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Core participation in mantle geochemistry: Geochemical Society Ingerson Lecture, GSA Denver, October 1999

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Abstract—The siderophile element problem in mantle geochemistry has not been solved by treating the mantle as the residue of core formation in a closed system. Conventional solutions to the problem involve the addition of new material to the mantle as late accretions from outer space. However more solution options are open if the core can return a little material to the mantle from inside. The notion that such a return flux of material from the outer core is occurring is suggested by the correlated anomalies in $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ seen in some plume materials by R. J. Walker and his colleagues (R. J. Walker et al., 1995; R. J. Walker et al., 1997; Brandon et al., 1998; Brandon et al., 1999). These isotopic anomalies could result from ^{190}Pt and ^{187}Re decay in the liquid outer core following Pt-Re-Os fractionation during crystallization of the solid inner core. Partition coefficients determined for solid/liquid metal fractionation of Pt, Re, and Os at 100 kbar are consistent with those required to produce the correlated Os isotope anomalies. Oxide exsolution from cooling and crystallization of a saturated liquid outer core provides a mechanism to reimplant the Os signal back into the mantle. Other siderophile elements may have their mantle abundances boosted by this process. The details of the reimplantation process present a worthy challenge for evaluation. *Copyright © 2000 Elsevier Science Ltd*

1. INTRODUCTION

It has been known for many years that the formation of the core has imprinted a large geochemical signal on the mantle; the mantle being slag residual to the smelting process that formed the core. Ringwood (1966) was an early exponent of the view that the footprint upon the siderophile elements was not strictly what was expected. The modest and highly siderophile elements (HSE) are depleted in the accessible mantle by comparison with their expected abundance in a chondritic Earth. Depletion is expected in smelting. But the HSE are quantitatively not depleted enough for the mantle to be explained as the residual silicate from an iron-producing smelting regime.

The depletion of moderately siderophile (Ni, Co) and highly siderophile elements (Au, Pt, Ir, etc. . . .) is not as large as expected for metal/silicate equilibrium at pressures sufficiently low to reduce oxidized Fe from silicates and oxides into neutral metal through the action of H_2 or C. Ni abundance in mantle silicates is greater than 1000 ppm, whereas in pallasite meteorites, which record a low-pressure metal-silicate equilibrium, the Ni abundance in olivine drops to a few ppm. Furthermore, the relative fractionations expected—of Ni from Co, or Ir from Au—in a metal/silicate equilibration process have not occurred. Ni is a factor of 10 more siderophile than Co and should be comparably more depleted in the mantle, but it is not. The overabundance of some siderophile elements compared to the expectations from low pressure fractionation, as well as the puzzling absence of relative fractionations between pairs like Ni and Co, are known collectively as the "siderophile element problem" in mantle geochemistry.

Many proposals for explaining the problem exist. For instance it might be more appropriate to use the depletion factors for metal sulfide liquids rather than those for solid Fe metal in modeling the initial stages of any terrestrial smelting process (e.g., Brett, 1984). Likewise it is possible that core formation was not completely efficient at removing smelted material from the mantle and that subsequent oxidation has reincorporated this material into the silicate mainstream of the mantle (e.g., Jones and Drake, 1986). A particularly effective remedy for some aspects of the siderophile element problem is the continued accretion of material to the Earth after the bulk of core formation occurs. The late material, if oxidized, may avoid being incorporated into the core. If it is chondritic in relative abundance of siderophile elements, it will give a depleted mix by mixing with depleted material, but a mix overabundant in HSE relative to smelting and of little relative fractionation of the HSE. Forms of this heterogeneous accretion model have been proposed by Chou (1978), Jagoutz et al. (1979) and Wanke et al. (1984). It is difficult to imagine that this process does not occur at some level because late accretion still occurs now. Nevertheless heterogeneous accretion has not been universally embraced for a number of reasons, including the need to dispose of an embarrassing amount of sulfur if a late salting of chondritic siderophile elements is boosting the inventory of mantle HSE. Many combinations of these paliatives for the siderophile element problem have been attempted with mixed results (Newsom, 1990; O'Neill, 1991).

Murthy (1991) set the community on a different track with his suggestion that the operative distribution coefficients for core formation were not those then available from low pressure and temperature laboratory study or meteorite studies. Instead, in a magma ocean phase of primordial terrestrial differentiation, much higher temperatures would be relevant to the fractionation of the siderophile elements between core and mantle protoliths. He predicted, using a questionable formulation, that

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the partition coefficient Ds of the HSE would decrease to about the level needed at about 3000–3500 K to successfully interpret the imperfectly depleted mantle abundance patterns. Predictably Murthy's formulation was questioned. Jones et al. (1992) and O'Neill (1992) took Murthy to task for neglect of pO_2 and they rejected his prediction of decreasing HSE Ds with temperature as unsound. They regarded high T as a step in the wrong direction. Thus it was a surprise when D. Walker et al. (1993) actually demonstrated decreasing Ds for fractionations of several siderophile elements up to 3100 K qualitatively consistent with the prediction of Murthy (1991). This demonstration was not a vindication of Murthy's formulation nor was it a complete rejection of the thermodynamics of Jones et al. (1992) and O'Neill (1992). Walker et al. (1993) believed that the decrease of HSE Ds was only a secondary consequence of high T. Mutual solubility increases of the metal and silicate liquids and melt structure changes with high T were the primary agents in driving the Ds toward unity. Constancy of pO_2 or FeO in the silicate fraction is not a relevant constraint on the behavior with temperature of coexisting masses of terrestrial metal and silicate. Although FeO in the silicate mass should be constrained by the mantle's composition at the end of the accommodation, FeO in the silicate of a silicate-metal assemblage will shift with temperature. Thus a narrow focus on sound thermodynamic extrapolation at constant pO_2 or constant FeO in silicate can be just as misleading in evaluating expectations of core/mantle fractionations as the use of an unsound formulation.

Murthy's (1991) paper stimulated much experimental work directed at understanding the siderophile element problem through the discovery of alternate physical conditions where the D values would give the appropriate mantle siderophile element abundances without resort to heterogeneous accretion. In this effort it was shown that pO_2, $a_{(SiO2),}$ $a_{(C)}$, pS_2, pressure, and T were all significant variables (Schmitt et al., 1989; Holzheid et al., 1994; Jones and Jurewicz, 1994; Walter and Thibault, 1995; Hillgren et al., 1996; Li and Agee, 1996; Jana and D. Walker, 1997a–c, 1999). Particularly attractive, elegant, and nearly convergent solutions to the siderophile element problem were outlined by Li and Agee (1996), and Righter et al. (1997). Their solutions involved the simultaneous increase of both T and pressure well beyond the conventional choices to 2000–2500°C and 200–300 kbar under which extreme conditions the applicable D values would provide an acceptable solution. Li and Agee (1996) showed experimentally that Ni and Co had D for liquid metal/liquid silicate drop to similar low values at 250 kbar and extrapolated this result to be the expected behavior for other elements. Righter et al. (1997) parameterized the existing experimental data base for a wider range of siderophile elements and found an acceptable extrapolated solution in generally the same window of pressure, temperature as Li and Agee, although there were differences in detail. The physical scenario of their proposed differentiations was the primordial terrestrial magma ocean. Smelted metal accumulating at the ocean's base would do its metal/silicate partitioning at the high pressure and temperature of the ocean's floor before descending through the lower mantle to form the core. The high pressure fractionation solution to the siderophile element problem seemed practically inescapable when Tschauner et al. (1997, 1999) reported diamond anvil cell (DAC) measurements of D_{Ni} and D_{Co} between perovskite and iron metal to 800 kbar.

As found by Li and Agee for liquid state metal/silicate partitioning, Tschauner's solid state partitioning also showed convergence of D_{Ni} and D_{Co} to each other and to near unity near a megabar. Ni and Co would be indifferently absorbed by the core metal from the mantle and no great siderophile element fractionations would be effected by high pressure transfer of material to the core. This simple, harmonious picture was somewhat soured by the further investigations of Tschauner et al. (1998) which demonstrated that other siderophile elements such as Mo, Mn, Cr, and V failed to follow the systematics shown by Ni and Co.

Thus it is likely that the high pressure, high T solution will fail to completely fix the siderophile element problem. This result is anticipated from the precedent of all the previous "fixes" which have failed as more evidence accumulates. We will probably be left scrabbling about checking for combinations of mechanisms that can in concert have the desired effects on as many elements as we have the strength to consider. In such a game of "alternatives evaluation" it is important to have as many of the alternatives identified as possible. Broadly the ones we have been considering for solution of the mantle's siderophile element problem are these.

1. The mantle can spawn the core under some set of physical conditions and be left with the budget of siderophile elements that it has.
2. The mantle spawns the core but cannot have the siderophile elements it does without input of additional material from above through delayed heterogeneous accretion.

It is the purpose of the present paper to highlight another potential part of the solution.

3. The mantle spawns the core but the mantle subsequently receives additional material from below—the core is not a passive, sealed siderophile element dump.

