Mesosiderite Clasts with the Most Extreme Positive Europium Anomalies Among Solar System Rocks

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Pigeonite-plagioclase gabbros that occur as clasts in mesosiderites (brecciated stony-iron meteorites) show extreme fractionations of the rare-earth elements (REEs) with larger positive europium anomalies than any previously known for igneous rocks from the Earth, moon, or meteorite parent bodies and greater depletions of light REEs relative to heavy REEs than known for comparable cumulate gabbros. The REE pattern for merrillite in one of these clasts is depleted in light REEs and has a large positive europium anomaly as a result of metamorphic equilibration with the silicates. The extreme REE ratios exhibited by the mesosiderite clasts demonstrate that multistage igneous processes must have occurred on some asteroids in the early solar system. Melting of the crust by large-scale impacts or electrical induction from an early T-Tauri–phase sun may be responsible for these processes.

The REEs, long used by geochemists as indicators of igneous petrogenesis, tend to be excluded from common rock-forming minerals during crystallization or melting. This incompatible geochemical behavior is a smooth function of atomic number because the REEs exist as trivalent species under most geological conditions, and the ionic radii of the REEs vary monotonically with atomic number. An exception to this systematic behavior occurs for Eu. Under typical geological conditions, a significant fraction of Eu is in the divalent state (*1*) and fractionation of Eu from Sm and Gd occurs during igneous processes. Both positive and negative Eu anomalies can be found in terrestrial and extraterrestrial igneous rocks.

In addition to Eu anomalies, large fractionations of light rare-earth elements (LREEs) from heavy rare-earth elements (HREEs) can be produced by the high-pressure phase garnet (*2*) or by any of several accessory phases such as zircon and monazite (*3*). Meteorite parent bodies generally did not produce igneous rocks with extreme HREE/LREE fractionations because pressures were not within the stability field of garnet, and accessory minerals were essentially absent (*4*). Meteorites having exceptional HREE/LREE fractionations and low overall REE contents—the cumulate orthopyroxenite meteorites (the diogenites) and the olivine-pigeonite achondrites (the ureilites)—were probably fractionated in a different way: low-Ca pyroxene and olivine exclude the LREEs more efficiently than the HREEs (*5*) and can lead to cumulates with CI chondrite–normalized (*6*) Yb/Sm ratios of ~10 to 20 from parent melts with chondritic Yb/Sm ratios. Chondrite-normalized Yb/Sm ratios for diogenites range up to 20 (*7*) and for ureilites up to 24 (*8*).

The basaltic achondrite meteorites and igneous clasts in mesosiderites (brecciated stony-iron meteorites) comprise suites of basalts and gabbros composed of roughly equal amounts of pyroxene (ferroan pigeonite) and anorthitic plagioclase, with minor amounts of tridymite, chromite, ilmenite, troilite, metallic Fe-Ni, and merrillite (*4*). These igneous rocks were formed under conditions of low oxygen fugacity, fO_2 (*9*). These conditions favor fractionation of Eu from Sm, especially in the presence of plagioclase (*10*). Nonetheless, Eu/Sm ratios in basaltic achondrites and basaltic mesosiderite clasts are generally not very different from those of their terrestrial counterparts. These basaltic meteorite samples generally have unfractionated REE patterns except for modest negative Eu anomalies (Eu/Sm ratios 0.6 times that of CI chondrites) and slight depletions in HREEs (Yb/Sm ratios 0.8 times that of CI chondrites) in some (*11*). Cumulate eucrites, formed by the accumulation of pigeonite and plagioclase from a silicate liquid, exhibit moderately high HREE/LREE ratios (Yb/Sm ratios up to 2.3 times that of CI chondrites) and Eu/Sm ratios up to about 6 times that of CI chondrites (*12*).

