



High-pressure solid/liquid partitioning of Os, Re and Pt in the Fe–S system

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ABSTRACT

Coupled enrichments in $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ in some ocean island basalts have been interpreted to reflect material transfer from Earth's outer core to the base of the mantle. The outer core is a viable source for these coupled enrichments if it is able to maintain sufficiently high Pt/Os and Re/Os ratios for sufficient time. Iron meteorite studies and some experimental data indicate that progressive crystallization of the inner core is a plausible mechanism for generating the required high Pt/Os and Re/Os ratios in the outer core. However, the conditions of the experiments and meteorite parent bodies are far different from those in Earth's core, particularly in terms of pressure. Here we present experimental results on the partitioning of Os, Re and Pt between solid iron and liquid iron sulfide solutions over a wide range of pressures, from 3.3 to 22 GPa. The solid/liquid partition coefficients for these elements decrease, and become more similar to each other, as pressure increases. This behavior is consistent with an increasing misfit of each element in the iron lattice with increasing pressure, due to the small compressibility of Os, Re and Pt relative to iron. The partition coefficients, and differences among them, are too small at the conditions of these experiments to generate the radiogenic Os isotope anomalies observed in some plume-derived lavas. At 22 GPa the partition coefficients are such that inner core crystallization elevates the Pt/Os ratio of the outer core by only 11%, and the Re/Os ratio by only 6%; after 4.5 Gyr, the calculated $^{186}\text{Os}/^{188}\text{Os}$ ratio of the outer core is only 0.0012% higher than it would be in the absence of inner core crystallization, and the $^{187}\text{Os}/^{188}\text{Os}$ ratio is only 1.4% higher. If the pressure effect is due to lattice strain, the partition coefficients are expected to decrease further at the pressure and temperature conditions relevant to Earth's core. Thus, the present data set does not support the idea that radiogenic Os isotope anomalies originate in the outer core.

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1. Introduction

Over the last several years there has been vigorous debate about whether a geochemical signature of the Earth's outer core is detectable in oceanic basalts. The ^{190}Pt – ^{186}Os and ^{187}Re – ^{187}Os isotopic systems have played a key role in this debate, with coupled enrichments in $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ providing the best case for an outer core signature (Walker et al., 1995; Brandon et al., 1998, 1999, 2003; Brandon and Walker, 2005). Earth's mantle has relative abundances of Os, Re and Pt similar to chondrites (Drake and Righter, 2002), and the same is likely true of the core as a whole, given the highly siderophile behavior of these elements. However, crystallization of the inner core may have fractionated Pt/Os and Re/Os ratios, which may have led to a present-day outer core with $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios different from those in the mantle. Experimental partitioning studies (Walker, 2000; Chabot et al., 2003), and studies of materials from asteroidal cores (Walker et al., 1995) indicate that the outer core would

develop elevated Pt/Os and Re/Os ratios during inner core crystallization, and on this basis the outer core seems to be a plausible source for elevated Os isotope signatures.

The hypothesis that high $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ in oceanic basalts reflect a material contribution from the outer core has several weaknesses. A negative ^{182}W anomaly should be part of the core signature, but has not been found (Scherstén et al., 2004). Metasomatic sulfides and pyroxenites have been shown to have Pt/Os and Re/Os high enough to produce the observed ^{186}Os and ^{187}Os enrichments (Luguet et al., 2008), making a core contribution unnecessary and perhaps invisible even if it did occur. Finally, there is doubt that the outer core itself has sufficiently high $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ to explain the values found in basalts, because it appears unlikely that the inner core crystallized early enough for significant ^{186}Os anomalies to develop in the outer core (Lassiter, 2006). It is also uncertain whether the differences in solid/liquid partition coefficients between Os, Re and Pt are large enough at the conditions relevant to inner core crystallization.

The inner core comprises a small fraction of the core's mass (~5.5%), and therefore has little leverage on element fractionation in the outer core unless the solid/liquid partition coefficient of at least one element is quite large. Assuming perfect fractional crystallization

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of the inner core (which appears to be a reasonable assumption; Yunker and Van Orman, 2007), the ratio of concentrations in the outer core is a power-law function of the difference in their solid/liquid partition coefficients. The atomic ratio Pt/Os, for example, is given by $(Pt/Os)_{o.c.} = F^{-(D_{Os} - D_{Pt})}$, where F is the liquid fraction and D_i is the ratio of the molar concentration of element i in the solid to its concentration in the liquid, at equilibrium. In the most favorable case, where the inner core is assumed to have attained its present mass just after Earth's formation, partition coefficient differences $D_{Os} - D_{Pt} \cong 25$ and $D_{Os} - D_{Re} \cong 10$ are required to produce the appropriate Os isotope signatures in the outer core (Brandon et al., 2003). In more realistic scenarios, where inner core crystallization is delayed and/or gradual, larger differences among the partition coefficients are necessary. Note that even if Pt were perfectly incompatible in the solid inner core (i.e. $D_{Pt} = 0$), Os would have to be highly compatible, with D_{Os} at least 25, in order to produce the required fractionation. Platinum is in fact found to be moderately to highly compatible in solid iron alloys in equilibrium with liquid metal, so this value for D_{Os} is clearly an extreme lower limit.

