

New insights into the Re–Os systematics of sub-continental lithospheric mantle from in situ analysis of sulphides

Olivier Alard^{a,b,*}, William L. Griffin^{a,c}, Norman J. Pearson^a,
Jean-Pierre Lorand^d, Suzanne Y. O'Reilly^a

^a ARC National Key Center for the Geochemical Evolution and Metallogeny Of Continents (GEMOC),
School of Earth and Planetary Sciences, Macquarie University, Sydney, NSW 2109, Australia

^b Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

^c CSIRO Exploration and Mining, P.O. Box 136, North Ryde, NSW 1069, Australia

^d Laboratoire de Minéralogie, Muséum National, d'Histoire Naturelle de Paris, 61 rue Buffon, 75005 Paris, France

Received 28 March 2002; received in revised form 18 June 2002; accepted 28 June 2002

Abstract

The Os isotopic compositions of mantle rocks generally are considered to be established during melt-depletion events and to be robust to subsequent disturbances (e.g. metasomatism). Consequently, Os isotopes are used to date the main melting event that a mantle section has undergone, i.e. transformation of fertile asthenospheric material into a depleted, buoyant lithosphere. However, Os resides almost entirely in Fe–Ni–Cu sulphides, which can be very mobile under mantle conditions. In situ laser ablation multi-collector ICP-MS measurement of Re/Os isotopic ratios in sulphides from spinel peridotite xenoliths demonstrates that whole-rock Os-isotope signatures record the mixing of multiple sulphide populations. Sulphides residual after melting events have unradiogenic Os isotopic compositions reflecting ancient melt depletion; those introduced by later metasomatism events contain more radiogenic Os. Therefore, the whole-rock Os isotopic signature can be strongly altered by metasomatic processes, and studies of mantle-derived xenoliths show that such disturbance is quite common in the lithospheric mantle. Because melt-depletion ages estimated from individual sulphide inclusions are systematically older than those obtained from whole-rock analysis, caution is essential in the interpretation of the Os model ages derived from whole-rock analysis, and their use and abuse in geodynamic models. This work suggests that sulphide could become a key phase in unravelling the formation and evolution of the lithosphere.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Re/Os; siderophile elements; sulfides; mantle; metasomatism; in situ

1. Introduction

The Re–Os isotopic system has been widely used, over the last 10 years, to study the timing and processes of the formation and evolution of the sub-continental lithospheric mantle (SCLM) [1–4]. The success of the Re–Os system in this

* Corresponding author. Tel.: +44-1908-659781;
Fax: +44-1908-655151.

E-mail addresses: o.alard@open.ac.uk (O. Alard),
wgriffin@els.mq.edu.au (W.L. Griffin),
npearson@laurel.ocs.mq.edu.au (N.J. Pearson),
lorand@mnhn.fr (J.-P. Lorand), sue.oreilly@mq.edu.au
(S.Y. O'Reilly).

field stems from the fact that Os is, in general, strongly compatible in mantle rocks, so that metasomatism due to the movement of fluids enriched in incompatible elements is unlikely to disturb or reset this isotopic system [1–4]. This is in contrast to the more commonly used lithophile isotopic systems such as Rb–Sr and Sm–Nd, whose parent and/or daughter elements may be strongly concentrated in metasomatic fluids that can thus seriously disturb the whole-rock signature [1].

However, the recent intensive use of the Re–Os system tends to overlook the fact that the behaviour of the highly siderophile elements (HSEs: Os, Re, Ir, Ru, Rh, Pt, Pd, Au) during mantle processes remains unclear [1–8]. Recently, the robustness of the Re–Os system against metasomatic processes has been challenged [5–8]. Analyses of mantle sulphides [9–14] have demonstrated the high solubility of the HSEs in base metal sulphides (BMSs) and confirm that the Os budget of mantle rocks is fully controlled by the BMSs. Refractory monosulphide solid solution (MSS) can accommodate up to 1000 ppm Os and Ir [12] while whole-rock Os or Ir contents vary from 1 to 6 ppb [2].

The behaviour of the BMS during melting and metasomatism is poorly constrained [14–17]. The BMSs have low melting temperatures [14–17] and dissolved volatile species will further lower their crystallisation temperatures [18]. Sulphide melts

have low viscosities, in the same range as volatile-rich melts [19]. Finally, S is strongly soluble in basaltic or volatile melts [16,17]. Thus, if not sequestered inside refractory silicate or oxide phases, sulphides are likely to be mobile in the lithospheric mantle. In situ analyses of mantle sulphides [12–14] have shown that this mobility is accompanied by severe fractionation of the HSEs, and that the absolute and relative abundances of these elements can be altered by metasomatic processes [12–14,20]. Recent analytical developments [21] allow the in situ determination of Os isotopes in single grains of mantle sulphides by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). This paper presents results obtained with this technique, which offer new insights on the Re–Os isotopic systematics of the lithospheric mantle.

2. Analytical techniques

S concentrations were measured using a high-temperature iodometric-titration method [15]. Selenium was analysed on 10 g powder splits by hydride generation and flameless atomic absorption spectroscopy at Geolab (Laurentian University, Canada). The detection limit is about 7 ppb. S and Se data are reported along with key petrographic features in Table 1.

Table 1
Compositional data for the selected samples

	Al ₂ O ₃ (wt%)	T (°C)	(La/Sm) _{PM}	N	S (ppm)	Se (ppb)	Sulphide (ppm)
Gam VL11	1.87	876 ± 16	4.12	15/4	53	22	201
Gam VL9	2.34	903 ± 7	0.96	17/4	49	25	230
Mgam 1	2.24	927 ± 25	0.651	21/4	69	28	257
Gam Tr6	1.87	897 ± 12	2.02	6/2	50	22	201
Gam VL8	3.55	972 ± 31	0.371	5/1	56	26	238
GRM-2	3.40	920 ± 23	0.188	9/3	23	29	266
MBR-11	3.09	1052 ± 10	0.942	7/3	4	16	146
Mtf-37	4.24	892 ± 19	0.571	23/2	60	25	300
Mbs-1	2.21	906 ± 21	18.40	11/1	89	52	490
Primitive mantle	4.2 ± 0.2		1.00		250 ± 50	70	700 ± 150

T (°C), equilibrium temperature using two pyroxene equilibrium [25]; *N*, number of sulphides having a diameter 50 µm/number of thin sections investigated. S content obtained by high temperature iodo-titration [15], Se analysed by hydride generation and flameless atomic absorption spectroscopy, detection limit ca. 7 ppb. Sulphide abundance was computed from Se content – more resistant to weathering effects [14] – using S/Se = 3300 [14,31,32] and using S content in sulphide [12,15,33,41], propagated error is ca. 20%.

Unless noted otherwise (see Tables 2 and 3), whole-rock Re–Os isotopic compositions and concentrations were analysed at the Open University. 1–2 g samples were digested in inverse aqua-regia in Carius tubes followed by solvent extraction [22,23]. Re separation was achieved after further solvent extraction and an anion column pass [23]. Samples were run on a Finnigan MAT-261 mass spectrometer in N-TIMS mode [23].

