

Re–Os fractionation in magmatic sulfide melt by monosulfide solid solution

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Abstract

In order to better evaluate the effect of monosulfide solid solution (MSS) crystallization on Re–Os fractionation in magmatic sulfide ore systems, MSS–sulfide melt partition coefficients for Re and Os have been measured in experiments in the Fe–Ni–Cu–S system at 1100°C. Samples were encapsulated in evacuated silica tubes, run for durations of 13.5–61 h, and the compositions of coexisting MSS–melt pairs were characterized by electron microprobe. Average MSS–sulfide melt partition coefficients for Re and Os are 2.5 and 3.8, respectively, and are independent of experiment duration and MSS metal/sulfur ratio. Comparison of D_{Os} measured in this study with values determined by Fleet et al. [Contrib. Mineral. Petrol. 115 (1993) 36–44] also suggests D_{Os} is constant for melt Os contents ranging from 0.2 to 2000 ppm. Combining these data with a simple model of closed-system MSS fractionation reveals that the Re and Os content of coexisting MSS–residual sulfide melt pairs decreases with increased differentiation (as gauged by melt or MSS Cu abundances), whereas Re/Os ratios increase. This model reproduces the overall Re–Os–Cu trends observed in the zoned massive sulfide ore bodies at Noril'sk (Russia), although in detail, modeled Re variation is better predicted than Os or Re/Os variation. This latter result could suggest that the variation in ore Os content is not completely controlled by primary magmatic processes. In general, such results lend further support for the role of in situ differentiation in producing zoned ore bodies, but they also allow a clearer distinction to be made between primary vs. post-solidification processes in affecting the Re–Os isotopic system in sulfide-saturated igneous rocks. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

There can be significant variation in the isotopic composition of osmium within massive sulfide ore systems associated with mafic igneous rocks. This variation may reflect the time-integrated response to Re–Os fractionation arising

from a number of processes, including: crustal contamination, sulfide–silicate melt immiscibility, separation of silicate, oxide or platinum group mineral phenocrysts, hydrothermal alteration or crystallization within the massive sulfide ore [2,3]. The osmium isotopic variation in some magmatic sulfide ores (e.g., Sudbury, Ontario; Noril'sk, Siberia) is not only correlated with the Re/Os ratio but is also coupled to intradeposit zonation in the concentrations of Re and Os, the platinum group elements (PGEs), iron and copper [4,5]. Specifically, Fe-rich, Cu-poor ores tend to have relatively high Re, Os and low Re/Os, with

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Re and Os concentrations decreasing and Re/Os increasing as ores become Fe-poor and Cu-rich. The concentrations of Ru, Ir and Rh show similar behavior to Os, whereas Pt and Pd are enriched along with Cu. This variation has been attributed to fractional crystallization of monosulfide solid solution (MSS), which is a primary liquidus phase in the Fe–Ni–Cu–S system [6–8]. The essential datum needed to accurately assess this process as being responsible for the observed behavior of Re and Os is the partitioning of these elements between MSS and sulfide melt. Past work in this regard has focused on laboratory measurements involving osmium only [1], or empirical estimates of the partitioning of Re and Os based on the compositional variation of these elements in massive sulfide ores [3]. Unfortunately, the former data cannot be used to directly determine if MSS can fractionate Re from Os, whereas the latter estimates are model dependent, requiring accurate knowledge of sulfide–silicate melt partitioning and the silicate/sulfide mass ratio, which are themselves somewhat uncertain. As such, in this paper I present the results of experiments in which the MSS–sulfide melt partitioning behavior of both Re and Os has been measured under controlled conditions of temperature and melt composition. Results indicate that Os is slightly more compatible than Re in MSS, thus substantiating the MSS fractionation hypothesis for some ore systems and better constraining the processes that result in Re/Os fractionation in igneous rocks.

2. Experimental and analytical techniques

Experiments performed in this study used bulk compositions chosen to represent a range in initial metal/sulfur ratios and were modeled after those employed in previous work involving MSS–melt partitioning (i.e., compositions B11-1 and L11-2 of [9]; C2b2 of [10]). A temperature of 1100°C was chosen for partitioning experiments to afford direct comparison to this previous work and because the phase equilibria for the chosen compositions at this temperature are well-known. Compositions had variable Fe/S ratios, contained

subequal amounts of Ni and Cu (~5 wt%) and Re and Os at the 0.5 wt% level or below. Although Re and Os concentrations exceed those found in sulfide ores, a comparison of Os partition coefficients measured in this study with those determined previously (see Section 3.2) suggests Henry's Law is obeyed in the MSS–sulfide melt system up to the abundance levels added to these experiments. Re and Os were run in separate experiments so as to avoid X-ray line overlap in subsequent electron microprobe analysis. Starting materials consisted of high purity metals and sulfur, which were weighed into closed-end silica tubes (5 mm OD×3 mm ID×30 mm long) for a total sample mass of ~50 mg. After loading, tubes were evacuated, then sealed. All experiments were run in a vertical tube furnace and samples were subject to one of two time–temperature histories: (1) initial superliquidus step at 1200°C for 1 h, followed by cooling at 1°/h to 1100°C, then an isothermal soak for 13.5–61 h or (2) no superliquidus step, direct heating to 1100°C, then soaking for 38–46 h. In both cases, samples were quenched by plunging into ice water. Temperature was monitored using a calibrated type-S thermocouple, and values varied by less than 2°C over the course of an experiment.