Such large values of D_{Os} , and large differences ($D_{Os} - D_{Pt}$) and ($D_{Os} - D_{Re}$), are found in some experiments on solid/liquid iron alloy partitioning at atmospheric pressure—but only when the concentration of non-metallic light elements (e.g. S) in the liquid is much higher than it is thought to be in Earth's outer core. The light element concentration of the liquid is a dominant factor controlling siderophile element partitioning in partially molten iron alloys, with solid/liquid partition coefficients increasing strongly with the light element concentration (e.g. Jones and Malvin, 1990; Chabot and Jones, 2003). In sulfur-bearing systems, which have been the most extensively studied, D_{Os} exceeds 25 only for sulfur concentrations in the liquid approaching 20 wt.% or more (Fleet et al., 1999; Chabot et al., 2003). Even higher concentrations are necessary in order for ($D_{Os} - D_{Pt}$) to exceed 25 and ($D_{Os} - D_{Re}$) to exceed 10 (Fleet et al., 1999; Chabot and Jones, 2003). These sulfur concentrations are much too high to be relevant to Earth's outer core, where the light alloying component must account for less than 12% of the mass, regardless of the mixture of light elements (Williams and Knittle, 1997; Alfè et al., 2002). Chabot and Jones (2003) found that in many cases siderophile partition coefficients could be parameterized very simply in terms of the molar fraction of pure iron in the liquid relative to ferrous-light element species, regardless of the identity of the light element (S, P, C or a mixture of these). Osmium and rhenium in carbon-bearing alloys were later found to be inconsistent with this simple parameterization (Chabot et al., 2006), but their solid/liquid partition coefficients are lower than in S or P bearing systems at the same mole fraction of light species. Hence, in the systems that have been studied to date, at atmospheric pressure and the appropriate light element concentrations, Os is not compatible enough to produce an outer core with sufficiently fractionated Pt/Os and Re/Os ratios.

The present study was undertaken to determine whether pressure has a significant influence on the partitioning behavior of Os, Re and Pt, and whether the pressure effect is in the direction of increasing or decreasing compatibility. Multi-anvil experiments were performed to determine partition coefficients between solid and liquid metal alloys in a single bulk composition in the Fe–S system, over a wide range of pressure, from 3.3 to 22 GPa. Walker (2000) reported partitioning experiments at 10 GPa on a range of Fe–Ni–S–P bulk compositions, with results generally similar to those at atmospheric pressure. The results presented here are also generally similar to those of Walker (2000), but reveal a systematic influence of pressure on the partitioning behavior of all three elements. Os, Re and Pt all become less compatible as pressure increases, therefore making it more difficult to fractionate the elements during inner core crystallization. The effect of pressure on the partitioning behavior is shown to be consistent with the Blundy and Wood (1994) model, in which local elastic strain

resulting from the misfit of an atom on the crystal lattice has a strong influence on the partitioning behavior.

2. Experimental methods

The starting mix was composed of 93 wt.% Fe and 7 wt.% S, to which approximately 1 wt.% each of Os, Re and Pt were added. The doping level was chosen to be high enough that high-precision, high spatial resolution analyses of the solid could be made using the electron microprobe, in order to avoid sampling portions of the solid that were not in partitioning equilibrium with the liquid during the experiment. The diffusive length scale in solid iron alloys at the conditions of these experiments is only on the order of 10 μm or less (Watson and Watson, 2003; Yunker and Van Orman, 2007); thus crystallization during the experiment is expected to have been a nearly fractional process, with only the outer rim of the solid in partitioning equilibrium with the liquid. The concentrations of Os, Re and Pt in our solid run products ranged between 8.3 and 17.4 wt.% (2.7–5.9 at.%), above the regime where Henry's Law behavior has been established in similar systems (up to ~3 wt.%; Chabot et al., 2003). It is possible that the dopant concentration has some influence on the partition coefficients determined in our study, but it is unlikely that this effect is large. The solid run products in the experiments of Walker (2000) had concentrations of Os, Re and Pt that were a factor of two or more higher than the highest values in our experiments, but the partition coefficients obtained from these experiments are similar to those determined by Chabot et al. (2003) at trace levels (albeit at different pressures; 10 GPa and 1 atm, respectively).

Metallic iron (99.99% pure; Alfa Aesar) and troilite (FeS, 99.99% pure; Alfa Aesar) powders were used to prepare the Fe–S bulk composition. The dopants (99.99% pure; Alfa Aesar) were added to the starting mix as metal powders, and to ensure homogeneity the whole mix was ground in an agate mortar for at least an hour. The grain size of the powdered starting mix is believed to have been less than ~10 μm . After grinding, the starting mix was kept in a desiccator.

High-pressure, high-temperature experiments were performed in multi-anvil presses (MA-6/8 module) at the Geophysical Laboratory. Experiments at 3.3 GPa and 18–22 GPa were performed using “Presnall-type” and “Walker-type” presses, respectively. Experiments at 3.3 GPa were performed in cast MgO octahedral pressure cells (Ceramacast; Aremco Products Inc., NY, USA) with fins that had an effective edge length of 18 mm. The furnace assembly in this type of cell consists of a thick zirconia sleeve (that acts as a thermal insulator) surrounding a straight graphite furnace with inner MgO–Al₂O₃ spacers and dense 4-bore alumina sleeves for the thermocouple leads. To ensure near anhydrous runs, the MgO octahedra, zirconia and thermocouple sleeves, and inner ceramics were fired in air at 1000 °C for at least 2–3 h just before the experiment. After construction, the entire cell was kept at 110 °C in a conventional oven. Tungsten carbide (WC) second-stage anvils with 11 mm edge length truncations were used to impart pressure on the cell. Sample pressure versus press load calibrations for the 18/11 (octahedron edge-length/truncation of the carbide cubes) were done using identical cell configuration, employing quartz-coesite, calcium germanate garnet/perovskite and pure fayalite, and coesite–stishovite mixtures. Further details on these aspects are reported in Corgne et al. (2007). On the basis of the pressure brackets reported in Corgne et al. (2007), the precision in pressure measurement in the experiments reported here is believed to be ± 0.2 GPa.

