presumably extraretinal in origin. However, it is still unclear whether these signals are derived from cues such as vergence angle or accommodation, or both, although psychophysical data suggest an important role for vergence (*7*). In both cases, the relevant information could be obtained from either corollary discharges or proprioceptive feedback; indeed, this second extraretinal signal contributes to the localization of objects in space (*8*).

The most surprising aspect of our study is the finding that the responses of disparity-selective neurons can be modulated by extraretinal factors, even at the level of the primary visual cortex. One might expect to find such units in higher order cortical areas, such as the parietal cortex, where neurons have been shown to integrate signals from the angle of gaze (*9*). However, our findings imply that stereoscopic processing in area V1 might no longer be considered only in relation to the pattern of light falling on the retina but also as a site in which a range of retinal and extraretinal signals involved in three-dimensional space perception are integrated.

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2. For a review, see G. F. Poggio and T. Poggio [*Annu. Rev. Neurosci.* **7**, 379 (1984)]. Disparity-sensitive cells were first discovered in the primary visual cortex of the anesthetized paralyzed cat. These cells respond to stimulation of disparate points on the two retinas, a stimulus condition that normally occurs only if an object is in front of or behind the fixation plane [H. Barlow, C. Blakemore, J. D. Pettigrew, *J. Physiol. (London)* **193**, 327 (1967); T. Nikara, P. O. Bishop, J. D. Pettigrew, *Exp. Brain Res.* **6**, 353 (1968); D. E. Joshua and P. O. Bishop, *ibid.* **10**, 389 (1970)]. Under normal conditions of binocular vision in behaving monkeys, distinct categories of cells exist in area V1: cells responding preferentially to stimuli in front of the fixation plane ("near" cells), behind the fixation plane ("far" cells), or around the fixation plane ("tuned" cells) [G. F. Poggio and B. Fischer, *J. Neurophysiol.* **40**, 1392 (1977)]. More recently, evidence for the existence of disparity-sensitive neurons was provided with the use of RDSs [G. F. Poggio, B. C. Motter, S. Squatrito, Y. Trotter, *Vision Res.* **25**, 397 (1985); G. F. Poggio, F. Gonzalez, F. Krause, *J. Neurosci.* **8**, 4531 (1988)].
3. We ensured fixation during the presentation of the stimuli by placing the monkeys (two *Macaca mulatta*) in darkness, with their heads fixed, and training them to fixate a small bright target that appeared at the center of the video monitor along the straight horizontal optical axis. The monkeys had to detect a slight dimming of the target at random times (between 500 ms and 4 s) after the start of fixation. For correct detections, the monkeys were rewarded with a drop of water. The training was performed at each of the three distances. The stability of the fixation of each eye was measured independently of the other and verified with the use of infrared oculometers. An examination of the refraction of the eyes (skiascopy) revealed no optical abnormality. Cortical recordings were made with insulated tungsten microelectrodes in area V1, in the representation of the central part of the visual field. During the fixation period, an RDS with one of the six disparity values was flashed on for a duration of 300 ms. At each fixation distance and for all disparity values, the RDSs were presented 9 to 15 times, randomly interleaved.
4. Of the 113 neurons tested with the viewing distance set at 40 cm, about half [59 out of 113 (52%)] were disparity-sensitive, of which 22 were in the tuned-zero category and the rest were either near or far neurons. These proportions are in agreement with those described in studies with RDSs at a fixed target fixation distance, usually 1 m (*2*). However, because most neurons showed a modulation of their responsiveness, the percentage of disparity-selective units was actually higher when the neurons were tested at more than one viewing distance [37 out of 50 cells (74%)]. This proportion is also higher than that previously reported in studies that tested only one fixed fixation distance.
5. We tested cortical neurons by using RDSs of different dot densities and frequently found that cells were driven more efficiently by patterns of a particular dot density, usually between 10 and 30%. The pattern that elicited the optimal neural response was chosen to show the optimal effect of viewing distance. In the example of Fig. 3A, the cell was more sensitive to a dot density of 20% than to one of 10%, which explains the difference in the visual responsiveness at viewing distances of 40 and 80 cm but not the weak responses to both patterns at 20 cm.
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10. Supported by grants from the Centre National de la Recherche Scientifique and the European Community, Esprit Basic Research Action (MUCOM).