Recently, exceptional Eu-Sm fractionations have been identified in a few gabbroic clasts from mesosiderites (*13*). These clasts have both Eu/Sm and HREE/LREE ratios that are more extreme than can be understood by the simple petrogenetic model, that is, by fractional crystallization of primary melts, which is usually invoked to explain basaltic achondrite petrogenesis (*13*). These clasts have Eu/Sm ratios greater than those of any previously known for rocks from the Earth, moon, or other meteorite parent bodies. Because positive Eu anomalies occur in feldspar, we compare the mesosiderite gabbros to rocks containing cumulus plagioclase, that is, lunar and terrestrial anorthosites, and cumulate eucrite meteorites (Fig. 1). Initial pigeonite-plagioclase cumulates that formed from melts with chondritic REE ratios would fall in the stippled field between plagioclase and pigeonite partition coefficients. As crystallization proceeded,

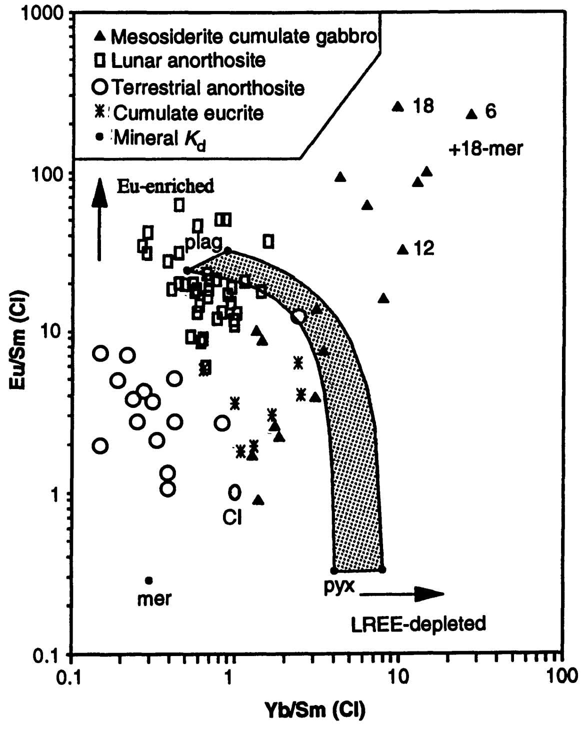

Fig. 1. CI chondrite–normalized Yb/Sm and Eu/Sm ratios for solar system igneous rocks with cumulus plagioclase. Some mesosiderite gabbro clasts have CI chondrite–normalized Eu/Sm ratios greater than those of any other known igneous rock in the solar system. Vaca Muerta pebbles 6, 12, and 18 (see text) and pebble 18 merrillite are labeled. Shown for comparison are typical plagioclase, pigeonite, and merrillite partition coefficients (K_d values) (*19*), which are assumed to be in equilibrium with melts of CI chondritic Eu/Sm and Yb/Sm (ellipse labeled CI). The stippled field is a mixing region between plagioclase and pigeonite in equilibrium with a melt with chondritic Yb/Sm and Eu/Sm ratios. REE data are from numerous sources (*31*); pyx, pyroxene.

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melts would evolve to lower Yb/Sm and Eu/Sm ratios. Therefore, all such cumulates should plot within or to the lower left of this field. Cumulate eucrites plot in this region, consistent with formation from melts with initial chondritic REE ratios.

Lunar anorthosites cluster around the plagioclase partition coefficient points, consistent with models that suggest that these rocks were formed from a lunar magma ocean with chondritic REE ratios (*14*). Terrestrial anorthosites plot at lower Eu/Sm and Yb/Sm ratios than the plagioclase partition coefficients. Because terrestrial anorthosites were formed under more oxidizing conditions than their lunar counterparts, less of the Eu is divalent. Thus, Eu partition coefficients will be lower (*1*), leading to less Eu/Sm fractionation. Calculated parent melts for terrestrial anorthosites typically have subchondritic Yb/Sm ratios (*15*).

Some of the mesosiderite gabbro clasts in Fig. 1 plot with the cumulate eucrites. These clasts may have been formed by simple igneous processes on the mesosiderite parent body, akin to those that formed the cumulate eucrites. That is, they may be cumulates that were formed from primary melts on the mesosiderite parent body. On the other hand, some mesosiderite gabbros have higher Eu/Sm and Yb/Sm ratios than the equilibrium field. These rocks must have had a complex petrogenetic history because their extreme REE fractionations cannot be due to formation from primary melts with chondritic REE ratios. The trend formed by all of the mesosiderite gabbros (Fig. 1) suggests that these rocks (including those below the equilibrium field) could have been formed by complex igneous processes.