Four recent bodies of work suggest that ongoing core participation in mantle geochemistry may not be unthinkable. R. J. Walker et al. (1995, 1997) and Brandon et al. (1998); Brandon et al. (1998) have presented evidence that there is a small return flux of material from the outer core to the mantle. The evidence is an excess of ^{187}Os relative to ^{188}Os positively correlated with excess ^{186}Os relative to ^{188}Os in some plume volcanic rocks. $^{187}Os/^{188}Os$ anomalies presumably arise from ^{187}Re decay and $^{186}Os/^{188}Os$ anomalies from ^{190}Pt decay. The excesses could conceivably be generated within old crust because crustal rocks have elevated Re/Os and Pt/Os ratios compared to the mantle (e.g., Schmidt and Palme, 1999). However Os anomalies are very difficult to achieve in mantle-derived lavas by crustal recycling because the crustal abundances of the PGE are so low compared to mantle materials (Brandon et al., 1998). Also crustal Re/Os is more elevated compared to the mantle than is Pt/Os. The reverse would need to be true to generate the correlated anomalies seen without additional fractionation and special timing in the recycling process. This is because the low isotopic abundance and long half life of ^{190}Pt require more Pt/Os enrichment to produce the $^{186}Os/^{188}Os$ anomalies seen. R. J. Walker et al. (1995, 1997) proposed that fractionation in

the outer core from growth of the solid inner core could produce the correct correlated anomalies, and that reinjection of some core material back into the mantle was the most probably cause of the correlated Os anomalies in some plumes. We examine experimentally the proposed fractionation process below and confirm its plausibility.

McDonough (1995) sought alternatives to the terrestrial late chondritic veneer for understanding mantle siderophile element anomalies because the analogous veneer seems to be absent from the moon. Like R. J. Walker et al. (1995, 1997) he also proposed that material escaping the core could contribute to the siderophile element budget. From the constancy of Sn/Sm and Ti/Pd ratios in basalts and komatiites of Archean and younger ages, however, he proposed that this transfer must have occurred earlier in the Hadean and was not ongoing to the present. There is not necessarily a contradiction between this inferred early timing of transfer and the observation of the ^{187}Os and ^{186}Os anomalies in Phanerozoic plume volcanism. A reconciliation would require either the Os signals to have been stored in the mantle for some time or else the currently active transfer from the core be so small as to be non-perturbing of the Sn/Sm and Ti/Pd ratios.

In the oral presentation based on the abstract of Carlson et al. (1999) excess ^{107}Ag was reported in one of the Hawaiian lavas that showed $^{186/188}$Os excesses. The authors interpreted this excess as derived from ^{107}Pd decay. Because Ag is less siderophile than Pd, the low Ag/Pd of the core would show the ^{107}Ag excess more than would the higher Ag/Pd of the mantle. The observed ^{107}Ag excess requires prompt core formation to take advantage of short-lived ^{107}Pd (half life 6.5×10^6 y) and requires material to be returned from the core to the mantle for the excess to be seen.

A more extreme version of the core-is-a-player-in-mantle-geochemistry scenario has been proposed by Snow and Schmidt (1998). HSE abundances measured in some MORB-related gabbros are nonchondritic and would seem to require very substantial core involvement on the HSE budget of the samples. It remains to be demonstrated how representative their samples are of MORB mantle and how quantitative are their fire assay HSE extractions. If these issues are satisfactorily resolved then it is clear that 3 above must be a very important agent in resolving the siderophile element problem. However the Pt-Re-Os isotopic systematics of similar abyssal peridotites examined by Brandon et al. (2000) offer little support for core involvement.

In the remainder of this paper the following questions are examined. What are the Pt/Re/Os fractionations expected in crystallizing metal from the liquid core of the Earth? Do they plausibly generate Pt/Re/Os ratios compatible with growth of the observed correlated ^{187}Os and ^{186}Os anomalies? Can we devise a plausible mechanism for delivering any signal generated in the core back into the mantle?

2. PT-RE-OS FRACTIONATION

The observed ^{187}Os and ^{186}Os anomalies require radiogenic Os growth in a reservoir which has been modestly enriched in Re/Os and strongly enriched in Pt/Os relative to chondritic. The differences in the relative enrichments required for Re/Os and Pt/Os arise from the scarcity of the ^{190}Pt isotope compared to ^{187}Re and its longer decay time. R. J. Walker et al. (1995, 1997) proposed that crystallization of solid iron metal from liquid alloy would give the correct sense of Pt-Re-Os fractionation. Their proposal was based upon the IIA iron meteorite suite's natural crystallization experiment. Pernicka and Wasson (1987) and Morgan et al (1995) measured and modeled the abundance of several HSE as if their variation were caused by fractional crystallization of Fe alloy. From the slopes of compositional arrays on log-log variation diagrams, the ratio of the partition coefficients can be inferred. Of course the crystallization of small asteroidal cores may not be an appropriate pressure, temperature analog for crystallization of the terrestrial core. The present data base for experimental high pressure partitioning of siderophile platinum group elements (PGE) between iron metal and liquid is limited. The pioneering study to near 100 kbar of Fleet et al. (1991) measured 6 siderophile PGE (including Pt and Os, but not Re) and the study of Wang (1993) tackled Ir. Fleet et al. (1991) found for Pt and Os partitioning between solid metal and near-eutectic sulfide liquid at 85 kbar that $D_{Os}/D_{Pt} = 6$. This is the same as the D_{Os}/D_{Pt} inferred from the slope of a log Os/log Pt plot for fractionated type IIA iron meteorites of Pernicka and Wasson (1987). The pressure and the sulfur and the Ni content of IIA meteorite fractionation are quite different from the conditions of the Fleet et al. study. Because the D ratios are the same, it is encouraging to think that the effect of pressure is minor and that these partition coefficients behave in a tractable manner which can be discovered by experiment without undue complication. But the absolute values of D_{Os} and D_{Pt} are almost an order of magnitude greater in Fleet et al. (1991) than would be inferred from the IIA meteorites for an assumed $D_{Ir} = 14$ (Morgan et al., 1995). This difference in absolute values can be anticipated to result from the much higher sulfur contents of the liquid in Fleet et al (1991) according to the formulation of Jones and Malvin (1990). The absolute values of Ds must be known to scale the expected ^{186}Os/^{188}Os and ^{187}Os/^{188}Os enrichments in the outer core. Thus more work is required on the partitioning systematics at high pressure to determine the absolute values of D_{Os} and D_{Pt}. Fleet et al. (1991) did not measure D_{Re} but Fleet et al. (1999) measured D_{Re}, D_{Os}, and D_{Pt} at 1 bar and low temperatures near 1200°C where sulfur contents of the liquids approach the eutectic. Low pressure studies of Ir, Re, and Os by Jones and Jurewicz (1994) and Pt and Os by Lauer and Jones (1998) have extended partitioning Ds for these elements to higher temperatures and lower sulfur contents. Fleet et al. (1999) made the very valuable contribution of determining the partitioning of a wide range of PGE at near-natural abundance by activation analysis. This study was an important community calibration point of comparison between studies done by electron microprobe analysis with PGE at minor element levels and those done at the more difficult but more relevant trace abundance levels by activation. Fortunately, it was shown that partitioning behavior across the range of abundance studied was internally consistent and that there were no obvious departures from Henrian behavior in this system. [This is not the same as showing ideal behavior!] Nevertheless, the D_{Re} values determined were at low pressure and high S. Higher pressure and lower S values for D_{Re} were reported by Jana and D. Walker (1997b), but the relevance to core crystallization was still marginal because the fractionation was not between crys-

talline metal and S-rich metal liquid but for liquid S-poor metal vs. S-rich liquid metal. The immiscible liquid partition coefficients obtained by Jana and D. Walker (1997b) are in reasonable apparent extrapolated agreement with D_{Re} of Fleet et al. (1999) at very high sulfur. Nonetheless a uniformly collected high-pressure partitioning data set on the 3 principal HSPGE elements of interest Os, Re, Pt would be a useful complement to the existing data.

Experience with already-known siderophile elements and known partitioning dependencies is an important guide to forming a strategy for exploring Pt-Re-Os partitioning systematics. Jones and Malvin (1990) showed that partitioning of all known siderophile elements in Fe-Ni-S-P could be understood much better as a consequence of nonmetal interaction in the liquid phase than as temperature dependence. Cooling solid metal/liquid sulfide (±phosphide) assemblages changes the partition coefficients. But the compositional change in the liquid has a much stronger effect on siderophile element partitioning than the intrinsically weak temperature dependence. For instance, the large Ds for Pt and Os found by Fleet et al. compared to the inferences from IIA iron meteorites could be a very natural consequence of the high sulfur abundance in their experimental near-eutectic liquids. Much sulfur in the liquid causes much S-avoidance and consequently high Ds both for Pt and Os which take preferential residence in the S-free metal. Jones and D. Walker (1991) extended this conclusion for several siderophile elements to 80–150 kb: Liquid composition is the principal determinant of siderophile element partitioning between metal and metal-sulfide liquid, not temperature or pressure. Thus, a study of partitioning systematics of Pt, Os, and Re will most plausibly explore the compositional dependencies involved. [This is in contrast to the case for partitioning of siderophile elements between metallic and silicate liquids where Li and Agee (1996) and Tschauner et al. (1999) have demonstrated important pressure dependencies. Evidently, the low compressibility of metallic melts compared to silicate melts renders their partitioning behavior with respect to similarly low compressibility metal rather pressure-insensitive.] Our strategy is to measure Pt, Os and Re abundances in assemblages of γ iron and polymetallic sulfide/oxide/phosphide liquids quenched from a variety of temperatures (1350–1500°C) relevant to producing a range of liquid compositions in the neighborhood of 100 kbar. Pt, Os, and Re abundances were doped to electron microprobable levels.