Samples were mounted in epoxy, polished with SiC, then 1 and 0.3 µm alumina and, finally, colloidal silica. The composition of coexisting phases was determined using the Cameca SX50 electron microprobe at the University of Toronto. All analyses were performed at an accelerating voltage of 20 kV and using a 30 µm diameter defocused electron beam. A 30 nA beam current and 20 s on-peak count times were used to measure Fe, Ni, Cu and S, whereas 100 nA and 60 s count times were used for Re and Os. Re was measured using the $L\alpha$ X-ray line, and Os using the $M\alpha$ line, the latter being necessary to avoid the Cu $K\beta$ interference on the Os $L\alpha$ line. Limits of detection for Re and Os in the phases analyzed are estimated to be 0.02 wt%, based on 3σ above background count rates. Typically, 8–20 spots were analyzed for each phase, then averaged. A summary of experiments and phase compositions is provided in Table 1.

Table 1
Summary of experiments and run product analyses

Sample	Type ^a	Duration ^b (h)	ReS ₂ or Os metal? ^c	Phase	Fe ^d	Ni	Cu	Re	Os	S	Sum
MSSRe1	1	61	yes	melt	52.01 (0.51)	4.87 (0.13)	7.67 (0.49)	0.13 (0.03)	–	35.79 (0.30)	100.47
				MSS	57.57 (0.61)	3.11 (0.18)	2.09 (0.34)	0.28 (0.02)	–	37.65 (0.20)	100.74
				D MSS/melt	1.11 (0.02)	0.64 (0.04)	0.27 (0.05)	2.21 (0.47)	–	1.05 (0.01)	
MSSRe4	1	13.5	yes	melt	53.91 (0.56)	4.49 (0.19)	6.55 (0.58)	0.12 (0.02)	–	35.26 (0.35)	100.34
				MSS	59.18 (0.24)	2.50 (0.07)	1.58 (0.11)	0.32 (0.01)	–	37.63 (0.13)	101.23
				D MSS/melt	1.10 (0.01)	0.56 (0.03)	0.24 (0.03)	2.65 (0.48)	–	1.07 (0.01)	
MSSRe5	1	22.5	N.O.	melt	54.10 (0.44)	5.13 (0.14)	5.80 (0.76)	0.12 (0.02)	–	35.20 (0.45)	100.38
				MSS	59.19 (0.10)	2.76 (0.11)	1.54 (0.12)	0.34 (0.02)	–	37.46 (0.17)	101.34
				D MSS/melt	1.09 (0.01)	0.54 (0.03)	0.27 (0.04)	2.73 (0.53)	–	1.06 (0.01)	
MSSRe7	1	22.5	N.O.	melt	54.14 (0.48)	5.05 (0.09)	5.64 (0.46)	0.050 (0.015)	–	34.91 (0.26)	99.79
				MSS	59.87 (0.16)	2.48 (0.05)	1.40 (0.07)	0.096 (0.020)	–	37.33 (0.11)	101.21
				D MSS/melt	1.11 (0.01)	0.49 (0.01)	0.25 (0.02)	1.92 (0.70)	–	1.07 (0.01)	
MSSRe10	1	23.5	yes	melt	50.37 (0.67)	5.21 (0.13)	5.74 (0.54)	0.12 (0.03)	–	38.24 (0.31)	99.79
				MSS	56.57 (0.17)	3.84 (0.05)	1.57 (0.08)	0.25 (0.01)	–	39.07 (0.16)	101.31
				D MSS/melt	1.12 (0.02)	0.74 (0.02)	0.27 (0.03)	2.06 (0.55)	–	1.02 (0.01)	
MSSRe17	1	44.5	N.O.	melt	55.39 (0.23)	5.58 (0.07)	4.46 (0.26)	0.028 (0.015)	–	34.66 (0.19)	100.14
				MSS	60.20 (0.19)	2.41 (0.04)	1.03 (0.16)	0.083 (0.015)	–	37.33 (0.15)	101.07
				D MSS/melt	1.09 (0.01)	0.43 (0.01)	0.23 (0.04)	3.02 (1.78)	–	1.08 (0.01)	
MSSRe20	2	38	yes	melt	51.71 (0.91)	5.62 (0.17)	4.05 (0.93)	0.11 (0.03)	–	37.35 (0.38)	98.90
				MSS	56.25 (0.26)	4.03 (0.07)	1.18 (0.07)	0.26 (0.02)	–	38.48 (0.13)	100.21
				D MSS/melt	1.09 (0.02)	0.72 (0.03)	0.29 (0.07)	2.35 (0.64)	–	1.03 (0.01)	
MSSRe21	2	46	yes	melt	53.29 (0.45)	4.75 (0.15)	6.16 (0.59)	0.12 (0.02)	–	34.88 (0.23)	99.24
				MSS	58.68 (0.24)	2.35 (0.07)	1.50 (0.08)	0.35 (0.02)	–	37.14 (0.18)	100.07
				D MSS/melt	1.10 (0.01)	0.50 (0.02)	0.24 (0.03)	2.96 (0.45)	–	1.06 (0.01)	
MSSOs1	1	61	yes	melt	52.62 (0.44)	4.59 (0.14)	7.77 (0.61)	–	0.092 (0.026)	35.44 (0.26)	100.53
				MSS	58.30 (0.21)	2.75 (0.07)	1.89 (0.14)	–	0.47 (0.02)	37.74 (0.11)	101.12
				D MSS/melt	1.11 (0.01)	0.60 (0.02)	0.24 (0.03)	–	5.16 (1.48)	1.06 (0.01)	
MSSOs2	1	13.5	yes	melt	53.62 (0.54)	4.62 (0.12)	6.51 (0.71)	–	0.036 (0.014)	35.00 (0.34)	99.81
				MSS	59.44 (0.23)	2.37 (0.05)	1.63 (0.07)	–	0.15 (0.02)	37.42 (0.09)	101.03
				D MSS/melt	1.11 (0.01)	0.51 (0.02)	0.25 (0.03)	–	4.23 (1.70)	1.07 (0.01)	
MSSOs3	1	22.5	N.O.	melt	54.59 (0.39)	5.08 (0.13)	5.90 (0.46)	–	0.055 (0.013)	35.21 (0.27)	100.82
				MSS	58.94 (0.52)	2.84 (0.20)	1.91 (0.20)	–	0.19 (0.01)	37.12 (0.19)	100.99
				D MSS/melt	1.08 (0.01)	0.56 (0.04)	0.32 (0.04)	–	3.39 (0.83)	1.05 (0.01)	
MSSOs6	1	23.5	N.O.	melt	51.60 (1.41)	5.09 (0.36)	4.75 (1.05)	–	0.085 (0.031)	38.03 (0.46)	99.57
				MSS	56.76 (0.13)	3.72 (0.05)	1.33 (0.05)	–	0.26 (0.01)	39.19 (0.12)	101.27
				D MSS/melt	1.10 (0.03)	0.73 (0.05)	0.28 (0.06)	–	3.07 (1.13)	1.03 (0.01)	
MSSOs11	2	38	N.O.	melt	49.82 (0.51)	7.53 (0.31)	4.52 (0.36)	–	0.18 (0.04)	37.19 (0.42)	99.18
				MSS	54.68 (0.28)	5.00 (0.10)	1.15 (0.10)	–	0.59 (0.03)	38.38 (0.20)	99.84
				D MSS/melt	1.10 (0.01)	0.66 (0.03)	0.25 (0.03)	–	3.28 (0.80)	1.03 (0.01)	