Experiments at higher pressures (18–22 GPa) were conducted using pre-cast MgO+5%–Cr₂O₃ octahedral pressure cells with an edge length of 8 mm. The furnace assembly in this type of cell consists of a lanthanum chromite thermal insulator that surrounds a straight, fringed Re-foil (0.0015" thick) that acts as a resistance furnace, inner MgO–Al₂O₃ ceramics, and dense 4-bore alumina sleeves for the thermocouple leads. Prior to each experiment, the pressure cell, thermal sleeve, and inner

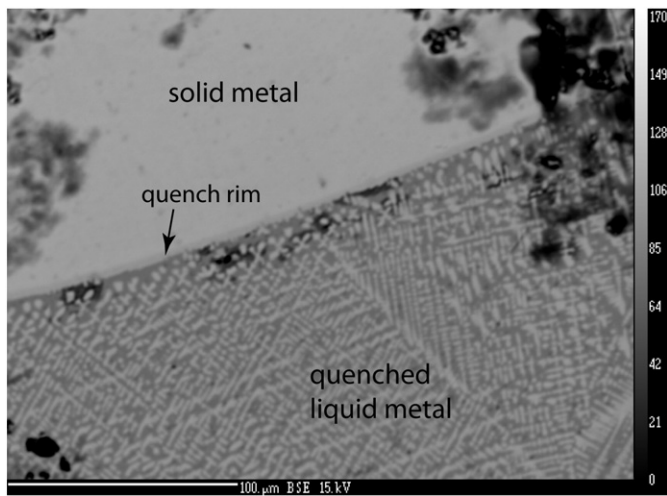


Fig. 1. Backscattered electron image of experiment M747 (18 GPa, 1750 °C). Note the thin, slightly darker rim on the solid metal, which is interpreted as a quench precipitate and was avoided when analyzing the solid.

ceramics were fired in air at 1000 °C for at least 2–3 h, and after construction the cell was kept at 110 °C. Pressure on the cell was imparted using WC anvils (Toshiba grade F) with 3 mm edge length truncation with pyrophyllite gaskets. Pressure calibration for the 8/3 (octahedron edge-length/truncation of the carbide cubes) cells at high temperature were done using the pyroxene–majorite, wadsleyite+stishovite–ilmeneite, and ilmenite–perovskite transitions in MgSiO_3 . Further details on the cells and calibration are given in Bertka and Fei (1997).

Polycrystalline MgO capsules, chosen as containers because they are unreactive with iron alloy systems over a wide range of conditions, were machined and drilled from pure MgO rods. For the 3.3 GPa experiments, approximately 0.8–1 mg of the starting mix was loaded in an MgO capsule that was ~2 mm long prior to compression. To minimize temperature gradients, the total length of the sample at 3.3 GPa did not exceed 1 mm. At 18–22 GPa, the total length of the MgO

capsule was ~1 mm prior to compression, and the sample length was less than 0.7 mm. To prevent leaking of the sample from the MgO capsule during the experiment, some MgO powder, which had initially been dried at 1000 °C for 12 h, was also loaded on top of the MgO capsule. Finally, an alumina plug encased in an MgO sleeve was used to close the cell and position the sample within the hot spot of the furnace. Temperatures in all the experiments were measured using type-C ($\text{W}_{26}\text{Re}-\text{W}_5\text{Re}$) thermocouples and were controlled to within ± 2 °C. The thermocouple was positioned along the axis of the pressure cell, and was in contact with the MgO capsule. Temperatures reported here have not been corrected for the effect of pressure on the thermocouple emf. On the basis of thermal gradient measurements in nearly identical assemblies (van Westrenen et al., 2003) using the same presses at the Geophysical Laboratory, the difference in temperature between the thermocouple junction and sample is estimated to have been less than 30 °C in the 18/11 experiments, and less than 50 °C in the 8/3 experiments. At 3.3 GPa, the cells were compressed at 0.75 GPa/hr and decompressed over a course of 6–7 h. At higher pressures, cells were brought to pressure and decompressed over a period of 10–24 h.

In all the experiments reported here, the temperature of a particular run was raised at 100 °C/min. To ensure dissolution of the Re, Os and Pt and avoid the formation of nuggets, the temperature was raised at least 50 °C above the liquidus (for the pure Fe–S composition; see Fei et al., 1997, 2000) and held there for 15–30 min before being lowered slowly, at 5 °C/min, to the target temperature. At the target temperature, the total run duration in all but one experiment ranged from 2 to 4 h. During each experiment reported here, the power, temperature, voltage, and current all were stable. Each experiment was quenched by shutting off the power, and cooled at an initial rate of 500–600 °C/s. After the run, the sample was mounted and ground longitudinally (i.e., along the axis of the pressure cell) for optical and electron microprobe examination. Run products were ground first in water using SiC (240–600 grit) paper. Subsequently, samples were brought to a mirror polish using water-based agglomerated alumina (3–0.25 μm) paste.

Compositions of the run products were determined using JEOL-JXA 8900 microprobe with five wavelength dispersive spectrometers at the Geophysical Laboratory. Concentrations of Fe and S were

Table 1
Experimental conditions and results

	LO317 22 GPa 1775 °C 6 min	M746 18 GPa ~1775 °C ^a 2 h	M747 18 GPa 1750 °C 2 h	PR-331 3.3 GPa 1370 °C 3 h	PR-334 3.3 GPa 1325 °C 3 h	PR-258 3.3 GPa 1300 °C 4 h
Quenched liquid (wt.%)	N=26	N=15	N=22	N=34	N=48	N=25
Fe	83.59±0.56	83.29±1.13	87.23±0.39	82.95±0.44	80.06±0.37	78.57±0.25
S	13.42±0.79	12.62±0.92	9.69±0.37	11.83±0.52	17.30±0.42	20.51±0.24
Re	0.775±0.143	0.784±0.105	1.09±0.39	1.116±0.047	0.477±0.019	0.089±0.011
Os	0.482±0.108	0.571±0.081	0.851±0.045	0.745±0.039	0.269±0.016	0.120±0.017
Pt	0.608±0.247	0.854±0.100	1.042±0.033	1.337±0.054	1.064±0.039	0.285±0.017
Total	98.87	98.12	99.90	97.99	99.18	99.58
Solid (wt.%)	N=9	N=7	N=11	N=23	N=30	N=24
Fe	91.72±3.21	91.75±1.11	91.49±0.48	82.24±1.74	83.35±1.34	92.05±2.06
S	0.453±0.029	0.373±0.024	0.384±0.015	0.024±0.015	0.029±0.017	0.046±0.019
Re	3.718±1.090	3.581±0.249	3.439±0.253	6.567±0.428	5.919±0.548	3.121±0.872
Os	2.857±0.930	3.329±0.185	3.391±0.161	6.400±1.107	4.823±0.433	2.824±0.843
Pt	2.196±0.317	2.695±0.153	2.437±0.134	4.441±0.517	5.838±0.552	2.399±0.294
Total	100.94	101.73	101.14	99.67	99.96	100.44
Partition coefficients (mol%)						
D_{Fe}	1.240±0.020	1.225±0.021	1.160±0.008	1.185±0.010	1.306±0.012	1.416±0.007
D_{S}	0.038±0.003	0.033±0.003	0.044±0.002	0.0025±0.0015	0.0021±0.0013	0.0029±0.0004
D_{Re}	5.39±1.99	5.06±0.79	3.49±0.32	7.03±0.57	15.54±1.73	42.38±5.64
D_{Os}	6.65±2.77	6.46±1.04	4.41±0.32	10.26±1.98	22.45±2.60	28.19±4.27
D_{Pt}	4.06±0.96	3.50±0.48	2.59±0.17	3.97±0.49	6.87±0.760	10.24±0.69
Mol% S in liquid	21.69±1.16	20.73±1.41	16.07±0.58	19.70±0.79	27.20±0.57	31.17±0.31