Pressure of 100 kbar is a nontrivial benchmark that is routinely achievable on large sample volumes in a multianvil environment. We achieved this pressure with the use of 250 tons thrust on a 6 mm TEL assembly (D. Walker, 1991). It is not, however, the pressure at the inner/outer core boundary, being over an order of magnitude lower. It is chosen so that routine multianvil techniques can be used to explore high-pressure compositional systematics in detail on a uniformly treated set of experiments for determining D_{Os}, D_{Re} and D_{Pt}. Although it is beginning to be possible to do meaningful geochemical partitioning experiments in diamond anvil cells at near-megabar pressures as shown by the recent heroic endeavors of Tschauner et al. (1999), such efforts on Pt, Os, and Re are remote. The principal uncertainty in the application of compositional systematics discovered at multianvil pressures to problems for which diamond anvil pressures are more relevant is likely to be with respect to the identity of the phase of solid iron involved. It may not be the γ iron we shall be studying. The difficulty in finding agreement in the current literature on the identity of the solid Fe polymorph (γ,ε,β, or δhcp) expected in the core suggests that it is premature to expect diamond anvil cell (DAC) experiments to be of much assistance in resolving the fine structure of PGE partitioning variations. [Compare e.g., Saxena and Dubrovinski (1997); Yoo et al. (1995); Yoo et al. (1997); Andrault et al. (1997), and Mao et al. (1998).] We anticipate that the identity of the solid iron phase will be rather less important than the composition of the liquid in determining the partitioning systematics anyway. We anticipate this because in sulfur-carbon-oxygen-free partitioning of siderophile elements between Fe liquid and Fe solid, most Ds are close to one: the phases of nonmetal-free iron as different as solid and liquid are only marginally selective between themselves with respect to siderophile elements. γ,ε,β, or δhcp are unlikely be more differentially selective.

3. EXPERIMENTAL

The sample preparation and operating procedures previously used successfully by Jones and D. Walker (1991) and Wang (1993) were used with some modifications. The recent work of Majewski and D. Walker (1998) suggests diffusivities in this system are rapid enough that experiments of about half an hour should be of more than sufficient duration to achieve liquid state equilibrium. Run times at pressure and temperature of 2.5 to 26 h were used to be sure. MgO capsules were presintered in situ for about 8 h at pressure and 800°C (below the sulfide eutectic) to seal them against sulfide liquid percolative escape. The use of MgO capsules instead of the graphite used by Fleet et al. (1991), D. Walker et al. (1993), and Jana and D. Walker (1997b) reduced some experimental complications. It is considerably easier to examine the contents of an MgO capsule than one which has been converted to diamond. Furthermore, carbon, like sulfur, has a strong effect on siderophile element partitioning (Jana and D. Walker, 1997a) and it also promotes rogue outcropping of refractory alloy immiscibility which is an undesirable complication for this study. The persistence of only-partly-dissolved Os-Ir nuggets in the Fleet et al. (1991); Fleet et al. (1999) studies was also encountered by Wang (1993) at relatively low temperatures. A particular strategy was adapted to eliminate the nugget problem in the multianvil experiments performed here.

Figure 1 illustrates the configuration of internal components and the placement of starting materials used in our 6 mm TEL assemblies. The $LaCrO_3$ heating tube generates a modest thermal gradient away from the central portion. The charge is placed with its lower end at the hottest portion of the heater. The top portion of the charge is in a cooler region roughly equivalent within the thermal gradient to the position of the thermocouple below the hot spot. The starting material is added as an elemental Fe-Ni-S or Fe-Ni-S-P powder. This powder is first used to fill a small part of the base of the charge. Then small amounts of elemental Pt, Re, and Os powders are added before the remainder of the cavity in the MgO container is filled with the base material. The original bulk compositions of the charges by weight added are given in Table 1.

The placement of ingredients causes redistribution of material in the small thermal gradient at experimental pressure and temperature. Solubility gradient diffusion (also called thermal migration by Buchwald et al., 1985) is a special case of traveling solvent zone refining (Pfann, 1958). It is treated in some detail for complex geological systems by Lesher and D. Walker (1988). In the present case the solubility of solid metal increases with temperature so that liquids in the system migrate through a metal matrix towards regions of higher temperature by solution at the hot side and precipitation of backfill at the cold side of melt parcels. This is in addition to any development of a Soret effect within the single-phase liquid as documented by Majewski and D. Walker (1998). Because the charge has its hot end down, the generation of Soret gradients of compositionally light S-rich liquids at the hot base of the charge reinforces the thermally driven convective stirring of the liquid once the PGE are uniformly dispersed within it.

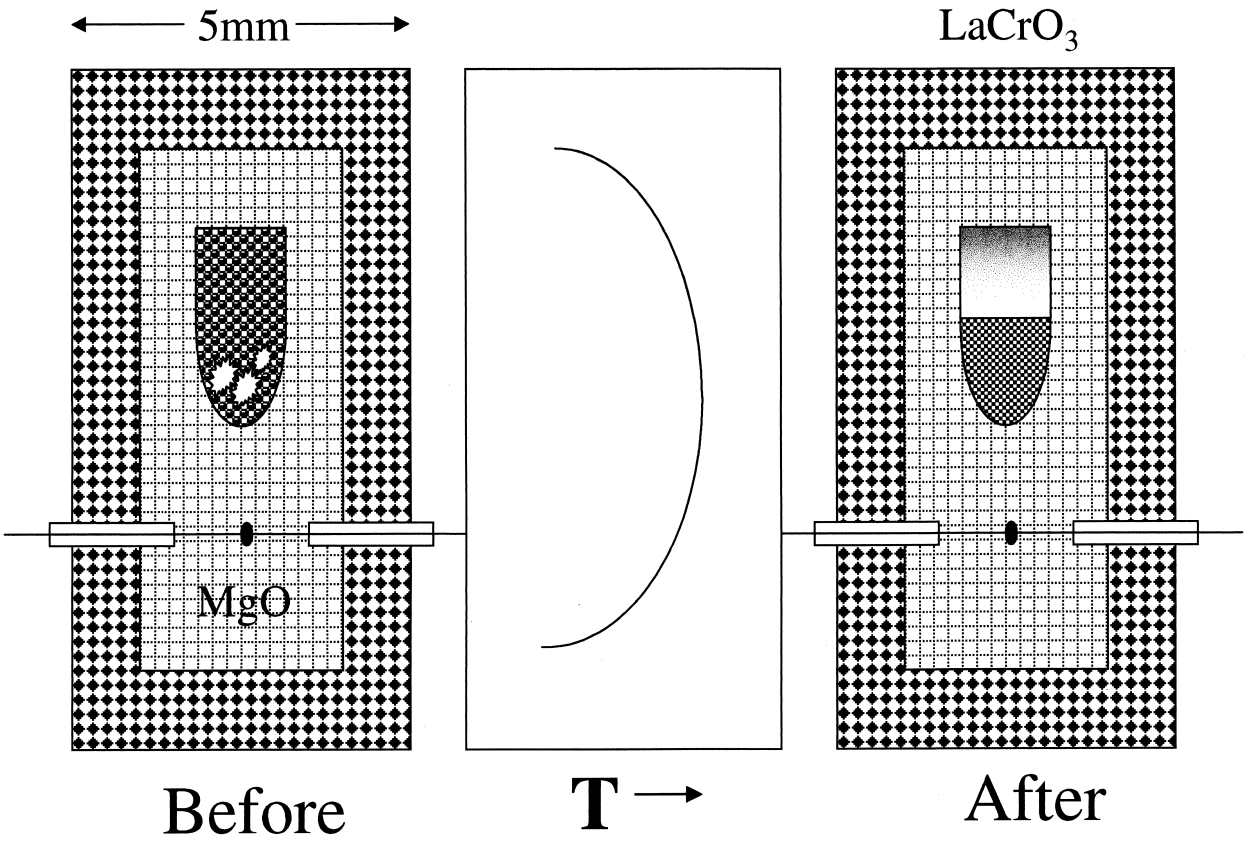

Fig. 1. Cross section through a cylindrical $LaCrO_3$ heater embedded within a 6mm TEL multi-anvil assembly. The 'before' panel shows the initial position of three splodges of elemental Pt, Re, and Os powder within the Fe, Ni, S, and phosphorous mixture in their MgO container. The center panel shows schematic temperature distribution within the heater. The 'after' panel shows the final configuration of quench sulfide liquid beneath zoned, solid Fe alloy. This configuration would have been gravitationally unstable at the experimental pressure and temperature except for the fact that the consolidating solid iron crystals have a firm bond with the capsule top and sides.

The sulfide-rich liquid formed collects at the low end hot spot whereas solid metal alloy compacts against the roof of the charge. This compaction defies gravity. The Pt, Re, and Os initially added to the hot base of the charge remain immersed in corrosive metal sulfide liquid for as long as it takes for them to dissolve. Diffusion in the liquid state transfers them to the cold end of the charge where they are reprecipitated in the metal alloy compacting there. This behavior is in contrast to the situation that develops when PG HSE are initially distributed uniformly through a thermally homogeneous charge. Local alloying of PGE with Fe-Ni produces refractory nuggets that can persist throughout the charge for extended periods making clean analysis of phases after the experiment difficult. This problem has been well documented by Fleet et al. (1991, 1999) and by Wang (1993).