^a Type 1 experiments were subject to a 1 h superliquidus step at 1200°C, followed by ramping at 1°/min to the final soak temperature of 1100°C. Type 2 experiments were brought directly to 1100°C.

^b The duration given corresponds to the time at 1100°C.

^c Indicates experiment contained visible rhenium sulfide or osmium metal. N.O. means not observed using the petrographic microscope.

^d Numbers in parentheses correspond to 1σ error based on 8–20 spot analyses.

3. Results

3.1. Textural observations

Run products consisted of a few large (100–500 μm) rounded MSS crystals in a mass of quenched sulfide melt (identical texture to Li et al. [9], their figure 1). The quench melt consisted of an intergrowth of acicular dendrites of MSS plus a Cu-rich phase (probably intermediate solid solution), and the relatively large standard deviation in microprobe analyses of the melt phase (Table 1) is a consequence of both this textural inhomogeneity and overall low concentrations. Quenched melt from the most sulfur-rich experiments (MSSRe10, MSSOs6) was highly vesicular (foam-like), and similar to textures reported by Ebel and Naldrett [10]. Table 1 also lists whether a particular experiment contained visible crystals of euhedral rhenium sulfide or osmium metal. For the case of rhenium-bearing experiments, all but three contained trace amounts of rhenium sulfide, and those that do have nearly identical Re concentrations (~ 0.12) in the melt, consistent with compositional buffering by phase saturation. An exception to this is experiment MSSRe5, which did not contain visible Re–sulfide despite having similar Re levels in the melt. It may be that this experiment contained a Re level sufficient to just saturate the melt phase, and thus a small amount of excess Re–sulfide may have been overlooked. Osmium metal was observed in only two of the osmium-bearing experiments and, although the Os content of those two experiments differ somewhat, they overlap in their standard deviation. As in the case for Re-bearing experiments, a small amount of excess metal may have been overlooked in the other experiments with similar Os concentrations in the melt.

3.2. Partition coefficients

MSS–melt equilibrium was assessed in two ways. First, multiple microprobe analyses were made across individual MSS crystals from all run products, which did not reveal any discernible zoning regardless of run time–temperature history. Second, run durations for experiments containing ~ 35 wt% sulfur were varied from 13.5

to 61 h, and partition coefficients for Re, Os, Ni and Cu all remained essentially constant (Fig. 1). Partition coefficients for Ni (0.54–0.74) and Cu (0.26–0.28) are also in excellent agreement with values determined in previous studies done at similar temperatures and over the same range of melt sulfur contents. For example, at temperatures of 1040–1100°C, for melts with 35–38 wt% sulfur, values of D_{Ni} are in the range of 0.40–0.88 (with a low value of 0.22 measured by Barnes et al. [11]) and D_{Cu} are 0.20–0.35 [1,9,10–13].

Although the range of Re and Os concentrations over which partitioning could be assessed was limited (by phase saturation at the high end and electron microprobe detection limits at the low end), partition coefficients for these elements appear to be independent of total Re or Os in the melt or MSS phase (Fig. 2). A robust test of Henry's Law can be made by comparing our values for D_{Os} with those of Fleet et al. [1] obtained from experiments containing ppm levels of Os (Fig. 2B). Values of D_{Os} measured in this study are 3.1–5.2 with 360–1800 ppm Os in the melt, which are in excellent agreement with D_{Os} of 3.7–5.3 measured by Fleet et al. [1] involving melts with 0.2–14 ppm Os.