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TECHNICAL COMMENTS

Siderophile Elements and the Earth's Formation

Siderophile (metal-seeking) element concentrations in the earth's upper mantle are indicators of how the earth accreted and differentiated. A long-standing problem in geology is that, although the earth has a large metallic core, mantle siderophile elements appear to be in much higher concentrations than can be explained by simple metal-silicate equilibrium (*1*). Murthy (*2*) suggests that the abundances of siderophile elements in the earth's mantle can be explained by equilibration at higher temperatures than those achieved in most laboratory experiments. Murthy (*2*) finds that metal/silicate partition coefficients (*D*), measured in the laboratory at temperatures of 1200° to 1600°C, can account for high abundances of mantle siderophile elements if these coefficients are extrapolated to higher temperatures, 3000 to 4000 K. This method of extrapolation allows one to predict mantle siderophile element abundances that agree reasonably well with observed abundances, which argues for an extensive magma ocean early in the history of the earth. However, we believe that the extrapolation technique used by Murthy is incorrect.

First, Murthy's method of extrapolation (*2*) is made without reference to a governing chemical reaction. Such reference is important when dealing with metal/silicate partitioning because of the change in valence that accompanies the transfer of the siderophile element from metal to silicate (Fig. 1). Murthy's extrapolation equates the chemical potential of the siderophile element in the metal to that in the silicate with no account taken of an oxidizing or reducing agent. This would require that the partitioning siderophile element does not undergo a change in valence during metal/silicate partitioning.

Second, Murthy's method implicitly assumes that the Gibbs free energy change for the partitioning reaction, ΔG^0, is constant, independent of pressure and temperature. This assumption, however, is generally incorrect. One could argue that pressure effects may fortuitously cancel those of temperature and allow ΔG^0 to remain constant. However, the proper calculation cannot be performed because speciations and partial molar volumes of the relevant siderophile elements in silicate systems are unknown.

Third, Murthy's method does not seem to agree with most experimental evidence. For the great majority of siderophile elements, higher temperatures promote siderophile behavior and the values of *D* should increase, not decrease, as Murthy calculates. Nickel and, possibly, cobalt are exceptions to this rule, presumably because their stoichiometry

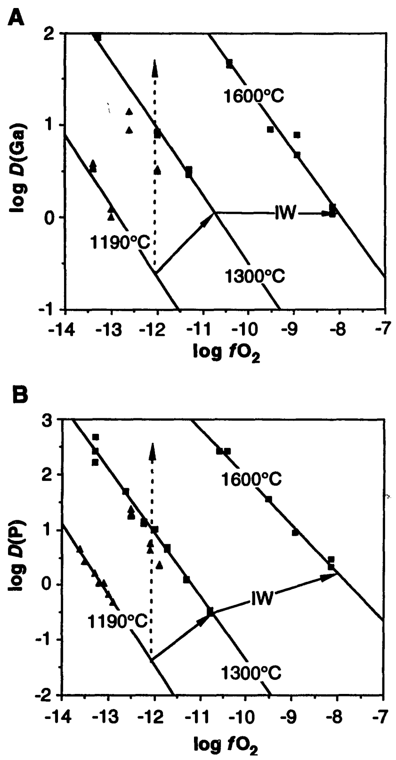

Fig. 1. Effect of temperature on metal-silicate partitioning. (■) indicates data from (*3*), (▲) indicates data from (*4*). Solid lines marked IW show how values of *D* change with increasing temperature when an oxygen buffer (iron-wüstite) curve is followed. Dashed lines show how values of *D* change with increasing temperature at constant fO_2. Lines are regressions (with the exception of the sparsely populated 1190°C Ga line, where a simple regression would be unacceptably steep). The slopes of these lines indicate (**A**) the valence of Ga and (**B**) the valence of P in the silicate liquid and show that Ga exists as Ga^{3+} and P as P^{5+}, which are the accepted valences.

parallels that of FeO, and because iron-oxygen reactions control oxygen fugacity (fO_2). However, the values of *D* for Ga and P (Fig. 1, A and B), W, Ge, and Mo increase with increasing temperature (*3*, *4*). Generally, metal/silicate liquid partition coefficients tend to either increase or remain constant as temperature increases along paths of buffered oxygen fugacity, such as that of iron-wüstite (IW). Because $\partial \ln D/\partial T = \Delta H/RT^2$, the IW path is expected to flatten at higher temperatures. In addition there may be complications from the phase change of metallic iron, which melts between 1300 and 1600°C. Even so, based on the available data, slopes are either positive or zero (Fig. 1, A and B).