In situ Os-isotope analyses were obtained using a Nu Plasma multi-collector ICP-MS coupled to a laser ablation system in the GEMOC Geochemical Analysis Unit, Macquarie University (Sydney, Australia). The laser ablation system is a Merchantek LUV266 nm operating at 5 Hz, with a beam energy of about 3–5 mJ/pulse, and the spot size varied between 60 and 80 μm . Ablation was carried out in a He atmosphere. The Nu Plasma mass spectrometer is a double-focussing Nier–Johnson instrument with a fast scanning laminated magnet [24]. A detailed description of the analytical techniques is given in Pearson et al. [21] and only a brief outline is given here. Measurements were made in static collection mode; masses 194, 193, 192, 191, 190, 189, 188, 186 were measured in Faraday cups, while masses 187 and 185 were measured in ion counters. This detector setting allows simultaneous measurement of Os, Re and Ir and permits analysis of low-Os sulphide (down to ≈ 10 ppm for a 5% 2 SE on $^{187}\text{Os}/^{188}\text{Os}$). Ir is introduced to the Ar component of the nebuliser gas stream, as a ‘dry’ vapour produced by desolvating an Ir solution (100 ppb) in a CETAC MCN6000, and is used to measure the mass bias of the instrument for correction of Re and Os. Daily analysis of Ir–Os, Ir–Re and Re–Os solutions shows that the fractionation behaviour and relative fractionation coefficients for Os, Re and Ir are internally consistent [21]. Because of the overlap of ^{187}Re on ^{187}Os , accurate measurement is only possible for sulphides having $^{187}\text{Re}/^{188}\text{Os} \leq 1.6$. Repeated analyses ($n=26$) of PGE-A, a synthetic sulphide standard, yield $^{187}\text{Os}/^{188}\text{Os} = 0.10636 \pm 0.00017$ (2σ); solution TIMS analysis of this same standard gave $^{187}\text{Os}/^{188}\text{Os} = 0.10645 \pm 0.00002$ (Ingo Horn, personal communication).

3. Samples

3.1. Petrography and geochemistry

The samples described here are peridotite xenoliths from the alkali basalts of the Newer Basalt Province in SE Australia (Mt Gambier xenoliths) and the Massif Central and neighbouring provinces in France (MBR-11, GRM-2, Mtf-37 and MBS-1). They have all equilibrated in the spinel facies. They illustrate the range of Re/Os sulphide relationships encountered during our study of ≈ 60 samples from these areas. All are large xenoliths ($\text{Ø} > 10$ cm). Samples for crushing and thin sections were taken from the cores of the samples in order to minimise lava contamination. Thorough investigation of several thin sections (up to five per sample) indicates that the samples studied are devoid of lava contamination.

Al_2O_3 contents of Mt Gambier xenoliths range between 1.87 and 3.55 wt% (Table 1) and mineral chemistry indicates equilibration between 876 and 972°C [25]. The xenoliths are devoid of metasomatic phases (e.g. amphibole, phlogopite, apatite). However, trace element patterns indicate that they have been affected to various degrees by metasomatic melts ($0.371 < (\text{La}/\text{Sm})_{\text{N}} < 4.12$, $(\text{Th}/\text{Ta})_{\text{N}} \geq 1$; N = normalised to primitive mantle values [26]).

The Massif Central xenoliths are from the Massif Central volcanic provinces (*sensus stricto*) and from the nearby Languedoc Province (Southern France). Two of them were previously investigated for incompatible trace element and HSE contents [14]. All selected samples are lherzolites ($2.21 \leq \text{Al}_2\text{O}_3 \leq 4.24$ wt%), and have equilibration temperatures between 892 and 1048°C. GRM-2 and MBR-11 show light rare earth element (REE)-depleted patterns ($0.188 \leq (\text{La}/\text{Sm})_{\text{N}} \leq 0.571$) and enrichment in other large ion lithophile elements. Mtf-37 contains disseminated amphibole, ($< 1\%$ modal abundance) but shows a light-REE depletion ($(\text{La}/\text{Sm})_{\text{N}} = 0.571$). However, there is pronounced enrichment of U and Sr relative to Th or La, respectively [27]. MBS-1 displays poikilitic clinopyroxenes, inferred to be metasomatic due to their petrographic character-

Table 2
Sulphide and whole-rock Re–Os isotopic compositions for Mt Gambier xenoliths

Sample	Sulphide ^a	¹⁸⁷ Re/ ¹⁸⁸ Os ± 2 SE	¹⁸⁷ Os/ ¹⁸⁸ Os ± 2 SE	$T_{RD} \pm 2\sigma$ (Ga)	$T_{MA} \pm 2\sigma$ (Ga)	
Gam VL11	T1 e(ol)-a	0.168 ± 0.022	0.1126	0.0025	2.13 ± 0.37	3.63 ± 0.71
	T2 int-a	0.478 ± 0.004	0.1282	0.0008	−0.16 ± 0.12	0.85 ± 0.62
	T2 int-b	0.516 ± 0.032	0.1270	0.0033	0.01 ± 0.49	−0.1 ± 1.7
	T2 int-b	0.710 ± 0.017	0.1257	0.0053	0.21 ± 0.79	−0.3 ± 1.0
Whole rock A, Os:3.86, Re:0.31		0.345 ± 0.007	0.1187	0.0001	1.30 ± 0.01	8.8 ± 1.1
Whole rock B, Os:4.82, Re:0.56		0.523 ± 0.010	0.1228	0.0002	0.70 ± 0.03	−2.35 ± 0.22
Gam VL9	T1 e(ol)-a	0.016 ± 0.001	0.1160	0.0007	1.64 ± 0.10	1.71 ± 0.11
	T2 int-a	0.035 ± 0.007	0.1283	0.0028	−0.18 ± 0.42	−0.20 ± 0.46
Whole rock, Os:3.36, Re:0.02		0.024 ± 0.001	0.1225	0.0001	0.74 ± 0.01	0.79 ± 0.01
MGam 1	T1 e(ol)-c	0.274 ± 0.019	0.1083	0.0040	2.75 ± 0.59	8.3 ± 2.1
	T2 e(cpx)-b	0.437 ± 0.022	0.1218	0.0032	0.79 ± 0.48	−9.5 ± 8.1
Whole rock A, Os:4.05, Re:0.33		0.391 ± 0.009	0.1202	0.0002	1.08 ± 0.03	34 ± 31
Whole rock B, Os:3.86, Re:0.30		0.425 ± 0.009	0.1214	0.0002	0.91 ± 0.03	−17.4 ± 6.5
Gam Tr6	T1 e(ol)-d	0.188 ± 0.006	0.1153	0.0013	1.74 ± 0.19	3.24 ± 0.37
	T2 e(cpx)-d	0.311 ± 0.058	0.1190	0.0028	1.20 ± 0.42	5.2 ± 3.8
Whole rock, Os:3.84, Re:0.23		0.281 ± 0.014	0.1185	0.0001	1.33 ± 0.03	4.35 ± 0.52
Gam VL8	T1 e(ol)-b	0.048 ± 0.003	0.1124	0.0022	2.16 ± 0.32	2.45 ± 0.37
	T2 int*-a	2.68 ± 0.138	0.1716	0.0052	−7.06 ± 0.83	1.16 ± 0.15
Whole rock, Os:2.50, Re:0.08		0.155 ± 0.013	0.1273	0.0002	0.03 ± 0.01	0.05 ± 0.02

All values are shown $\pm 2\sigma$. Note that the method used, laser ablation MC-ICP-MS, only allows determination of mass ratio, and not Re and Os concentrations, as internal normalisation is not possible. Whole-rock Re and Os concentrations in ppb. SE, standard error of means; A, B denote different powder aliquots from the same sample. T_{MA} is the Re–Os model age, defined as $T_{MA} = (1/\lambda) \ln[1 + ((^{187}\text{Os}/^{188}\text{Os})_{\text{sample}} - (^{187}\text{Os}/^{188}\text{Os})_{\text{REF}}) / ((^{187}\text{Re}/^{188}\text{Os})_{\text{sample}} - (^{187}\text{Re}/^{188}\text{Os})_{\text{REF}})]$ and relies on the assumption that there has been no disturbance of the Re/Os ratio. It is obviously not the case here, given that T_{MA} model ages for some sulphides or samples are unrealistic, giving future ages or ages older than 4.5 Ga. T_{MA} is model-dependent, here we have chosen a CHUR (chondritic uniform reservoir) reference model, which assumes that the primitive mantle has a chondrite-like composition ($^{187}\text{Re}/^{188}\text{Os}_{\text{REF}} = 0.40186$, $^{187}\text{Os}/^{188}\text{Os}_{\text{REF}} = 0.1275$, [42]). T_{RD} , the Re depletion age, assumes that all Re has been removed from the residue ($^{187}\text{Re}/^{188}\text{Os}_{\text{sample}} = 0$) and thus yields a minimum depletion age ($= T_{MA}$), but is more ‘robust’ to addition or removal of Re by recent secondary processes. Uncertainties for T_{RD} and T_{MA} (σ) were calculated following Albarède’s [43] formulation; λ is the ^{187}Re decay constant ($1.666 \times 10^{-11} \text{ a}^{-1}$ [44]).