Uncertainties for the solid and liquid concentrations are reported as two standard deviations and two standard deviations of the mean, respectively. Uncertainties in partition coefficients were determined by propagating the error in the solid and liquid concentrations, and are reported as 2σ .

^a The thermocouple failed during this experiment, and the temperature was estimated based on its correlation with output power in previous experiments using the same assembly. Based on the measured S content in the liquid, the temperature estimate appears to be high by ~50 °C.

determined using pyrite as a standard, and pure element standards were used for Re, Os and Pt. Operating conditions were 15 kV accelerating voltage and 30 nA current (at the Faraday Cup). Counting times were 30 s and 15 s, on peak and background, respectively. Counts to concentrations were reduced with the ZAF correction procedure.

The quenched liquid portion of the charge had a dendritic texture, but optical and backscattered electron images (Fig. 1) revealed no evidence for Pt–Re–Os-enriched nuggets. Prior to quenching, the liquid should have been uniform in composition, since diffusion in Fe–S liquids is sufficiently rapid (Dobson, 2000) to homogenize the charge within the first few minutes of the isothermal anneal. To reconstruct the liquid composition, concentrations of the elements were determined in raster mode with a square area 50 μm on a side being scanned during each analysis. Fifteen to forty-eight separate analyses were made, covering as much of the quenched liquid portion as possible. The composition of the liquid was taken to be the average of the raster analyses, and the standard deviation of the mean was taken to represent the uncertainty. The solid metal was analyzed in spot mode, with all reported analyses performed within 10 μm of the interface with the liquid. Metal that appeared to have precipitated on the solid rim during the quench (Fig. 1) was avoided during analyses of the solid metal. Seven to thirty separate analyses were made, and in this case the standard deviation (rather than the standard deviation of the mean) was taken as a measure of the uncertainty. Phase compositions in the quenched experimental charges, retrieved solid/liquid partition coefficients and their associated 2σ uncertainties are presented in Table 1.

3. Results

The solid/liquid partition coefficients determined in this study are listed in Table 1, and plotted against the molar sulfur concentration in the liquid in Fig. 2. As in previous studies of highly siderophile element partitioning in sulfur-bearing alloys, the partition coefficients determined here increase strongly with the sulfur concentration in the liquid. The curves shown in Fig. 2 are derived from the model presented by Chabot and Jones (2003), with the 3.3 GPa data fit to the model by least squares. The Chabot and Jones model parameterizes the solid-metal/liquid-metal partition coefficient as a power-law function of the molar fraction of iron in the liquid, relative to light-element-bearing species (in this case FeS):

$$D_{\text{molar}}(1-X_S) = D_0[(1-2X_S)/(1-X_S)]^{-\beta} \quad (1)$$

where D_{molar} refers to the partition coefficient based on molar concentrations in the solid and liquid, X_S is the molar fraction of sulfur in the liquid, D_0 corresponds to the partition coefficient in the pure sulfur-free system, and β describes the sensitivity of the partition coefficient to the sulfur concentration in the liquid. The partition coefficients for Os, Re and Pt are systematically lower at high pressure than at 3.3 GPa; the pressure dependences are consistent with a lattice strain model, as discussed below.

In Fig. 3, the partition coefficients determined in this study, as functions of liquid sulfur content, are compared to those obtained by Walker (2000) at 10 GPa and those compiled by Chabot and Jones (2003) from experiments at atmospheric pressure. The partition coefficients for Os and Re at 3.3 GPa are similar to the prior results. The Pt partition coefficients from this study at 3.3 GPa are slightly but systematically higher those reported by Walker (2000) and Chabot and Jones (2003).

4. Discussion

4.1. Modeled Os isotope composition of the outer core

The partition coefficients for Pt, Re, and, most importantly, Os, decrease significantly with pressure between 3.3 and 22 GPa—i.e. they

