Craton and suggest that the bulk of the Kaapvaal SCLM had formed prior to 3 Ga.

The age structure of the SCLM beneath the Udachnaya kimberlite pipe in the eastern Siberian craton has been studied using *in situ* Re-Os analysis of sulfides enclosed in olivine (Griffin et al., 2002). The olivine grains were selected from coarse (5-8 mm) mineral concentrate and their composition and grain size suggest derivation from the 'megacrystalline dunites' that occur at depths of 150-180 km. The sulfide inclusions range in size from 20-250 µm and several olivine grains contained multiple sulfide inclusions. Typically the sulfides consist of interfingered Ni-rich and Fe-rich MSS, surrounded by discontinous zones of pentlandite and an outer zone of chalcopyrite. No alloys were observed in section although irregular signals during laser ablation indicate the presence of Pt-rich nuggets.

The Os, Pt and Re contents of the sulfides allow the recognition of 5 populations with the compositional features: Group 1(67-6009 ppm Os; Os/Pt 256; Re/Os 0.0006); Group 2 (320-20000 ppm Os; Os/Pt <1.8; Re/Os 0.0007); Group 3A (40-225 ppm Os; Os/Pt <1-7; Re/Os 0.003); Group 3B (3-85 ppm Os; Os/Pt 9.5; Re/Os 0.006); Group 3C (~8 ppm Os; Os/Pt 1.1; Re/Os 0.067). The Os isotopic data for most sulfides from Groups 1, 2 and 3A give T_{RD} and T_{MA} ages > 2.5 Ga. Although Proterozoic model ages are derived from some Group 3A and 3B sulfides, most of the Group 3 sulfides have $^{187}Os/^{188}Os$ above the present-day CHUR, giving negative T_{RD} ages. In some cases where multiple sulfide inclusions occur in a single olivine grain, the sulfides belong to the same group and are similar in isotopic composition. In other olivine grains the sulfides are from different groups and have widely varying isotopic compositions and Re/Os ratios. In general these do not yield Re-Os isochrons with meaningful ages and initial ratios, implying that the inclusions represent different generations of sulfides.

The distribution of T_{MA} ages indicates that the SCLM beneath the Udachnaya pipe formed during the period 3.0-3.5 Ga, culminating with a major lithosphere-forming event at 2.9 Ga. It is suggested that partial melting of eclogites (3.2 to 2.9 Ga) produced melts with high $^{187}Os/^{188}Os$ and high Re/Os. Varying degrees of interaction between these melts and the Os-rich MSS produced the range of observed Os isotope compositions.

The T_{MA} age distribution plot for sulfides from peridotite xenoliths from the Slave Craton has a pronounced peak at 2.7 Ga (Aulbach et al., 2004). Thus the sulfide age distributions for the Kaapvaal, Siberian and Slave Cratons all have distinct modes between 2.7 and 3.0 Ga, suggesting that c.2.7 Ga corresponds to the timing of final stabilization of the lithospheric mantle beneath those cratons that still exist.

Discussion

The development of the *in situ* analysis method of mantle sulfides has shown that Re-Os isotope systematics in mantle-derived peridotites are complex. The microanalytical technique has demonstrated that different generations of sulfide, recognised on the basis of mineralogy and PGE compositions, have very different Os-isotope composition and that Os is mobile during metasomatism. The *in situ* data indicate that whole-rock Re-Os analyses of mantle-derived peridotites reflect the mixing of several generations of sulfides and that the interpretation of these data in terms of depletion ages may be ambiguous. Evidence for the scale of this mixing is shown by the range of Os isotope compositions for sulfide inclusions in single olivine grains. Thus analysis of separated olivine might overcome the effects of recent Re addition but may still give an $^{187}Os/^{188}Os$ for a mixture of different generations of sulfide. At best whole-rock T_{RD} ages provide minimum estimates for the age of melting in cratonic peridotites.

Meaningful interpretation of Re-Os data in terms of mantle events requires understanding of the occurrence and mobility of sulfides in mantle peridotites. Heterogeneity of Os isotopes in the convecting mantle is used as evidence to negate the significance of the age of a single sulfide grain (Pearson & Wittig, 2008; Rudnick & Walker, 2009). Because sulfide is one of the first phases to enter the melt during peridotite melting, then all of the sulfide present in highly depleted cratonic peridiotites might be metasomatic and could have mixed isotopic signatures. The whole-rock derived depletion ages for these samples will have little significance, especially if there are multiple generations of sulfide. It is important to note that the oldest sulfide model ages should also be considered to be minimum depletion ages. Although Os isotope ratios in low-Os sulfides may be less precise than conventional techniques, the *in situ* analyses provide the spatial context to recognise different sulfide generations and provide more readily interpretable depletion ages.

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