Rubin and Mittlefehldt (*13*) evaluated three possible means of generating the extreme REE fractionations observed for some of the mesosiderite gabbro clasts. (i) The clasts may represent partial melt residues of an earlier generation of cumulates similar to cumulate eucrites (*13*). (ii) They may represent cumulates formed from a melt with REE contents similar to those of cumulate eucrites (*13*). (iii) They may be an artifact of terrestrial weathering (*16*). Rubin and Mittlefehldt (*13*) have shown that this latter model is incorrect.

Vaca Muerta pebble 18 is the mesosiderite gabbro clast with the highest Eu/Sm ratio (Fig. 1). Although the bulk clast composition and mineralogy of pebble 18 strongly indicate that it equilibrated with a melt highly depleted in incompatible elements, trace element analyses of the constituent minerals would provide firm evidence of this notion. We therefore analyzed merrillite, the major REE carrier, from pebble 18 with the ion microprobe. In determining the elemental concentrations, we followed the procedures of Davis *et al.* (*17*); the results are presented in Table 1. The merrillite has a Eu/Sm ratio 140 times that of CI chondrites (Fig. 2). This ratio firmly rules out the weathering hypothesis (*16*), which would require the merrillite to have a Eu/Sm ratio of <1. Because merrillite has a large positive Eu anomaly (Fig. 2), the extreme Eu/Sm fractionation observed for pebble 18 cannot be an artifact of undersampling merrillite in the split used for instrumental neutron activation analysis. The ion-probe data therefore indicate that the melt that equilibrated with pebble 18 was very depleted in the incompatible elements and had a fractionated REE pattern.

Mesosiderite gabbro clasts with Yb/Sm and Eu/Sm ratios slightly higher than equilibrium values (Fig. 1) may have formed either as cumulates from melts similar in trace element characteristics to common cumulate eucrites (pigeonite-plagioclase cumulates) or as partial-melt residues of common cumulate eucrites (*13*). Hence, a two-stage igneous process is required for the formation of these clasts. The mesosiderite gabbros with the largest Yb/Sm and Eu/Sm ratios, such as Vaca Muerta pebbles 6 and 18 [Eu/Sm ratios 223 times and 255 times that of CI chondrites, respectively (*13, 18*); Fig. 1], however, may require a more extreme fractionation process because the high Eu/Sm ratios are difficult to achieve by the two-stage processes outlined above (*13*). The extreme Eu/Sm ratios may reflect a multistage (≥3) fractional crystallization process (*13*).

Merrillite in mesosiderite gabbros is a late-stage phase, probably crystallizing from interstitial melt, which may not have been completely trapped in the rock. This inference is supported by the observation that merrillite in pebble 18 occurs at the boundaries of plagioclase and pyroxene and is associated with tridymite. Because pebble 18 is strongly LREE-depleted and has a CI chondrite–normalized Eu/Sm ratio of 255, it was expected that this clast equilibrated with an LREE-depleted, Eu-enriched melt (*13*). We estimate that the Eu/Sm ratio of the melt would be in the range of about 12 to 30 times that of CI chondrites. [This estimate uses the modal mineralogy of pebble 18 (*13*) to infer that it is composed of 39% plagioclase, 56% pyroxene, 2% REE-free minerals, such as metal, in equilibrium with a melt, plus 3% trapped melt. The Eu/Sm ratio of the melt is then calculated from mineral melt partition coefficients (*19*) and mass balance.] In Fig. 2 we compare the CI chondrite–normalized REE pattern for merrillite from pebble 18 with that of an equilibrium liquid calculated using merrillite-liquid partition coefficients (*19*). This calculated liquid has a CI chondrite–normalized Eu/Sm ratio of ~490, too high to be plausible

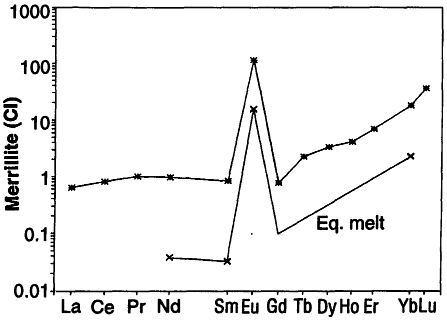

Fig. 2. CI chondrite–normalized REE pattern for pebble 18 merrillite and for an equilibrium liquid calculated from merrillite-liquid partition coefficients (*19*). The REE pattern of the merrillite requires that the parent melt of pebble 18 had a large positive Eu anomaly and was strongly LREE-depleted.