Finally there is an example of a naturally occurring, extremely reduced system that forms at very high temperatures. Fulgurites, produced when lightning strikes the soil, can have highly reduced phase assemblages. In one well-documented case, not only was Fe metal present, but a substantial amount of silicate was reduced to silicon, which existed both as Si metal and in solid solution with Fe (*5*). Organic C was probably the smelting agent for this reduction. Even so, high temperature is crucial, as C will not smelt SiO_2 to Si at temperatures below 2000 K (*5*). Thus, we argue that high temperatures tend to promote reducing conditions and siderophile behavior, not the other way around.

In summary, the basis of Murthy's extrapolation is the assumption that $\Delta G°$ is independent of temperature. As this is generally not a valid assumption thermodynamically, and as it is contradicted by most experimental data, the issue of mantle siderophile elements remains unresolved.

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Murthy suggests (*1*) that the excess abundances of the siderophile elements in the earth's mantle reflect metal-silicate equilibrium at high temperatures (above 3000 K) that would be appropriate for a magma ocean in an initially molten earth. This hypothesis is based on extrapolation to these temperatures of experimentally measured metal-silicate distribution coefficients. However, the method of extrapolation used by Murthy does not appear to be valid thermodynamically; and an extrapolation based on generally accepted thermodynamic assumptions yields different results.

For his formulation of the thermodynamic equilibrium for the distribution of a siderophile element, M, between metal and silicate melt at equilibrium, Murthy proposes, with slightly different notation, the equation

$$\mu^0_{M,met} + RT \ln X^{met}_M = \mu^0_{M,sil\ melt} + RT \ln X^{sil\ melt}_M \quad (1)$$

where μ^0 represents the chemical potential of the pure component in a hypothetical standard state in which the component at unit concentration has the properties that it would have at infinite dilution, M is the component, *R* is the gas constant, *T* is temperature, and X^{met}_M and $X^{sil\ melt}_M$ are the equilibrium concentrations of M in the metal and silicate melt, respectively. The component in the silicate melt is implied to be atomic M. However, the term "component" has a restricted meaning in chemical thermodynamics; for example, it has been defined (*2*) as "those constituents the concentrations of which may be *independently varied* in the various phases" (italics as in the original). But if M dissolves in a silicate melt as an oxidized species, its concentration cannot be *independently* varied, as the concentration of the accompanying oxygen must be varied concomitantly. Because the chemical potential of a component is defined as $\mu_M = (\partial G/\partial n_M)_{T,P,n_x}$, where G is Gibbs free energy, a "component" which cannot be varied independently cannot have a definite chemical potential. Equation 1 does not apply except in the unlikely circumstance that the siderophile element dissolves in the silicate melt only as the zero-valence species.

The choice of valid components in a silicate melt is not unique, but a convenient option for all M is $MO_{x/2}$, where *x* is the formal valence. Therefore

$$\mu^0_{M,met} + RT \ln X^{met}_M + x/4[\mu^0_{O_2} + RT \ln fO_2] = \mu^0_{MO_{x/2}\ sil\ melt} + RT \ln X^{sil\ melt}_{MO_{x/2}} \quad (2)$$

where fO_2 is oxygen fugacity. The distribution coefficient is given by

$$D^{met\text{-}sil\ melt}_M = k(fO_2)^{-x/4} \exp\{\Delta\mu^0_M/RT\} \quad (3)$$

where the change in the chemical potential of component M

$$\Delta\mu^0_M = \mu^0_{MO_{x/2},\ sil\ melt} - \mu^0_{M,\ met} - \frac{x}{4}\mu^0_{O_2}$$

and *k* converts from mole fractions to the usual parts per million. Equation 3 might then be used to extrapolate $(D^{met\text{-}sil\ liq}_M)_{1573}$ to $(D^{met\text{-}sil\ melt}_M)_{3000\ K}$, for example, keeping all the other assumptions used by Murthy apart from the neglect of oxygen fugacity. The main assumption is that $\Delta\mu^0_M$ remains constant, and therefore

$$(D^{met\text{-}sil\ melt}_M)_{3000\ K} = [(D_M{}^{met\text{-}sil\ melt}{}_{1573\ K}\left((fO_2)^{x/4}_{1573}\right)]^{\frac{1573}{3000}} (fO_2)^{x/4}_{3000})\ k^{\left(1-\frac{1573}{3000}\right)} \quad (4)$$

This further implies that *x* remains constant, which is not likely for those siderophile elements which show more than one oxidation state in silicate melts under the conditions of interest (for example, V, Cr, W, Mo, and probably P, As, and Sb). Equation 4 shows that neglecting the change in fO_2 with temperature will result in errors in the high temperature distribution coefficients which depend on x (x is 1 for Cu, but is 4 to 6 for Mo and W or 3 to 5 for P, As, and Sb).