Li et al. [9] have shown that MSS–melt partition coefficients for the PGEs increase with decreasing metal/sulfur ratio of MSS. Their results were obtained from experiments in which MSS contained several wt% of total PGEs. In experiments doped at trace PGE levels, Ballhaus et al. [12] did not observe this behavior, and concluded that the experiments of Li et al. [9] were done at concentration levels that exceed the Henrian range. Consistent with the results of Ballhaus et al. [12], values of D_{Os} and D_{Re} measured in this study are independent of MSS composition (Fig. 3).

Average values of D_{Re} and D_{Os} obtained in this study are 2.5 and 3.8, respectively, thus indicating that both of these elements will be selectively retained in MSS relative to sulfide melt, with a slight preference for Os relative to Re in the solid phase. The compatibility of osmium in MSS is also consistent with the behavior of the other high melting point PGEs, Ir and Ru, in that previous studies have consistently reported partition

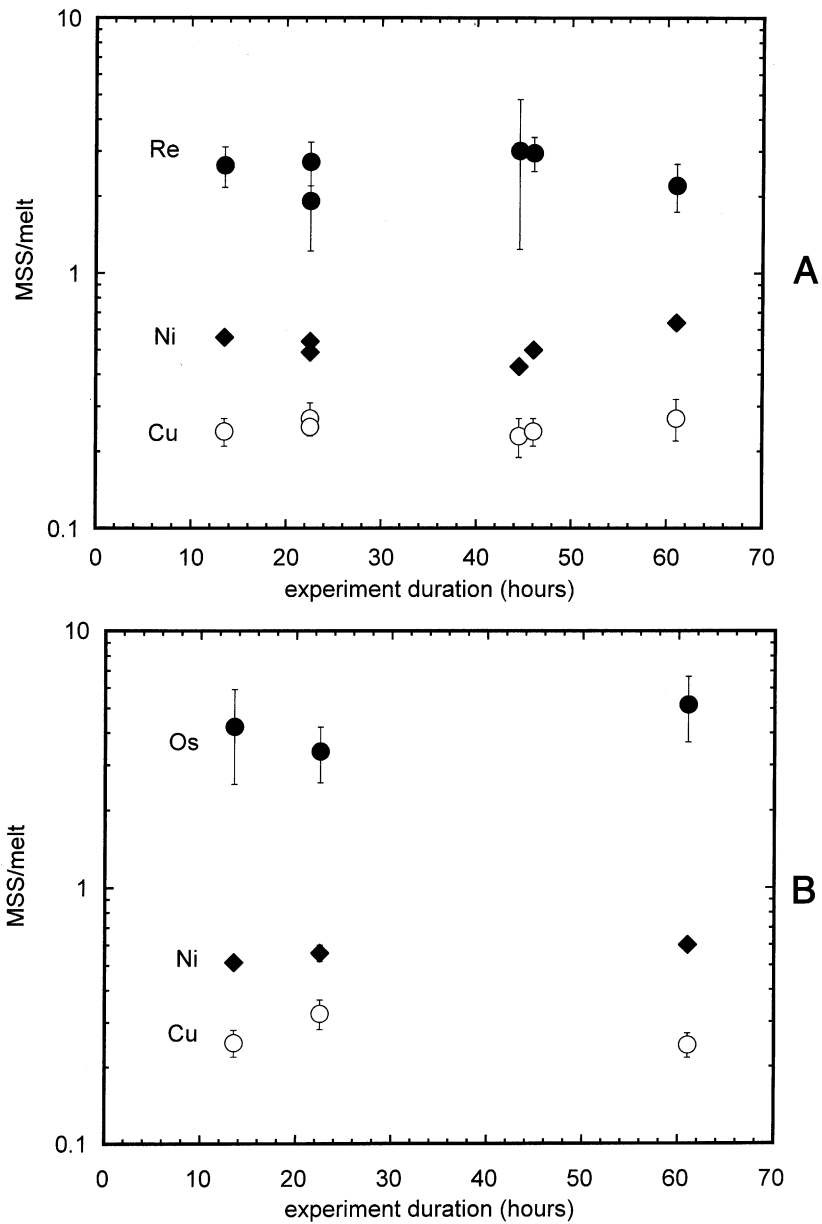


Fig. 1. MSS–melt partition coefficients as a function of experiment duration. (A) Experiments doped with rhenium. (B) Experiments doped with osmium.

coefficients for these elements of > 1 [1,9,11,12]. Moreover, Lambert et al. [3] modeled the compositional variation in massive sulfide ores from Kambalda (Australia), Noril'sk (Russia) and Sudbury (Canada), using combined data for Re, Os and other PGEs, and obtained an empirical esti-

mate for D_{Re} of 1.5 and D_{Os} of 2.6. These values are in close agreement with those reported here, and it is also notable that the ratio for $D_{\text{Os}}/D_{\text{Re}}$ of 1.5 estimated by Lambert et al. [3] is identical to the value derived from the experiments reported in this study.