Table 1. Composition of merrillite in Vaca Muerta pebble 18 gabbro determined by ion microprobe. Oxide concentrations are in percent by weight; elemental concentrations are in micrograms per gram. Uncertainties due to counting statistics are given when they exceed 10% of the concentration.

Component	Merrillite	
SiO_2	0.85	
TiO_2	0.0038	± 0.0008
Al_2O_3	0.27	
Cr_2O_3	0.03	
FeO	1.5	
MnO	0.13	
MgO	2.5	
CaO	48	
Na_2O	0.96	
K_2O	0.05	
P_2O_5	45	
Li	7.2	
B	7.3	
F	63	± 12
Sc	76	
V	9.7	
Sr	66	
Y	5.8	
Zr	1.5	± 0.2
Nb	0.19	± 0.06
Ba	4.8	
La	0.15	± 0.02
Ce	0.48	± 0.05
Pr	0.088	± 0.28
Nd	0.43	± 0.10
Sm	0.12	± 0.05
Eu	6.4	
Gd	0.15	± 0.07
Tb	0.081	± 0.019
Dy	0.81	± 0.09
Ho	0.23	± 0.04
Er	1.1	
Yb	2.9	
Lu	0.85	
Hf	0.50	± 0.09
U	0.25	± 0.04

on the basis of our estimated equilibrium melt (above). If the late-stage melt was completely trapped in the rock, then the merrillite would contain essentially the entire REE inventory of the trapped melt. The CI chondrite–normalized Eu/Sm ratio of the merrillite (140) would then be a minimum value for the parent melt of pebble 18 because early plagioclase crystallization would have depleted the late-stage melt in Eu. Again, the measured Eu/Sm ratio in merrillite is too high for a plausible late-stage melt. Thus, we do not believe that the REE content of the merrillite reflects solely igneous processes.

Another possibility is that the REE content of the merrillite reflects metamorphic equilibration with the rest of the gabbro. In this case, the Eu anomaly of the merrillite would be a lower limit for the Eu anomaly of the bulk silicate fraction of the clast because Sm is more strongly partitioned into merrillite than is Sr (Eu^{2+} analog) (*19*) and plagioclase strongly partitions Eu^{2+} (*19*). For the modal abundance of merrillite and REE concentrations of pebble 18 (*13*) and the merrillite REE data (Table 1), we find that merrillite contains about 39% of the Sm and about 21% of the Eu of the bulk clast. This is consistent with equilibration of early crystallized, Eu-rich plagioclase with late crystallized, Eu-depleted merrillite. The merrillite-plagioclase partition coefficient for Sr (Eu^{2+} analog) is near unity, whereas that for Eu^{3+} is $>>1$ (*19*). Hence, metamorphic equilibration will result in merrillite with a Eu/Sm ratio greater than can be explained by plausible igneous crystallization, as we demonstrated above for pebble 18. We conclude that the REE content of merrillite reflects an approach to internal equilibrium with the silicate fraction of the clast and that the Eu/Sm ratio of the bulk clast represents that of a cumulate or partial-melting residue from the mesosiderite parent body. A recent ion-probe study of Vaca Muerta pebble 12, another gabbro, has shown that merrillite is in equilibrium with the silicates (*20*). Pebble 12 is petrographically similar to pebble 18 (*13*) but has a less fractionated REE pattern (Fig. 1).

The Eu/Sm ratios of Vaca Muerta pebbles 6 and 18 (223 and 255 times that of CI chondrites, respectively) are far greater than any observed for any other igneous rocks in the solar system. Those cumulate eucrites that are mineralogically and petrologically similar to the mesosiderite gabbros have Eu/Sm ratios <6 times that of CI chondrites (*12*). The highest ratio reported for lunar anorthosites for Apollo 16 rock 67455,30 is 61 times that of CI chondrites (*21*). The SNC meteorites (shergottites, nakhlites, and Chassigny), igneous rocks widely believed to have come from Mars, have Eu/Sm ratios <2 times that of CI chondrites (*22*). The highest ratio we have found reported for terrestrial anorthosite is 13 times that of CI chondrites for a sample from the Bad Vermilion Lake anorthosite complex (*23*). The highest Eu/Eu* ratio (measured Eu divided by that interpolated from Sm and Gd; approximately equivalent to the Eu/Sm ratio) observed for terrestrial lower crustal granulites is 11 times that of CI chondrites (*24*). Many lower crustal granulites that are depleted in large-ion lithophile elements and that have positive Eu anomalies are believed to be restites after crustal melting (*24*), which is one of two possible models we invoke for the genesis of mesosiderite gabbros.