The magnitude of the change in fO_2 with temperature may be estimated from the distribution of Fe

$$\ln fO_2 \cong 2(\Delta\mu^0_{\text{Fe-FeO}}/RT - \ln X^{\text{met}}_{\text{Fe}} + \ln X^{\text{sil melt}}_{\text{FeO}}) \qquad (5)$$

For convenience I use thermodynamic data for liquid FeO and for solid Fe from (3), with $X^{\text{met}}_{\text{Fe}} = 0.85$ (which allows for Ni and the light element in the earth's core), and $X^{\text{sil melt}}_{\text{FeO}} = 0.055$ from (4). Thus $fO_2 = 10^{-11.3}$ at 1573 K, and $fO_2 = 10^{-3.5}$ at 3000 K. For

$$(\Delta\mu^0_{\text{Fe-FeO}})_{3000\text{ K}} = (\Delta\mu^0_{\text{Fe-FeO}})_{1573\text{ K}}$$

fO_2 would be calculated to be $10^{-5.9}$ at 3000 K, which illustrates that the assumption of constant $\Delta\mu^0_{\text{M}}$ is inappropriate.

Nevertheless, it is possible to consider Murthy's extrapolation as a purely empirical algebraic device, the effect of which is that all $D^{\text{met-sil melt}}_{\text{M}}$ tend towards unity with increasing temperature. The effectiveness of this extrapolation may be tested thermodynamically by considering two-component distribution coefficients corresponding to balanced exchange reactions of the type

$$x/2\ \text{Fe} + \text{MO}_{x/2} = x/2\ \text{FeO} + \text{M} \qquad (6)$$

thus using the observation implicit in Eq. 5, that fO_2 during planetary differentiation is effectively controlled by the equilibrium between FeO in the silicate and Fe in the metal. The advantages of the two-component distribution coefficient approach are further discussed in (5). Then, for reaction 6

$$\frac{\Delta G_{(6)}}{RT} = \frac{x}{2} \ln \left(\frac{X^{\text{sil melt}}_{\text{FeO}} \ \gamma^{\text{sil melt}}_{\text{FeO}}}{X^{\text{met}}_{\text{Fe}} \ \gamma^{\text{met}}_{\text{Fe}}} \right) + \ln \left(\frac{X^{\text{met}}_{\text{M}}}{X^{\text{sil melt}}_{\text{MO}_{x/2}}} \right) + \ln \left(\frac{\gamma^{\text{met}}_{\text{M}}}{\gamma^{\text{sil melt}}_{\text{MO}_{x/2}}} \right) \qquad (7)$$

where each γ represents an activity coefficient, and where

$$(X^{\text{met}}_{\text{M}}/X^{\text{sil melt}}_{\text{MO}_{x/2}})k_{\text{M}} = D^{\text{met-sil melt}}_{\text{M}}$$

where k_{M} represents a normalizing constant. This $D^{\text{met-sil melt}}_{\text{M}}$ is defined for a particular ratio of the concentration of FeO in silicate to Fe in metal. This definition is convenient because this is the condition under which different values of $D^{\text{met-sil melt}}_{\text{M}}$ are measured experimentally and applied in practice. If one assumes that all values of γ remain constant and that x does not change with temperature, and with $\Delta G_{(6)} = \Delta H_{(6)} - T\ \Delta S_{(6)}$, where H is enthalpy and S is entropy, then Eq. 7 may be written for two temperatures, T_1 and T_2, and the constant terms eliminated to give, with rearrangement

$$D^{\text{met-sil melt}}_{\text{M},T_2} = D^{\text{met-sil melt}}_{\text{M},T_1} \exp\left[\frac{-\Delta H_{(6)}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \qquad (8)$$