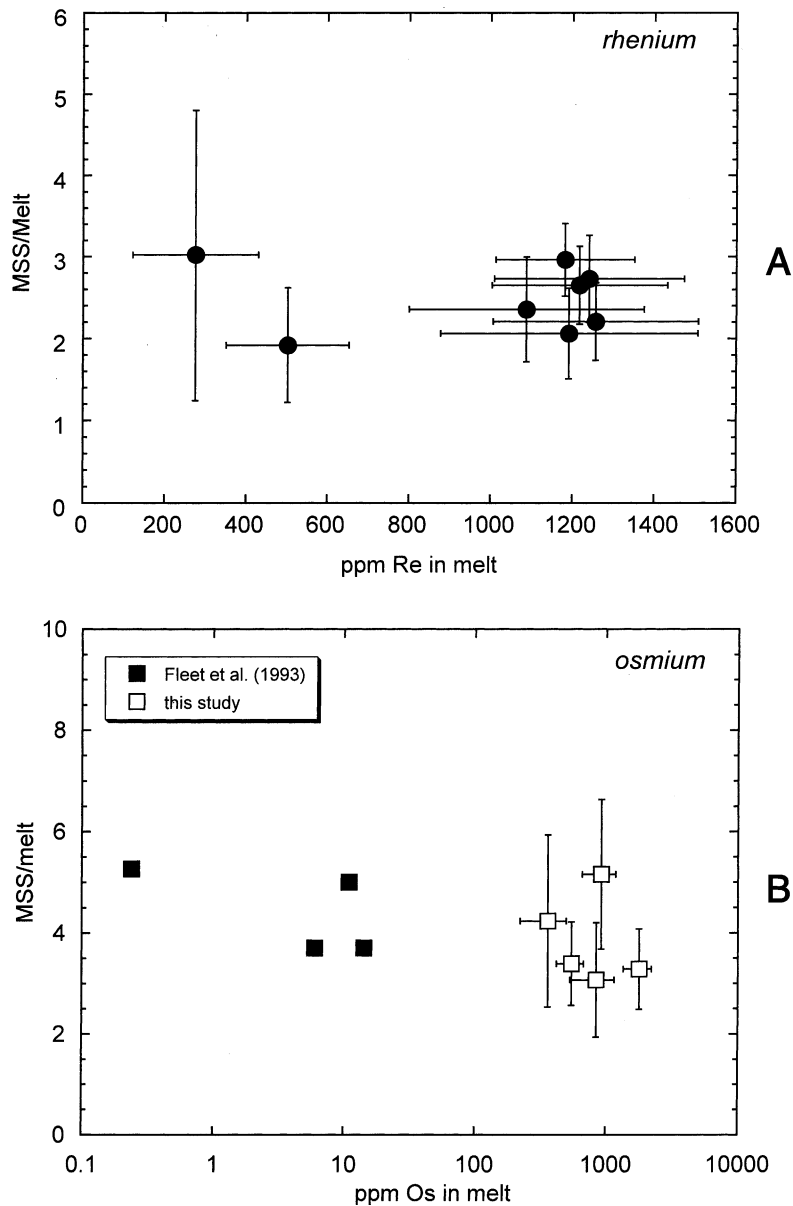


Fig. 2. MSS–melt partition coefficients as a function of (A) rhenium and (B) osmium content of the sulfide melt. For comparison is the osmium partitioning data of Fleet et al. [1] from experiments at 1000–1040°C, in which coexisting phases were analyzed by SIMS.

4. The effect of MSS fractionation on Re and Os abundances in sulfide ore

The values of D_{Os} and D_{Re} measured in this study can be used to predict the variation in Re and Os in melt and MSS cumulates arising from

the crystallization of massive sulfide ores. This information can be used to assess directly whether the Re–Os variation in such systems represents the original magmatic signature or has been subject to post-crystallization disturbance. As an example of this application, partitioning data are

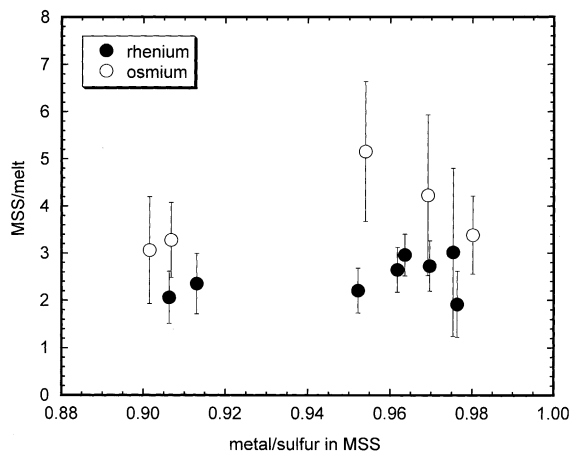


Fig. 3. MSS–melt partition coefficients for rhenium and osmium as a function of the metal/sulfur (atomic) ratio in the MSS.

combined with a simple model of MSS crystallization to assess the origin of the Re–Os variation in Ni–Cu ores from the Noril’sk region (Russia).

Massive sulfide ores from the Noril’sk region occur within and are adjacent to mafic intrusive bodies that are spatially and temporally associated with the ca. 250 Ma Siberian Flood Basalt Province [14,15]. A distinctive aspect of these deposits is the large variation in abundances of Ni, Cu and PGEs within the ore bodies [16,17], which is well-correlated with mineral-assemblage zonation. For example, the massive-sulfide ores of the Oktyabr’sky Mines area within the Kharaelakh intrusive body are concentrically zoned with a pyrrhotite-rich margin, grading to inner zones rich in chalcopyrite and cubanite, to a core of mooihoekite ($\text{Cu}_9\text{Fe}_9\text{S}_{16}$)–cubanite or talnakhite ($\text{Cu}_9[\text{Fe},\text{Ni}]_8\text{S}_{16}$)–cubanite-bearing assemblages. In parallel with the mineralogical zonation, samples that are Fe-rich and Cu-poor are enriched in Ru, Os, Ir and Rh, and depleted in Pd and Pt relative to those that are Cu-rich and Fe-poor. Zonation of these elements has been successfully modeled in terms of closed system MSS fractionation, as Ru, Ir and Rh are compatible in MSS, whereas Pt, Pd and Cu are incompatible [1,8,9,11,12]. Thus the Fe-rich portions of Noril’sk ore bodies are interpreted to represent early-formed MSS cumulates, with the corresponding Cu-rich portions as differentiated melts,

and intermediate compositions representing varying degrees of entrapment of melt within the MSS cumulate pile [15–18].

