Superheating Effects on Metal-Silicate Partitioning of Siderophile Elements

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Liquid metal–liquid silicate partition coefficients for several elements at 100 kilobars and temperatures up to about 3000 kelvin in carbon capsules experimentally converge on unity with increasing temperature. The sense of change of the partition coefficients with temperature resembles the extrapolation of Murthy and may partially contribute to, but by no means provide a complete resolution of, the "excess" siderophile problem in the Earth's mantle. Sulfur and perhaps carbon successfully compete with oxygen for sites in the metallic liquid at these temperatures and pressures. This observation casts doubt upon the hypothesis that oxygen is the light element in the Earth's core.

If the Earth's metallic core segregated from the whole Earth, rather than being accreted directly in a differentiated state, the Earth's silicate mantle should have chemistry reflecting this extraction process. The siderophile ("iron-loving") elements should be depleted in the mantle; the most strongly siderophile elements, such as Ir and Au, should be the most depleted. These conditions are generally what is observed. However, the quantitative extent of the depletions is not as large as expected on the basis of depletion factors seen in coexisting metal and silicate in meteorites or in laboratory experiments at low pressure and temperature in the range of 1200 to 1600°C. The discrepancies, up to a factor of ~1000 or more, are largest for the most siderophile elements. These discrepancies are a longstanding puzzle in geochemistry: The "excess" siderophile element problem (*1*)—the "excess" being with respect to the expected depletion caused by core formation.

Many resolutions to the excess problem have been proposed. Iron sulfide eutectic liquid, instead of iron-metal alloy, might be the operative carrier of most of the siderophiles from mantle to core. And such a liquid might not be as receptive to siderophile elements as is iron-nickel metal (*2*). Core formation might be physically inefficient, and residual alloy in the mantle could boost the siderophile inventory there (*3*). Continued accretion—even to the present through the cycling of cosmic dust into subduction zones—might also boost the mantle's siderophile element inventory (*4*). Each of these mechanisms has some merit, but none alone appears capable of explaining all the details of the mantle's siderophile element abundances (*5*).

The problem might be evaded by modification of the expected partition coefficients through changes of physical conditions [for example, (*2*)]. Proposals that high pressure might substantially modify the partition coefficients have not been encouraged by subsequent laboratory experiments [for example, (*6*)]. Recently, Murthy (*7*) suggested that the highly superheated temperatures implicit in some Earth formation models could substantially change the expected partition coefficients in the correct sense. His suggestion was criticized because of the inattention to thermodynamic detail in his extrapolations and the failure of the existing, but limited, data base to follow those extrapolations (*8*). Nevertheless, it was felt that additional experiments over a large temperature range would be useful.

Ultrabasic silicate [MT7 (*9*)] and polymetallic iron-nickel sulfide [SS7, containing Ge, Au, Ni, and P (*6*)] powders were mixed together, encapsulated in graphite, pressurized to 10 GPa in a multi-anvil apparatus (*10*), and heated to 2180° and 2800°C with $LaCrO_3$ heaters. Sample geometry and containment were similar to the methods of Johnson and Walker (*11*). Pyrometry was accomplished by extrapolation of W3Re-W25Re thermocouple voltages. During runs of 1/2-hour duration, temperatures were controlled by off hot-spot W-Re thermocouples at 2000° and 2400°C, respectively; the temperature difference to the charge temperature was calibrated in a separate run with two thermocouples.

Quenching, sectioning, and optical examination of the charges were followed by electron microprobe chemical analysis with the use of a Cameca (Stamford, Connecticut) CAMEBAX and standard wavelength dispersive techniques. The accelerating voltage and beam current were 15 kV and 200 nA, respectively. Counting times for tracer elements were 60 s each on peak and background. Detection limits and interferences were evaluated by the analysis of appropriate standards that nominally contained none of the elements of interest, as well as by wavelength scans. Pulse-height analysis of the detected x-rays assured that possible interferences from higher order refractions was not a problem. Oxygen was measured directly with the use of the Kα line and the lead stearate (ODPB) crystal. Synthetic hematite was used as the oxygen standard and gave excellent results for the direct analysis of oxygen in a standard silicate glass.