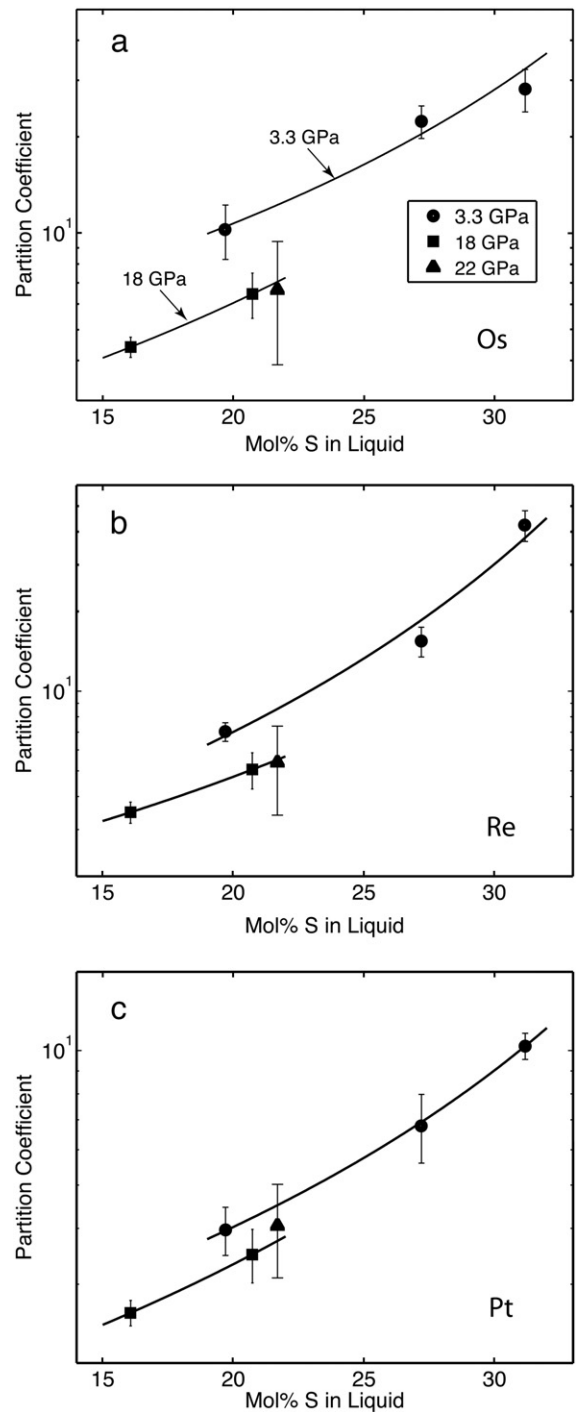


Fig. 2. Partition coefficients (in mol%) from this study plotted against the molar sulfur concentration of the quenched liquid. The curves are fits of the Chabot and Jones (2003) model to the 3.3 GPa and 18 GPa data, as described in the text.

move in the wrong direction to produce strong fractionations in Pt/Os and Re/Os during crystallization of Earth's inner core. We calculated the Os isotope composition of the outer core based on a simple, extreme model in which inner core crystallization is a perfectly fractional process, and in which the inner core reaches its present size very early in Earth history (4.5 Ga). These assumptions maximize Pt/Os and Re/Os fractionation and radiogenic ingrowth, and thus lead to the highest outer core $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios, for a given set of partition coefficients. The results are plotted and compared with Os isotope data for plume-related lavas in Fig. 4. In our calculations we used the same initial $^{186}\text{Os}/^{188}\text{Os}$, $^{187}\text{Os}/^{188}\text{Os}$, $^{187}\text{Re}/^{188}\text{Os}$, and $^{190}\text{Pt}/$

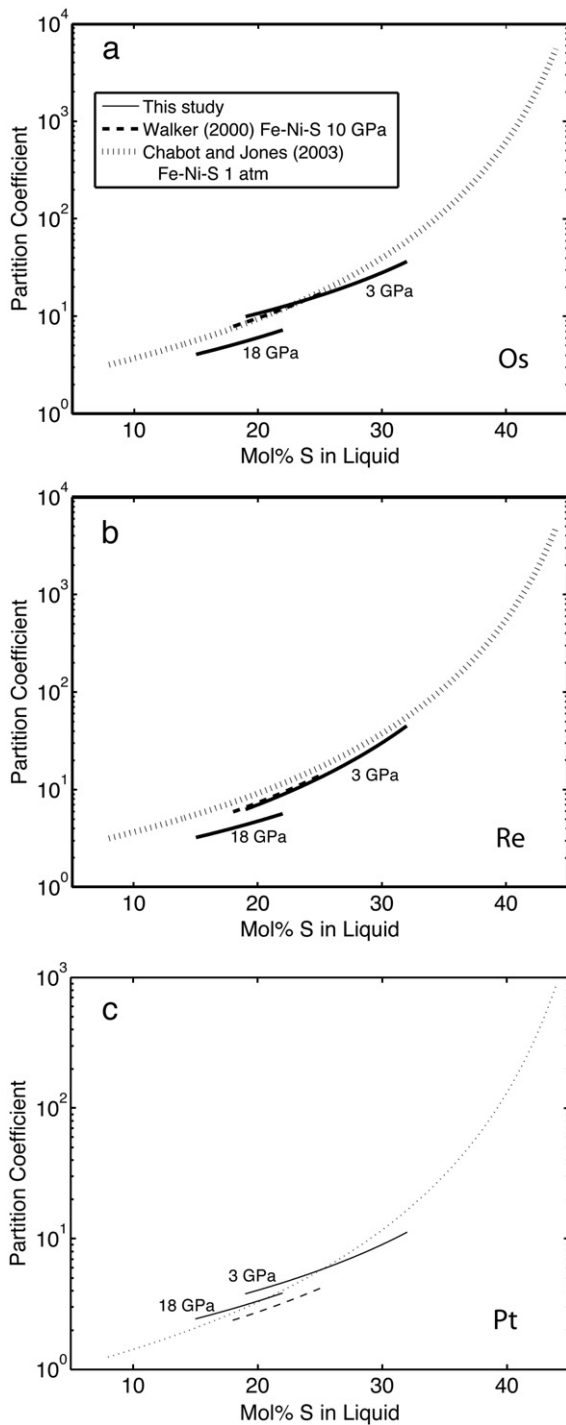


Fig. 3. Comparison of partitioning data from this study with 1 atm (Chabot and Jones (2003), and references therein) and 10 GPa experimental data (Walker, 2000). The curves are fits to the Chabot and Jones (2003) model.

^{188}Os for the bulk core used by Brandon et al. (2003) in their modeling (their Table 2). The inner core was assumed to undergo instantaneous fractional crystallization (5.5%) that modified the $^{187}\text{Re}/^{188}\text{Os}$ and $^{190}\text{Pt}/^{188}\text{Os}$ ratios in the outer core, after which the $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios in the outer core evolved by simple radiogenic ingrowth over a period of 4.5 billion years. The partition coefficients used to calculate the fractionation due to inner core crystallization were adjusted to correspond to a liquid sulfur content of 12 wt.% (the maximum light element concentration in the outer core) using the model of Chabot and Jones (2003). For the experiment at 22 GPa

(13.42 wt.% S in the liquid) the regression parameters (D_0 and β) determined from the 18 GPa experiments were used to adjust the data to the reference S concentration; the adjustment is insensitive to the precise values of the parameters used because the extrapolation to the reference concentration is small.

