The Canadian Mineralogist
Vol. 43, pp. 1553-1564 (2005)

CORE–MANTLE CHEMICAL ISSUES

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Abstract

Is the core's chemical isolation from the mantle complete? This is an important question for the balancing of the persistently enigmatic budgets of the highly siderophile elements and PGE, to which Fleet's work has contributed so much. On redox criteria alone, it is clear that the core and the mantle cannot be in bulk equilibrium, and therefore that there are chemical incentives for core–mantle exchange. Recent Os isotope evidence suggests that the core may indeed be leaking chemically (although some W isotope evidence does not encourage this view). Possible mechanisms of chemical transfer between core and mantle include the following. (1) Cooling of the Earth provides a temperature perturbation that affects solubility in the outer core of the oxides, sulfides, carbides, hydrides, and silicates with which inevitably the outer core becomes saturated. Cooling and buoyancy lead to a progressive transfer of liquid (or crystalline) precipitates to the mantle. Solubilities of nonmetals in the core need determination. (2) Electromagnetic effects arising from core dynamo action can also drive core–mantle transfers. Interesting phase-changes, electrowetting, and dramatic trace-element chemical fractionation effects are driven by ~1 V potentials. The electronic character of, and voltages across, the core–mantle boundary (CMB) need determination. (3) Chemical transfers can be forced by emplacement of chemically incompatible assemblages into the CMB region. The redox imbalance between the core and oxidized slab material subducted to the CMB will certainly require chemical re-adjustments, most plausibly leading to core-to-mantle transfer of mass. The current debate about whether the chemical signature seen in some plumes is recycled crust or core need not have an exclusive "either/or" resolution. Recycled material could be key in refluxing core material into the mantle.

Keywords: Earth's core, mantle geochemistry, redox, oxygen solubility, electrochemistry, titration, crustal recycling, reflux digestion.

Sommaire

L'isolation chimique du noyau en présence du manteau est-elle complète? Il s'agit d'une question importante pour le bilan des budgets toujours enigmatiques des éléments fortement sidérophiles et des éléments du groupe du platine, domaines auxquels Michael Fleet a tellement contribué. En considérant seuls les critères de redox, il semble évident que le noyau et le manteau ne peuvent pas globalement être à l'équilibre, et donc il y aurait des incitations chimiques favorisant les échanges entre noyau et manteau. D'après les données récentes sur les isotopes d'osmium, le noyau pourrait bien être en train de subir des fuites, quoique certaines observations au sujet des isotopes de W ne favorisent guère ce point de vue. Parmi les mécanismes possibles de tranfert chimique entre noyau et manteau se trouvent les possibilités suivantes. (1) Un refroidissement de la Terre provoque une perturbation thermique qui affecte la solubilité dans le noyau externe des oxydes, sulfures, carbures, hydrides, et silicates avec lesquels le noyau externe devient inévitablement saturé. Le refroidissement et la flottabilité mènent à un transfert progressif de liquide ou de précipités cristallins vers le manteau. La solubilité des matériaux non-métalliques dans le noyau demeure méconnue et doit être étudiée. (2) Les effets électromagnétiques résultant de l'action de dynamo du noyau peuvent aussi favoriser les transferts entre noyau et manteau. Des transformations de phase intéressantes, le mouillage électrique et le fractionnement des éléments traces sont provoqués par des potentiels d'environ un volt. Le caractère électronique et les voltages en traversant l'interface entre le noyau et le manteau doivent faire l'objet de recherche. (3) Les transferts chimiques peuvent être imposés par la mise en place d'assemblages chimiquement incompatibles dans la zone de transition entre le noyau et le manteau. L'imbalance redox entre le noyau et les matériaux oxydés arrivés par subduction demanderont surement des réajustements chimiques, et tout probablement un transfert de masse du noyau vers le manteau. Le débat actuel à propos de la signature chimique de certains panaches, attribuée soit à la croûte recyclée ou au noyau, n'a pas besoin d'être résolu exclusivement en optant pour l'une ou l'autre des possibilités. Les matériaux recyclés pourraient bien tenir la clé favorisant le reflux des matériaux du noyau dans le manteau.

(Traduit par la Rédaction)

Mots-clés: noyau de la Terre, géochimie du manteau, redox, solubilité de l'oxygène, électrochimie, titration, recyclage de la croûte, digestion du reflux.

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INTRODUCTION

The platinum-group elements (PGE) have such low abundances in the crust and mantle of the Earth that they are a high-value resource. Illuminating the petrological processes responsible for their occurrences has been an objective of the research of Michael E. Fleet for a sustained period. We are considerably better informed about the partitioning behavior and the petrology of these materials because of his efforts (*e.g.*, Fleet & Stone 1991, Fleet *et al.* 1991, 1996, 1999a, b, Crocket *et al.* 1997, Liu & Fleet 2001). An additional characteristic of the PGE documented by Fleet, besides rarity, is their highly siderophile nature. They partition into metals or polymetallic sulfides if given the chance. If core formation produced the mantle (and crust) as a differentiation complement, then it is remarkable that there is such a supply of PGE for extraction and study as there is. It has long been known (Ringwood 1966, Jagoutz *et al.* 1979) that the Earth's mantle has roughly 1000 times the PGE abundances expected if the core were in equilibrium with the mantle. Although the PGE are depleted with respect to chondritic abundances, consistent with the sequestration of some PGE in the core, they are much more abundant than expected from experimental equilibrations of metal and silicate. The PGE quintessentially illustrate the problem of "excess" siderophile elements in the mantle.

There are several possible explanations for the "excess" of siderophile elements. Their budget may have been supplemented in the mantle after core formation by continuing accretion (Chou 1978, Wanke *et al.* 1984). Or core formation was "sloppy" in achieving bulk equilibrium (Jones & Drake 1986). Or there would be no excess if the correct physical conditions of the pressure and temperature of core formation could be found (Murthy 1991, Li & Agee 1996, Righter *et al.* 1997). To this incomplete list of potential solutions can be added the possibility that the PGE-rich core is leaking material back into the mantle.