This may be compared to Murthy's extrapolating equation

$$D^{\text{met-sil melt}}_{\text{m},T_2} = (D^{\text{met-sil melt}}_{\text{M},T_1})^{T_1/T_2} \qquad (9)$$

Whether $D^{\text{met-sil melt}}_{\text{M}}$ increases or decreases with temperature thus depends on the sign of $\Delta H_{(6)}$. Generally, one expects that for an M that is more siderophile than Fe (that is, reaction 6 tending toward the right-hand side), $\Delta H_{(6)}$ will often be negative, causing $D^{\text{met-sil melt}}_{\text{M}}$ to decrease with increasing temperature, and vice versa for an M that is less siderophile than Fe. This is in the same direction as predicted by Murthy's extrapolation. However, comparison of Eqs. 8 and 9 indicates that the magnitude of the effect is likely to be quite different, perhaps by orders of magnitude, and for some elements (which are more siderophile than Fe by virtue of high $\gamma^{\text{sil melt}}_{\text{MO}_{x/2}}$, low $\gamma^{\text{met}}_{\text{M}}$, or large positive $\Delta S_{(6)}$), Eq. 8 predicts that $D^{\text{met-sil melt}}_{\text{M}}$ could increase rather than decrease with increasing temperature. The effect of pressure on $D^{\text{met/sil melt}}_{\text{M}}$ may be assessed in the same way as that for high temperatures. With the customary approximations

$$D^{\text{met-sil melt}}_{\text{M},P} = D^{\text{met-sil melt}}_{\text{M},1\text{ bar}} \exp\left(\frac{-\Delta V_{(6)}\, P}{RT} \right) \qquad (10)$$

(compare with Eqs. 7 and 8) where ΔV is the change in volume. $\Delta V_{(6)}$ may be either positive or negative, independent of the siderophile tendency of M, so that increasing pressure, unlike increasing temperature, is not expected to have any systematic effect on the direction of change of $D^{\text{met/sil melt}}_{\text{M}}$

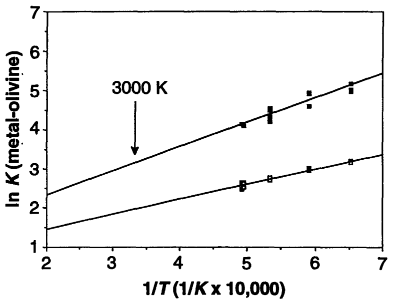

Fig. 1. Distribution coefficients of Co-Fe and Ni-Fe metal-olivine. The experimental data are from (6) and were corrected to 1 bar pressure. The upper line indicates Ni-Fe, the lower line indicates Co-Fe.

For a core with a mass equal to 32% of the earth, of which 10% is a light element, the observed upper mantle abundances of Fe, Co, and Ni require that $D^{\text{met-sil}}_{\text{Fe}} = 15$, $D^{\text{met-sil}}_{\text{Co}} = 24$, and $D^{\text{met-sil}}_{\text{Ni}} = 25$ in order to maintain bulk earth chondritic Co/Fe and Ni/Fe ratios (4). Like Fe, Co and Ni enter silicate melts overwhelmingly in the divalent state under the reduced conditions appropriate for equilibrium with metal, so it is convenient to consider the metal/silicate partitioning in light of the two-component distribution coefficients, K

$$K^{\textit{met-sil}}_{\textit{Co-Fe}} = \frac{X^{\text{met}}_{\text{Co}}\ X^{\text{sil}}_{\text{FeO}}}{X^{\text{met}}_{\text{Fe}}\ X^{\text{sil}}_{\text{CoO}}} = D^{\text{met-sil}}_{\text{Co}} / \text{D}^{\text{met-sil}}_{\text{Fe}} \qquad (11)$$

and similarly for Ni. These two-component distribution coefficients are independent of fO_2 (5). The partitioning of Co-Fe and Ni-Fe between metal and $(\text{Mg,Fe})_2\text{SiO}_4$ olivine has been measured from 1543 to 2043 K (6) and extrapolated to 3000 K (Fig. 1). In terms of $1/T$, this extrapolation is over a range similar to that over which the measurements were obtained. The conversion from metal/olivine (met/ol) to metal/silicate melt distribution coefficients