The diffusive redistribution of material into spatially separated single-phase regions is key to the strategy of achieving clean phase analysis. Even so the process is complex. The first solid metal alloys to compact on the charge roof are free of Pt, Re, and Os because the first solid metal grows from local materials. The Pt, Re, Os from the hot end of the charge take time to be dissolved into the liquid phase and be transported to the cold end for reprecipitation in the compacting metal zone. As a consequence there is a very pronounced chemical stratigraphy within the precipitated metal. This zonation is very well preserved in experiments of a day when any zonation within the liquid phase has long disappeared. Thus to discover the Ds, the solid metal analyses must be performed on metal near the interface with the liquid. This strategy must not be followed for the liquid phase which shows a small quench metal depletion and sulfur enrichment a few 10's of μm away from the interface with the metal but is elsewhere homogeneous.

It may seem perverse to attempt to do equilibrium partitioning studies with deliberate growth of zoned metals from heterogeneous starting mixes. Conventional wisdom is that equilibrium is best achieved from homogeneous mixes. Previous attempts by Wang (1993) to study the partitioning of Ir using such a convention-based strategy were made particularly difficult by the persistence in experiments of several weeks duration of nuggets of Ir-Fe alloy throughout the charge. Wang used piston-cylinder techniques with small thermal gradient and exceptional longterm thermal stability to no avail. Each small nugget was compositionally zoned, requiring particular care in the microprobe analyses of codispersed phases and their edges, as in the study of Fleet et al. (1991). The point of the current strategy is to make the zoning in metal macroscopic in scale and to produce a nugget-free liquid. These characteristics materially aid the recovery of clean analyses.

CAMEBAX electron microprobe analyses were performed in raster mode with a 30 μm square raster at 30 kV and 50 nA. Kα lines for Fe, Ni, S, phosphorous, and O and Lα lines for Pt, Re, and Os were compared to elemental standards for all metals and to hematite, pyrite, and GaP for O, S, and phosphorous. The MBXv1.32 operating system of Carl Henderson (University of Michigan) was employed with PAP correction procedures to reduce X-ray intensity ratios to amounts of the elements present. Analytical results are reported in Table 1 as atomic fractions.

4. RESULTS

Figure 2A shows a photomicrograph of charge GG-741 which ran for 12 h at 1400°C at 100 kbar and segregated

Table 1. Experimental partitioning results at 100 kbar.

Bulk composition			Metal	At. Frac.	Liquid	At. Frac.	D	+/−	+/−
	Wt.%	At. Frac.	avg	stdev	avg	stdev mean			%
GG-741 (*12 hours 1400°C*)									
Fe	73.1	0.8034	0.8249	*0.0024*	0.7188	*0.0032*	**1.1**	*0.01*	*1*
Ni	7.7	0.0805	0.0647	*0.0007*	0.0758	*0.0007*	**0.9**	*0.02*	*2*
S	3.8	0.0727	0.0016	*0.0002*	**0.1853**	*0.0040*			
O			0.0000	*0.0000*	0.0000	*0.0000*			
Pt	3.2	0.0101	0.0163	*0.0002*	0.0068	*0.0002*	**2.4**	*0.08*	*3*
Re	5.1	0.0168	0.0482	*0.0011*	0.0078	*0.0002*	**6.2**	*0.29*	*5*
Os	5.1	0.0165	0.0442	*0.0018*	0.0055	*0.0001*	**8.1**	*0.54*	*7*
GG-742 (*11 hours 1500°C*)									
Fe	70.1	0.7922	0.7808	*0.0039*	0.6679	*0.0018*	**1.2**	*0.01*	*1*
Ni	7.5	0.0806	0.0642	*0.0005*	0.0780	*0.0016*	**0.8**	*0.02*	*3*
S	3.6	0.0709	0.0007	*0.0002*	**0.2296**	*0.0025*			
O			0.0054	*0.0061*	0.0029	*0.0012*			
Pt	8.8	0.0285	0.0563	*0.0016*	0.0145	*0.0002*	**3.9**	*0.17*	*4*
Re	5.0	0.0169	0.0378	*0.0020*	0.0033	*0.0000*	**11.4**	*0.78*	*7*
Os	3.3	0.0109	0.0548	*0.0030*	0.0038	*0.0001*	**14.4**	*1.00*	*7*
BB-662 (*26 hours 1350°C*)									
Fe	75.1	0.8050	0.7642	*0.0035*	0.6495	*0.0033*	**1.2**	*0.01*	*1*
Ni	7.8	0.0795	0.0679	*0.0012*	0.0842	*0.0012*	**0.8**	*0.03*	*3*
S	3.9	0.0728	0.0009	*0.0001*	**0.2464**	*0.0045*			
O			0	*0*	0.0007	*0.0003*			
Pt	5.6	0.0172	0.0389	*0.0005*	0.0104	*0.0003*	**3.7**	*0.16*	*4*
Re	3.8	0.0122	0.0576	*0.0009*	0.0044	*0.0001*	**13**	*0.50*	*4*
Os	4.2	0.0132	0.0704	*0.0012*	0.0044	*0.0001*	**15.9**	*0.64*	*4*
GG-729 (*2.5 hours 1400°C*)									
Fe	62.5	0.6751	0.3427	*0.0191*	0.6199	*0.0027*	**0.6**	*0.03*	*6*
Ni	8.0	0.0822	0.0160	*0.0009*	0.0823	*0.0006*	**0.2**	*0.01*	*6*
S	8.0	0.1505	0.0044	*0.0035*	**0.1853**	*0.0013*			
P	1.6	0.0312	0.0004	*0.0005*	**0.0299**	*0.0002*			
O			0.0000	*0.0000*	0.0139	*0.0042*			
Pt	4.5	0.0139	0.0095	*0.0006*	0.0163	*0.0001*	**0.6**	*0.04*	*7*
Re	7.9	0.0256	0.3618	*0.0092*	0.0191	*0.0002*	**18.9**	*0.69*	*4*
Os	6.8	0.0216	0.2652	*0.0078*	0.0154	*0.0002*	**17.3**	*0.71*	*4*
GG-747 (*13.5 hours 1400°C*)									
Fe	68.8	0.6936	0.6100	*0.0120*	0.6131	*0.0023*	**1.0**	*0.02*	*2*
Ni	8.8	0.0844	0.0451	*0.0026*	0.1013	*0.0005*	**0.4**	*0.03*	*6*
S	8.8	0.1545	0.0007	*0.0010*	**0.2081**	*0.0016*			
P	1.8	0.0327	0.0012	*0.0009*	**0.0358**	*0.0003*			
O			0.0020	*0.0056*	0.0179	*0.0025*			
Pt	5.0	0.0144	0.0258	*0.0015*	0.0124	*0.0003*	**2.1**	*0.17*	*8*
Re	3.6	0.0109	0.1801	*0.0085*	0.0072	*0.0002*	**24.9**	*1.84*	*7*
Os	3.2	0.0095	0.1349	*0.0062*	0.0043	*0.0001*	**31.7**	*2.36*	*7*
GG-725 (*16 hours 1450°C*)									
Fe	58.7	0.6611	0.5649	*0.0047*	0.5856	*0.0011*	**1.0**	*0.01*	*1*
Ni	7.5	0.0804	0.0352	*0.0007*	0.0941	*0.0001*	**0.4**	*0.01*	*2*
S	7.5	0.1471	0.0017	*0.0023*	**0.2254**	*0.0005*			
P	1.5	0.0305	0.0002	*0.0005*	**0.0290**	*0.0001*			
O			0.0000	*0.0000*	0.0307	*0.0000*			
Pt	8.6	0.0277	0.0341	*0.0006*	0.0230	*0.0001*	**1.5**	*0.03*	*2*
Re	4.1	0.0139	0.0884	*0.0019*	0.0027	*0.0004*	**33.0**	*5.98*	*18*
Os	11.9	0.0394	0.2755	*0.0048*	0.0094	*0.0011*	**29.2**	*3.89*	*13*

cleanly into zoned metal above and homogeneous liquid below which quenched to a dendritic intergrowth of metal and troilite. A small band of quench depletion of the liquid in metal components is barely visible at the interface between metal and quenched liquid. Also visible in Figure 2A are lines of burn marks left by electron microprobe rasters. The compositional profiles obtained along the right track across all of the metal and liquid are presented in Figure 3.

