

In-situ Re-Os analysis of mantle sulfides: a new microanalytical technique to unravel the evolution of the lithospheric mantle

Pearson, N.J.¹, Griffin, W.L.^{1,2}, Spetsius, Z.³ and O'Reilly, S.Y.¹

1. *GEMOC Key Centre, Dept. of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia*

2. *CSIRO Exploration and Mining, North Ryde, NSW 2113, Australia*

3. *Institute of Diamond Industry, ALROSA Co. Ltd., Mirny, Yakutia, 678170, Russia*

Introduction

Re-Os isotopic analyses of mantle-derived peridotites have contributed much of what is currently known about the age of the sub-continental lithospheric mantle. Model ages from mantle-derived samples 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?

Sulfide has been shown to be 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 (e.g. Mitchell & Keays, 1981; Morgan & Baedekker, 1983; Hart & Ravizza, 1996; Burton et al., 1999; Alard et al., 2000; Lorand & Alard, 2001). For many years these elements were regarded as occurring in chondritic relative proportions (e.g. Jagoutz et al., 1979; Mitchell & Keays, 1981; Morgan, 1986). The recent identification of non-chondritic ratios for Pd/Ir, Pt/Ir and Rh/Ir in mantle-derived rocks (e.g. Pattou et al., 1996; Snow & Schmidt, 1998; Lorand et al., 1999; Rehkämper et al., 1999) has stimulated renewed interest in the PGE distribution in these rocks and in particular the sulfides.

Using *in situ* laser ablation analyses of sulfides in mantle-derived peridotites Alard et al. (2000) have shown that the sulfides in general do not have chondritic patterns for the highly siderophile elements (PGE + Au + Re). The data also show that multiple generations of sulfide occur within many peridotites as evidenced by the variations in PGE patterns with microstructural context.

Two distinct types of sulfide can be recognised:

1. Sulfides enclosed in silicate minerals are characterised by fine intergrowths of Ni-poor and Ni-rich monosulfide solution (MSS) and pentlandite, with minor chalcopyrite, and have high Os and Ir contents (in some samples > 100,000 times primitive mantle (PM)) and low Pd/Ir

ratios ($\text{Pd}/\text{Ir} < 0.5$) giving rise to arch-shaped PM-normalised highly-siderophile elements (HSE) patterns.

2. Interstitial sulfides have a bulk composition of Cu-pentlandite with low Os and Ir contents but high Pd/Ir ratios (up to 1000).

Both types of sulfide commonly occur in the same sample and can show a variety of HSE patterns. The silicate-enclosed MSS sulfides are thought to represent the residues of partial melting and the interstitial Cu-Ni rich sulfides are considered to be the crystallisation products of sulfide-bearing metasomatic fluids (Alard et al., 2000).

The development of in-situ analysis techniques for Re-Os isotopes using laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) enables the determination of $^{187}\text{Os}/^{188}\text{Os}$ in single sulfide grains (Pearson et al., 2001). The significance of this development, as with all *in situ* techniques, is that it preserves the microstructural context necessary for interpretation and eliminates the difficult and time-consuming task of separating the small and rare sulfide grains. Thus the technique allows the assessment of the contribution of enclosed and interstitial sulfides to the whole-rock Os isotope systematics, as has been shown by Pearson et al. (2001) and Alard et al. (2001).

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 $^{187}\text{Os}/^{188}\text{Os}$ 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., 2001; Pearson et al., 2001). The observed trends also indicate the mobility of radiogenic Os, but not Re, and the disturbance of the Re-Os isotopic system during metasomatism.

Pearson et al. (2001) reported in-situ Os isotope data for 3 sulfides enclosed in olivine macrocrysts from the Udachnaya kimberlite (Siberian Craton, Russia). $^{187}\text{Os}/^{188}\text{Os}$ ratios of these sulfides range between 0.1033 ± 0.0002 and 0.1118 ± 0.0013 , while the low $^{187}\text{Re}/^{188}\text{Os}$ ratios (0.006 to 0.081) are consistent with their low Pd/Ir. Unradiogenic Os isotopic ratios and low Re/Os ratios indicate that these sulfides have evolved in a low Re/Os environment since roughly 3 Ga. T_{RD} ages vary from 3.6 to 2.3 Ga and T_{MA} range from 2.9 to 3.6 Ga. The in-situ results are in good agreement with data for diamond-enclosed sulfides from the same locality (Pearson et al., 1999) and demonstrate the accuracy and precision of the in-situ method relative to the micro-chemistry N-TIMS method.