Both the liquid metal and liquid silicate present at run conditions quenched to complex phase intergrowths. The metallic liquid quenched to dendrites of metal and sulfide, with interstitial oxygen- and carbon-bearing phases. The silicate liquid quenched to dendrites of olivine and graphite or diamond, globules of (Fe,Ni) metal sulfide, and silicate glass. Averages of multiple microprobe rasters $(30\ \mu m)^2$ over the quench intergrowths (*6, 12*) are reported as the composition of the immiscible liquid phases. Carbon analysis could not be reliably done this way because it could not be determined to what extent the large crystalline carbon polymorphs present within the charge (diamond at lower temperature, graphite at the higher temperature) were recrystallized capsule material and what fraction was quench growth recovered from solution. Crystalline carbon was avoided in the placement of the analytical rasters.

Because metallic liquids are extremely difficult to quench to a homogeneous phase [for example, (*12*)], the dendritic structure of the metal phase caused us no alarm. Initially, however, we were concerned that the metal-sulfide globules within the silicate phase might represent a mechanical emulsion of liquid metal and silicate that pre-existed the quench. In that case, raster analysis of the silicate would not yield a meaningful partition coefficient. However, textural evidence suggests that the sulfide globules formed during the quench, after the quench growth of carbon-rich dendrites but before the transition of the silicate to glass. This qualitative observation is supported by the fact that Ge/Ni and P/Ni ratios of the metal-sulfide globules differ substantially from those of the bulk metal. Thus, we interpret the complex phase assemblage within the silicate portion of the charge to represent the quench products of an originally homogeneous liquid.

All well-defined partition coefficients (*D*) for the constituents of our system are given in Table 1. Uncertainties are quoted as errors of the mean because much of the compositional variation that we observed occurred during the quench and is not indicative of our approach to equilibrium. Consequently, the average of our analyses is important, not the variation about that value [for example, (*6*)]. For completeness, Table 1 also reports elements for which the values of *D* are not well determined by electron microprobe analysis.

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Table 1. Electron microprobe analyses (percent by weight). For the experimental runs BB-119 and BB-123, the numbers in parentheses are the last two digits of the standard error of the mean. Values of *D* represent the metal (met) to silicate (sil) ratio; *n*, number of analyses.

Element	BB-119, met (*n* = 55)	BB-119, sil (*n* = 71)	*D* (2180°C)	BB-123, met (*n* = 62)	BB-123, sil (*n* = 74)	*D* (2800°C)
Fe	61.69 (15)	9.98 (04)	6.2	65.17 (10)	14.23 (11)	4.6
O	1.96 (05)	44.92 (06)	0.044	1.35 (06)	42.93 (09)	0.032
P	0.073 (04)	0.206 (05)	0.36	0.118 (04)	0.321 (04)	0.37
Cr	0.019 (06)	0.118 (02)	0.16	0.024 (05)	0.183 (02)	0.13
S	21.30 (16)	0.197 (06)	108	18.71 (09)	0.430 (44)	44
Ge	0.862 (21)	0.027 (01)	32	1.09 (02)	0.078 (02)	14
Ni	10.94 (07)	0.063 (03)	175	10.53 (07)	0.163 (24)	65
Ca	0.000 (00)	5.92 (01)		0.000 (00)	4.98 (02)	
Al	0.022 (02)	4.10 (01)		0.011 (02)	3.73 (01)	
Mg	0.000 (00)	15.25 (02)		0.000 (00)	13.81 (03)	
Si	0.000 (00)	19.62 (02)		0.008 (02)	18.98 (05)	
Ti	0.001 (00)	0.157 (00)		0.001 (00)	0.204 (02)	
Mn	0.003 (00)	0.073 (01)		0.003 (00)	0.077 (01)	
Au	0.925 (07)	0.010 (01)		1.09 (01)	0.021 (02)	
Total	97.80	100.64		98.10	100.12	

Figure 1 shows the variation of partition coefficients as a function of temperature. Elements with $D > 1$ are siderophile, and those with $D < 1$ are lithophile, preferring the silicate liquid. The only other partitioning experiments performed in carbon capsules, of which we are aware, are those of Peach and Mathez (*13*) at 8 kbar and 1450°C. We have included these data (at a different pressure) in Fig. 1 because it is our thesis (6) that the effects of composition and temperature on partitioning are much more important than those of pressure, and this data set allows a significant extension of the temperature range.