Walker *et al.* (1995) and Brandon *et al.* (1998, 1999) have found evidence in some plume-related lavas of a correlation between the isotopic ratios ^{187}Os/^{188}Os and ^{186}Os/^{188}Os. These ratios can be increased by radioactive decay from ^{187}Re and ^{190}Pt, respectively, in reservoirs that have sustained Pt–Re–Os fractionation relative to chondritic ratios involving Pt, Re and Os. To explain the observed ^{187}Os–^{186}Os covariations, ratios involving Pt–Re–Os in some reservoir should be changed to substantially increase Pt/Os and modestly increase Re/Os over chondritic values. Such a fractionation is thought to characterize the outer core, from growth of the inner core (Walker *et al.* 1995, 1997, Walker 2000). The discovery of correlated radiogenic Os isotope ratios that could be generated in the core is the reason to propose a core component in some plume lavas showing those correlations. The proposal is not based on the premise that the core is a unique source of these correlated ratios, but on the likelihood that it is the only plausible one identified so far that might have the correct isotopic characteristics *and* sufficient concentrations of the PGE.

Other evidence suggesting core involvement in mantle geochemistry includes Morse's (2000) analysis of the melting relations at the core–mantle boundary. Humayun *et al.* (2004) have argued that the anomalous Fe/Mn value of some plumes also may result from a core signal.

Agreement on these issues is not uniform. The core should be depleted in Hf relative to the mantle. For scenarios involving early formation of the core (where ^{182}Hf was still present), the core might be expected to have a lower abundance of ^{182}W relative to ^{185}W because ^{182}Hf decay has not contributed to ^{182}W in the core as in the mantle. Schersten *et al.* (2004) examined the same plume lavas as did Brandon *et al.* (1999) for evidence of relatively unradiogenic W isotopes, and found no such anomaly. An anomaly might be expected if the plumes contained a core signal. Another circumstance that undermines the power of the Os system for pointing uniquely to a core signal is that plume lavas contain a number of additional signals. These strongly indicate that recycled oceanic crust has flavored the source regions of plumes in general (Hofmann & White 1982). Elevated ^{187}Os/^{188}Os values could plausibly arise from crustal recycling (Hauri & Hart 1993). Elevated ^{187}Os/^{188}Os values also correlate in some Hawaiian lavas with Sr, Nd, Pb, and O isotope signatures of the oceanic lithosphere (Lassiter & Hauri 1998). It is difficult to imagine why radiogenic Sr, for example, should correlate with radiogenic ^{186}Os from the core, because Sr and Rb are on no plausible list of core ingredients. Rather, the signals might all correlate with recycled crust. Indeed, the radiogenic Sr in plumes has been previously interpreted as a seawater signature of recycled hydrothermally altered crust (Hofmann & White 1982). The Pt/Os and Re/Os values of altered crust are not outrageously incompatible with those needed to cause the correlated anomalies. But the abundances in recycled crust are so low that adding recycled crust to mantle levels of Pt, Re, and Os is not expected to cause observable correlations, a point made by Brandon *et al.* (1999). Thus, the conclusion that all the isotopic signals come from recycled crust is as insecure as the conclusion that the Os signals come from the core.

It may seem premature to inquire into the mechanism of implanting a core signal into mantle-sourced lavas in advance of having unequivocal evidence that such core signals are actually seen. However, the theme of this paper will be to ask (and partially answer) the question of how might the signals come to be seen if they were there. The reason for asking "how do the signals get from the core to the mantle?" is that if there were no plausible mechanisms for implanting such a signal, the evidence for such a signal should be doubly subject to scrutiny. If, on the other hand, as is the case here, there are several plausible mechanisms, then knowledge of the possible mechanisms can focus the search for patterns in the signals sought.

CORE–MANTLE TRANSFER

For a transfer of material to be achieved between the core and the mantle, the core–mantle boundary (CMB) must be crossed. The nature of the CMB has been proposed to be one of violent on-going reaction between a core and a mantle that are out of chemical equilibrium (*e.g.*, Knittle & Jeanloz 1989, 1991). This view is compatible with the obvious displacement of the mantle from redox equilibrium with core metal. However, the CMB has been at several thousand degrees for several billion years. At these temperatures, equilibria in the laboratory take only seconds to achieve. Anything less equilibrated than local equilibrium at the CMB is inconceivable. Transfers across the CMB thus must be treated as locally perturbed equilibria, not as reactions.

At least three sorts of perturbations may be effective agents of CMB transfer. Thermal perturbations, like a cooling of the Earth, may change solubility balances. Electromagnetic perturbations consequent on the core's magnetic field may drive electrochemical transfers. Also, chemical shifts in local reservoirs on one side or the other of the CMB may drive transfers akin to a titration process. Each of these types of perturbations is examined here.

THERMAL PERTURBATIONS

The notion that the cooling of the Earth drives core processes is not new. Variations and embellishments on this theme have been given by many, including Braginskiy (1964), Stevenson (1981), Ito *et al.* (1995), Walker (2000), and Buffett *et al.* (2000). In outline form, cooling causes crystallization of the solid metal inner core from the molten alloy of the outer core. Light element solute is concentrated in the liquid outer core, providing buoyancy, complementary to the release of latent heat of crystallization, to drive dynamo action in the outer core. Not only is the solubility of crystalline metal lowered by cooling, but also the solubility of potential carrier phases of the light elements from liquid metal alloys is lowered. Precipitation of oxide immiscible liquids (Ito *et al.* 1995), oxide crystals (Buffett *et al.* 2000), sulfide liquids or crystals, carbides, hydrides, among others, will result. All these materials are buoyant with respect to the liquid metal outer core. They would collect at the CMB and eventually become incorporated into the lower mantle. Mantle convection might bring signals of this material to the surface in plumes.