^a T1, T2: Type 1 and Type 2 sulphide, respectively, see text; e and int denote enclosed and interstitial sulphides, respectively; ol, olivine; cpx, clinopyroxene; a–e denote thick section numbers.

istics and trace element compositions. Both Cpx and whole rock show high Ca/Al ratios, and trace element patterns ($(\text{La}/\text{Sm})_N = 18.4$, [14]) commonly ascribed to metasomatism by a volatile-rich melt [28].

Thus all samples, from both the Mt Gambier and the Massif Central suites, show evidence for varying degrees of melting and moderate metasomatism by small-volume melts, variably enriched in incompatible and volatile elements, as do the vast majority of SCLM samples worldwide [29].

3.2. Sulphide abundance and S and Se content

All samples except Mtf-37 and MBS-1 have low sulphide abundances, with only one to four grains ($\varnothing \geq 50 \mu\text{m}$) per section. This observation is confirmed by the low contents of S (23–89 ppm) in both the Mt Gambier and the Massif Central suites. However, because S is particularly sensitive to weathering effects [15,30] and Se is less affected by this process, Se contents are probably a better indicator of original sulphide abundance [31]. The Se contents of the Mt Gambier suite define a nar-

Table 3
Sulphide and whole-rock Re–Os isotopic compositions for the Massif Central xenoliths

Sample	Sulphide ^a	¹⁸⁷ Re/ ¹⁸⁸ Os ± 2 SE	¹⁸⁷ Os/ ¹⁸⁸ Os ± 2 SE	$T_{RD} \pm 2\sigma$ (Ga)	$T_{MA} \pm 2\sigma$ (Ga)	
Sulphides in GRM-2 peridotite xenolith (Grand Magnon, Languedoc, Southern France)						
	T1 e(opx)-a	0.167 ± 0.009	0.1248	0.0036	0.34 ± 0.54	0.59 ± 0.92
	T1 e(ol)-b	0.029 ± 0.004	0.1236	0.0012	0.52 ± 0.18	0.56 ± 0.19
	T2 int-a	0.500 ± 0.034	0.1389	0.0055	−1.79 ± 0.84	6.7 ± 3.9
Whole rock [‡] , Os:1.74, Re:0.13		0.383 ± 0.007	0.1349	0.0015	−1.12 ± 0.23	−32 ± 14
Sulphides in MBR-11 peridotite xenolith (Mont Briançon, Vivarais, France)						
	T1 e(ol) b-s3a	0.089 ± 0.002	0.1169	0.0011	1.57 ± 0.08	2.01 ± 0.22
	T1 e(ol) b-s3b	0.240 ± 0.019	0.1210	0.0022	0.97 ± 0.17	2.39 ± 0.91
	T1 e(ol) b-s1	0.055 ± 0.052	0.1145	0.0046	1.92 ± 0.68	2.22 ± 0.85
	T2 e(cpx) b-s4	0.223 ± 0.034	0.1272	0.0027	0.05 ± 0.40	0.12 ± 3.24
	T2 int a-s1	0.791 ± 0.140	0.1354	0.0014	−1.20 ± 0.20	1.20 ± 0.96
Whole rock [‡] , Os:1.63, Re:0.17		0.491 ± 0.009	0.1336	0.0004	−0.92 ± 0.06	3.93 ± 0.47
Sulphides in Mtf-37 peridotite xenolith (Montferrier, Languedoc, Southern France)						
	int(a-s1)	0.072 ± 0.012	0.1316	0.0042	−0.68 ± 0.63	−0.83 ± 0.77
	int(a-s2)	0.060 ± 0.010	0.1337	0.0034	−1.00 ± 0.51	−1.17 ± 0.61
	int(a-s3)	0.211 ± 0.008	0.1209	0.0026	0.92 ± 0.39	1.93 ± 0.81
	int(a-s4)	0.072 ± 0.012	0.1316	0.0042	−0.68 ± 0.63	−0.83 ± 0.77
	int(c-s3)	0.137 ± 0.008	0.1361	0.0014	−1.36 ± 0.21	−2.08 ± 0.33
	int(e-s9)	0.310 ± 0.030	0.1151	0.0032	1.77 ± 0.47	7.4 ± 3.2
	int(e-s6)	0.240 ± 0.012	0.1267	0.0010	0.06 ± 0.15	0.15 ± 0.37
	int(e-s1)	0.256 ± 0.002	0.1194	0.0024	1.14 ± 0.36	3.11 ± 0.97
	int(e-s4)	0.186 ± 0.002	0.1175	0.0017	1.42 ± 0.25	2.62 ± 0.47
Whole rock [‡] , Os:5.24, Re:0.16		0.144 ± 0.003	0.1277	0.0002	−0.03 ± 0.03	−0.05 ± 0.05
Sulphides in Mbs-1 peridotite xenolith (Montboissier, Northern Massif Central, France)						
	T2 e(cpx)-a	0.258 ± 0.020	0.1218	0.0054	0.79 ± 0.8	2.19 ± 2.25
	T2 e(cpx)-a	0.225 ± 0.024	0.1229	0.0050	0.63 ± 0.74	1.42 ± 1.7
	T2 e(cpx)-a	0.00043 ± 0.0003	0.1365	0.0024	−1.42 ± 0.36	−1.43 ± 0.36
	T2 e(cpx)-b	0.364 ± 0.016	0.1157	0.0040	1.68 ± 0.59	16 ± 9

Caption as for Table 2; [†] and [‡], data from Meissel et al. [34] and Lambert et al., [39], respectively.

row range between 22 and 28 ppb. The Massif Central suite has Se abundances between 16 and 52 ppb. Using the S/Se ratio measured in mantle sulphide [14,31,32] we can estimate the primary abundance of sulphide in these samples as between 200 and 260 ppm for the Mt Gambier suite and between 150 and 500 ppm for the Massif Central suite. The estimated sulphide contents are independent of any fertility indices (e.g. Al₂O₃). Such sulphide abundances are well below those estimated for the primitive mantle (700 ± 150 ppm, Table 1), but are characteristic of alkali basalt-hosted peridotites [14–16,31].