Based on these preliminary results a reconnaissance study has been undertaken of the age structure of the lithospheric mantle beneath the Udachnaya kimberlite pipe in the eastern Siberian craton using in-situ Re-Os analysis of sulfides enclosed in mantle-derived olivine grains.

Analytical Methods

The in-situ measurement of Os isotopes in sulfides uses a Merchantek LUV266 laser microprobe and a Nu Plasma multi-collector ICP-MS with 12 Faraday cups and 3 ETP ion counters. We use two combinations of collectors:

Masses 194, 192, 190, 189, 188, 187, 186, 185 in Faraday cups

Masses 194, 193, 192, 191, 190, 189, 188, 186 in Faraday cups; 187 and 185 in ion counters.

The all-Faraday configuration allows the simultaneous measurement of Os, Re and Pt, whereas the repositioning of the ion beams by changing the magnet field and zoom lens voltages to direct masses 187 and 185 into ion counters also allows Ir to be measured.

Mass bias is corrected by normalisation of $^{189}\text{Os}/^{192}\text{Os} = 0.39593$ (Völkening et al., 1991) using the exponential law for measurements with the Faraday array. The mixed Faraday-ion counter setup allows the use of $^{191}\text{Ir}/^{193}\text{Ir}$ for this correction, using either (1) the Ir in the sulfide; (2) addition of Ir to the nebuliser gas as a 'dry' vapour from a CETAC MCN6000. The overlap of ^{187}Re on ^{187}Os is corrected using a $^{187}\text{Re}/^{185}\text{Re} = 1.6742$, determined from measurement of a mixed Ir-Re solution. Typical precision ($\pm 2\text{se}$) for analysis of a 25ppb Os solution is ± 0.0002 for the Faraday setup and ± 0.00005 for the combined Faraday-IC setup. The accuracy of the Re correction can be demonstrated up to $^{187}\text{Re}/^{188}\text{Os} = 1.6$ using the Faraday array and up to $^{187}\text{Re}/^{188}\text{Os} = 0.26$ using the Faraday-IC setup. Typical precision on $^{187}\text{Os}/^{188}\text{Os}$ with $^{187}\text{Re}/^{188}\text{Os} = 0.26$ is ± 0.0001 (2se). The accuracy of the Re correction can be demonstrated up to $^{187}\text{Re}/^{188}\text{Os} = 1.6$ using the Faraday array and up to $^{187}\text{Re}/^{188}\text{Os} = 0.26$ using the Faraday-IC setup.

Typical laser operating conditions used in this study were a frequency of 5 Hz and beam energy of 3-5 mJ/pulse producing spot sizes in sulfide minerals in the range 60-80 microns. Ablation was carried out in a He atmosphere and the He-sample mixture was passed through a 30 ml mixing chamber (Norman et al., 1996) before blending with Ar prior to introduction into the ICP.

The LAM analysis has been tested using a synthetic NiS bead (PGE-A) with 204 ppm Os (Alard et al., 2000) of known isotopic composition (I. Horn, pers. comm.) and PGE pattern. Analyses of PGE-A were undertaken to assess the precision of the measured $^{187}\text{Os}/^{188}\text{Os}$ as a function of signal intensity (laser energy, spot size) and analysis time. Repeated LAM analysis of PGE-A demonstrates the precision expected for peridotite sulfides as a function of signal intensity, laser

spot size and analysis duration. Precision equivalent to N-TIMS is achieved using the Faraday array for Os > 200ppm and the Faraday-IC setup for Os > 50ppm. Better precision is obtained when Ir is used to correct for mass discrimination.

Results

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. 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 monosulfide solution (MSS), surrounded by discontinuous 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 summarised in the following table and Fig. 1:

	Os ppm	Os/Pt	Re/Os
Group 1	67-600	9-256	0.0006
Group 2	320-20000	<1.8	0.0007
Group 3A	40-225	<1-7	0.003
Group 3B	3-85	9.5	0.006
Group 3C	~8	1.1	0.067