Highly siderophile elements (HSE) like the PGE are expected to chemically partition into core metal alloy, rather than join mantle-bound precipitates. Thus thermal perturbation might be fairly ineffective at chemically transferring siderophile material back into the mantle. The thermal-perturbation-induced mechanism of transfer does not make the characteristic HSE partitioning disappear. Thus for this mechanism to be useful in recharging the PGE to the mantle, one must argue that the HSE went into the core under different conditions than they are now escaping the core. Li & Agee (1996) and Tschauner *et al.* (1999) have argued that Ni and Co become dramatically less siderophile with pressure. Righter *et al.* (1997) have parameterized many siderophile elements for their partitioning behavior. Most siderophile elements become less siderophile with increasing temperature and pressure. Thus if the original smelting leading to core formation took place at P–T conditions of significantly lower P and T than the present CMB, then the high-P–T CMB presents a less restrictive gate for PGE escape than the tenacity with which the HSE were originally trapped at lower P–T. This is a qualitative conjecture that awaits detailed experimental evaluation.

A more important implicit qualification in these thermal perturbation scenarios is that light-element carrier phases are sufficiently soluble in the core to eventually deliver an interesting amount of material to the mantle. They must also have a large enough prograde temperature-dependence to the solubility (increases with temperature) for the cooling to deliver interesting amounts of material to the mantle. Unfortunately, detailed knowledge of the solubilities in metallic liquid or their temperature dependencies for O, S, C, and H at a megabar is lacking. The current stage of exploration of this phase-equilibrium terrain is comparable to that 50 years ago in matters dealing with partial melting in the Earth's upper mantle to give basaltic magma. However, theory and extrapolated observations are not zero with respect to light element solubilities in liquid metal with pressure. The discussion will focus on oxygen. This choice does not exclude S, C, or H as potentially important ingredients. The choice is simply one to aid a start on the issues and their resolution.

OXYGEN SOLUBILITY IN LIQUID METAL

O'Neill *et al.* (1998) gave the most complete and recent account of oxygen solubility in liquid metal alloy to 25 GPa and 2500°C. They concluded that oxygen solubility is too limited to be of interest in the context of the light element in the Earth's core. Furthermore, they claimed that oxygen solubility *decreases* with increasing pressure. The factor of five increase in pressure needed to make their experimental pressures relevant to the CMB would lower the solubility even below "not interesting".

Additionally distressing from the point of view of entertaining oxygen solubility as an interesting framework for understanding the core, their data show essentially the same low solubility for oxygen at 2200, 2400, and 2500°C. This apparent high-T invariance of the dependence of solubility on temperature stands in marked contrast to the prograde solubility shown at lower T. Strong prograde solubility with T has been previously demonstrated for liquid Fe by Fischer & Schumacher (1978) and Ohtani & Ringwood (1984). Walker *et al.* (2002) suggested that this anomalous static solubility in T at high T is an artifact of the quenching method used by O'Neill *et al.* (1998). O'Neill *et al.* excluded their 2400°C data from their fitting procedure, and thus concluded that the solubility is prograde in T, as Ohtani & Ringwood (1984) had claimed earlier. O'Neill *et al.* were aware of their experiments' vulnerability to quench effects, but did not give quench problems as the reason for the exclusion of data. Recently, Rubie *et al.* (2004) have extended the pO_2 dependence of the data of O'Neill *et al.* (at a smaller range of P and T) and fit P, T, and pO_2 dependencies to the combined dataset. They repeated, again excluding the same data, the conclusion that oxygen solubility is prograde in T, arriving at, without acknowledging, the earlier conclusion of Ohtani & Ringwood (1984).

Rubie *et al.* (2004) also reiterated the conclusion of O'Neill *et al.* that oxygen solubility is retrograde in pressure in Earth's upper mantle. Walker *et al.* (2002) suggested reasons why the retrograde pressure-effect claimed by O'Neill *et al.* might also be a quenching artifact, a suggestion that could apply equally to the study of Rubie *et al.* (2004). Experimental documentation of variations in capsule size and quench rate are not sufficient in the Rubie *et al.* (2004) study to be sure about this either way. One might be tempted simply to accept the two agreeing multianvil studies, were it not for the first-order discrepancy with the DTA-based experimental study of Ohtani *et al.* (1984), which did not have vulnerability to quenching effects.

In the absence of a definitive experimental reading on the P coefficient of oxygen solubility in liquid metal, one does have volume considerations on which to fall back. If volumes in the system Fe–O were well enough known, it would be possible to predict whether oxygen solubility increases or decreases with pressure. Walker *et al.* (2002) synthesized these arguments in detail. An important quantity to track is the molar volume of the FeO dissolving in liquid metal. This could be the molar volume of wüstite itself dissolving directly, or it could be the partial molar volume of FeO in ferroan periclase or other oxide or silicate solution that is contributing FeO to the liquid iron. The molar volume or partial molar volume of solute FeO, $^{\text{Wüs}}\bar{V}$, must be compared to the partial molar volume of FeO in metallic liquid solvent, $^{L}\bar{V}_{FeO}$. For this second partial molar volume, $^{L}\bar{V}_{FeO}$, O'Neill *et al.* (1998) cited the value of ~19 cm^3/mole at 1350°C, 1 bar, from Kaiura & Toguri (1979). This is a remarkably large value compared to $^{\text{Wüs}}\bar{V} \approx$ 13 cm^3/mole for wüstite at the same P and T (Hazen & Jeanloz 1984). Thus a transfer of FeO from wüstite into liquid metal would have a large positive volume of reaction, ~6 cm^3/mole. Pressurizing this system would favor transfer to the solid, and so a lower solubility of oxygen would be expected with increasing pressure, as claimed by O'Neill *et al.* (1998) and Rubie *et al.* (2004).

However, it is difficult to reconcile this large positive volume of reaction and these claims with the experimental observations of Ohtani *et al.* (1984) at 20 kbar. They used *in situ* DTA to track the increase of the melting T of iron and the eutectic T in the system Fe–O. These temperatures both increase with pressure, but the melting of pure Fe metal increases faster. The retardation of the rise of the Fe–O eutectic temperature was inferred to be a consequence of the increasing acceptance of oxygen by the liquid with pressure. This line of argument is powerful, it is not vulnerable to quenching effects, and it must be taken as least as seriously as the multianvil results at higher P. It implies that the volume relations with ~+6 cm^3/mole as the reaction volume at 1 bar should have become negative by 20 kbar. This is in contradiction to the stated inferences of O'Neill *et al.* (1998) and Rubie *et al.* (2004) that the reaction volume for solution remains positive to in excess of 250 kbar.