The high frequency, low amplitude compositional variability seen in the right hand part of Figure 3 reflects the heterogeneity introduced by the growth of quench dendrites from the liquid portion of the charge. The analyses made in the liquid region of the charge with the exception of the 50 μm region near the interface with the crystalline metal are averaged to reconstruct the liquid composition. Table 1 gives these averages. The standard deviation of the mean of these averages is given as a measure of the statistical uncertainty associated with measurement of the average liquid composition. The standard deviation of the mean is a better measure of uncertainty in the pre-quench liquid composition than is the standard deviation of all the measurements which includes the heterogeneity introduced by the quenching process which on spatial average should not

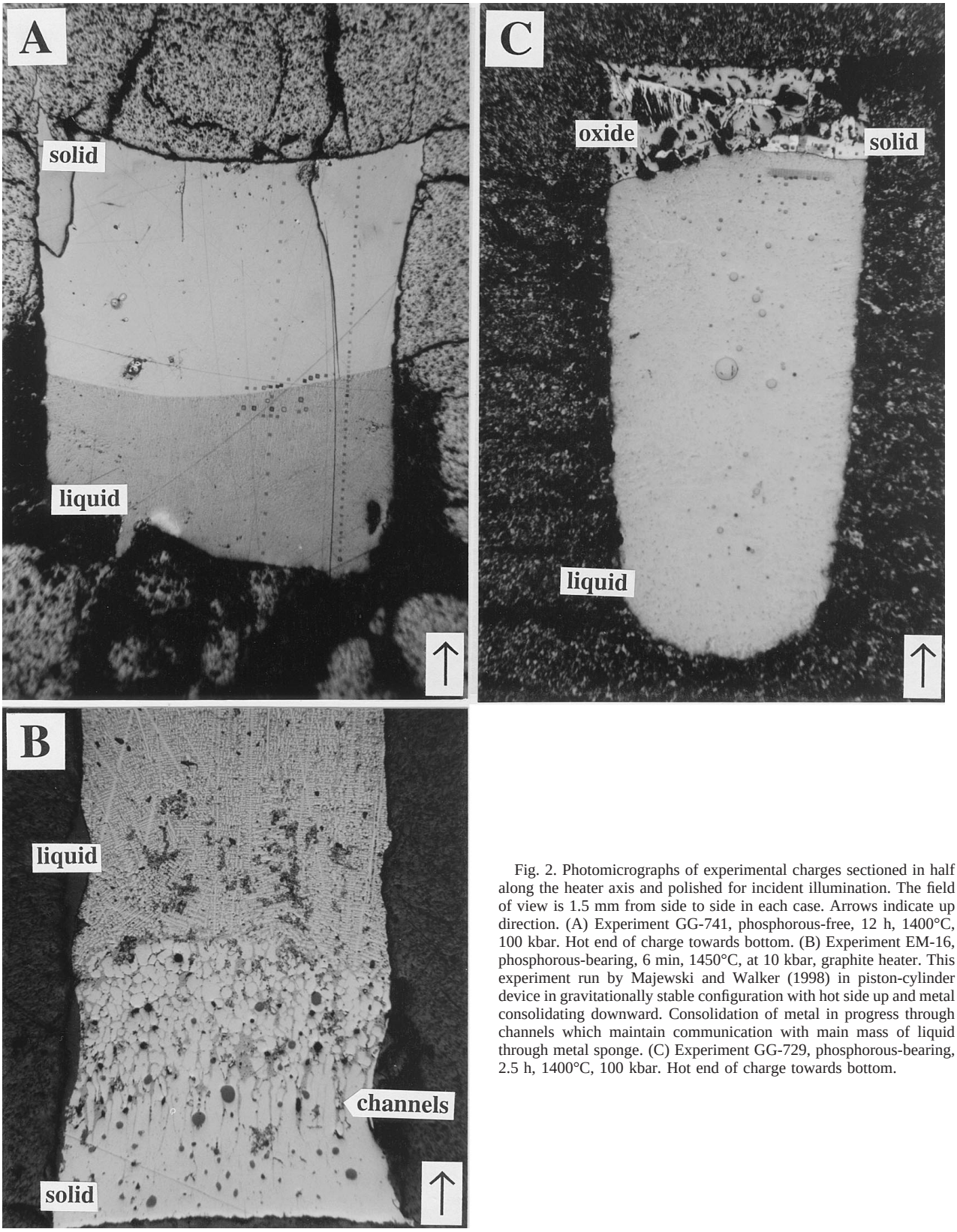

Fig. 2. Photomicrographs of experimental charges sectioned in half along the heater axis and polished for incident illumination. The field of view is 1.5 mm from side to side in each case. Arrows indicate up direction. (A) Experiment GG-741, phosphorous-free, 12 h, 1400°C, 100 kbar. Hot end of charge towards bottom. (B) Experiment EM-16, phosphorous-bearing, 6 min, 1450°C, at 10 kbar, graphite heater. This experiment run by Majewski and Walker (1998) in piston-cylinder device in gravitationally stable configuration with hot side up and metal consolidating downward. Consolidation of metal in progress through channels which maintain communication with main mass of liquid through metal sponge. (C) Experiment GG-729, phosphorous-bearing, 2.5 h, 1400°C, 100 kbar. Hot end of charge towards bottom.

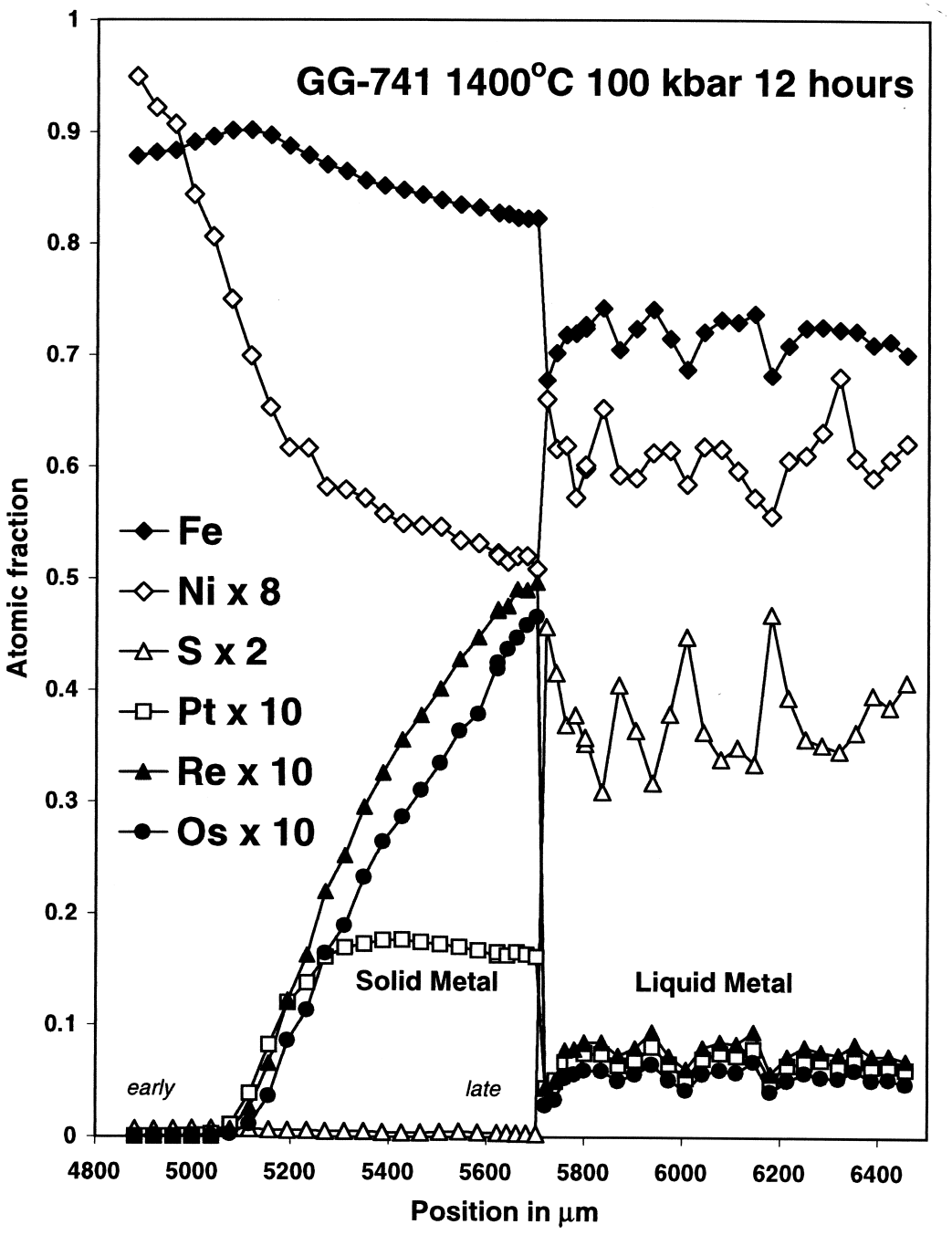

Fig. 3. Compositional profile through charge GG-741 seen in figure 2A. The series of probe burn rasters from top to bottom on the right side of the charge corresponds to this profile from left to right. Metal stratigraphy proceeds from old metal on left to young metal on the right in this figure.

distort the bulk composition of a sufficiently large sampling. To obtain the composition of the metal alloy relevant to the calculation of experimental Ds for this experiment, we average the compositions of rasters taken in the metal, very close to the interface with the liquid. Several such rasters can be seen in Figure 2A. Table 1 gives these averages and their standard deviations. We use the standard deviation because we interpret the small amount of variability encountered near the interface as present at the pressure and T of interest and not as an artifact of the quenching process.

The compositional profiles within the metal show little high frequency noise in contrast to those within the liquid. Yet, there is considerably more total variation in the solid metal which reflects the great change in alloy composition during growth. The zonation patterns displayed in the metal stratigraphy of Figure 3 are typical of the phosphorous-free experiments. The

stratigraphy in the metal has details which result from a complex interplay of dissolution rate of PGE elements into the hot end liquid, diffusive transport of the PGE through the liquid to the cold end metal precipitation zone, and activity-composition effects within the metal phase. For instance, the absence of PGE from the coldest quarter of the metal on the left of Figure 3 is a function of the delay in their arrival in this region from the other end of the charge. The very slightly earlier arrival of Pt means that a combination of its dissolution rate and diffusive transport rate is marginally faster than for Re and Os. Ni decreasing with time in the metal before the PGE arrive must be more of a consequence of its partitioning than its transport behavior because it is initially uniformly present in the basic PGE-free portion of the starting material. Ni/Fe in the first alloy precipitated against the cold roof of the charge is slightly larger than Ni/Fe of the starting material. This is as expected for D_{Ni} slightly greater than 1 which is characteristic of systems of this sulfur content, temperature and pressure (Jones and Walker, 1991). Depletion of the cold end liquids in Ni leads to precipitation of metals with decreasing Ni with time, as observed with the monotonically falling Ni content in the metal with increasing time in the stratigraphy.