3.3. Sulphide occurrence, mineralogy and geochemistry

Despite this low sulphide abundance, the Mt Gambier xenoliths contain two types of sulphide. Type 1 occurs as rounded inclusions in silicate (typically olivine) and consists of the exsolution products of MSS (Ni-rich MSS+Ni-poor MSS+pentlandite) which occupy the centre of the inclusions, whereas Cu sulphides are confined to the rims of the sulphide grains (Fig. 1a). Type 2 sulphides are interstitial (Fig. 1b), or associated with clinopyroxene or with interstitial

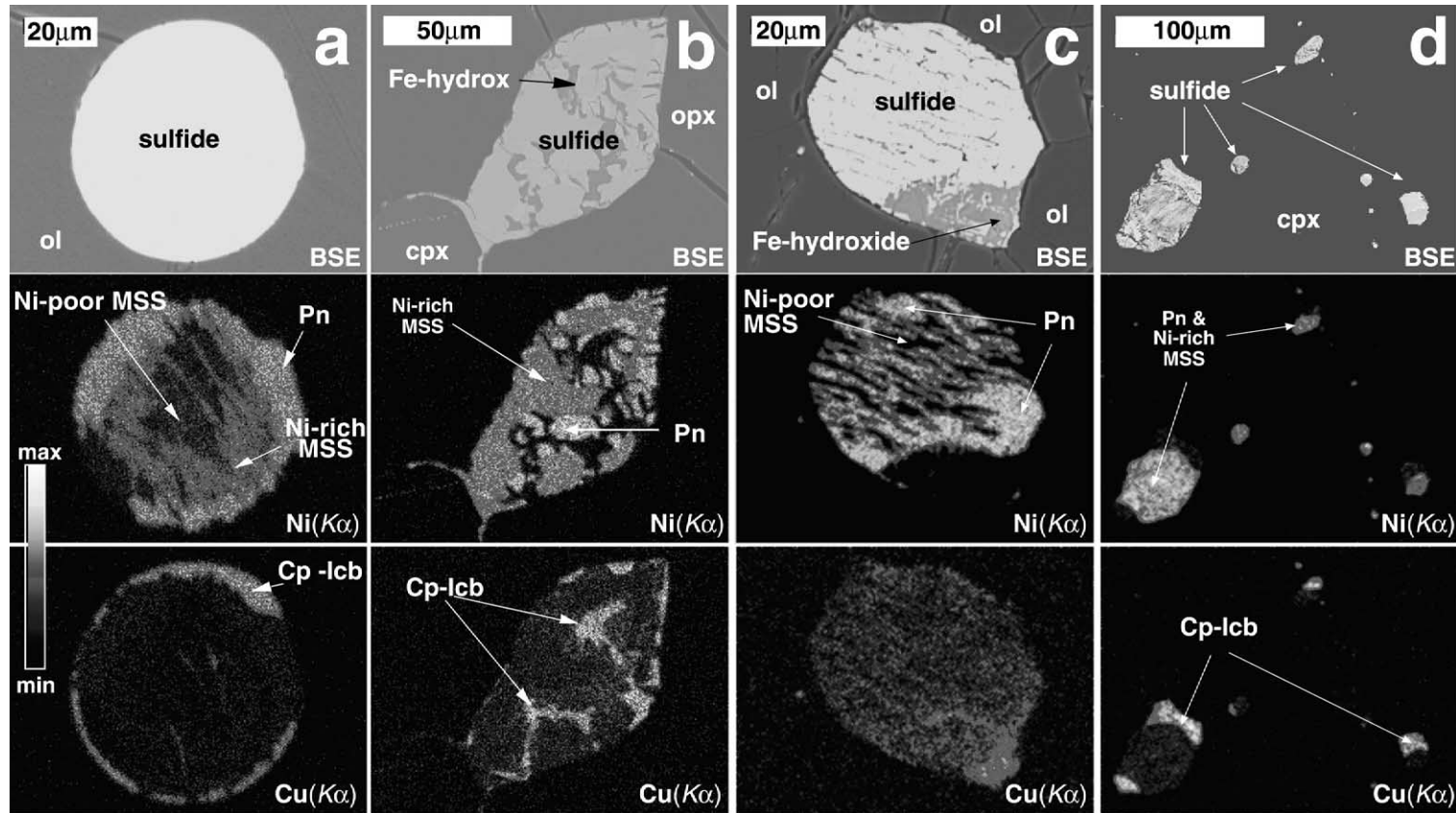


Fig. 1. Backscattered electron and chemical maps of typical mantle sulphides. (a) Enclosed; (b) interstitial sulphides, both from Mt Gambier peridotites; (c) Mtf-37 intergranular sulphide; (d) MBS-1 cpx-enclosed sulphide. BSE, backscattered electron; MSS, monosulphide solid solution; Pn, pentlandite; Cp-Icb, chalcopyrite-isocubanite. Note the difference in Cp-Icb distribution and occurrence: thin film on the edge of the enclosed sulphide (a) and networked patches in the interstitial sulphide (b). Chemical maps produced using a LINK energy dispersive X-ray detector coupled to a CAMECA SX-50 microprobe. Colour scales indicate the relative abundance of a given element.

melt pockets, and are more abundant than Type 1. They show anomalously high modal abundances of Cu-rich sulphides, which occur as networked patches and veinlets (Fig. 1b). Type 1 sulphides display strong enrichment in refractory HSE (Os, Ir, Ru, Rh) over Pt and Pd (low Pd/Ir sulphide), while Type 2 sulphides show the inverse HSE pattern and are characterised by high Pd/Ir ratio [12]. Sulphides in Mt Gambier lava are characterised by a Ni-poor chemistry and consist mainly of Ni-poor MSS (almost pure monoclinic pyrrhotite), with minor amounts of pyrite and isocubanite-like sulphide. The Type 2 sulphides therefore are distinct from those in the host lava.

Although sulphides in MBR-11 and GRM-2 are heavily altered, we recognise the same two types described for the Mt Gambier suite. In situ PGE analyses of Type 1 and Type 2 MBR-11 sulphides reveal the same systematics described for the Mt Gambier suite [14].

Due to the sheared microstructure all sulphides are intergranular in Mtf-37; however, they are in textural equilibrium with the ‘polygonal’ neoblastic matrix. They consist of abundant pentlandite intergrown with low-Ni pyrrhotite, chalcopyrite \pm valeriite (Fig. 1c).

All sulphides in MBS-1 are enclosed in poikilitic clinopyroxene (Fig. 1d). Sulphide mineralogy is dominated by pentlandite and Ni-rich MSS. Chalcopyrite and isocubanite are relatively abundant (≈ 10 – 15% , Fig. 1d). For both MBS-1 and Mtf-37, this mineralogy yields an original Ni-rich and S-poor bulk composition intermediate between typical mantle MSS and pure pentlandite [15,33]. In situ LAM-ICP-MS analyses of MBS-1 sulphides show variable and extremely fractionated HSE patterns ($0.14 < \text{Pd/Ir} < 1430$). This fractionation is correlated with modal abundances of Cu sulphides [14].

4. Results

4.1. Whole-rock Re–Os characteristics

Whole-rock analyses of the Mt Gambier xenoliths yield $^{187}\text{Os}/^{188}\text{Os}$ between 0.1185 and 0.1273

and $^{187}\text{Re}/^{188}\text{Os}$ ranging from 0.024 to 0.523 (Table 2). While we obtain slightly more radiogenic values, the range of Os-isotope composition is in agreement with previous studies of these rocks [4]. It should also be noted that analyses of different powder aliquots from the same samples yield different Re–Os isotopic compositions; compare whole rocks A and B for Gam VL11 and Mgam1 (Table 2). Re-depletion ages (T_{RD} , Table 2) range from 0.04 to 1.35 Ga, while most of the model ages are unrealistic (T_{MA} , Table 2). These features indicate that the Re–Os system has been perturbed.