There are additional reasons to be wary of accepting the multianvil results to 250 kbar at face value. A troubling aspect of the supposed pressure-variation in the multianvil labs is that for a pressure range achieved in a single size of truncated edge-length assembly, there is no pressure variation observed in the solubility. Variation of the solubility with pressure is only introduced by comparison of results from assemblies of different size, where quenching effects play a role, more so at higher pressure with smaller assemblies. This is particularly obvious in the results of O'Neill *et al.* (1998) because the experiments are particularly well documented. Furthermore, the reaction volume for solution recovered from a fit to the data for the high-P data of both O'Neill *et al.* and Rubie *et al.* is ~1.5 cm^3/mole instead of the ~6 cm^3/mole mentioned above for 1 bar. The signs of the two estimates agree, but it is difficult to imagine a parameter space with compressibilities of phases sufficiently elastic to accommodate both these estimates, unless the reaction volume is rapidly approaching zero at 250–300 kbar. These relations are summarized in Figure 1. If the reaction volume does go to zero, then further increases in pressure should encounter *increasing* dissolution of oxygen in liquid metal with pressure. This increase in solubility of oxygen in liquid metal is exactly what was reported by Knittle & Jeanloz (1991) and by Goarant *et al.* (1992). Both sets of investigators using diamond-anvil cells (DAC) reported seeing a major increase in oxygen solubility at 300 kbar, which is not observed at lower pressures with their techniques. This is the DAC limit line shown in Figure 1. Rubie *et al.* (2004) discussed this change in sign of the volume of reaction as if it were a remote possibility, in on-line archival material linked to their paper. They did not seem to notice the experimental claims that this increase had already been observed by Knittle & Jeanloz (1991) and Goarant *et al*. (1992), and analyzed by Walker *et al*. (2002).

The molar volume of fluid oxygen may be taken as a very conservative lower bound on the partial molar volume of oxygen in metallic liquid. Measurements of the volume of fluid oxygen then provide additional insight into these volume issues, as discussed in detail by Walker *et al*. (2002). At pressures below a megabar, the conventionally accepted volumes of fluid oxygen are large enough that no reasonable construction leads to negative volumes of solution for oxygen in liquid metal.

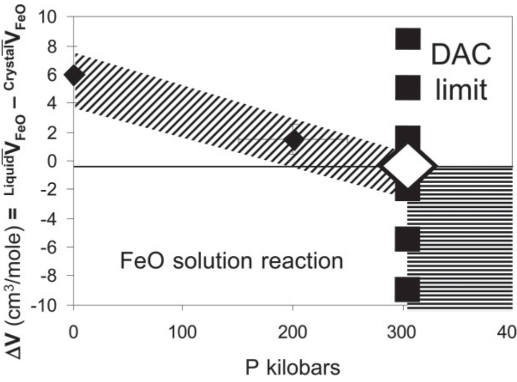

FIG. 1. FeO solubility increases or decreases with pressure depending on the sign of the volume change associated with the solution reaction. This volume is shown as a function of pressure. The zero-pressure data point is the difference between a $^{L}\bar{V}_{FeO}$ of ~19 cm^3/mole from Kaiura & Toguri (1979) and ^{Wüs}V of ~13 cm^3/mole from Hazen & Jeanloz (1984). The data point centered on 200 kbar is based on fitting the multi-anvil (MA) data of Rubie *et al*. (2004). The vertical dashed line labeled DAC limit is the pressure of reaction-onset reported by Knittle & Jeanloz (1989). The dark quadrant ($P > 300$ kbar, $\Delta V_{sol} < 0$) is where high-pressure ΔV_{sol} must lie to be consistent with the DAC observations. The open diamond is placed at the pressure expected for $\Delta V_{sol} = 0$ based on the analysis of oxygen volumes by Walker *et al*. (2002), in close agreement with the DAC limit. The small, positive value of ΔV_{sol} reported from multi-anvil studies needs to be seen in the context of this number compared to its value at $P = 0$ of ~+6 cm^3/mole. A simple extrapolation through the two points is consistent with ΔV_{sol} becoming negative, and therefore FeO solubility increasing, beyond 300 kbar, as claimed by the DAC community and supported by measurements of oxygen volume . Even though the MA solubilities are grossly discrepant with respect to the early projections of Ohtani & Ringwood (1984) of oxygen solubility from lower pressure, the MA results do not contradict the DAC results or the measurements of oxygen volume that are compatible with increasing oxygen solubilities in liquid Fe above 300 kbar. None of these techniques give a firm quantitative measure of how much the solubility of FeO actually increases above 300 kbar.

This is consistent with the claims from multianvil labs, and is inconsistent with the findings from DAC labs at considerably higher pressure, or even with lower-pressure DTA results. The new measurements of oxygen volume using static techniques by Walker *et al*. (2002) change the oxygen volume landscape considerably. Oxygen volumes from static thermal decomposition of three different chlorates and perchlorates all agree with each other and are ~50% smaller than shock-wave measurements (Nellis & Mitchell 1980) and results of impulsively stimulated scattering (Abramson *et al*. 1999). The new smaller volumes of oxygen are quantitatively consistent with the DAC observations of a large increase in solubility of oxygen in liquid iron at pressures above 300 kbar (open diamond in Fig. 1). As satisfying as this new vista on oxygen volumes may be in terms of rendering more plausible the DAC results from two different labs, it does nothing to reconcile the first-order discrepancy at lower pressures between the Ohtani *et al*. (1984) results and those from multianvil labs.