The lithophile element phosphorous appears to become slightly less lithophile with increasing temperature; all siderophile elements become less siderophile. The values of *D* are convergent on unity, suggesting that the distinction between the silicate and metallic liquid diminishes at high temperature. That these liquids might actually become miscible at some accessible temperature (but one well beyond our ability to control or monitor) was suggested by a "failure." An experiment headed for a 2400°C temperature became unstable and engaged in a thermal runaway reaction between the $LaCrO_3$ and MgO internal parts. This reaction promoted excessive power consumption and wholesale melting, including that of the W-Re thermocouples, before the experiment was manually terminated about ~10 s into the runaway. The diamond capsule, although partially reconverted to graphite, remained intact. The product, instead of well-segregated silicate and metallic liquids, was an intimate dispersion of one in the other. Inasmuch as this experiment started with the silicate and metal powders unmixed, this dispersion may reflect exsolution after wholesale miscibility at transient high-temperature conditions. Thus, we interpret the principal control on the partitioning results in Fig. 1 as temperature closing a solvus, with the consequence that values of *D* approach unity.

The exceptions to this discussion are chromium and oxygen. Chromium may be anomalous, as an artifact of contamination from the $LaCrO_3$ heater at the highest temperature, although the expected complementary La contamination is not observed. Chromium has shown anomalous behavior in other contexts in which contamination is not a possibility. In the iron-nickel system, chromium is modestly compatible in iron-nickel metal. However, in the iron-nickel-sulfur system chromium is clearly chalcophile and its solid metal–liquid metal partition coefficient drops rapidly as the sulfur content of the liquid increases (*14*). We similarly interpret chromium behavior in the present context, with chromium becoming more "lithophile" at high temperatures, as a consequence of its chalcophile tendencies. The shrinking of the sulfur partition coefficient with temperature is more strongly a function of the sulfur concentration increasing in the silicate melt than decreasing in the metallic melt. Thus, the increased availability of sulfur in the silicate melt for chromium complexing as the solvus closes may constrain the chromium distribution.

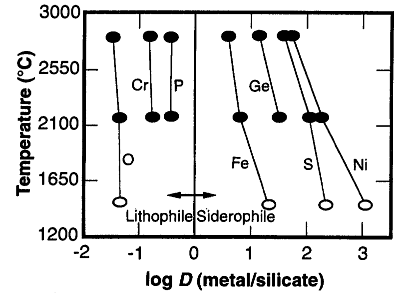

Fig. 1. Temperature versus metal-silicate partition coefficient. The experimental results for the partitioning of several siderophile elements between metallic and silicate liquids in carbon capsules are shown as a function of superheated temperatures. Filled symbols are from this study at 100 kbar. Open symbols are from Peach and Mathez (*13*) at 8 kbar. Carbon was in the graphite form at the highest and lowest temperatures and in the diamond form at 2180°C at 100 kbar. Siderophile elements become less strongly siderophile at high temperature as the two liquids become more mutually soluble. Oxygen remains strongly lithophile, more so with increasing temperature, and is a poor candidate for the light ingredient of the Earth's core when it must compete with sulfur and carbon to enter metallic liquid.

An additional possible complication is that the highest temperature experiment may have a small amount of entrained or emulsified metal in the silicate liquid before quench. The reason for this concern in the highest temperature experiment, and not in the 2180°C experiment, is that variations of the individual analyses in the 2800°C silicate trend away from a dominant cluster, which reflects the siderophile element signature of the silicate, toward compositions that are indistinguishable from the equilibrium metal. This variation would be expected if the most siderophile-rich silicate analyses contained a small dispersed component of prequench metal droplets. However, this variation is also expected if the first metal to exsolve upon quenching has a composition similar to that of the equilibrium metal. The latter scenario is more appealing if there is some mechanical redistribution of the quench-grown droplets within the silicate. Textural inspection of the charge reveals that the metal droplets present in the quench silicate are modestly concentrated by quench-crystal fascicles rather than randomly dispersed, although textural arguments are notoriously ambiguous in resolving problems of this sort.