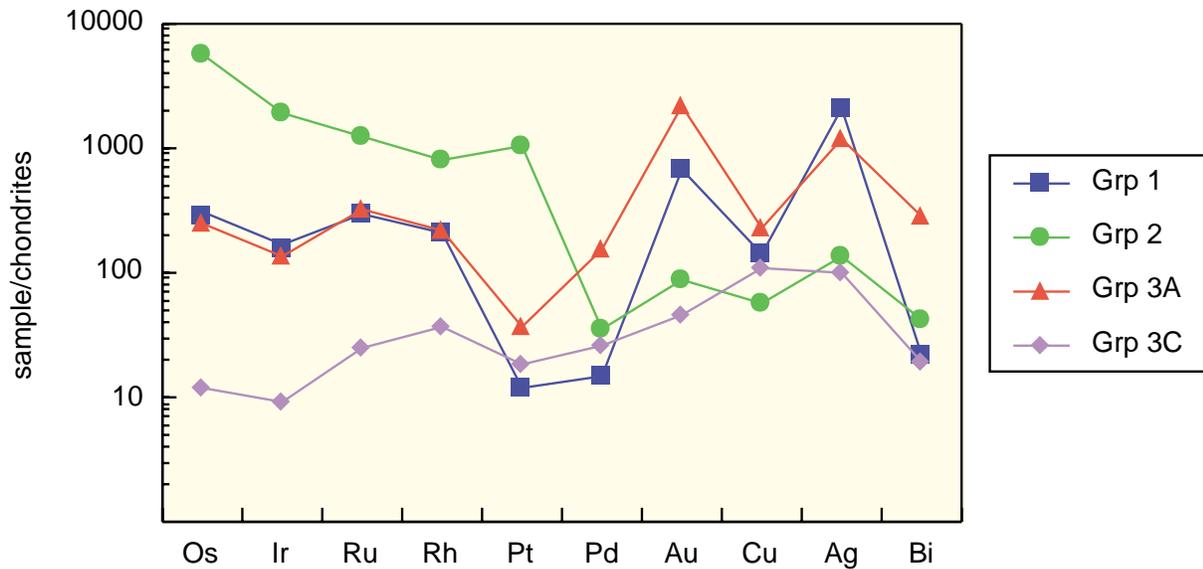


Fig. 1: Trace element abundances for Group averages of sulfide inclusions analysed by ICPMS

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 $^{187}\text{Os}/^{188}\text{Os}$ 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 (Fig. 2). It is suggested that partial melting of eclogites (3.2 to 2.9 Ga, Pearson et al., 1995) produced melts with high $^{187}\text{Os}/^{188}\text{Os}$ and high Re/Os. Varying degrees of interaction between these melts and the Os-rich MSS produced the range of observed Os isotope compositions.

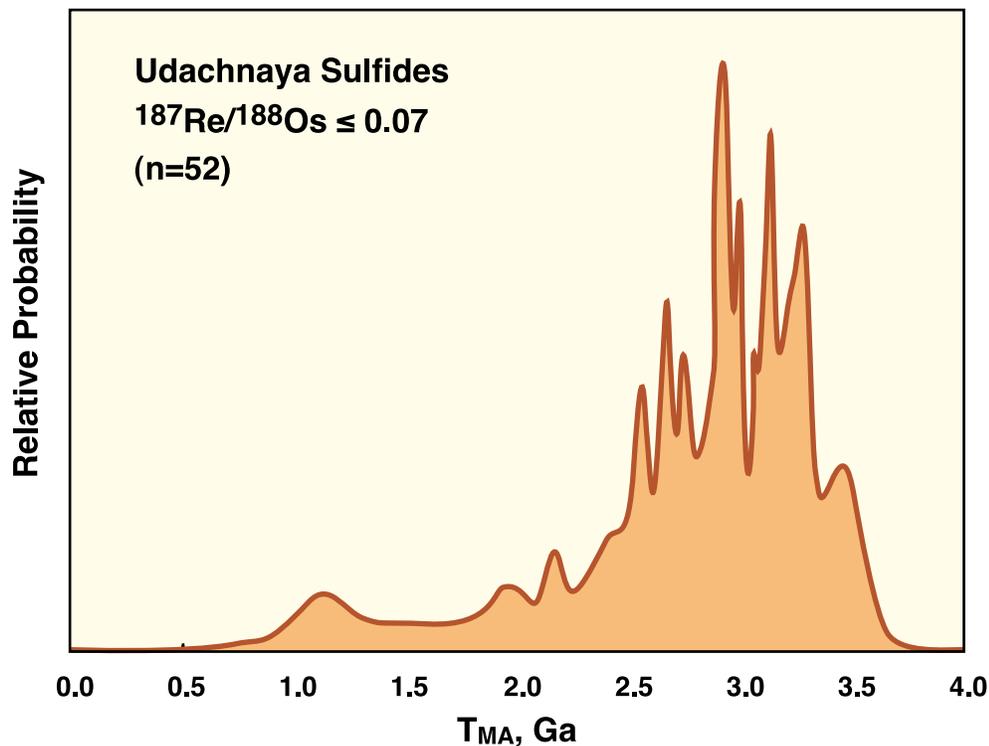


Fig.2: Cumulative probability plot of T_{MA} model age data

Conclusions

The development of a method for 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 $^{187}\text{Os}/^{188}\text{Os}$ for a mixture of different generations of sulfide.