How then to understand the fact that the partitioning derived from the interface metal/liquid measurements shows $D_{Ni} < 1$? This is unprecedented for liquids of this sulfur content. However another unprecedented aspect of these experiments is the fact that the metal has more than 10% total PGE which are substantially more siderophile (higher D) than Ni. It is easy to rationalize the anomalous D_{Ni} as a consequence of the competition between Ni and the PGE for sites in the metal. Ni loses the competition. One might view the interactions of Ni with Re and Os as leading to an increase in the activity coefficient of Ni in the solid alloy. It is not that Ni has suddenly become chalcophile; it is just less siderophile than the PGE, and is forced into the liquid with the sulfur it usually avoids. An additional indication that the PGE are the culprits in this anomalous Ni partitioning is that the break in slope of the Ni depletion stratigraphy occurs when the PGE arrive.

The thermal migration process produces single-phase separations of chemically zoned metal and homogenous liquid. Liquid leaves the region that becomes consolidated as single-phase solid metal. It may migrate in connected or unconnected packets. The PGE profiles in the metal are consistent with the existence of open liquid channels connecting the PGE-rich liquid reservoir at the hot end with the front where solidification is being completed. Such open channels are required for PGE transport against the bulk transport direction of the liquid. It is not preordained that liquid pockets remain connected in the consolidating metal sponge. Migration of unconnected liquid blobs in a system of high enough metal/liquid ratio is an alternate mode seen in meteorites (e.g., Buchwald et al., 1985).

The reality of open, thermally migrating liquid channels in this experimental system can be seen in Figure 2B. A charge of the same base composition (but without PGE) was run at a similar temperature, at 10 kbar, in a larger thermal gradient, and with the gradient arranged hot-end-up rather than down, to preserve any Soret effect which might develop. The charge was quenched after 6 min at temperature. The fingering structure resulting from liquid packet migration is by this time well developed between regions which are all metal and those which are all liquid. This fingering structure provides the diffusion transport path for PGE arriving from the hot end in the configuration of the present experiments at much higher pressure. If the melt remained as unconnected, separately-migrating globules as in systems of larger metal/liquid ratio there would be no PGE throughout the bulk of the metal of the experiment because there would be no liquid access path. PGE would remain confined only to those regions of the metal quite near the metal/liquid interface of Figure 2A which were in diffusive communication with the hot end liquid. The process of producing clean regions of single-phase, compositionally zoned metal and homogeneous liquid takes less than 1/2 hour (Majewski and Walker, 1998). The large compositional variation in the stratigraphy of the PGE in the metal grown during that short time is well preserved on the much longer time scale of the experiment. Therefore it is clear that PGE diffusion in solid metal is slow enough to have prevented significant penetration of the solid metal by PGE. The PGE are quickly distributed by diffusion through the liquid channels in the solid sponge and they are locked into their stratigraphic profile by torpid solid state diffusion.

The complexities of the Fe, Ni, and PGE stratigraphic profiles within the solid metal are entertaining but are of limited interest to the present study. Because the liquid achieves uniform composition so quickly (Majewski and Walker, 1998), it is safe to assume that the liquid achieved partitioning equilibrium with the youngest stratigraphic metal surface adjacent to it. That youngest solid metal surface was consolidated from a liquid with the composition measured at the end of the experiment. As an additional indication that partitioning equilibrium between liquid and adjacent metal was achieved, the present Ds for Pt, Re, and Os are in excellent agreement with the low-pressure equilibration results of Jones and Jurewicz (1994) and Lauer and Jones (1998) at comparable sulfur contents as reviewed below. This agreement mutually reinforces the complementary experimental techniques and further supports the conclusion of Jones and Walker (1991) that the Ds have only minor sensitivity to pressure.

5. DISCUSSION

Table 1 provides a summary of the D values recovered from the interface metal and average liquid. These Ds are plotted as a function of the liquid composition in Figure 4. Two series of results, one with and one without phosphorous, plot separately. The function of liquid composition used is that of Jones and Malvin (1990). The J-M parameterization is an analytical template for checking the effects of nonmetal avoidance on partitioning. Straight lines are expected on lnD plots as a function of the J-M parameter. The more S or phosphorous or C or O etc. present, the fewer sites available in the liquid where Ni, Pt, Os, etc. can avoid the nonmetals and the more likely that they will be found in the metal. The $-\ln(1-N_n\alpha_nX_n)$ form reflects the probability of site availability, where α_n is a constant related to the eutectic composition in the Fe-nonmetal (n) system and shown by Jones and Malvin from fitting to be independent of which siderophile element is fit. N_n is a stoichiometric constant based on the expectation that nonmetal n such as sulfur or phosphorous will tie up Fe making FeS or Fe_3P conglomerations in the melt. N_S is then 2 and N_P is 4 and N_O might be 2

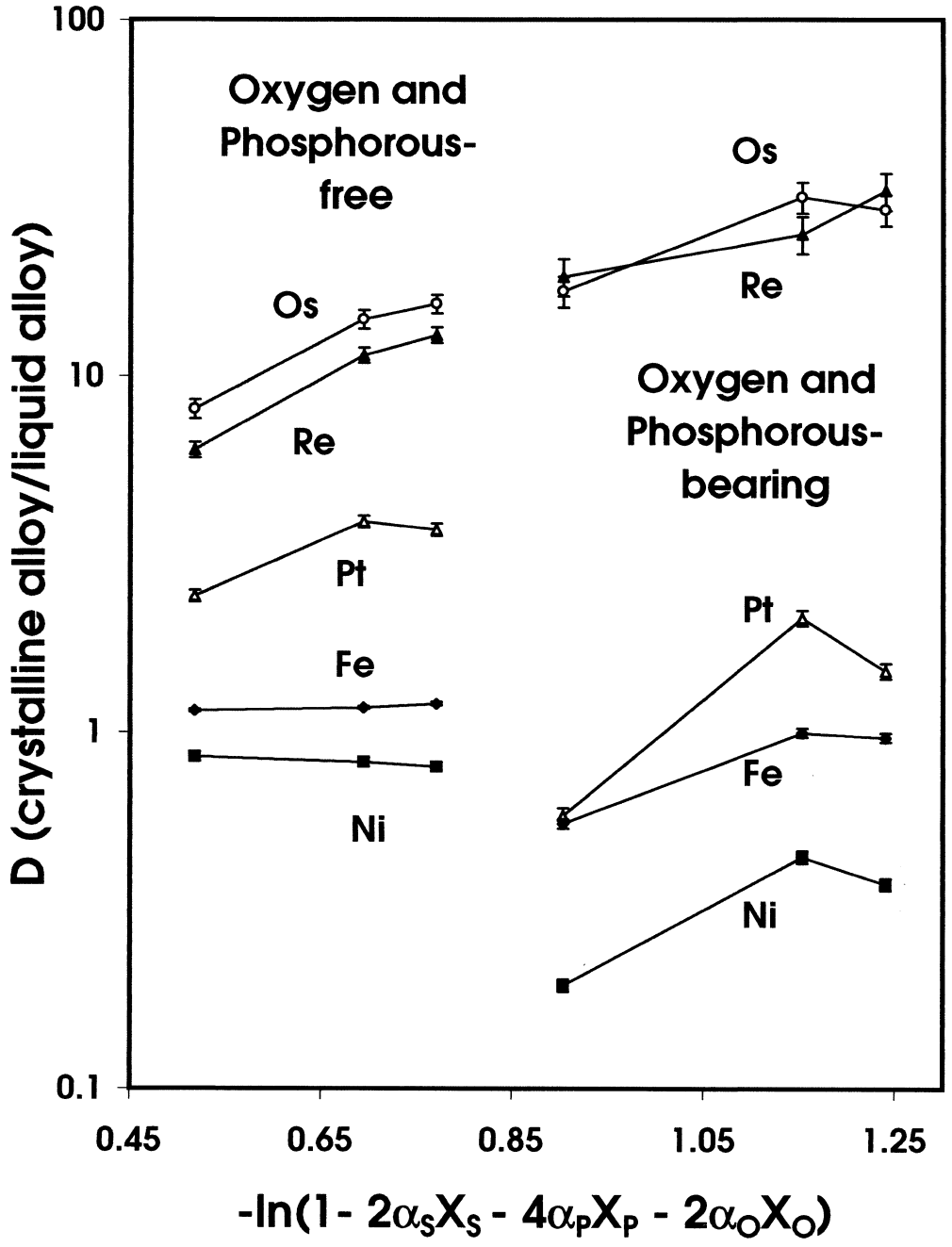

Fig. 4. Summary of partitioning results from Table 1. D(metal/liquid) versus the Jones-Malvin parameter computed to include additive nonmetal interactions from sulfur, phosphorous, and oxygen. Oxygen and phosphorous-bearing charges plot separately in J-M space and have poorer systematics because the phosphorous and oxygen parameters are not well known and the additive combination may not be appropriate at the high abundance of PGE used in these experiments. Nevertheless it is clear that phosphorous and oxygen have a much bigger effect on Pt, Fe, and Ni than on Re and Os.

for FeO units in the melt. The theoretical and microscopic observational basis for this formulation is quite modest and relies on the impressive success of Jones and Malvin in fitting known data with this form.