The difficulties in originally accepting the DAC results were in part based upon the highly altered state of the charges after quenching. Homogeneous alloys or glasses were not recovered from laser-heated spots in the DAC. Instead, the fine-grained aggregates of metal, wüstite, and FeSi recovered were interpreted as products of quench crystallization of an oxygen-charged liquid. The multianvil results appear to have quenching problems in both their T and P variations of oxygen solubility in liquid metal. The only study not vulnerable to quenching effects is that of Ohtani *et al*. (1984), based on *in situ* DTA. However, DTA is vulnerable to difficulties in unambiguous recognition of small electrical signals in an electrically noisy piston–cylinder environment and their unambiguous correlation with the equilibria claimed. Progress in these matters might result from an alternate experimental strategy using neither quenching nor DTA to measure FeO solubility in liquid metal.

AN ALTERNATIVE STRATEGY: LH–DAC–XRI–SRI

To access the pressure and temperature range of the CMB or the lower mantle, the laser-heated (LH) diamond-anvil cell (DAC) is the only viable static experimental approach available at present. Experimentalists have already learned much from this approach, including the difficulties of interpretation that attend the autopsies of its quench products. *In situ* sensing of phase compositions could lead to more certain interpretations. Optical emissions are insufficiently excited at CMB temperatures for useful analytical information to be available. Likewise, X-ray fluorescence in conjunction with excitation in a synchrotron beam is not very useful for X-rays emitted by oxygen (~½ keV), which would be too strongly absorbed by the diamond anvils to be detectable. Excitation of Fe X-rays (~6 keV) is more promising from the perspective of escaping the diamond anvils. But the spatial resolution with which one can tell from what part of a sample the X-rays come is a practical limit on their use. It may be marginally possible at some time in the future with extremely fine beam-size and a well-collimated detector geometry that some analytical progress with DAC charges could eventually be made with X-ray microprobes at a synchrotron facility.

On the other hand, the X-ray absorption characteristics of oxygen and iron are sufficiently different that absorption measurements of phases produced *in situ* may well provide a useful characterization of the composition of experimental phases in terms of Fe/O. The very low divergence of synchrotron-sourced X-radiation makes very-high-resolution imaging of experimental phases a practical possibility. Figure 2 shows an absorption-contrast X-radiographic image (XRI) of a DAC experiment in which an indented steel gasket contained an eccentric plug of wüstite in the sample chamber. The image was taken in a beam of 20 keV X-rays with the camera system on Station 8.3.2 at the Advanced Light Source (ALS) at the Lawrence Berkeley National Lab (LBNL). The dark background

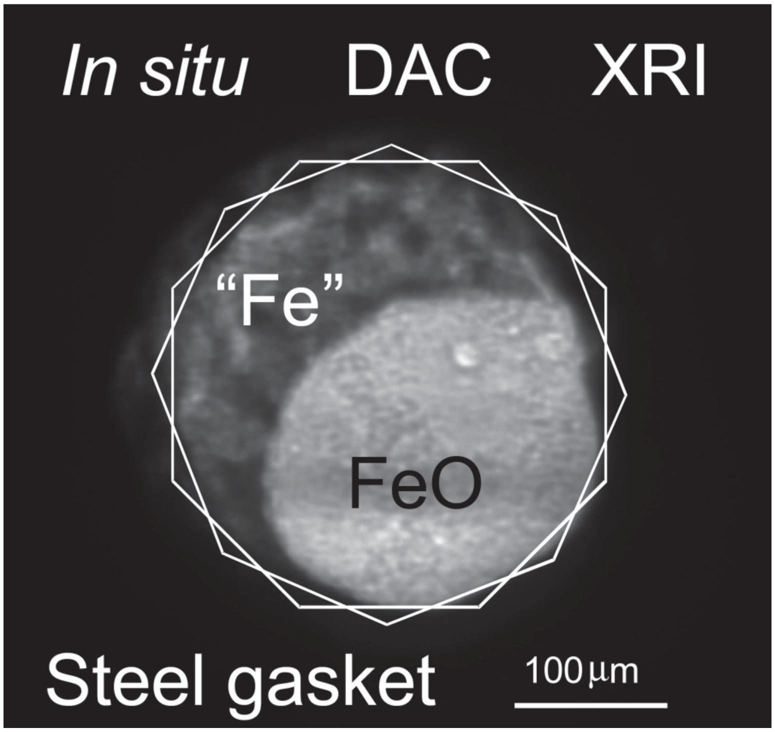

FIG. 2. X-radiographic image (XRI) of the region thinned between the culets of a diamond anvil cell (DAC). The faceted circle is drawn to indicate the trace of the culet edge. The dark area outside the faceted circle is the unthinned gasket, which is locally thickened near the culet trace, as the gasket flows outward during DAC compression. An eccentric hole was filled with crystalline wüstite before compression. The XRI shows very strong absorption contrast between the thinned steel ("Fe") of the gasket and the FeO, indicating the potential for analyzing the oxygen content of liquids generated at the interface between these two spatially resolved ingredients (SRI) by laser-heating (LH) at the interface. The gasket labeled "Fe" is a Cr-rich stainless steel with less contrast in X-ray absorption with FeO than pure Fe would have. The gray-scale modulations within the "Fe" are variations in thickness, not chemistry, caused by flow during DAC compression of the Al_2O_3 layers placed between the target and the diamond anvils. The Al_2O_3 acts as a thermal insulator and chemical separator to keep C out of the melting experiment. Refinements of the loading and fabrication technique have reduced but not eliminated these "wrinkles". Thickness and geometry changes during loading provide one set of limiting circumstances on the precision of chemical estimates that can be made with this technique.

is due to the original thickness of the gasket (260 μm), which transmits few X-rays. In the thinned region of the gasket between the diamond culets (about 50 μm separation), the difference between the thin gasket steel and the FeO (of the same thickness as the thinned gasket material) is very apparent. Evidently X-ray transmission intensity is sensitive enough to phase chemistry to be a useful analytical tool. For chemical systems with only two ingredients, Fe and O, it should be possible to do quantitative analysis given suitable standards. Iron and wüstite at experimental P and T, and at the uniform culet-imposed thickness, would be suitable standards for analysis of the liquid phase produced as the result of Fe–FeO melting. The excellent spatial resolution of the imaging in this system, a little less than 2 μm, is this good as a combined consequence of the low divergence of the X-ray beam and the thinness of the imaging phosphors in the camera system. The image quality in Figure 2 implies that DAC-scale experimental phases and laser-heating spots should be resolvable. *In situ* XRI would seem to constitute a direct determination technique for oxygen solubility in liquid metal grown by laser heating of a spot on the junction of spatially resolved ingredients (SRI), metal and oxide.