Both GRM-2 and MBR-11 have $^{187}\text{Os}/^{188}\text{Os}$ higher than estimated for the primitive upper mantle (PUM) ($^{187}\text{Os}/^{188}\text{Os}_{\text{PUM}} = 0.1290 \pm 0.0006$ [34]). In GRM-2 this radiogenic value is not supported by the Re/Os ratio (Table 3), which is slightly lower than estimated for the PUM ($^{187}\text{Re}/^{188}\text{Os}_{\text{PUM}} \approx 0.4$ [34]). Conversely, the almost PUM-like $^{187}\text{Re}/^{188}\text{Os}$ ratio of MBR-11 yields an extremely old T_{MA} model age ($\approx 3.9 \pm 0.3\text{Ga}$, Table 3), unlikely for this Proterozoic to Phanerozoic area. Thus, in both cases the Os-isotope composition of the whole rock does not seem to be directly related to the measured Re/Os ratio. Mtf-37 has $^{187}\text{Os}/^{188}\text{Os}$ close to the PUM value and overlapping the chondrite range [34]. This feature, along with the extreme fertility of this sample and a Pd/Ir (1.3 ± 0.1) within error of the chondrite values, could suggest that the sample has a very primitive composition [34]. However, the Re/Os ratio is significantly lower than that estimated for the PUM.

4.2. Sulphide Re–Os isotopic compositions

Mt Gambier Type 1 inclusions (olivine-enclosed sulphides with MSS bulk chemistry) have $^{187}\text{Os}/^{188}\text{Os}$ between 0.1083 and 0.1160 and $^{187}\text{Re}/^{188}\text{Os}$ from 0.016 to 0.274 (Table 2, Fig. 2a,b). In contrast, Type 2 sulphides (interstitial, Ni- and Cu-rich sulphides) have more radiogenic Os ($^{187}\text{Os}/^{188}\text{Os} = 0.1190$ – 0.1282) and higher Re/Os ratio. One Type 2 sulphide in sample Gam VL8 yields an even more radiogenic composition ($^{187}\text{Os}/^{188}\text{Os} \approx 0.172$). Its $^{187}\text{Re}/^{188}\text{Os}$ ratio ($\approx 2.68 \pm 0.14$) is over the limit of the analytical

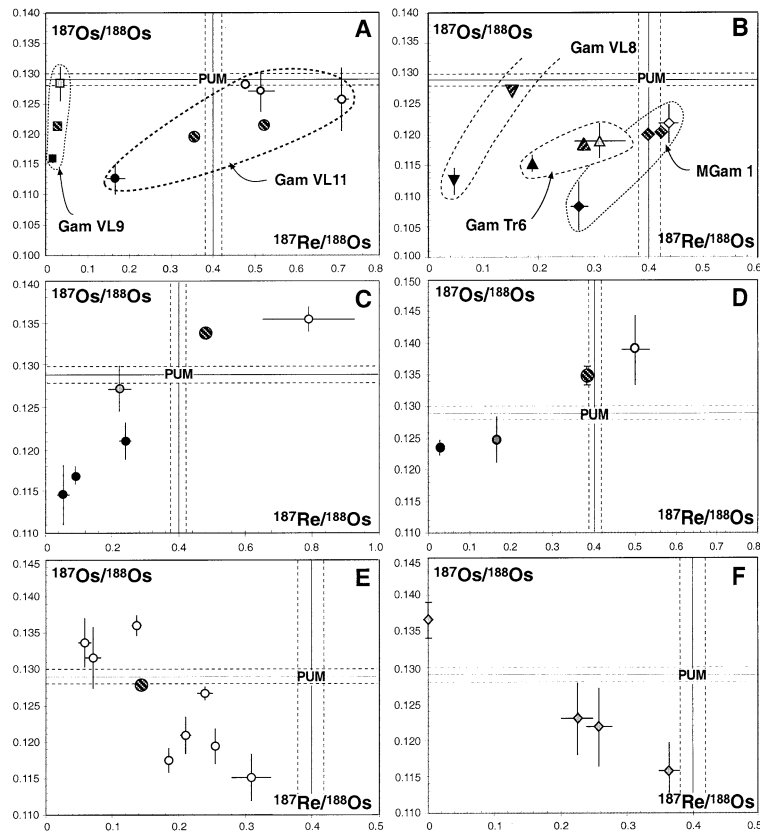


Fig. 2. $^{187}\text{Os}/^{188}\text{Os}$ versus $^{187}\text{Re}/^{188}\text{Os}$ in sulphides and whole rock. Olivine-enclosed sulphides, black symbols; pyroxene-hosted sulphides, grey symbols; interstitial sulphides, empty symbols; whole rocks, hashed enlarged symbols. (A) Mt Gambier sulphides: Gam VL11, circle; Gam VL9, square. (B) Mt Gambier. MGam 1, diamond; Gam Tr6, triangle; Gam VL8, inverted triangle. (C) GRM-2 lherzolite. (D) MBR-11 lherzolite; open circles, interstitial and enclosed sulphides; hashed box, whole rock. (E) Mtf-37, all sulphides are interstitial. (F) MBS-1, all sulphides are enclosed in poikilitic cpx. PUM, primitive upper mantle values [34].

technique (i.e. $^{187}\text{Re}/^{188}\text{Os} \geq 1.6$; [21]), but it indicates the presence of highly radiogenic sulphides in these samples.

Sulphides enclosed in silicate phases in GRM-2 have low $^{187}\text{Os}/^{188}\text{Os}$ ($< \text{PUM}$, Table 3, Fig. 2c). T_{MA} ages are ca. 0.6 Ga for these sulphide inclusions. In contrast, interstitial sulphides show high Re/Os and high $^{187}\text{Os}/^{188}\text{Os}$ ($> \text{PUM}$, Fig. 2c). Similar systematics are found in sample MBR-11. Olivine-enclosed sulphides have $^{187}\text{Os}/^{188}\text{Os}$ from 0.1145 to 0.1210 and $^{187}\text{Re}/^{188}\text{Os}$ between 0.055 and 0.240 (Fig. 2d). T_{RD} ages range between 1 and 2 Ga and T_{MA} ages cluster about 2.2 Ga. The clinopyroxene-hosted sulphide has more radiogenic Os ($^{187}\text{Os}/^{188}\text{Os} = 0.1272 \pm 0.0027$) and

higher $^{187}\text{Re}/^{188}\text{Os}$ (0.223). The interstitial sulphide contains still more radiogenic Os ($^{187}\text{Os}/^{188}\text{Os} = 0.1354 \pm 0.0014$ and has a higher $^{187}\text{Re}/^{188}\text{Os}$ (≈ 0.791).

The $^{187}\text{Re}/^{188}\text{Os}$ of Mtf-37 sulphides ranges from 0.06 to 0.31; $^{187}\text{Os}/^{188}\text{Os}$ varies from 0.1151 ± 0.0032 to 0.1361 ± 0.0014 . Cpx-enclosed sulphides in MBS-1 have $^{187}\text{Re}/^{188}\text{Os}$ between 0.0004 and 0.36 and $^{187}\text{Os}/^{188}\text{Os}$ from 0.1157 ± 0.0040 up to 0.1365 ± 0.0024 (Fig. 2d, Table 3). The noteworthy feature of these two samples (Mtf-37 and MBS-1) is the inverse correlation between $^{187}\text{Os}/^{188}\text{Os}$ and the Re/Os ratio (Fig. 2e,f).

5. Discussion

5.1. Origin of Type 1 sulphides

The unradiogenic Os composition of the enclosed sulphides indicates that they have evolved for a long time in a low Re–Os environment. Their bulk composition (MSS), occurrence (enclosed in refractory silicate, e.g. olivine), low Pd/Ir [12–14] and overall low Re–Os characteristics strongly suggest that these sulphides are residual from ancient melting events.

5.2. Origin of Type 2 sulphides

Type 2 sulphides show a wider range of Re–Os isotopic composition, but display common characteristics. They are interstitial or associated with clinopyroxene and have S-poor (relative to MSS), and Ni and/or Cu-rich bulk compositions. They have higher Re/Os and Pd/Ir, and more radiogenic Os isotopic compositions, than the Type 1 sulphides from the same samples. These features, taken together, indicate a metasomatic origin for Type 2 sulphides.