Walker et al. [5] report Re and Os¹ concentrations and Os isotopic compositions of massive sulfide ores from the Noril’sk 1, Talnakh and Kharaelakh intrusions, which are part of the Noril’sk igneous suite. General overlap in the initial $^{187}\text{Os}/^{188}\text{Os}$ between ore bodies suggests that the parental sulfide melts for these systems were derived from similar magmas. The overall behavior of Re and Os in the ores is similar to that of other MSS-compatible PGEs, in that concentrations of Re and Os fall with increased differentiation as judged by increases in the Cu content of the massive sulfide ore (Fig. 4A–C). Moreover, Re/Os ratios increase with Cu concentration, suggesting that Re is somewhat less compatible than Os in MSS. Both sets of observations are qualitatively consistent with the partition coefficients measured in this study. Following the methods set forth by Li and Naldrett [19], a more quantitative model of this behavior was developed by calculating the Re, Os and Cu content of coexisting MSS and melt undergoing fractional crystallization, and results are superimposed on the compositional data portrayed in Fig. 4. The composition of the melt in a system undergoing fractional crystallization can be calculated from the expression:

$$\frac{C_1}{C_0} = F^{D-1} \quad (1)$$

in which C_0 is the concentration of a specific element in the initial sulfide melt, C_1 is the concentration in the melt for a given fraction remaining (F) and D is the mineral–melt partition coefficient. The concentration of coexisting MSS at a given value of F can be calculated from the product of C_1 and D . Values of D_{Re} (2.5) and D_{Cu} (0.25) used

¹ In lieu of monitoring total Os, the concentration of ^{192}Os is used to describe the primary Os distribution in the ores, as it is the most abundant stable isotope of Os, and ores with high Re/Os may contain significant radiogenic ^{187}Os produced by in situ decay [5]. Therefore, unless stated otherwise, all reference to Os abundance variations implicitly refers to variations in primary Os concentrations, as represented by ^{192}Os .