Figure 3 shows the schematic X-ray absorption traces across experiments in which spatially resolved areas of Fe and FeO were laser-heated to first melting at their interface. The trace on the left side indicates that the first liquid has an amount of Fe intermediate between Fe and FeO, a situation appropriate for eutectic melting. The right side of the figure shows the potential situation for the case where the melting is peritectic. Although the right half of Figure 3 is not expected to be the outcome, there is no evidence at present to exclude it. That possibility is given here to underline that with the XRI absorption method, one should be able to determine whether peritectic melting occurs, as well as the melt composition. The extra information comes from the strategy of using spatially resolved ingredients (SRI). Observation of the spatial distribution of the melting product at the interface between ingredients provides evidence of the type of melting reaction. An interesting feature of the use of SRI, as opposed to mixtures of those ingredients, which is the more normal approach, is that the type of melting reaction, eutectic or peritectic, should be discernable from the pattern of distribution of products, independent of whether the exact composition of the liquid can be determined. This is also a feature in systems compositionally more complex than binary. This point will be addressed later. This strategy of constraining thermocompositional phase-equilibria may be more usefully employed in DAC work than in more conventional experimental petrology because of size limits to, coupled with optical paths into, the expe-

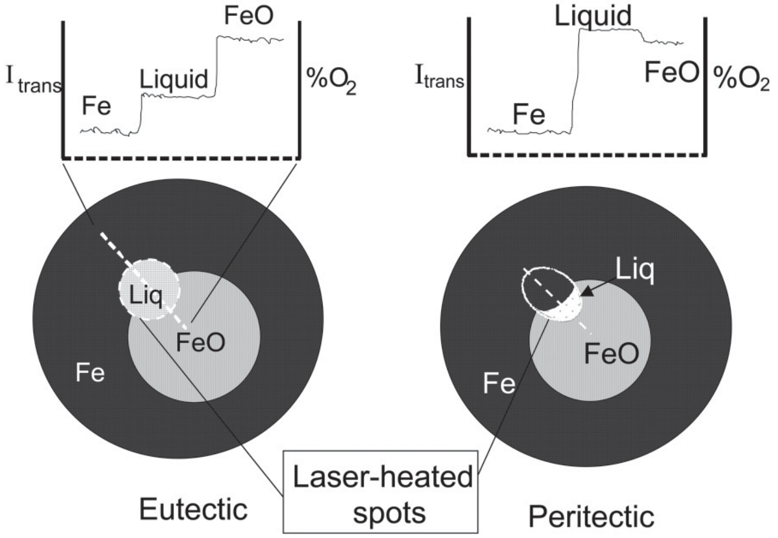

FIG. 3. Conceptual traces of X-ray intensity as a function of position across an experiment placed between the culets of a diamond-anvil cell (DAC). A laser-heated (LH) spot has caused first melting at the interface between spatially resolved ingredients (SRI), crystalline Fe and FeO. The geometrical distribution of melt and the intensity of X-ray transmission, a proxy for the proportion of oxygen, differ in the case of eutectic melting and peritectic melting. Patterned circles below show conceptual X-radiographic images (XRI) for the two cases. This experimental strategy should be effective in determining the oxygen solubility and melting equilibria at high P–T in the system Fe–O.

riment. A program of experiments to use the XRI–SRI strategy is under development in collaboration with Michael Walter, Simon Clark, and Martin Kunz at the ALS at LBNL. This team hopes, within a year or two, to have usefully direct *in situ* measurements of oxygen solubility in Fe liquid at CMB conditions in order to resolve the presently irreconcilable conflicts that exist among the various extrapolated datasets. If oxygen has an interesting solubility and temperature coefficient of solubility, the core-to-mantle transfer by cooling can be more usefully evaluated. Until such determinations are made, the question remains open. In the meantime, it is desirable to consider additional possible mechanisms of transfer.

ELECTROCHEMICAL TRANSFER

Ringwood (1959) was an early exponent of electrochemical transfers at the CMB. He started from the obvious redox disequilibrium between core and mantle, and estimated the electrochemical voltages that could characterize the disequilibrium. His proposition was that these voltages lead to transfers of substances (more substantial than electrons) between the disparate redox reservoirs.

As mentioned earlier, it is almost inconceivable that an interface that has been as hot as the CMB for as long as it has would not be at local equilibrium. Therefore, Ringwood's scenario for electrochemical transfer at the CMB is currently considered unlikely. However, the Earth has an active magnetic field generated within the core, that must have complementary electrical fields. These fields change in time and space in a synchronous manner. Changing electrical potentials undoubtedly develop across interfaces such as the CMB as a result of these fields. The buoyancy-driven magnetic dynamo of the core can supply the electrical perturbations necessary to effect CMB electrochemical transfer. If the CMB interface involved a standard metal and an aqueous electrolyte solution at 1 bar, and if the voltages from dynamo perturbations were known, tables of standard redox potentials would specify the result expected. The premises for such a prediction are not met, so one cannot predict CMB transfers with as much confidence as in an electroplating or corrosion experiment. Nevertheless, general principles such as "oxidation at the anode" are not expected to change with CMB pressures, temperatures, or materials.

Kavner & Walker (2001) and Kavner *et al.* (2005) have explored experimentally the range of phenomena that can result at metal – sulfide – silicate interfaces at high temperature in the presence of an electric field. Although these experiments were not run at a P or T pertinent to the CMB , they form a guide to what might be expected if the electrolyte is a silicate or polymetallic sulfide melt instead of an aqueous solution and if the applied emf is in the range 0.1–10 V. This modest range of electrical driving forces produces a rich range of easily observed transformations in phase assemblages, wetting properties, and phase compositions. Interestingly, this range of emf values is similar in magnitude to what Ringwood (1959) concluded might result from purely chemical driving forces. However, cause and effect are inverted. Ringwood produced emf from imbalances in chemical potential, whereas the approach of Kavner and coworkers is to investigate chemical transfers that arise from emf values produced by other means, power supplies in the lab or magnetic fields in the core.

