differentiation model, as Ni and Co have similar cosmochemical volatility to Fe and their abundances are so well known. Other tight constraints come from the chondritic relative abundances of the refractory noble metals (such as Ir, Os, Re, and Au), best indicated by Re/Os isotope systematics. These chondritic relative abundances argue strongly for a “late veneer” after all core-mantle equilibrium had ceased (7, 8), and the large differences in their compatibilities indicate a well-mixed primitive mantle without chemical stratification. In particular, chondritic Re/Os rules out the olivine flotation mechanism as a means of obtaining near chondritic Ni/Co in the upper mantle, as suggested (1), because Os is compatible in olivine, whereas Re is not (9). Also, the value for $D_{\text{met-sil}}$ of ~$10^6$ adopted by Murthy is a lower limit (10). A recent estimate finds $D_{\text{met-sil}}$ $\approx 10^{12}$ (11), so the apparent agreement of the mantle abundance of Ir with that predicted by Murthy’s model appears fortuitous [(11), figures 2 and 3].

A further constraint on the role of a magma ocean during core formation comes from depletion of S in the mantle; the upper present mantle abundance of S is only ~200 ppm, or $10^{-4}$ CI/Si normalized (12). S is thus more depleted (relative to CI) than the noble metals, or such highly volatile elements as Pb, Bi, or In (4, 12). S is effectively insoluble in solid silicates, but is extensively soluble in silicate melts, and this solubility increases with increasing temperature (13). Thus, if core formation had occurred by separation of metal from silicate melt, an appreciable amount of S would be expected to remain behind, dissolved in the silicate melt. On crystallization, immiscible sulfide would separate out, fractionating siderophile elements according to their silicate melt/sulfide distribution coefficients. For all but the least chalcophile of the elements, this would in any case obliterates the evidence of the original high-temperature equilibration. Such a sulfide signature is not seen, particularly in the noble metal abundances.

Quantitative explanations of the mantle siderophile element abundances, based on heterogenous accretion models, are given in (12) and (14).

Hugh O’Neill
Bayerisches Geoinstitut,
Universität Bayreuth,
W8580 Bayreuth,
Federal Republic of Germany

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Response: Before replying to the comments of Jones et al. and O’Neill, I wish to recall the two main points of my report (1). The first is that chemical differentiation in a planet occurs at its characteristic size-dependent internal temperature because of the effect of pressure on the melting points of the materials in the planet. If the earth were molten at its final stages of accretion, differentiation in a significant fraction of its mass would have occurred at temperatures on the order of 3000 to 4000 K. The second point is that the direct use of $K_d$ values determined at low temperatures may not be relevant to deciphering the earth’s high-temperature differentiation, because partition coefficients are exponential functions of temperature and tend to approach unity as temperature increases. For siderophile elements with metal-silicate $K_d$ values greater than 1, this implies a decrease in $K_d$ with increasing temperature. I presented “a heuristic exercise” (1) in the context of the above two points. That is why I called it “A New Approach” to the problem.

Jones et al. say that $K_d$ values for Ga, P, W, Ge, and Mo increase with temperature rather than decrease. The experiments they cite do not directly measure partition coefficients as a function of temperature in a closed IW-buffer system, which is generally considered relevant to metal-silicate differentiation in the earth. In this buffer, $f$O$_2$ is a function of temperature and changes from about $10^{-11.3}$ at 1573 K to about $10^{-3.5}$ at 3000 K. Jones et al. have consistently used low temperature, low $f$O$_2$ ($\sim 10^{-12}$) partition data to make inferences about the chemical differentiation of the earth. Direct measurements of the temperature dependence of metal-magnesiowustite $K_d$ for Ni (2), and the metal-silicate $K_d$ of Ni and of Co (3) in such a buffer system, show the suggested decrease with temperature. Even the indirect estimates that Jones et al. cite suggests that $K_d$ values for Ni, Ga, and P (because of its partitioning behavior between liquid-metal and solid-metal) decrease with temperature, as discussed in (4). For W and Ge, the stated uncertainties of $f$O$_2$ measurements and other experimental uncertainties (4) preclude any judgment. No statement can be made for Mo, because data are available only at approximately 1573 K, and two separate investigations provided data that differ by nearly a factor of ten (4). Indirect estimates such as those cited by Jones et al. are inherently subject to greater uncertainties than direct measurements, which confirm my prediction.