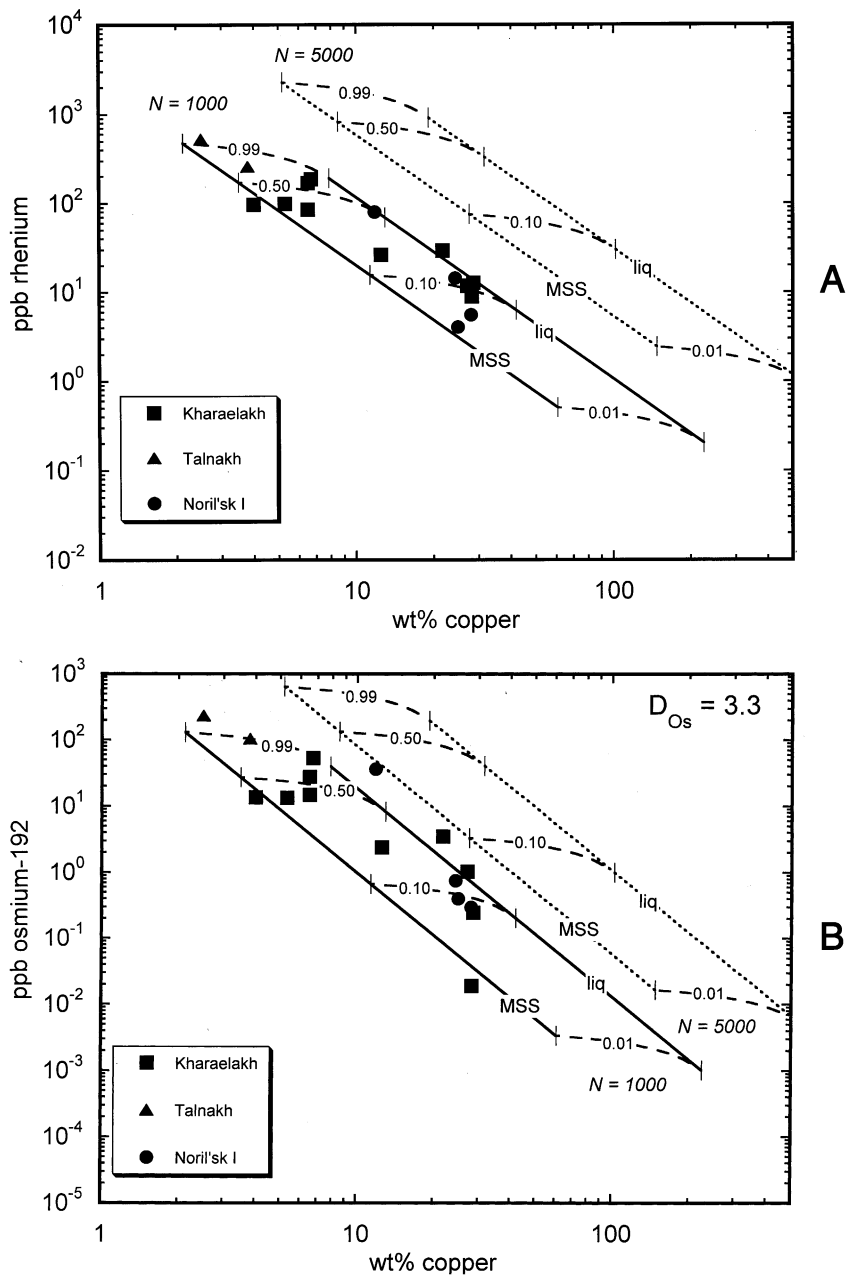


Fig. 4. Compositional variation in massive sulfide ores from the Noril'sk Ni-Cu-PGE deposit compared to models of MSS fractional crystallization (data from Walker et al. [5]). (A) Re vs. Cu, (B) and (C) ^{192}Os vs. Cu (variable D_{Os}) and (D) Re/ ^{192}Os vs. Cu. Curves portray the composition of MSS and sulfide melt undergoing fractional crystallization, and tie lines connect coexisting MSS-melt pairs for systems with remaining melt fractions (F) of 0.99, 0.5, 0.1 and 0.01. Sets of curves have been calculated assuming the Re and Os content of the initial sulfide melt was produced for N of 1000 and 5000. The concentration of ^{192}Os (the most abundant stable isotope of Os) is used in lieu of total Os, as ores with high Re/Os may have a significant amount of radiogenic ^{187}Os produced in situ, thus obscuring the osmium distribution when the ore was initially formed [5]. See text for further details.

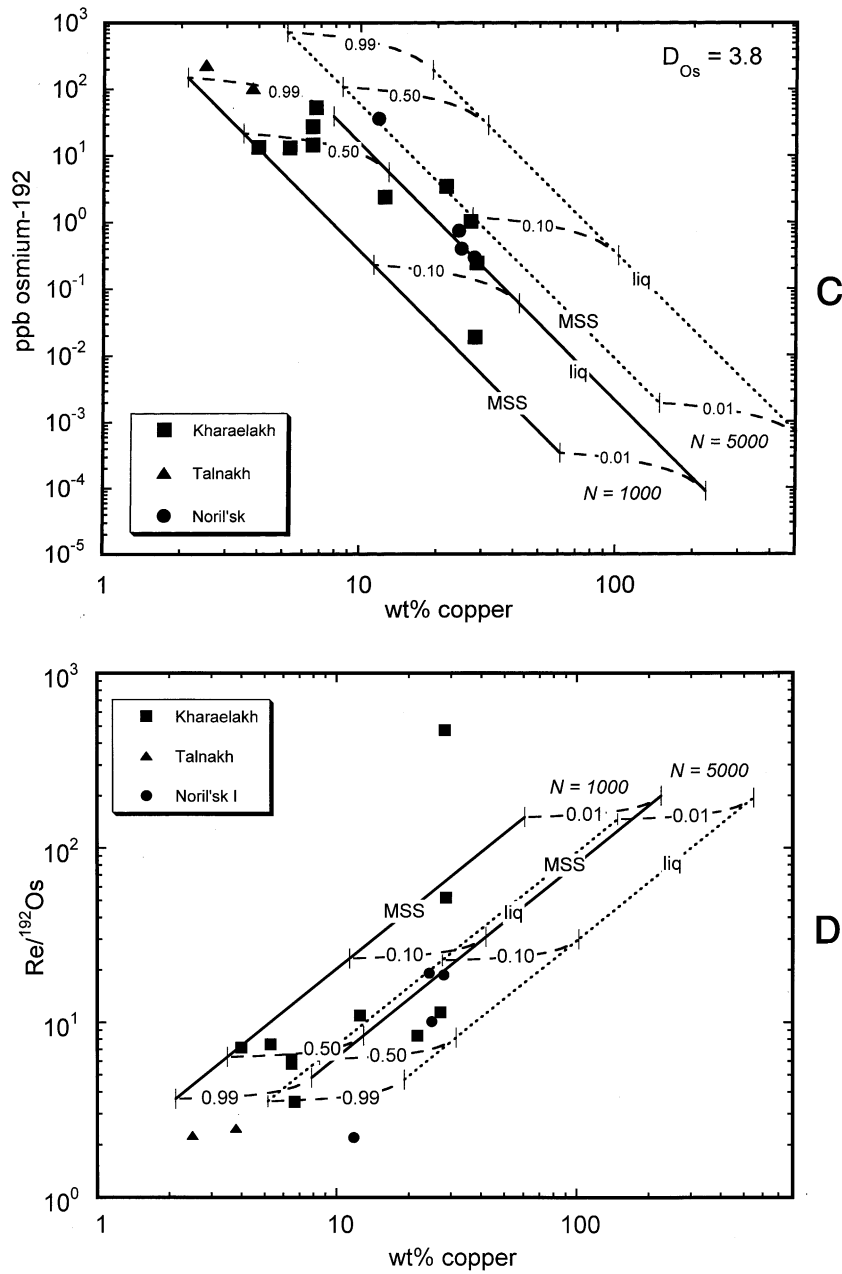


Fig. 4. (Continued).