The maximum $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios calculated for the outer core, based on the partition coefficients determined in the present study and those of Walker (2000) for the Fe–Ni–S system, are not high enough to explain the elevated ratios in plume-related lavas. At 22 GPa the partition coefficients are such that inner core crystallization changes the Pt/Os ratio of the outer core by only 11%, and the Re/Os ratio by only 6%. After 4.5 billion years of closed system evolution, the $^{186}\text{Os}/^{188}\text{Os}$ ratio is only 0.0012% higher than it would be in the absence of inner core crystallization, and the $^{187}\text{Os}/^{188}\text{Os}$ ratio is only 1.4% higher. In terms of the elastic model discussed below, the systematic decrease with pressure in chemical fractionation and Os isotope ratios between 3.3 and 22 GPa is expected to continue to higher pressures. Therefore, if partition coefficients determined experimentally for sulfur-bearing metallic systems are appropriate for chemical fractionation of the core, it is unlikely that the outer core could evolve appropriately radiogenic Os isotope ratios due to inner core crystallization.

4.2. Elastic model

The highest pressure studied here is more than a factor of two higher than has been studied previously, but still more than an order of magnitude lower than pressures relevant to inner core crystallization (~330–364 GPa). To have any confidence in extrapolating the data to inner core pressures it is essential to consider the physical mechanism(s) responsible for the observed negative influence of pressure on the solid/liquid partition coefficients. It is not possible in a strict sense to separate the effect of pressure from the effect of temperature, because these vary simultaneously at constant liquid S content. However, in the context of the elastic model presented below, pressure appears to be the primary influence on Os, Re and Pt partition coefficients.

In contrast to silicate mineral/melt systems, where the liquid often has a small influence on the partitioning behavior and the dominant factor is the elastic strain that results from the misfit of an ion on its lattice site in the mineral (e.g. Blundy and Wood, 1994), the liquid

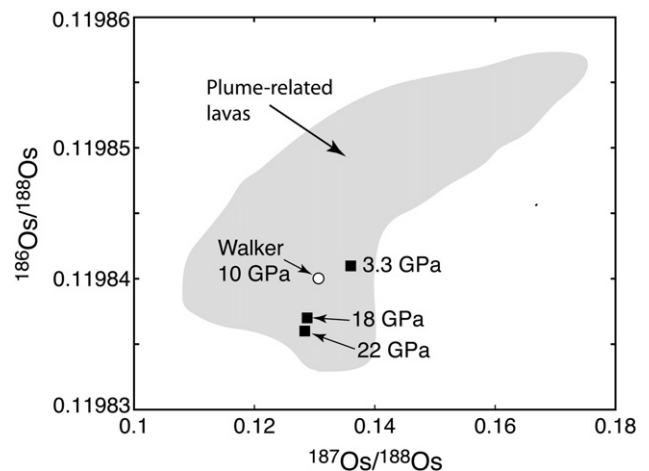


Fig. 4. Calculated maximum $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios in the outer core based on experimental high-pressure partition coefficients from this study (squares) and the Walker (2000) study (circles), adjusted to 12 wt.% sulfur in the liquid. The grey field represents plume-related lavas (Walker et al., 1997; Brandon et al., 1999; Brandon et al., 2003; Puchtel et al., 2005). The calculations assume rapid fractional crystallization of the inner core at 4.5 Ga, followed by closed-system isotopic evolution of the outer core up to the present day.

clearly dominates the partitioning behavior of highly siderophile elements in the Fe–S system. It is possible that at higher pressures the Fe–S liquid repels highly siderophile elements less effectively; i.e. that the exponent β in the Chabot and Jones parameterization (Eq. (1)) decreases with pressure. Owing to the limited range of S concentrations in the liquid in our study, especially at the higher pressures, β is not well constrained and it is not possible to determine whether its value for Os, Re or Pt varies significantly with pressure. Experiments covering a much larger range of liquid S content might allow the effect of pressure on β to be resolved.

Although the liquid dominates the partitioning behavior of highly siderophile elements in the Fe–S system, lattice strain of the solid should also play a role—and it offers a plausible explanation for the decrease in Os, Re and Pt partition coefficients with pressure. The influence of lattice strain on the partitioning of these elements may be important despite the strong control of the liquid composition because all are excluded from the Fe–S liquid to a similar extent; i.e. they all have similar values of β at atmospheric pressure (Chabot and Jones, 2003). At the relatively low liquid S contents in most of the experiments reported here the partition coefficients are not very sensitive to small variations in the value of β . The atomic radii of Os, Re and Pt, based on the crystallographic data tabulated by Wyckoff (1963) for the pure metals, are 0.1352 nm, 0.1375 nm, and 0.1387 nm, respectively, at room temperature and pressure (Os and Re are hcp metals and have c/a ratios slightly smaller than the ideal value, indicating that the atoms are not precisely spherical; the spherical atomic radii are estimated based on the unit cell volume, assuming the ideal c/a ratio). These atoms are all larger than iron, which has an effective radius of 0.1241 nm at room temperature and pressure (Wyckoff, 1963). Platinum, the largest of the three highly siderophile elements studied here, has the greatest misfit on iron lattice sites, and the lowest partition coefficient; the misfit for Os is the least, and it has the largest partition coefficient. Upon compression, the radii of all of the atoms decrease. Osmium, rhenium, and platinum are very incompressible metals, with bulk moduli of 435 GPa (Voronin et al., 2005), 360 GPa (Zha et al., 2004), and 277 GPa (Fei et al., 2007), respectively, at room temperature and pressure, compared to the more compressible γ -iron with a bulk modulus of ~ 155 GPa (Anderson and Isaak, 2000). Therefore, as pressure increases the lattice sites in iron compress at a rate that is greater than that for Os, Re or Pt atoms. This results in an increasing misfit of each atom, and is consistent with a decrease in the solid/liquid partition coefficient with pressure (Fig. 5a). The rate of decrease in the partition coefficient with pressure correlates with the bulk modulus (Fig. 5b), which is also consistent with lattice strain having a significant influence on solid metal/liquid metal partitioning. Fig. 5c shows detailed calculations of the lattice site mismatch for Os, Re and Pt in fcc (γ) iron at the conditions of two of the experiments reported here (3.3 GPa/1370 °C and 22 GPa/1775 °C, respectively). The effective atomic radii were calculated at the pressure and temperature of interest based on the thermal equations of state of Boehler et al. (1990) for Fe, Voronin et al. (2005) for Os, Zha et al. (2004) for Re, and Fei et al. (2007) for Pt. The lattice site mismatch increases with pressure for all elements, consistent with the observed decrease in solid metal/liquid metal partition coefficients with pressure.