One could argue that Type 2 sulphides are related to contamination by the host. However, this is very unlikely for several reasons: (1) No petrographic or geochemical features (e.g. REE patterns) indicate lava contamination; (2) infiltrated sulphides from the lava in xenoliths usually occur as veinlets and are strictly interstitial, whereas some of the Type 2 sulphides are enclosed in Cr-diopside of typical mantle composition (Gam Tr6, Gam VL9, MBS-1); (3) analyses of sulphide from Mt Gambier lavas reveal an extremely Ni-poor and S-rich bulk composition, in contrast to the Ni-rich and S-poor composition characteristic of Type 2 sulphides; (4) basaltic sulphides show highly fractionated HSE patterns and Re/Os [35] and Pd/Ir [14,36] at least an order of magnitude higher than those observed here; (5) Os in alkali basalts is usually quite radiogenic ($^{187}\text{Os}/^{188}\text{Os} > 0.135$ [2]), whereas most of the Type 2 sulphides at Mt Gambier have $^{187}\text{Os}/^{188}\text{Os} \leq 0.130$.

Mt Gambier sulphides show a positive correlation between $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$, and

each sulphide pair defines an ‘isochron’. However, unrealistic ages or initial Os compositions are obtained for Gam VL9 and Mgam 1. Furthermore, Type 2 sulphides in Gam VL11 (Fig. 2a) show similar $^{187}\text{Os}/^{188}\text{Os}$ over a large range of $^{187}\text{Re}/^{188}\text{Os}$ (0.478–0.710), demonstrating that their Os isotopic compositions are not related to time-integrated in situ ^{187}Re decay. The high Re/Os ratios, but relatively unradiogenic Os compositions, of the Type 2 sulphides indicate that the sulphide-bearing metasomatic fluids/melts have scavenged Os from a reservoir with low Re/Os, which is most likely the surrounding SCLM. This observation also indicates that the Re/Os ratios of the Type 2 sulphides are not representative of their source reservoir(s) and thus that Re has been enriched relative to Os during the metasomatic process(es) which led to the crystallisation of the Type 2 sulphides. These features also suggest that the metasomatic event is recent, since little or no ^{187}Os ingrowth by Re decay has occurred.

Interstitial sulphides in GRM-2 yield future T_{RD} ages and unrealistic T_{MA} ages, again indicating that the Os isotopic composition is not related to time-integrated in situ Re decay. This suggests that Re has been fractionated relative to Os during the metasomatic process that led to the recent crystallisation of this interstitial sulphide. In contrast, the radiogenic composition of the MBR-11 interstitial sulphide is consistent with its Re/Os ratio, as shown by its ‘realistic’ T_{MA} model age. Although it is not possible to dismiss Re–Os fractionation, as demonstrated in GRM-2 and for the Mt Gambier xenolith suite, in this case the Os isotopic signature could have been produced by in situ decay of ^{187}Re .

The inverse correlation between $^{187}\text{Os}/^{188}\text{Os}$ and Re/Os in samples Mtf-37 and MBS-1 (Fig. 2e,f) demonstrates that the high $^{187}\text{Os}/^{188}\text{Os}$ of the sulphides cannot be ascribed to in situ Re decay. However, the development of radiogenic Os ($^{187}\text{Os}/^{188}\text{Os} > \text{PUM}$) requires a reservoir with high Re/Os ($> \text{PUM}$). The relationships shown here suggest that radiogenic Os, but not Re, has been preferentially scavenged from a high-Re/Os reservoir via a metasomatic fluid. Alternatively, Os may have been fractionated relative to Re

by the transporting fluid during its percolation through the lithosphere. This is reminiscent of the Re–Os characteristics of subduction-related peridotites, where transport of Os has been related to the percolation into a mantle wedge of a highly oxidising subduction-related fluid [5].

The occurrence of amphibole in Mtf-37 and a pronounced enrichment in U ($U/Th \geq 30$) indicate the percolation of an oxidising fluid [37]. The geochemical and petrological features of Mtf-37 suggest that pre-existing sulphides have re-equilibrated with an Os-rich fluid. LA-ICP-MS analyses of Mtf-37 sulphides show constant Os, Ir, Ru contents and variable subchondritic Pd/Ir ratios (O. Alard, unpublished data), similar to those of Type 1 sulphide [12,14]. Thus these sulphides are probably not of metasomatic origin. Their microstructural position (interstitial in an ol-rich matrix) and the rapid diffusion of Os in sulphide probably allowed these sulphides to partially re-equilibrate with the percolating fluid.

The highly enriched and fractionated incompatible trace element pattern of the poikilitic cpx in MBS-1 [14] also suggests the percolation of a highly evolved, volatile-rich metasomatic melt. However, in contrast to Mtf-37, the occurrence of the sulphides (in the poikilitic cpx) and their highly fractionated PGE patterns [14] suggest that part of these sulphides have crystallised from the percolating melt. This is also suggested by the high sulphide abundance of MBS-1, which is in contrast to its relatively depleted composition ($Al_2O_3 = 2.21$ wt%), especially when compared with the sulphide and Al_2O_3 contents of Mtf-37 (≈ 300 ppm, 4.2 wt%, respectively).

There is no straightforward relationship between the occurrence, abundance and geochemistry of metasomatic (Type 2) sulphides and the usual indices of metasomatism such as LREE enrichments or HFSE/LILE fractionation (e.g. Mt Gambier xenoliths, Tables 1 and 2). There are several reasons for this. First, each of these mantle sections has a complex history of multiple melting and metasomatism episodes (see below). Each of these events may well have added or removed sulphides and/or modified the HSE characteristics of pre-existing sulphides. It is also extremely difficult to decipher the cumulative effects

of those events on the abundance and fractionation of the lithophile elements. Secondly, a metasomatic fluid will have drastically different effects upon the sulphide systematics of a mantle section depending on the equilibrium temperature (above or below sulphide solidus/liquidus), fluid composition (e.g. S saturation, fO_2 , PCO_2), and shielding of sulphide by silicate. The lithophile trace elements are either insensitive or behave differently to those parameters. Thus, clear relationships between lithophile element fractionation and sulphide-controlled elements such as Re and Os are not expected, except in very specific and unusual conditions such as in Mtf-37 and MBS-1. These two samples, however, provide compelling evidence that Os transport via sulphide-barren (Mtf-37) or sulphide-bearing (MBS-1) volatile-rich metasomatic fluids is possible and is not restricted to subduction settings.

5.3. Sulphide–whole-rock relationships and implication for Os model ages

Whole-rock analyses show Re/Os ratios and Os isotopic compositions intermediate between Type 1 and Type 2 sulphides. This indicates that the whole-rock Re–Os signature reflects only the mixing proportions between the residual and metasomatic sulphides. This observation is consistent with the poor reproducibility between aliquots of the same sample, which is ascribed to the so-called ‘nugget effect’. Our results strongly suggest that the ‘nugget effect’ is in fact an expression of the heterogeneous distribution of the various sulphide populations defined above. Therefore, Re–Os model ages for whole-rock samples would rarely correspond to any real melt-depletion event, but would instead be determined by the relative abundance of the different sulphide generations. The age of the melt-depletion event as estimated by T_{RD} and T_{MA} for Mt Gambier enclosed sulphides varies from 1.7 ± 0.2 to 2.8 ± 0.6 and from 1.7 ± 0.1 to 3.6 ± 0.7 Ga, respectively (Table 2). Whole-rock Re–Os data, both from this study (Table 2) and from previous studies of xenoliths from the same locality [4], yield much younger model ages (≤ 2 Ga).