One example of the effects observed by Kavner & Walker (2004) is illustrative. Where a Pt90%–Rh10% wire served as the anode in a basaltic liquid, spinel grains with 2% Rh and 0.2% Pt were produced at the anode–silicate interface with a 1 V potential at 1450°C, 20 kbar. No such spinels grains form in the absence of the voltage, much less ones that result from fractionation of the PGE such that the Rh/Pt ratio is enhanced by a factor of ~100 during the transfer leading to spinel growth. This is instructive of the type of effects that could operate at the CMB. The interested reader is referred to Kavner's work for a more extensive discussion of the subject with more examples.

Of the perturbations proposed to drive cross-CMB transfer, electrochemistry-based transfers are the least controversial and also the most poorly known in detail. They certainly operate at some level. But that level may be too small or transient to be interesting. It is not known whether one should expect the effects to manifest themselves as a foil-like coating on, or as a surface corrosion of, the CMB, or as a seismically observable layer. The voltages existing across the CMB are not known, not is it known how long they are sustained, or what is the electronic nature of the interface. Nor are the rates of transfer and couplings known. This ignorance is a source of current frustration but may provide an impetus for further work.

TITRATION-LIKE TRANSFERS

A third sort of perturbation occurs where reagents are combined and a chemical equilibrium is displaced. The beakers and stirring rods of the laboratory have cruder counterparts in nature. Convective mixing of the mantle can juxtapose chemically incompatible feedstocks in the grand, container-less laboratory of nature. An example of such a mixing and reaction-perturbing process may occur at the CMB where mantle convection delivers descending plates as far as the CMB. These plates reside there for some time and become reincorporated (reprocessed) into plumes (Hofmann & White 1982). From the work of Garnero & Helmberger (1996) and Williams & Garnero (1996) has come the suggestion that patchy, modulated zones of melting occur within the slab graveyard at the CMB. Williams *et al.* (1998) proposed that these magma chambers correlate with hot spots and feed into plume sources. A complex magmatic solution of silicate, oxide, metal and sulfide at the CMB would be stabilized there in part by the incorporation of chemically dense outer-core ingredients rich in iron. The digestion into a CMB magmatic stew of material from the top of the subducted slab will add a strongly oxidized component to the solution. The oxygen of Earth's atmosphere results in oxidized hydrothermal alteration of, weathering of, and sedimentation upon subducted crust. Such oxidized material will certainly shift the redox equilibria in any magma chambers at the CMB, should such oxidized material be digested. Hydrothermal alteration by oxidized seawater may also be a source of the radiogenic Sr isotopic signature of seawater. This signature would quite naturally be incorporated into the CMB magma and would flavor plumes derived therefrom. The oxidative titration of the CMB magmas by oxidized subducted material would undoubtedly shift the equilibria in the same way that cooling of the Earth does. Material of the core should be oxidatively transferred to the D" region. Instead of this transfer being driven by a long-term thermal perturbation, it would be a titrative transfer driven by the tectonic delivery of oxidized crustal material to the CMB. This scenario provides a ready explanation for the correlation of radiogenic Sr with radiogenic Os. It is likely the delivery of oxidized material with its radiogenic Sr signature that causes transfer of siderophile material with its Os signature from the outer core into the plume-source mantle. What phase equilibria control this magmatic transfer?

PHASE RELATIONS IN A CMB MAGMA?

The phase relations and density relations that drive the dynamics of a large magma-chamber at the CMB are largely conjectural. Petrologists are on generally safe grounds in postulating that adding oxidized material will shift equilibria in favor of core to mantle transfer. But the composition and density of the phases involved are unknown. According to Morse (2000), the perovskite-group phase (hereafter, "perovskite"), "magnesiowüstite" and liquid iron would first produce upon heating an oxide-rich, eutectic-like melt. Figure 4 reproduces the conjectural phase-relations on which Morse based his dynamical arguments on how such a CMB magma chamber would behave. The primary element of conjecture is that the melting is eutectic-like. The secondary element of conjecture involves the compositional details of the crystals and liquids involved. Morse's conjectures are perfectly reasonable, but they are conjectures (see also Morse 2002). There is no assurance that the melting is eutectic-like, much less the detailed composition of the first melt in the appropriate triangle. These comments are not made with a spirit of criticism, as Morse is to be commended for taking an educated first cut at the problem of how a CMB magma chamber would behave. Rather, these comments emphasize how poor is the understanding of the basic phase and density relations that govern possibly important Earth processes. This emphasis is intended to stimulate an approach to remediating this ignorance.

In the same vein as a strategy for determining oxygen solubility in liquid metal at the CMB was offered above, the following approach may be useful in unraveling the phase relations relevant to a CMB magma chamber. The first-order question of whether "perovskite" – "magnesiowüstite" melting is eutectic-like, as proposed by Morse (2000), may be addressed with the XRI–SRI strategy proposed for oxygen solubility. The problem is more complex in a ternary system, the minimal compositional complexity needed to capture the essence of Morse's scenario. In a binary system with end members of contrasting atomic number, XRI absorption measurements are sufficient to specify phase composition. In the system Fe–Mg–O, at least two independent analytical parameters are needed to specify phase compositions, so that XRI absorptometry alone is not sufficient to specify phase composition. X-ray fluorescence of Fe might marginally be capable of *in situ* determination of Fe abundances, as discussed above. Unfortunately, XRI absorption is largely set by Fe abundance, so XRI and XRF are not sufficiently independent to give good information on ternary compositions. Some additional analytical parameter or measurement would be needed to fix phase composition in this ternary system. With the synchrotron-based LH–DAC–SRI–XRI approach, it may be possible to develop such a parameter by looking at differential X-ray absorption among phases