These two scenarios would result in two different strategies for reducing the data for the 2800°C silicate. If the metal droplets are all grown on the quench, all analyses should be averaged, as reported in Table 1. However, if a small amount of the metal is a dispersion of prequenched material, the silicate analysis should exclude from the average those analyses that extend beyond the main cluster. The effect of the latter method would be to increase the metal-silicate partition coefficients of the siderophile elements. For example, in the case of Ge the *D* value at 2800°C would increase from 14 to 16 but would still be lower than the value of 32 measured in the 2180°C experiment. Nickel and sulfur partition coefficients that are calculated in this same manner also steepen the slopes of *D* with temperature but do not reverse the trends shown in Fig. 1. Thus, regardless of which data reduction technique is chosen, our main conclusions remain unchanged.

An alternative interpretation, at least for the siderophile element data (Fig. 1), is that changes in the partition coefficient are attributable to changes in oxygen fugacity (fO_2) as opposed to changes in temperature. Conceivably, there are concomitant changes in fO_2 with temperature that might be difficult to unravel. Evaluation of this proposal is not as straightforward as it might first appear. Our system was not buffered and neither was the experiment of Peach and Mathez (*13*). An upper limit of oxygen fugacity is provided by the pressure-dependent C-CO_2 equilibrium boundary. Peach and Mathez (*13*) infer from an internally consistent analysis of their experimental results that the fugacity of their experiments was within 0.5 log unit of this upper bound [$\log fO_2 \approx -8.5$ (or 1 log unit above the iron-wüstite buffer)].

The compositional difference between our experiments and those of Peach and Mathez (*13*) is such that our redox conditions should be more reducing. The sulfide liquid of the Peach and Mathez (*13*) experiments closely approximated that of a monosulfide such as FeS or NiS. Thus, the activity of metal in their experiments is thought to be small (*15*). The SS7 component of our starting material, however, contains excess metal. Following Sharma and Chang (*15*), we make the simplifying approximation that sulfur in our metallic liquids exists primarily as monosulfide species. If approximately ideal mixing is assumed and small fractionations between nickel and iron are ignored, this sulfide stoichiometry implies that the activity of iron metal in our experiments is 0.27 and 0.32 at 2400 and 3100 K, respectively. Thus, our experiments are more reducing than those of Peach and Mathez (*13*). Consequently, if fO_2 were the primary control on partition coefficients in our experiments, then values for siderophile element *D*'s should have increased with increasing temperature. Thus, the lowering of siderophile element partition coefficients with increasing temperature is not an artifact of changes in fO_2 values.

The same rationale argues that our observed changes in the partition coefficient are not artifacts of changes in the activity of sulfur in the metallic phase. Experimentally, increasing sulfur in the iron-nickel-sulfur system also increases solid metal–liquid metal partition coefficients, implying that most siderophile elements avoid sulfur (*14*), the sole documented counter-example is chromium, as discussed above. Consequently, we would have predicted that decreasing the sulfur content of our metallic liquids from that of Peach and Mathez (*13*) would have increased, not decreased, metal-silicate partition coefficients. Therefore, as in the case of oxygen fugacity, it appears that changes in sulfur activity are not responsible for the trends in Fig. 1.

The values of siderophile depletion factors at ~3100 K obtained in this study may be compared to those predicted by Murthy (*7*) in this temperature range. Although a generally satisfying comparison for the elements overlapping both studies can be made, phosphorus constitutes an unsatisfactory exception. It is lithophile in our experiments, so no amount of extrapolative prestidigitation will successfully explain its depletion in the mantle as a consequence of siderophile behavior. Possibly a competition with sulfur, carbon, or both renders this phosphorus behavior anomalous.

Although the generally satisfactory agreement of Murthy's predictions and our measurements might be construed as a strong vindication of Murthy's extrapolation, some caution is in order. Murthy clearly got the sign of the temperature variation correct, no matter how controversial the merits of the basis of the prediction may have been. Siderophile *D* values decrease rather than increase with temperature, in spite of some expectations based on lower temperature experiments. However, the rate of change of variation of *D* with temperature for some elements may not be as large as Murthy predicted. Thus, some of the agreement between the measurements and the predictions at the highest temperatures may be an artifact of the experimental inclusion of carbon and sulfur in the system, which also can reduce the *D* values. These reservations notwithstanding, it is clear that the temperature effect is in the right direction and is not trivial.