Further evidence for the influence of solid elasticity on the partition coefficients is the consistency of the results with the lattice strain model developed by Blundy and Wood (1994). The equation for the partition coefficient in this model, for a given set of experimental conditions (e.g. P and liquid S concentration), is:

$$D_i = D_0 \exp\left(-4\pi EN_A \left(\frac{r_0}{2}(r_i - r_0)^2 + \frac{1}{3}(r_i - r_0)^3\right) / RT\right) \quad (2)$$

where D_0 is the partition coefficient for an atom with the ideal radius (i.e. one with the same radius as a neutral Fe atom at the conditions of interest), r_i is the radius of the atom, r_0 the ideal radius, E is the

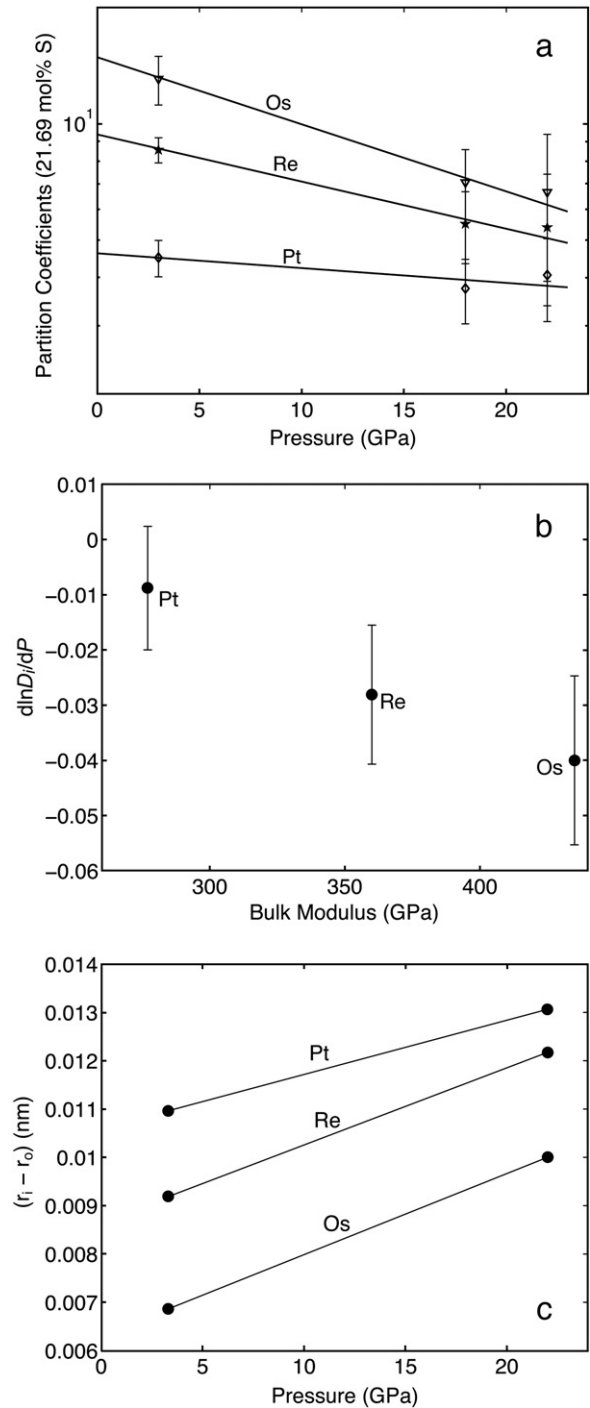


Fig. 5. (a) Partition coefficients (mol%) from this study, at a fixed liquid sulfur concentration of 21.69 mol%, plotted versus pressure. The data at 3.3 GPa and 18 GPa were interpolated/extrapolated to 21.69 mol% S along the curves shown in Fig. 2. The lines show least-squares fits to the data. In (b) the pressure dependence of the partition coefficient for Os, Re and Pt are plotted against the bulk moduli of the close-packed pure metal at room temperature and pressure (Pt: Fei et al., 2007; Re: Zha et al., 2004; Os: Voronin et al., 2005). In (c) the lattice mismatch of Os, Re and Pt in solid iron, calculated as the difference between the radius of the atom and the radius of an Fe atom in the pure fcc (γ) metal, are shown at 3.3 GPa/1370 °C and 22 GPa/1775 °C. The atomic radii are based on the lattice parameters of the pure metals at the pressure and temperature of interest, calculated using the thermal equations of state of Boehler et al. (1990) and Anderson and Isaak (2000) for fcc-Fe; Voronin et al. (2005) for Os; Zha et al. (2004) for Re; and Fei et al. (2007) for Pt. Note that Pt has the greatest misfit in the fcc-Fe lattice at both PT conditions, and Os the smallest, consistent with their relative partition coefficients, and that the misfit for all atoms increases with pressure, consistent with the observed decrease in solid/liquid partition coefficients with pressure.