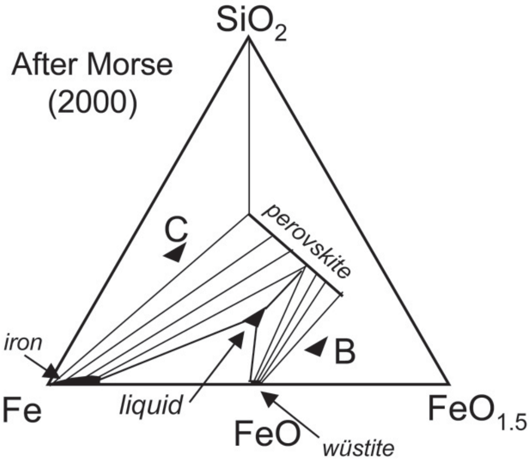

FIG. 4. Ternary projection of the phase relations postulated by Morse (2000) to be relevant to the behavior of magma chambers at the core–mantle boundary. Dark triangles are the first liquids produced on melting. Dark triangles B and C are the first liquids in cases of peritectic melting not considered by Morse (2000), but which could be possible.

as a function of X-ray energy. Such a notion has yet to be realized.

Even so, the absorption images of SRI should provide a useful reading on whether the CMB melting is eutectic or not in character in a ternary system. Figure 5 shows the images expected from an SRI experiment laser-heated at the triple junction of an iron – wüstite – "perovskite" assemblage. Figure 5a shows the eutectic case, whereas Figure 5b shows the case appropriate to liquid B in Figure 4 of Morse's conjectural phase-relations. The spatial distribution of first melts developed should be a useful guide to melting character. If all boundaries of the triple junction in the laser-heated spot are occupied by a first melt, a eutectic-like character is inferred. However if, as in Figure 5b, the boundary between wüstite and "perovskite" remains solid, peritectic melting with melt composition in the same triangle as B in Figure 4 is indicated. The present state of knowledge does not preclude a peritectic in which "perovskite" – Fe boundaries would remain solid at first melting, as in liquid C of Figure 4. Thus it is possible that significant progress can be made on these issues in the near future with techniques that are in the process of current development.

RECAP

The issue of whether some of the enigmatic budgets of the highly siderophile elements and the PGE in the mantle may be resolved by core involvement in mantle

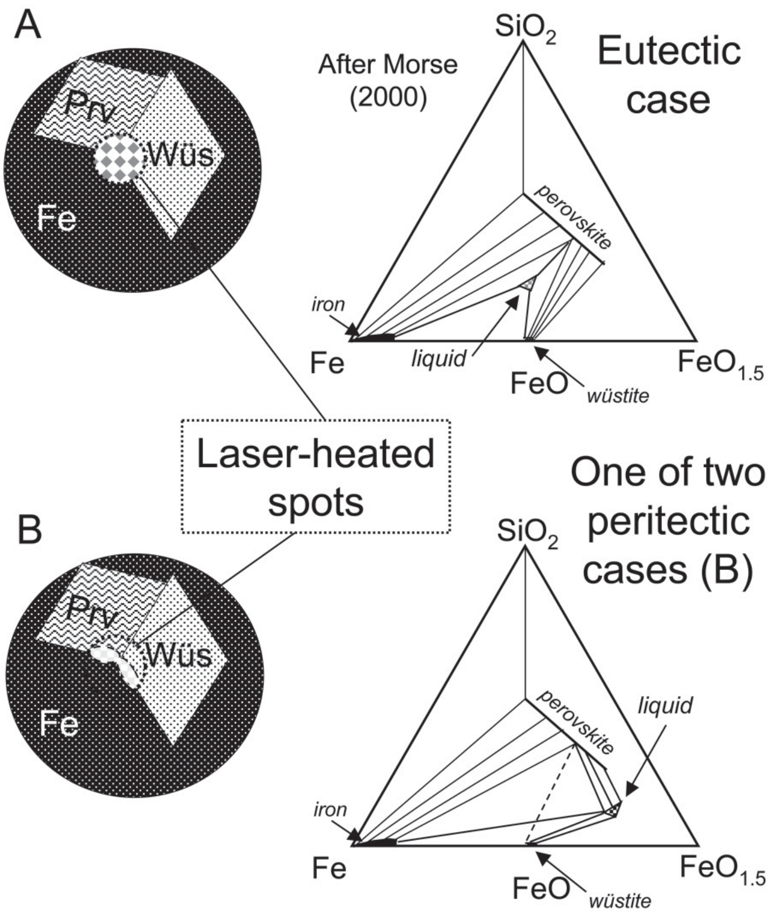

FIG. 5. Geometrical consequences of laser-heating the triple junction between crystalline spatially resolved ingredients (SRI). Eutectic case A after Morse (2000) produces melt from each ingredient. Peritectic case B does not produce melt at the "perovskite" – wüstite interface. Patterned circles on left are conceptual X-radiographic images (XRI) of the region thinned between the culets in a laser-heated (LH) diamond-anvil cell (DAC).

geochemistry is not settled. But it remains unsettled not for want of plausible mechanisms that could drive a return flux from core to mantle. Progress toward settling the matter could come from the examination of more isotopic evidence that targets core processes, and also from a determination of the phase relations operating at the CMB. Strategies for determining such phase relations are currently being developed by the application of synchrotron-based X-radiographic imaging of spatially resolved ingredients in laser-heated experiments in a diamond-anvil cell.

ACKNOWLEDGEMENTS

We all thank Mike Fleet for providing an example of the benefits of a broad perspective and for pioneering many of the issues important to the geochemistry of the core and mantle. I thank Grant Henderson and Yuanming Pan for organizing the event to celebrate Mike's career. I thank my collaborators Abby Kavner, Mike Walter, Simon Clark, Martin Kunz, and Richard Walker for their parts in all this. I thank reviewers James Brenan and Rick Secco for their comments. I thank Jamie Nasiatka for assistance with the X-radiographic imaging facility at ALS Station 8.3.2. This work was supported by the COMPRES initiative, by the NSF, and by the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy, under Contract No. DE–AC03–76SF00098 at Lawrence Berkeley National Laboratory. This is LDEO contribution #6801.

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Received August 10, 2004, revised manuscript accepted July 2, 2005.