The range of S contents is the same for both sets of experiments but the extra phosphorous and O are able to bring the phosphorous-bearing experiments to a separate part of J-M parameter space through the large multipliers for phosphorous: $\alpha_P = 1.36$ instead of $\alpha_S = 1.09$ and $N_P = 4$ instead of $N_S = 2$. The phosphorous-free experiments show lower errors in the measurements of individual Ds and show better behavior of the compositional systematics than the phosphorous-bearing experiments. In the phosphorous-free series $D_{Os} > D_{Re} \gg D_{Pt}$ with $D_{Os}/D_{Pt} \sim 4$ and $D_{Os}/D_{Re} \sim 1.3$ for atomic S from 18–25% in

the liquid. This D_{Os}/D_{Re} ratio compares remarkable well with the value of 1.27 used by Morgan et al. (1995) to successfully model the crystallization of group IIA iron meteorites. This correspondence is remarkable because the concentrations of Re and Os are roughly 4 orders of magnitude greater in these 100 kbar experiments than in the low-pressure, most primitive IIA iron meteorites. This suggests the Henrian region may be extensive in this solution and that pressure effects on the Ds are minimal in this range of pressures and Re-Os abundance. Pressure independence for the Ds would be anticipated from that found for Ge, phosphorous, Au, and Ni by Jones and D. Walker (1991).

Lest one imagine some hideous coincidental trade of pressure dependence for composition dependence that renders the appearance of neither having much effect, one may compare these Ds to known 1 bar results. D_{Pt} and D_{Os} values of Table 1 here are in good agreement with the results of Lauer and Jones (1998) in this range of S content. At $X_S = .185$, D_{Pt} of 2.4 compares with 2.6 and D_{Os} here of 8.1 compares with 7.4 in Lauer and Jones. The values for D_{Os} and D_{Re} in Table 1 are numerically quite close to those determined at 1 bar by Jones and Jurewicz (1994). For instance at $X_S = .185$, D_{Re} of 6.2 here compares to 6.9 and D_{Os} of 8.1 here compares to 8.4 in Jones and Jurewicz (1994) which also compares well with 7.4 in Lauer and Jones (1998). Jones and Jurewicz (1994) found that D_{Os}/D_{Re} increased with increasing S in contrast to this study at 100 kbar which shows that D_{Os}/D_{Re} decreases with increasing S. However if the compositional dependence of D_{Os} from Lauer and Jones (1998) is compared to the compositional dependence of D_{Re} from Jones and Jurewicz (1994), D_{Os}/D_{Re} would be expected to decrease slightly with increasing S as found here. Decreasing D_{Os}/D_{Re} is in accord with the natural experiment of the group II irons. Morgan et al. (1995) required that D_{Os}/D_{Re} drop from 1.27 to 0.88 if they were to successfully model the fractionation of IIB irons as a continuation of the IIA series. This is consistent with the drop in D_{Os}/D_{Re} we observe when phosphorous is added to S to make liquids representative of more fractionated systems. The very good quantitative agreement between the group II iron trends and our experimental D_{Os}/D_{Re} suggests that the group II irons form a very good analog of the expected behavior of natural systems even to 100 kbar. Therefore the calculations of R. J. Walker et al. (1995) and Brandon et al. (1998, 1999) on the evolution of the isotopic systems and fractionations expected do not need revision in light of the new results presented here.

This is not to say that there is nothing new here. The unprecedented low values of $D_{Ni} < 1$ for this S content and the flat-to-negative slope for the composition dependence are clearly not consistent with Jones-Malvin systematics and their extension to high pressure (Jones and Walker, 1991). The most plausible explanation for these anomalies is the unusually heavy loading of the PGE into the metal. They are not tracers but major constituents. One may understand the Ni pathology as the result of Ni losing a competition with the more strongly siderophile Os, Re, and Pt for sites in the metal. Or else it can be described as particularly nasty activity-composition relations in the metal solution. Such pathologies are quite common (D. Walker et al., 1993; Jana and Walker, 1997b, 1999; Capobianco et al. 1999). To follow this reasoning the slight decrease in D_{Pt} in the highest-S, phosphorous-free experiment may be a reflection of the modestly siderophile Pt being edged out by the much more siderophile Re and Os for metal site occupancy. Because the effects do not show up in the Ni systematics of the group II irons we are reinforced in the conclusion that the anomalies are an artifact of the experimental loading of PGE near saturation levels. J-M systematics have the best chance of being applicable to the most siderophile elements present and at modest loadings. The example of PGE interference with Ni is an indication that the siderophile elements interact not only with nonmetals but with each other, especially obviously at high concentrations. These interactions are not covered in the J-M formulation. Furthermore the lack of a uniform slope in these PGE plots makes any discussion of the J-M slope parameter β pointless. It is somewhat surprising that these considerations do not disrupt Re and Os systematics.

The phosphorous-bearing experiments are noisier than the phosphorous-free. Even so D_{Os} and D_{Re} crudely follow the extension of the trends established in the phosphorous-free experiments. The D_{Os} and D_{Re} converge to high values scattered about one another. In contrast Pt, Fe, and Ni show a step function change in their behavior between the phosphorous-free and phosphorous-bearing experiments. Fe and Ni are no longer siderophile, having $D < 1$! Clearly something else is at work here besides the addition of phosphorous to the nonmetal inventory. Figure 2C shows a micrograph of a phosphorous-bearing charge. There are several pronounced differences from the phosphorous-free charge shown in Figure 2A. Both charges were run at 1400°C, 100 kbar, and have nearly identical S content in the liquid. The proportion of metal in 2C is an order of magnitude less than 2A. There is a reaction with the MgO container in 2C making magnesiowustite around the edge of the charge although this is difficult to see in this incident illumination presentation. There is a band of wustite compacted at the very top of the charge that obliquely truncates the metal of 2C, and there are some texturally complex metal fingers within the wustite layer. There are spheres of a second immiscible phosphate liquid within the sulfide liquid. These differences can be understood as a consequence of oxygen contamination, the likely carrier being the phosphorous. Use of this material previously did not give these effects and it is likely that the seal on the vial in which it was stored was ineffective; over a shelf life of a few years, atmospheric oxygen and moisture were incorporated into the starting material. Further indication that there is oxygen contamination comes from direct analysis of the liquids. Phosphorous-free runs have virtually no detectable oxygen whereas all 3 of the phosphorous-bearing liquids have from 1.4–3% atomic oxygen present. Care was take to avoid phosphate immiscible liquids with the microprobe rasters so that this oxygen is presumably distributed between Fe, S, and phosphorous species in the sulfide liquid in some unknown manner. Variable oxygen contamination in the phosphorous-bearing data makes the noisiness in the J-M presentation of Figure 4 understandable. Some of the S and phosphorous will not be participating in the FeS and Fe_3P speciations of the J-M formulation, although the mix of SO_2, PO_4, FeO, etc., is unknown. Also unknown is the exact form in which the oxygen is entering as a contaminant. P_2O5, H_2O, etc., are possible but the factor of 2 variation in analysed O compared to the less than 20% variation in phosphorous content suggests that the contaminant is not uniformly distributed with the phosphorous.

This nonuniformity is consistent with a previously well-mixed material being partially contaminated in storage by a leak and then being sampled for the present experiments without further homogenization. Knowing that oxygen is present in the liquid, and how much, the J-M parameterization is extended in Figure 4 to include O assuming FeO-like aggregates ($N_O = 2$) and chosing α_O arbitrarily as 1. The qualitative features of the arrangement of phosphorous-bearing experiments to each other are insensitive to whether just S is included in the J-M parameter or whether phosphorous and O are also included. If only S is used the phosphorous-free and phosphorous-bearing arrays overlap in the J-M parameter. The inclusion of phosphorous and O shifts and separates the phosphorous-free and phosphorous-bearing experimental arrays from each other as in Figure 4.

This unfortunate lapse of laboratory hygiene has some useful lessons. There is the first obvious one that it would have been better to introduce O in a controlled manner by design than by accident so that the systematics controlled by O could be more easily unraveled from those caused by phosphorous. Even so it is clear that O is a player and that at increased pO_2 transfer of Fe and Ni from metal into the liquid and wustite does occur. Figure 4 shows this to be a large effect for Fe and Ni. This is not new or surprising. But Pt seems to also be somewhat vulnerable to this transfer whereas Re and Os show little effect distinguishable from simple extension of the phosphorous-free systematics, which fit the group II iron meteorite systematics. Knowledge that O is a player and its probable effect, whether phosphorous is also involved or not, brings a second lesson. The strong separation of Os from Pt as required to generate $^{186}Os/^{188}Os$ anomalies in the liquid outer core is a very durable feature of all experimental conditions examined by design or accident. We do not expect the Pt/Os fractionations that are so critical to the Os-from-the-core-hypothesis will be diminished by the presence of elevated O in the liquid outer core. Elevated O in the present experiments increases the signal. This is an important lesson because we argue below that elevated O in the core is indeed realistic and may also in fact be responsible in part for the retrieval of the Os isotopic signal from the core. The issue of whether D_{Re} is greater or less than D_{Os} at large fractionations (i.e., at large phosphorous and O concentrations) is not clearly resolved with the present data because the O vs. phosphorous vs. pressure systematics are not unraveled yet. When the systematics become known, it would also be necessary to know the concentration of O, S and phosphorous, etc., in the core fairly accurately to predict which D should be larger and by how much, because D_{Re} and D_{Os} are close to one another. A full prediction of the Re/Os fractionations and $^{187}Os/^{188}Os$ anomalies expected in the outer core from the crystallization of the inner core await partitioning experiments at pressures above those where O becomes increasingly soluble in liquid metal. Such experiments are not needed to be confident that $^{186}Os/^{188}Os$ anomalies will result. In the meantime the group II iron meteorites remain the best guide to the expected fractionations. This guide leads us to expect that the fractionations of Pt, Re, and Os required to explain the Os isotopic anomalies can occur in the Earth's core as proposed by R. J. Walker et al. (1995) and Brandon et al. (1998).