It is our hypothesis that the effect is as strong as it is for trace siderophile elements only as an indirect result of temperature. Temperature and entropy of mixing of the major constituents promote the solvus closure between silicate and metallic liquids, but the trace siderophile elements respond more to site population opportunities set up by the solvus closure than to the direct effect of temperature. The rationale for this view is more fully developed in (*6*).

Can this mechanism, in isolation, solve the long-standing problem of excess siderophiles in the Earth's mantle? Taking our experiments at face value, we believe that the answer to this question is likely "no." The most immediate objection is that our experiments predict a different mantle composition than what is observed. Our experiments predict that mantle Ge/Ni and P/Ni ratios should be considerably higher than chondritic, which is not the case.

However, even this analysis, which seems straightforward, may be oversimplified. We have not reproduced the correct (pressure, temperature, and oxygen fugacity) conditions that were present during core formation. For example, the iron contents of the silicate liquids in our experiments are about a factor of 2 higher than those of the Earth's upper mantle. The sulfur contents of these silicate liquids are factors of 7 to 15 times higher than those of the mantle. Thus, our experimental silicate liquids are not yet a good compositional match for the Earth's upper mantle. It is also unclear how to extrapolate from these laboratory experiments to natural systems. Additional experiments, ones that reproduce upper-mantle iron and sulfur abundances, will be required to help settle this issue.

Despite these difficulties, there are still possible applications of our experiments to the Earth's upper mantle. One popular model for understanding mantle siderophile element abundances is that of heterogeneous accretion (*4*), which culminates in a "late veneer" of chondritic material, rich in noble siderophiles, after core formation has ceased. Jones and Drake (*3*) spent considerable effort devising alternative models to heterogeneous accretion because they perceived (rightly or wrongly) that physical mixing of this late veneer into the upper mantle might be difficult.

Our experiments suggest that, if the early upper mantle were superheated, any late veneer could be assimilated and mixed in the liquid, as opposed to the solid, state. Total assimilation of both the silicate and metal-sulfide components of a chondrite could provide the noble element signature of the mantle as we now observe it. This mechanism, in principle, could overcome many of the difficulties envisioned by Jones and Drake (*4*). However, as with other magma ocean scenarios, the late stages of such a process are difficult to envision clearly [for example, (*16*)].

Thus, our conclusion with regard to the siderophile excess problem and chondritic late veneers is that the effect of high temperature may be another contributory mechanism for reducing the anomaly. But as with all the previous suggestions, it is imperfect by itself. The geochemical impact of core formation on the mantle is complex and so will be the resolution of the siderophile abundances.

Unlike the sulfur anion, the oxygen anion in our experiments does not show *D* values approaching unity with increasing temperature; it remains strongly lithophile, becoming more so with higher temperature. Oxygen abundance in the metallic liquid decreases over the temperature range of this study. This observation is difficult to reconcile with the closure of a miscibility gap modeled on Fe-FeO at high pressure [for example, Ringwood (*17*)] in which oxygen abundance should increase in the metallic liquid with temperature. The competition between oxygen, sulfur, and carbon for sites in the metallic liquid in our experiments is strongly resolved in favor of sulfur and carbon. Thus, if these two elements are present, high oxygen abundance in the mantle is apparently a doubtful criterion to establish that oxygen will be the major light element in the core.

The steepness of the solvus between liquid metals and silicates becomes measurably less dramatic at high temperatures. Consequently, we envision that there are regions of pressure–temperature–oxygen fugacity space in which the chemical distinction between silicates and metals is diminished and partition coefficients approach unity. However, our experiments do not predict in detail the siderophile element signatures of the Earth's upper mantle. Complete assimilation and dissolution of chondritic materials at high temperatures could, however, explain the pervasive, homogeneous distribution of mantle noble siderophiles that is attributed in some models to a late veneer. Finally, if our experiments are a useful guide, it does not appear that oxygen successfully competes with sulfur and carbon for sites in metallic liquids. This observation casts some doubt on the likelihood that oxygen is the dominant light element in the Earth's core.