in the modeling correspond to the average values determined from all experiments. Owing to the somewhat lower precision of the partition coefficients for osmium, the sensitivity of the model to the D for Os was tested by constructing model

curves using the average D_{Os} of 3.8 and the most precise value for D_{Os} of 3.3. Model curves for the variation in Re/Os ratio (Fig. 4D) were calculated using a D_{Os} of 3.3. Values of C_0 for Re, Os and Cu were estimated using an initial

silicate melt with 0.013 wt% Cu [8], 0.2 ppb Re and 0.1 ppb Os [20], and sulfide/silicate melt partition coefficients of 1500, 3.3×10^4 and 1×10^5 for Cu, Re and Os, respectively. Silicate melt abundances are based on values measured by Brugmann et al. [21] and Horan et al. [20] for the Tuklonsky picrites, which are considered to be a viable candidate for the magma that gave rise to the intrusive ore bodies. Sulfide–silicate melt partition coefficients for Cu and Os are the preferred values from Barnes et al. [8], whereas the value for Re is based on the measurements of Sattari et al. [22]. Naldrett et al. [15], have successfully reproduced the PGE variation in disseminated ores from Noril'sk using a model in which sulfides are progressively upgraded in their tenor by interaction with successive batches of magma in the feeder channels to the Noril'sk intrusions. These workers employed a zone refining model, in which the metal concentration in the sulfide (Y) is calculated by the relation:

$$Y = X_i [D - \{(D-1)e^{-(1/DN)}\}] \quad (2)$$

where X_i is the initial metal concentration in the silicate melt, D is the sulfide/silicate melt partition coefficient and N is the ratio of magma passing through and reacting with the sulfide to the amount of sulfide present. Values of N required to reproduce the range of disseminated ore PGE concentrations at Noril'sk range from ~ 1000 to $\sim 10\,000$ [15]. For the model parameters employed in this illustration, N of 1000 results in a reasonable fit to the data, and the results of calculations based on $N=5000$ are also included to illustrate the effect of varying this parameter². Consistent with the qualitative predictions of the MSS fractionation model, as the fraction of remaining melt decreases, the concentrations of Re and Os in sulfide melt and MSS decrease, whereas

both Re/Os ratios and Cu levels in both phases increase (Fig. 4A–D). In general, the Noril'sk ores can be described as mixtures of the MSS and fractionated sulfide melt produced by the crystallization of a parental sulfide melt that was subject to N of ~ 1000 , as most bulk compositions plot within the field defined by permissible MSS–melt endmembers. This fit is best for Re, whereas the data for Os is less well ‘bracketed’ by the permissible compositions of MSS and sulfide melt, regardless of the choice of D_{Os} . The deviation between model and data does not appear to be systematic, so it seems unlikely that the choice of model parameters is the origin of this discrepancy. Alternatively, it is certainly possible that the primary variation in Os concentration arising from sulfide fractionation may be partially obscured by subsolidus modification. For example, local redistribution of metals could in part result from low temperature exsolution of MSS. Moreover, given the large Os compositional gradients that undoubtedly existed (and persist) in the Noril'sk ores, combined with the low closure temperature for Os in sulfide minerals (i.e., $\sim 300^\circ\text{C}$ for pyrrhotite [24]), some internal homogenization of the ores seems inescapable. That this process may have affected Os systematics more than Re might be a consequence of differential fluxes of these elements to available exchange media (e.g., hydrothermal fluids). Although Xiong and Wood [25,26] have shown that Re metal is significantly more soluble than Os metal under moderately oxidizing hydrothermal conditions, the mineral–fluid partitioning behavior of these elements is unknown. Alternatively, varying degrees of homogenization may result from more sluggish solid-state exchange kinetics for Re relative to Os, possibly reflecting different predominant host phases for these elements. Disturbance of the Os concentrations within portions of the massive sulfide ore was probably a closed system event that acted soon after the ores solidified, however, given the overall uniformity in initial $^{187}\text{Os}/^{188}\text{Os}$ documented by Walker et al. [5]. Thus, differentiation of sulfide melt at the magmatic stage appears to be the process responsible for the overall variation in Re, Os and Re/Os in the Noril'sk ores, as has been suggested based on the behavior of the other

² It is important to note here that increasing N will result in a simultaneous *increase* in the Cu, Re and Os levels of derivative sulfide melts, and based on available data for sulfide–silicate melt partitioning, Re/Os of the sulfide melt will *decrease*, as D_{Os}/D_{Re} is at least 3 [22,23]. Thus, variations in N alone cannot account for the Re–Os trends within the ore bodies.

PGEs [17], although second-order effects appear to have influenced Os concentrations. In addition to the Noril'sk ore system, other massive sulfide ore systems that appear to have undergone internal differentiation by MSS fractionation include Sudbury [7] and Kambalda [27]. Preliminary modeling of those suites using the partitioning data presented here also suggests that the variation in Re, Os and Re/Os is consistent with the MSS fractionation hypothesis.

5. Conclusions

Measured MSS–sulfide melt partition coefficients for Re and Os reveal that both of these elements are compatible in MSS, relative to sulfide melt, with Os being slightly more so ($D_{Os}/D_{Re} = 1.5$). Combining these data with a simple model of closed system fractional crystallization of MSS from sulfide melt reveals compositional variations in MSS and melt that are generally consistent with trends seen in compositionally zoned massive sulfide ores, such as Noril'sk. In detail, however, the Noril'sk dataset for Os is not as well modeled as that for Re, as the Os abundance of some ore samples plots outside the expected range for MSS cumulates or evolved sulfide melt. This deviation is also reflected in Re/Os ratios that do not adhere well to expected variations, and such results might reflect some postmagmatic disturbance in Os concentrations. Such results underscore the value of this partitioning data in allowing for a clearer distinction to be made amongst primary vs. post-solidification processes in affecting the Re–Os isotopic system. This, in turn, results in a more complete interpretation of the osmium isotopic composition of sulfide-saturated igneous rocks.

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