The remaining question is how could any such anomalies generated escape from the core into the mantle to become seen at the Earth's surface? To understand the transmittal of a core signal to the mantle requires an understanding of the interface of the core with the mantle: the D″ layer. This is a physical as well as a chemical problem because the transfer of mass may have parallel transfers of heat and momentum across this boundary.

6. HOW DOES IT HAPPEN?

The proposal that siderophile element signals, fractionated ones, are escaping the core is burdened with some implausibilities even after the fractionations required are shown to be plausible. One imagines that a physical and chemical separation as profound as dense metal from light oxide is pretty well irreversible. If the separation happened, as suggested by the actual presence of a core, what could change the parameters sufficiently for the separation process to run backwards after running forward? Simple diffusive transfer of an Os isotopic signal from the core into the mantle is entirely inadequate quantitatively even though it must happen at some level. Majewski and D. Walker (1998) showed that even fast-diffusing, high-pressure sulfide liquids diffuse too slowly for diffusion to be an important process on this scale. This conclusion is even firmer for the solid oxide mantle. Percolative processes drawing core liquid into the base of the mantle solids by capillarity have been examined without hopeful conclusion (Poirier and le Mouel, 1992). Such processes beg the question of how the transfer of metallic liquid to an oxidized state is effected. Some more active process(es) must operate to provide both the mechanical transfer and the state change of the siderophile material.

Knittle and Jeanloz (1989, 1991) and Goarant, et al. (1992) observed complex reactions to occur between Fe-bearing solid silicates and molten Fe alloy at pressures greater than 300 kbar in diamond anvil cells (DAC). The observations were quite controversial and raised more questions about laboratory procedures than about the implications of these observations for D″. The basic proposition of these experiments was that above some threshold pressure of about 300 kbar oxygen became significantly more soluble in Fe liquid alloy and that the reactions observed were driven by the transfer of FeO from the silicates and oxides into the liquid alloy. The waste byproducts of the reaction which put FeO into liquid Fe were Fe-stripped silicates, SiO_2, and FeSi which might accumulate to form D″ as the core attempts to eat the mantle. Knittle and Jeanloz (1991) offered a permissive calculation at 300 K in support of the notion that their reaction could proceed at high pressure as a consequence of negative reaction volume. [If the reaction volume were positive, the reaction would be precluded from proceeding to a high pressure, higher volume equilibrium product.] Unfortunately their calculation was for solid product FeO, not for FeO entering the Fe liquid solution, and is not a valid guide to whether the reaction proceeds with pressure. To capture the essential feature that drives the reaction, the partial molar volume of FeO in solution at temperature is required instead of the volume of solid FeO.

O'Neill et al. (1998) cited the 1 bar partial molar volume of FeO of ~19 cc/mole in Fe-S-O liquid at 1350°C of Kaiura and Toguri (1979) as being ~6 cc/mole greater than the partial molar volume of FeO in solid oxide. The partial molar volume

of FeO in Fe liquid being greater than the partial molar volume of FeO in solid oxide (or silicate) should lead to decreasing solubility of FeO in liquid with increasing pressure. O'Neill et al. (1998) observed low and decreasing solubility of FeO in Fe liquid with pressure to 250 kbar and implicitly noted the difficulty of reconciling these observations with the DAC results. Calculations of the minimum expected FeO partial molar volumes in Fe liquid can be made from combining the volumes of liquid Fe and liquid oxygen in proportion to make FeO. For instance 2500°C and 300 kbar is a pressure and temperature threshold for the beginning of the Knittle and Jeanloz (1989) D″ reaction (Fig. 2) and is a reference condition for the following calculations. For conventionally accepted oxygen volumes (Nellis and Mitchell, 1980; Belonoshko and Saxena, 1991; Abramson et al., 1999) the partial molar volume of FeO in liquid Fe is calculated to be ~12.5 cc/mole. This is ~2 cc/mole greater than the volume for solid FeO at this P and T and therefore is consistent with the observations of O'Neill et al. (1998) of a low and decreasing solubility with pressure. Such calculations preclude Knittle and Jeanloz's D″ reaction from proceeding forward at any pressures much short of a megabar where the partial molar volume of FeO in Fe liquid may begin to fall below that of solid FeO.

However the new oxygen volume measurements of D. Walker et al. (1999a,b) are much lower than the conventionally accepted values and could lead to calculations of lower partial molar volumes and higher FeO solubility in liquid Fe with pressure. These much lower volumes for high-pressure oxygen are derived from the stable decomposition of $KClO_4$. They confirm and refine the measurements of Johnson et al. (2000) on the metastable decomposition of $KClO_3$. Using the equation of state parameters of D. Walker et al. (1999a) and the oxygen volumes of D. Walker et al. (1999b) the partial molar volume of FeO in liquid becomes that of solid FeO at the 300 kbar, 2500°C threshold, ~10.5 cc/mole. These new volumes and calculations do not contradict the observations of O'Neill et al. (1998) because they still predict that the partial molar volume of FeO in liquid Fe is greater than that of solid FeO below the 300 kbar threshold. The revised calculations are compatible with Knittle and Jeanloz's D″ reaction proceeding forward at about the pressure they claimed, reducing anxiety about lab hygiene problems being the cause of the DAC observations.

Nevertheless anxiety is conserved because the cause of the large discrepancy between the new oxygen volumes and those conventionally accepted is not yet understood. And anxiety about the DAC observations is shifted to concern about whether the D″ reaction could be going forwards as proposed by Knittle and Jeanloz (1991). If it were, siderophile elements and their signals would be effectively trapped in the core because in the forward direction the D″ reaction transfers material from the mantle to the core, not the reverse. The waste products in D″ are derived from the mantle—not the core. This is an extremely unpromising arrangement for delivering Os isotope signals to the mantle. The core is corroded shut. However there is a back-reaction for each forward one. The D″ reaction would reach an equilibrium once the core reached saturation in oxygen and would run in reverse if oxygen in the liquid alloy were increased beyond saturation.

Cooling of the core after its initial formation is one such process that would change the parameters sufficiently to make the D″ reaction run backward. Stevenson (1988) proposed that core cooling would bring out of solution the oxygen and other ingredients dissolved during its high temperature formation. This was extended by Ito et al. (1995) who invoked crystallization of the solid inner core to drive the oxygen content in the residual liquid of the outer core past saturation and cause it to exsolve supersaturated oxides which would accumulate as D″. Both these mechanisms lead to transfer of siderophile elements and Fe out of the core and into oxidized form in D″. This is an ideal pumping mechanism to reimplant Os and other siderophile element signals back into the mantle. At least it is ideal from the point of view that the mass transfer is in the correct direction and the issue of oxidation does not need a separate resolution as do percolation or mechanical entrainment mechanisms. Implicit in this exsolution mechanism is the fractionation of Pt, Re, and Os by inner core growth which generates the Os isotopic anomalies in the first place.

The DAC results do not tell us how much O is soluble in the metal after the pressure threshold is crossed. O solubility reported by Ito et al. (1995) and O'Neill et al. (1998) in S-free systems at 250 kbar (close to the threshold pressure) was only a few %. The potential objection that there may not be enough O solubility to give an interesting yield of material from the D″ reaction running backwards is answered in outline by appeal to two phenomena. The new calculations based on revised, lower O volumes suggest partial molar volumes for FeO in liquid above 300 kbar which are less than for solid FeO, whereas they are greater at lower pressure. Thus O solubility is expected to increase above 300 kbar in contrast to its observed decrease with increasing pressure at pressures below 250 kbar (O'Neill et al., 1998). The second phenomenon that can reduce concern that there is enough O solubility to be interesting comes from Table 1. The 250 kbar solubility of O in S-free liquid metal of Ito et al. (1995) and O'Neill et al. (1998) is comparable to or less than that observed here at only 100 kbar in S- and phosphorous-bearing liquids. Evidently the nonmetals can interact with each other too and increase the solubility of O without recourse to pressure alone. Naturally these issues would best be resolved with experimental observations of the solubility of O in liquid Fe at 400–500 kbar. These measurements should be a near-term goal of experimental programs designed to understand core-mantle interactions.

The ability to perform such experiments would encourage more work upon the Ds of the PGE in a pressure and oxygen solubility range more appropriate to the core differentiation regime than previously undertaken. Determination of the very high pressure PGE Ds will allow evaluation of the extent to which any PGE reemerging from the core to boost the mantle's inventory of HSE will have to pass through a fractionation filter. Presumably this filter should resemble the one through which the PGE passed during transfer into the core. Therefore with the exception of the fractionations imposed by internal processes in the core, the PGE might not be much internally fractionated by the round trip to and from the core. This lack of fractionation is a required characteristic of the material needed to explain the anomalous overabundance of HSE in the mantle. Considerably more experimental detail is required before this proposal can be fully evaluated. It is a proposal that may increase options in the search for a solution to the long-standing siderophile element problem in mantle geochemistry.

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