Several olivine-enclosed sulphides in Mt Gam-

bier xenoliths (e.g. Mgam 1, Table 2) display aberrant T_{MA} , while showing realistic Re depletion age (T_{RD} , i.e. > 3.0 Ga), thus indicating late Re addition to the sulphides themselves. The possibility of Re addition, as discussed above, casts some doubt on the meaning of some Early Archean T_{MA} ages which are associated with relatively high Re/Os in enclosed sulphides ($^{187}\text{Re}/^{188}\text{Os} > 0.16$, i.e. Gam VL11, Gam Tr6). These ages can be considered only as maximum depletion estimates of the depletion age. In contrast, T_{RD} ages do not take into account the amount of Re and therefore have to be considered as minimum age estimates. Despite these considerations, Os model ages for the Mt Gambier samples spread from 1.64 up to 2.75 Ga. For instance, the T_{RD} age for the Mgam 1 enclosed sulphide indicates a minimum age of depletion of about 2.16 Ga, while the maximum age depletion (T_{MA}) for Gam VL9 is 1.82 Ga. Thus, those sulphides have recorded different discrete events, either of melting, or of the crystallisation of monosulphide from sulphide liquids. The small size of the data set and the relatively large uncertainty associated with these age estimates precludes a more detailed discussion of the meaning of these data in terms of crustal formation or geodynamic events. Rocks of Proterozoic ages are not known in the Mt Gambier area; the nearest outcrop is 400 km to the west (see [4]).

The Os isotopic composition of the MBR-11 and GRM-2 whole rocks does not seem directly related to the measured Re/Os ratio. However, in both cases, the whole-rock composition is well explained by the mixing in various proportions of the Type 1 and Type 2 sulphides (Fig. 2c). Although model ages for Type 1 sulphides have relatively large uncertainties, they allow the construction of a rough melt-depletion history, otherwise not available with whole-rock data (Table 3). MBR-11 enclosed sulphides show T_{MA} ages clustering about 2.2 Ga for a range of $^{187}\text{Re}/^{188}\text{Os}$ from 0.055 to 0.240. GRM-2 olivine-enclosed sulphide shows consistent T_{RD} and T_{MA} ages of ca. 0.6 Ga. Proterozoic and Pan African crustal ages are well documented throughout the Variscan Belt and the Mediterranean Basin (e.g. [38]).

6. Conclusions

The Os sulphide paradox can be summarised as follows: Os is highly compatible in the mantle and this should limit the disturbance of its isotopic composition by metasomatism. However, the physical properties and reactivity of its carrier phases (the BMSs) allow Os to become highly mobile. Furthermore, during the percolation of highly oxidising fluids, Os can become mobile in metasomatic fluids.

Although the technique used here does not allow the precise measurement of Os content for each sulphide, it is obvious from the sulphide–whole-rock systematics (Fig. 2a–f) that whole-rock Re–Os analyses reflect various degrees of mixing between several sulphide generations, as do HSE abundances in sub-continental and oceanic peridotites [7–9, 17]. Therefore, these data provide compelling evidence that the Os isotopic composition of mantle rocks is altered by metasomatic processes. Furthermore, they show that small-scale isotopic heterogeneities can be preserved for billions of years. The preservation for 1–2 Ga of a depleted signature in the silicate-enclosed sulphide inclusions suggests that they have been effectively armoured by the silicate and that Os has an extremely low rate of diffusion in olivine [11].

These results clearly call for caution in the interpretation of the Os model ages derived from whole-rock analysis and their use and abuse in geodynamic models. Melt-depletion ages estimated from individual sulphide inclusions are systematically older than those obtained from whole-rock analysis. Thus, whole-rock model ages can only be considered as minimum depletion ages. We therefore suggest that the age of the off-craton SCLM derived from peridotite xenoliths may have been underestimated and that ancient lithospheric material may survive beneath off-craton areas despite multiple orogenic events [4,39,40].

Our study of 60 samples from the Massif Central and Eastern Australia volcanic provinces [41] has shown that the occurrence of the two types of sulphide is an extremely common feature of off-craton mantle xenoliths. Ongoing studies demonstrate that this is also true of cratonic xenoliths

from Canada, Siberia and South Africa (W.L. Griffin et al., unpublished data). Samples such as GRM-2 and MBR-11 demonstrate that these two types of sulphides occur in samples with low sulphide abundances and in samples with whole-rock Re–Os characteristics representative of depleted mantle lithosphere (e.g. Mt Gambier xenoliths). At the other end of the scale, Mtf-37 has a whole-rock composition akin to the primitive mantle. Therefore, this study illustrates the potential of the in situ technique for deciphering the behaviour of the HSEs during geological processes. Although sulphides are a minor phase, they are ubiquitous in the mantle and are a key phase in our understanding of the formation and evolution of the lithosphere. Although the in situ Re–Os technique is subject to larger analytical uncertainties than conventional analysis [21], its spatial resolution and the preservation of the petrographic context allow the data to be interpreted with a higher degree of confidence.

Acknowledgements

Thanks to K.W. Burton, B.F. Schaefer, N. Vigier and M. Gounelle for discussion and comments. This paper has benefited from constructive reviews by C. Class, M. Rehkämper and J. Snow. This is Publication 290 from the ARC National Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC). [BARDJ].

References

- [1] D.G. Pearson, The age of continental roots, *Lithos* 48 (1999) 171–194.
- [2] S.B. Shirey, R.J. Walker, The Re–Os isotope system in cosmochemistry and high-temperature geochemistry, *Annu. Rev. Earth Planet. Sci.* 26 (1998) 423–500.
- [3] L. Reisberg, J.P. Lorand, Longevity of sub-continental mantle lithosphere from osmium isotope systematics in orogenic peridotites massifs, *Nature* 376 (1995) 159–162.
- [4] M.R. Handler, V.C. Bennett, T.M. Esat, The persistence of off-cratonic lithospheric mantle: Os isotopic systematics of variability metasomatised southeast, Australian xenoliths, *Earth Planet. Sci. Lett.* 151 (1997) 61–75.
- [5] A.D. Brandon, R.A. Creaser, S.B. Shirey, R.W. Carlson, Osmium recycling in subduction zones, *Science* 272 (1996) 861–864.
- [6] A.H. Peslier, L. Reisberg, J. Ludden, D. Francis, Re–Os constraints on harzburgite and lherzolite formation in the lithospheric mantle: A study of Northern Canadian Cordillera xenoliths, *Geochim. Cosmochim. Acta* 64 (2000) 3061–3071.
- [7] A.E. Saal, E. Takazawa, F.A. Frey, N. Shimizu, S.R. Hart, Re–Os isotopes in the Horoman peridotites: evidence of Refertilization?, *J. Petrol.* 42 (2001) 25–37.
- [8] J.T. Chesley, R.L. Rudnick, C.T. Lee, Re–Os systematics of mantle xenoliths from the East African Rift: Age, structure, and history of the Tanzanian craton, *Geochim. Cosmochim. Acta* 63 (1999) 1203–1217.
- [9] S.R. Hart, G.E. Ravizza, Os partitioning between phases in lherzolite and basalt, in: A. Basu, S.R. Hart (Eds.), *Earth Processes: Reading the Isotope Code*, Am. Geophys. Union, Washington DC, 1996, pp. 123–134.
- [10] K.W. Burton, P. Schiano, J.L. Birck, C.J. Allegre, Osmium isotope disequilibrium between mantle minerals in a spinel-lherzolite, *Earth Planet. Sci. Lett.* 172 (1999) 311–322.
- [11] K.W. Burton, P. Schiano, J.L. Birck, C.J. Allegre, M. Rehkämper, A.N. Halliday, J.B. Dawson, The distribution and behaviour of rhenium and osmium amongst mantle minerals and the age of the lithospheric mantle beneath Tanzania, *Earth Planet. Sci. Lett.* 183 (2000) 93–106.
- [12] O. Alard, W.L. Griffin, J.P. Lorand, S.E. Jackson, S.Y. O'Reilly, Non-chondritic distribution of the highly siderophile elements in mantle sulfides, *Nature* 407 (2000) 891–894.
- [13] A. Luguet, O. Alard, J.P. Lorand, N.J. Pearson, C.G. Ryan, S.Y. O'Reilly, Laser-ablation microprobe (LAM)-ICPMS unravels the highly siderophile element geochemistry of the oceanic mantle, *Earth Planet. Sci. Lett.* 189 (2001) 285–294.
- [14] J.P. Lorand, O. Alard, 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* 65 (2001) 2789–2806.
- [15] J.P. Lorand, Are spinel lherzolite xenoliths representative of the abundance of sulfur in the Upper Mantle, *Geochim. Cosmochim. Acta* 54 (1990) 1487–1492.
- [16] D.A. Ionov, J. Hoefs, K.H. Wedepohl, U. Wiechert, Content and isotopic composition of sulphur in ultramafic xenoliths from central Asia, *Earth Planet. Sci. Lett.* 111 (1992) 269–286.
- [17] H.St.C. O'Neill, The origin and the early history of the Earth – A chemical model. Part 2: The Earth, *Geochim. Cosmochim. Acta* 55 (1991) 1159–1172.
- [18] T. Andersen, W.L. Griffin, S.Y. O'Reilly, Primary sulfide melt inclusions in mantle derived megacrysts and pyroxenites, *Lithos* 20 (1987) 279–294.
- [19] G.A. Gaetani, T.L. Groves, Wetting of mantle olivine by sulfide melt/implications for Re:Os ratios in mantle peridotite and late stage core formation, *Earth Planet. Sci. Lett.* 169 (1999) 147–163.