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Orphan Strontium-87 in Abyssal Peridotites: Daddy Was a Granite

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The ^{87}Sr/^{86}Sr ratios in some bulk abyssal and alpine peridotites are too high to be binary mixtures of depleted mantle and seawater components. The apparent excess, or "orphan," ^{87}Sr appears to be separated from its radioactive parent. Such observations were widely held to be analytical artifacts. Study of several occurrences of orphan ^{87}Sr shows that the orphan component in abyssal peridotite is located in the alteration products of olivine and enstatite in the peridotite. The orphan ^{87}Sr is most likely introduced by infiltration of low-temperature (<200°C) seawater bearing suspended detrital particulates. These particulates include grains of detrital clay that are partly derived from continental (that is, granitic) sources and thus are highly radiogenic. Orphan ^{87}Sr and other radiogenic isotopes may provide a tracer for low-temperature seawater penetrating into the oceanic crust.

The available sources for Sr in oceanic and alpine peridotites are the mantle reservoir (^{87}Sr/^{86}Sr $\cong$ 0.7023) and seawater (^{87}Sr/^{86}Sr $\cong$ 0.7092). If these are the only sources, the Sr isotopic composition of abyssal peridotites must lie somewhere in between. The first measurements of Sr isotopes and Rb and Sr concentrations in peridotites (*1, 2*) immediately turned up the problem of excess ^{87}Sr in altered alpine peridotite. Although some rocks showed ^{87}Sr/^{86}Sr ratios consistent with a mantle origin, many had ^{87}Sr/^{86}Sr values much higher than those of seawater (*3*). Some of these samples could not have evolved in a single stage from the bulk Earth. Ultramafic nodules, by contrast, have ^{87}Sr/^{86}Sr ratios comparable to those in basalts. This led to the conclusion that alpine peridotites are not related to basalts, either by partial melting or by crystal accumulation (*4*). The most favored explanation for the high ^{87}Sr/^{86}Sr ratio of alpine peridotites was partial melting, resulting in an increase of the Rb/Sr ratio in the residual peridotite. Nonetheless, alpine peridotites were not considered parental to basalts (*2, 4, 5*).

This conclusion extended to abyssal peridotites as well (*6*). On the basis of isotopic evidence, as well as petrographic and trace-element data, abyssal peridotites strongly resembled the alpine peridotites and thus could not be considered parental to mid-ocean ridge basalts. At the time, the lowest ^{87}Sr/^{86}Sr ratio measured on an alpine or abyssal peridotite was 0.7046 (*1*), which was approximately the average of measurements for basalts. The highest alpine peridotite ^{87}Sr/^{86}Sr measurement was 0.7864 (*4*), and the highest abyssal peridotite measurement was 0.7227 (*6*). Ancient continental crust underlying the mid-ocean ridges was proposed to account for the high ^{87}Sr/^{86}Sr ratios (*7*). These results posed a minor but significant problem for plate tectonics, which required a genetic link between abyssal peridotites and mid-ocean ridge basalts.

The first indication that the high ^{87}Sr/^{86}Sr problem in abyssal and alpine peridotites was an alteration effect came when clinopyroxene from an abyssal peridotite turned out to have a significantly lower ^{87}Sr/^{86}Sr ratio than the bulk peridotite (*8*). Metamorphic minerals plagioclase and hydrogrossular had isotopic compositions that showed significant seawater interaction (0.7088 and 0.7089, respectively), but clinopyroxene from that rock had a much lower ^{87}Sr/^{86}Sr ratio of 0.7067 (*8*). Later reanalysis of leached clinopyroxene reduced this number somewhat to about 0.7052 (*9*).

Subsequently, consistently mantle-like Sr isotopic compositions were found by analysis of clinopyroxenes separated from alpine peridotites (*10*). This showed that alpine peridotites were in fact a plausible residual material for basalt, in terms of Sr isotopes. Since that time, a variety of other lines of evidence (*11–16*) have amply demonstrated the genetic link between abyssal peridotite and mid-ocean ridge basalt. The earlier measurements were ascribed to analytical error or to a metasomatic component. We refer to these ^{87}Sr/^{86}Sr ratios as containing orphan ^{87}Sr because there is a radiogenic component of unknown origin. We present new measurements that suggest an origin for the orphan ^{87}Sr reservoir.

Orphan ^{87}Sr has not been observed in unaltered peridotites or in leached mineral separates from alpine or abyssal peridotites (*8, 10, 16*). This strongly suggests that the process of alteration itself has a fundamental role in the formation of the orphan ^{87}Sr reservoir in abyssal peridotites. In order to

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