References

- Alard, O., Griffin, W.L., Lorand, J.P., Jackson, S.E., O'Reilly, S.Y., 2000. Non-chondritic distribution of the highly siderophile elements in mantle sulfides. *Nature*, 407, 891-894.
- Burton, K.W., Schiano, P., Birck, J.L., Allègre, C.J., 1999. Osmium isotope disequilibrium between mantle minerals in a spinel lherzolite. *Earth Planet. Sci. Lett.*, 172, 311-322.
- Hart, S.R., Ravizza, G.E., 1996. Os partitioning between phases in lherzolite and basalt. In: Hart, S.R., Basu, A., *Earth Processes: Reading the Isotope Code*, Vol. 95, Am. Geophys. Union, Washington DC, pp 123-134.
- Jagoutz, E., Palme, H., Baddenhausen, H., Blum, K., Cendales, M., Dreibus, G., Spettel, B., Lorenz, V., Wanke, H., 1979. The abundance of major, minor and trace elements in the earth's mantle as derived from primitive ultramafic nodules. *Proc. Lunar Planet. Sci. Conf. 10th (USA)*, 2031-2050.
- Lorand, J.-P. and Alard, O., 2001. Platinum-Group Element abundances in the upper mantle: New constraints from *in-situ* and whole-rock analyses of Massif Central xenoliths (France), *Geochim. Cosmochim. Acta*, *In press*.
- Lorand, J.P., Gros, M., Pattou, L., 1999. Fractionation of platinum-group elements in the upper mantle: a detailed study in Pyrenean orogenic peridotites. *J. Petrol.*, 40, 951-987.
- Mitchell, R.H., Keays, R.R., 1981. Abundance and distribution of gold, palladium and iridium in some spinel and garnet lherzolites. Implications for the nature and origin of precious metal rich intergranular components in the upper mantle. *Geochim. Cosmochim. Acta.*, 45, 2425-2445.
- Morgan, J.W., 1986. Ultramafic xenoliths: clue to earth's late accretionary history. *J. Geophys. Res.*, 91, 12375-12387.
- Morgan, J.W., Baedekker, P.A., 1983. Elemental composition of sulfide particles from an ultramafic xenolith and the siderophile element content of the upper mantle. *Lunar Planet. Sci. Conf. XIV*, 513-514.
- Pattou, L., Lorand, J.P., Gros, M., 1996. Non-chondritic PGE ratios in the terrestrial upper mantle. *Nature*, 379, 712-715.
- Pearson, D.G., Shirey, S.B., Bulanova, G.P., Carlson, R.W., Milledge, H.J., 1999. Re-Os isotopic measurements of single sulfide inclusions in a Siberian diamond and its nitrogen aggregation systematics. *Geochim. Cosmochim. Acta*, 63, 703-711.
- Pearson, D.G., Shirey, S.B., Carlson, R.W., Boyd, F.R., Pokhilenko, N.P., Shimizu, N., 1995. Re-Os, Sm-Nd and Rb-Sr isotope evidence for thick Archean lithospheric mantle beneath the Siberia Craton modified by multi-stage metasomatism. *Geochim. Cosmochim. Acta*, 59, 959-977.

Pearson, N.J., Alard, O., Griffin, W.L., Jackson, S.E., O'Reilly, S.Y. 2001 *In situ* measurement of Re-Os isotopes in mantle sulfides by Laser Ablation Multi-Collector Inductively-Coupled Plasma Mass Spectrometry: analytical methods and preliminary results. *Geochim. Cosmochim. Acta* (in press).

Rehkämper, M., Halliday, A.N., Alt, J., Fitton, J.G., Zipfel, J., Takazawa, E., 1999. Non-chondritic platinum-group element ratios in oceanic mantle lithosphere: petrogenetic signature of melt percolation. *Earth Planet. Sci. Lett.*, 172, 65-81.

Snow, J.E., Schmidt, G., 1998. Constraints on Earth accretion deduced from noble metals in the oceanic mantle. *Nature*, 391, 166-169.

Völkening, J., Walczyk, T., Heumann, K.G., 1991. Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. *Int. J. Mass Spec. Ion Proc.* 151, 147-159.