- [20] M. Rehkämper, Tracing the Earth's evolution, *Nature* 407 (2000) 848–849.
- [21] N.J. Pearson, O. Alard, W.L. Griffin, S.E. Jackson, S.Y. O'Reilly, In-situ measurements of Re–Os isotopes in mantle-sulfides by laser ablation multi-collector inductively-coupled mass spectrometry: analytical methods and preliminary results ICP-MS, *Geochim. Cosmochim. Acta* 66 (2002) 1037–1050.
- [22] S.B. Shirey, R.J. Walker, Carius tube digestion for low blank digestion rhenium-osmium analysis, *Anal. Chem.* 67 (1995) 2136–2141.
- [23] A.S. Cohen, F.G. Waters, Separation of osmium from geological material by solvent extraction for analysis by thermal ionisation mass spectrometry, *Anal. Chim. Acta* 332 (1996) 269–275.
- [24] N.S. Belshaw, P.A. Freedman, R.K. O'Nions, M. Frank, Y. Guo, A new variable dispersion double-focussing plasma mass spectrometer with performance illustrated for Pb isotopes, *Int. J. Mass Spectrom. Ion Phys.* 181 (1998) 51–58.
- [25] G.P. Brey, T. Khöler, Geothermobarometry in four-phase lherzolites; II, New thermobarometers, and practical assessment of existing thermobarometers, *J. Petrol.* 31 (1990) 1353–1378.
- [26] W.F. McDonough, S.S. Sun, The chemical composition of the Earth, *Chem. Geol.* 120 (1995) 223–253.
- [27] O. Alard, J.-L. Bodinier, X. Lenoir, J.M. Dautria, Uranium enrichment in the lithospheric mantle: Case studies from the French Massif Central, *Mineral. Mag.* 62A (1998) 30–31.
- [28] J.M. Dautria, C. Dupuy, K. Tahkerist, Carbonate metasomatism in the lithospheric mantle: peridotitic xenoliths from a melilitic district of the Sahara Basin, *Contrib. Mineral. Petrol.* 111 (1992) 37–52.
- [29] D. McKenzie, Some remarks on the movement of small melt fractions in the mantle, *Earth Planet. Sci. Lett.* 95 (1989) 55–72.
- [30] A. Luguët, J.P. Lorand, Supergene weathering and sulphur contents of basalt-hosted mantle xenoliths: an appraisal from Montferrier lherzolites (Languedoc, France), *C. R. Acad. Sci. Paris* 327 (1999) 519–525.
- [31] J.P. Lorand, O. Alard, A. Luguët, R. Keays, Sulfur and selenium systematics of the sub-continental lithospheric mantle beneath the Massif Central (France), *Geochim. Cosmochim. Acta* (2002) submitted.
- [32] J. Guo, W.L. Griffin, S.Y. O'Reilly, Geochemistry and origin of sulfide minerals in mantle xenoliths: Qilin, southeastern China, *J. Petrol.* 40 (1999) 1125–1149.
- [33] J.P. Lorand, F. Conquéré, Contribution à l'étude des sulfures dans les enclaves de lherzolites à spinelle des basaltes alcalins (Massif Central et Languedoc, France), *Bull. Mineral.* 106 (1983) 585–606.
- [34] Th. Meisel, R.J. Walker, A.J. Irving, J.P. Lorand, Osmium isotopic compositions of mantle xenoliths: a global perspective, *Geochim. Cosmochim. Acta* 65 (2001) 1311–1323.
- [35] M. Roy-Barman, G.J. Wasserburg, D.A. Papanastassiou, M. Chaussidon, Osmium isotopic and Re–Os concentrations in sulfide globules from basaltic glasses, *Earth Planet. Sci. Lett.* 154 (1998) 331–347.
- [36] M. Rehkämper, A.N. Halliday, J.G. Fitton, D.-C. Lee, M. Wieneke, N.T. Arndt, Ir, Ru, Pt and Pd in basalts and komatiites: New constraints for the geochemical behavior of the platinum group elements in the mantle, *Geochim. Cosmochim. Acta* 63 (1999) 3915–3934.
- [37] J.M. Brenan, H.F. Shaw, F.J. Ryerson, D.L. Phinney, Mineral-aqueous fluid partitioning of trace elements at 900°C and 2.0 GPa: Constraints on the trace element chemistry of mantle and deep crustal fluids, *Geochim. Cosmochim. Acta*, 59 (1995) 3331–3350.
- [38] J.J. Peucat, P. Jegouzo, P. Vidal, J. Bernard-Griffiths, Continental crust formation seen through the Sr and Nd isotope systematics of S-type granites in the Hercynian belt of western France, *Earth Planet. Sci. Lett.* 88 (1988) 60–68.
- [39] D.R. Lambert, O. Alard, J.L. Bodinier, L. Frick, Evidence for interaction of Proterozoic (2 Ga) sub-continental mantle with an enriched mantle plume from Re–Os isotope systematics in French Massif Central peridotite xenoliths, *Mineral. Mag.* 62A (1998) 848–849.
- [40] S.Y. O'Reilly, W.L. Griffin, Y. Poudjom Djomani, P. Morgan, Are lithospheres forever? Tracking changes in sub-continental lithospheric mantle through time, *GSA Today* 11 (2001) 4–9.
- [41] O. Alard, Chalcophile and siderophile elements in the mantle, Ph.D. Thesis, Macquarie University, Sydney, 2000, 427 pp.
- [42] R.J. Walker, J.W. Morgan, Rhenium-osmium systematics of carbonaceous chondrites, *Science* 243 (1989) 519–522.
- [43] F. Albarède, Introduction to Geochemical Modelling, Cambridge University Press, Cambridge, 1995, 543 pp.
- [44] M.I. Smoliar, R.J. Walker, J.W. Morgan, Re–Os ages of group IIA, IIIA, IVA, and IVB iron meteorites, *Science* 271 (1996) 1099–1102.