$$K^{\text{met-sil melt}}_{\text{Co-Fe}} = K^{\text{met-ol}}_{\text{Co-Fe}}\ K^{\text{ol-sil melt}}_{\text{Co-Mg}} / K^{\text{ol-sil melt}}_{\text{Fe-Mg}} \qquad (12)$$

makes use of the well-known constancy of $K^{\text{ol-sil melt}}_{\text{Fe-Mg}}$, $K^{\text{ol-sil melt}}_{\text{Co-Mg}}$, and $K^{\text{ol-sil melt}}_{\text{Ni-Mg}}$, with temperature, pressure, and melt composition (5) equal to 0.33 ± 0.05, 0.7 ± 0.1, and 1.5 ± 0.5, respectively (5, 6). The transition from solid to liquid metal cancels out across the exchange reaction and may thus be ignored.

At 1573 K, $D^{\text{met-sil melt}}_{\text{Co}} = 730$, and $D^{\text{met-sil melt}}_{\text{Ni}} = 10^4$ (both values are larger than those used by Murthy because there is a lower fO_2 implicit in the use of $D^{\text{met-sil melt}}_{\text{Fe}} = 15$). At 3000 K, $D^{\text{met-sil melt}}_{\text{Co}}$ decreases to 230 and $D^{\text{met-sil melt}}_{\text{Ni}}$ to 1600; clearly, neither are near the required values, nor do they converge as would be required by the almost chondritic Ni/Co ratio of the mantle. There would be little improvement at 5000 K (Fig. 1). There is a large difference between these results, from a thermodynamically reasonable extrapolation, and the distribution coefficients obtained by Murthy [$D^{\text{met-sil melt}}_{\text{Co}} = 15.0$ and $D^{\text{met-sil melt}}_{\text{Ni}} = 66.6$ at 3000 K from (1), table 1].

The ability to explain satisfactorily the upper mantle abundances of Ni and Co must be a first requirement in any earth 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 $D_{\mathrm{Ir}}^{\text{met-sil melt}}$ of $\sim 10^6$ adopted by Murthy is a lower limit (*10*). A recent estimate finds $D_{\mathrm{Ir}}^{\text{met-sil melt}} \cong 10^{12}$ (*11*), so the apparent agreement of the mantle abundance of Ir with that predicted by Murthy's model appears fortuitous [(*1*), 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 present upper 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 obliterate 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*).

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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, fO_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 fO_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 show that values of K_d 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 fO_2 measurements and other experimental uncertainties (*4*) preclude any judgement. 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 "metallize" 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 $\Delta\mu^0$ 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

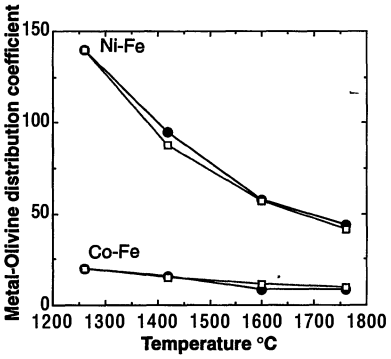

Fig. 1. A comparison of the measured distribution coefficients of Ni-Fe and Co-Fe in the metal-olivine system as a function of temperature (*3*) with those calculated by my approximation (*1*). Closed circles are measured values; open squares are calculated values.

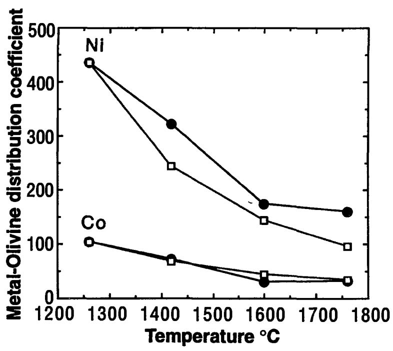

Fig. 2. Data for Ni and Co from (*3*) plotted as metal-olivine elemental distribution coefficients, for example, $K_d = X_M$ (metal)/X_M (olivine), as a function of temperature and for comparison, those calculated (*1*). Closed circles are measured values; open squares are calculated values.

paper. In general, for any exchange reaction we have

$$\Delta\mu^0(P_2,T_2) = \Delta\mu^0(P_1,T_1) + \int_{T_1}^{T_2} - \Delta S_r \, dT + \int_{P_1}^{P_2} \Delta V_r \, dP \qquad (1)$$

where ΔS_r and ΔV_r 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 $\Delta\mu^0$ 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 $\Delta\mu^0$ 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 Eucrite 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.

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