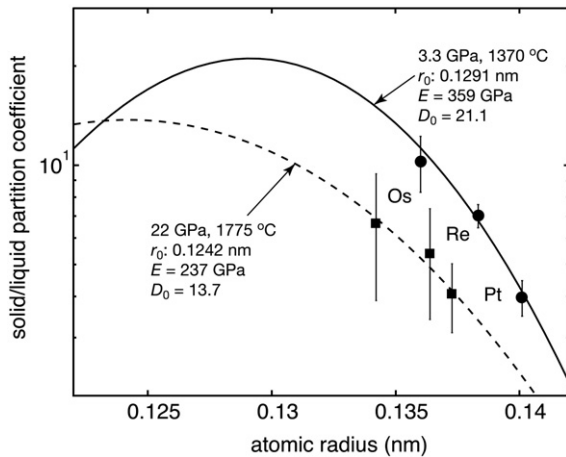


Fig. 6. Partition coefficients (mol%) for Os, Re and Pt from experiment PR-331 (3.3 GPa, 1370 °C) and LO317 (22 GPa, 1775 °C) plotted on a semi-log scale versus the calculated atomic radius at the pressure and temperature of each experiment. The curves are two-parameter fits to the elastic model of Blundy and Wood (1994), as described in the text. The ideal atomic radius is set to the neutral atomic radius of iron in the fcc phase at the *PT* conditions of the experiment; *E*, the apparent Young's modulus, and *D*₀, the partition coefficient for an atom with ideal radius, are the fit parameters.

apparent Young's modulus, N_A is Avogadro's number, R is the gas constant, and T is temperature (in K). Fig. 6 shows the Os, Re and Pt partitioning results from experiments at 3.3 GPa/1370 °C and 22 GPa/1775 °C, along with model curves that are two-parameter fits to Eq. (2). The two parameters fit to the data are D_0 and E ; the ideal radius, r_0 , is taken to be the radius of an iron atom at the pressure and temperature of interest, inferred from the unit cell volume according to the Boehler et al. (1990) equation of state for γ -Fe. The atomic radii of Os, Re and Pt are also calculated at the pressure and temperature of interest, based on the equations of state for the pure metals as referenced above. The model fits to the data are quite good, and the effective Young's moduli are reasonable, but due to the similarity in atomic radius of the three elements there are fairly large uncertainties in the fit parameters ($\sim 25\%$ error in D_0 and E at 3.3 GPa/1370 °C, and $\sim 100\%$ error at 22 GPa/1775 °C). One puzzling feature of the data is that the best-fit value of E is higher (and the parabola thus has higher curvature) at lower pressure. The opposite trend is expected, since the bulk modulus of γ -Fe increases from ~ 145 GPa at 3.3 GPa/1370 °C to ~ 230 GPa at 22 GPa/1775 °C (Anderson and Isaak, 2000). Due to the large uncertainty in fitted values of E the trend is not clearly resolved, and it thus seems premature to speculate on possible reasons for it.

If lattice strain is responsible for the pressure dependence observed in this study, then the decrease in partition coefficients with pressure is expected to continue to even higher pressures. The greater compressibility of iron relative to Os, Re and Pt would lead to a continuously increasing misfit of these atoms on lattice sites in iron, and thus a continuous decrease in solid/liquid partition coefficients. At pressures of 18–22 GPa and liquid sulfur concentrations near or beyond the maximum light element concentration of the outer core, D_{Os} , $(D_{Os}-D_{Pt})$ and $(D_{Os}-D_{Re})$, are already too small for inner core crystallization to produce significantly radiogenic Os isotope signatures over the age of the Earth. Increasing misfit of Os, Re and Pt in the Fe lattice at higher pressures would drive the partition coefficients (and their differences) to even smaller values, resulting in even less fractionation. Therefore the present data set, in combination with other published experimental studies, does not support the idea that the outer core is a source of radiogenic Os isotopes.

Many uncertainties remain regarding the partition coefficients that are relevant to inner core crystallization. In this study, solid iron was stable in the fcc (γ) structure at the conditions of the experiments, while the inner core is likely to have an hcp, or possibly bcc structure.

The fcc/hcp transition may have an influence on partitioning, but it seems unlikely that this influence is large. The experiments of Chabot et al. (2003) included conditions where the bcc (at high temperatures and low S concentration) and fcc (at lower temperatures and higher S concentrations) phases were stable, but a discontinuity in partition coefficients across the bcc/fcc boundary was not observed. One would expect a larger difference in partitioning between the bcc and fcc phases than between fcc and hcp, since the coordination environment differs, and in general there are much greater differences in properties (diffusion and creep strength, for example) between bcc and close-packed metals than between fcc and hcp metals (Frost and Ashby, 1982).

This study focused on sulfur as the light element in the liquid, while other light elements, notably oxygen and silicon, may be significant constituents of Earth's outer core. It is possible that O and/or Si in the liquid exclude Os, Re and/or Pt even more effectively than S does, boosting the Os partition coefficient into the range that would allow large Re/Os and Pt/Os fractionations. Even in this case, the lattice strain effect is expected to depress the partition coefficients at high pressures.

5. Conclusions

We have determined a significant influence of pressure on the solid/liquid partition coefficients for Os, Re and Pt in the Fe–S system. The partition coefficients, at the same sulfur concentration in the liquid, drop by a factor of two between 3.3 and 22 GPa for Os, by $\sim 60\%$ for Re and by $\sim 10\%$ for Pt. The pressure dependence of the partition coefficient correlates with the bulk modulus of the element, and is consistent with an increasing misfit of the neutral atoms on lattice sites in solid iron. The partition coefficients, and differences among them, in particular D_{Os} , $(D_{Os}-D_{Pt})$ and $(D_{Os}-D_{Re})$, are too small for inner core crystallization to produce sufficiently radiogenic Os isotope ratios in the outer core, even if inner core crystallization happens very early in Earth history. The differences in partition coefficients are expected to decrease further at higher pressures, due to an increasing misfit of Os, Re and Pt in solid iron. Systems that involve non-metallic light elements other than S, especially O and Si, are worthy of investigation, but it appears likely that solid/liquid partition coefficients in all systems will decrease with pressure due to an increasing lattice site mismatch of Os, Re and Pt in solid iron.

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