O’Neill’s formulation assumes that one can assign a “convenient” formal valence state of an oxide for the siderophile elements dissolved in liquid silicates, drawing from the experience of experiments at low temperature and low pressure. It is not clear whether this holds true for the high-temperature–high-pressure differentiation in the deep earth. There is evidence that some of these siderophile elements may well dissolve in silicate melts as zero-valence species (5). Similarly, many experiments have shown that pressure has a significant effect on valence state and tends to “metalitize” oxides in the deep earth (6). If so, oxidation-reduction reactions may not control the partitioning of siderophile elements.

O’Neill and Jones et al. question whether $\Delta M^{*}$ can be held constant for the high-temperature extrapolations. This simplification was made not for thermodynamic reasons, but to explore possible consequences of the two main points of my
Fig. 2. Data for Ni and Co from (3) plotted as metal-olivine elemental distribution coefficients, for example, \( K_d = X_M \) (metal)/\( X_M \) (olivine), as a function of temperature and for comparison, those calculated (1). Closed circles are measured values; open squares are calculated values.

In general, for any exchange reaction we have

\[
\Delta \mu^o(P_2, T_2) = \Delta \mu^o(P_1, T_1) + \int_{T_1}^{T_2} -\Delta S\,dT + \int_{P_1}^{P_2} \Delta V\,dP
\]

(1)

where \( \Delta S \) and \( \Delta V \) refer to the changes in the entropy and volume for the reaction. We have no useful data on these two variables at present. My approximation assumes that the sum of the last two terms on the right side of Eq. 1 is about zero. If this is so, the calculated and observed siderophile element abundances in the mantle are acceptably matched (1).

The only experimental evidence so far on the behavior of \( \Delta \mu^o \) comes from data on Ni and Co (3) that are discussed by O'Neill. The measured distribution coefficients for Ni-Fe and Co-Fe in the metal-olivine system in the temperature range of 1533 to 2033 K (3) can be compared to those calculated when \( \Delta \mu^o \) is kept constant (Fig. 1). The elemental distribution coefficients, defined in the customary fashion, \( K_d = X_M \) (metal)/\( X_M \) (olivine), are shown in (Fig. 2). At least for Ni and Co, my approximation seems qualitatively reasonable; \( K_d \) clearly decreases with increasing temperature (Figs. 1 and 2; figure 1 of O’Neill). Moreover, the magnitude of the decrease over a range of 500 K (3) demonstrates that it would be inappropriate to use the low-temperature partition coefficients to understand the earth's high-temperature geochemical differentiation.

O’Neill’s discussion of the required \( K_d \) of Ni and of Co to satisfy the near chondritic Ni/Co ratio seems beside the point. I have explicitly stated (1) that the high-temperature partition coefficients alone would not solve this problem. I attributed the chondritic Ni/Co of the upper mantle specifically to one or both of two causes: core formation occurring in a molten mantle containing a small percentage (~5%) of solid silicates and olivine addition to the upper mantle (1). For example, with O’Neill's 3000 K metal-silicate partition coefficients for Ni and Co, a liquid mantle with 5% solid silicates present during core separation and a subsequent 30% olivine addition to the upper mantle has a Ni/Co ratio of 0.9, equal to that in the upper mantle. The near chondritic Ni/Co ratio seems unique to the upper mantle of the earth and is not found in samples of other differentiated planetary bodies [the moon, the Shergottite parent-body (possibly Mars), and the Euclite parent-body]. Of these, only the earth, because of its size and the pressure-density relationships in its body, can significantly meet the condition for olivine fractionation (7).

The Re/Os isotopic systematics in the mantle constrain not only the proposed olivine flotation, but also metal-silicate fractionation in the earth. The metal-silicate \( K_d \) for Os is not known. The compatibility of Os in olivine relative to Re suggests that olivine addition to the upper mantle will decrease its Re/Os ratio, but says nothing about the ratio established initially in the mantle after metal-silicate differentiation. That initial ratio depends on the ratio of the metal-silicate \( K_d \) of Re to that of Os. These effects can not be quantitatively modeled at present because of our lack of knowledge of the metal-silicate \( K_d \) for Os, and the uncertainty of our knowledge of the \( K_d \) for Re, as shown recently in the case of Ir (8). The behavior of these highly siderophile elements in metal-silicate differentiation, their speciation in mantle silicates, and their abundances in the mantle are so poorly known at present that definitive statements are precluded. The rest of O'Neill's comments do not address the main points of my paper.

The continued use of low-temperature partitioning data to infer the early differentiation history of the earth does not appear to be an useful exercise. Next-generation experiments with the IW-buffer system, with attention given to the temperature and pressure dependence of partition coefficients, will help refine our understanding of the early differentiation of the earth.

V. Rama Murthy
Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455

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Response
V. Rama Murthy

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