The extreme REE fractionations observed for mesosiderite gabbro clasts indicate that complex igneous processes occurred on some asteroid-sized bodies in the early solar system. Both mesosiderite silicates and the basaltic achondrites are composed of petrologically and mineralogically similar basalts, gabbros, and orthopyroxenites. Because of this general similarity, one would not a priori expect that there would be large differences among the igneous histories of the parent bodies. Many mesosiderites, including Vaca Muerta, contain impact melt matrices and clasts (*13*, *25*), whereas the basaltic achondrites are typically fragmental breccias (*26*). This difference suggests that melting in large-scale, basin-forming impacts on the mesosiderite parent body may have been the heat source that produced the mesosiderite clasts with extreme REE fractionations. In this scenario, basin-forming impacts melted crustal cumulates and formed large melt sheets that underwent fractional crystallization during slow cooling. Alternatively, crustal cumulates at the basin floor may have been heated to the point where eutectic melts formed, leaving behind highly fractionated restites.

A second difference between mesosiderites and the basaltic achondrites is the presence of $\sim$50% by weight (30% by volume) metallic Fe-Ni in the mesosiderites (*27*). Heating driven by electromagnetic induction from a dense primordial solar wind will be concentrated in conductive regions of meteorite parent bodies (*28*). In this model, metal-silicate mixing occurred when an Fe core of a disrupted asteroid accreted onto the mesosiderite parent asteroid (*29*) and was mixed into the crust by further impacts. The metal-rich crust would then have coupled more strongly with the existing dense solar wind and been subjected to stronger heating than the metal-poor basaltic achondrite crust. Heating could have then produced the highly fractionated mesosiderite gabbros as restites or as cumulates from remelted cumulate rocks as described above for the basin impact model. However, heating of metal-silicate mixtures will work only if the metal occurs as isolated grains or pods in a silicate matrix (*30*). Once melting started, the metal could either have segregated from the silicates or have formed a continuous, highly conductive network that effectively shut off the heating process (*30*). Later impacts would then have remixed the metal and silicate into the breccias.

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Thermoelasticity of Silicate Perovskite and Magnesiowüstite and Stratification of the Earth's Mantle

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Analyses of x-ray-diffraction measurements on (Mg,Fe)SiO$_3$ perovskite and (Mg,Fe)O magnesiowüstite at simultaneous high temperature and pressure are used to determine pressure-volume-temperature equations of state and thermoelastic properties of these lower mantle minerals. Detailed comparison with the seismically observed density and bulk sound velocity profiles of the lower mantle does not support models of this region that assume compositions identical to that of the upper mantle. The data are consistent with lower mantle compositions consisting of nearly pure perovskite (>85 percent), which would indicate that the Earth's mantle is compositionally, and by implication, dynamically stratified.

The lower mantle is the largest single region of the Earth's interior, accounting for 55% of its volume. In contrast to the case for the upper mantle, from which we have samples, we cannot determine the composition of the lower mantle by direct observation, yet its major element chemistry has important implications for the evolution of our planet and its current thermal and chemical state. The possibility of compositional stratification—distinct upper and lower mantle compositions—implies that the Earth's mantle convects in at least two layers and that the planet has evolved slowly and retained much of its primordial heat and large-scale geochemical heterogeneities. Despite its importance, the most direct approach to determining lower mantle composition, comparison of laboratory experiments with seismic observations, has been subject to substantial uncertainties, and the question of compositional stratification remains open. The greatest difficulty has been the acquisition of accurate measurements at the relevant conditions. Experiments have only recently achieved high temperatures at pressures greater than 1 bar and high pressures at temperatures greater than 300 K (*1*, *2*). In this report we present a thermodynamic analysis and the geophysical implications of these measurements.

Constraints on lower mantle composition can be obtained from accurate experimental measurements of thermoelastic properties of the constituent materials. This approach requires determination of the room temperature equation of state, the thermal expansivity, α, and the dimensionless Anderson-Grüneisen ratio

$$\delta_X = -\frac{K_X}{\alpha}\left(\frac{\partial\alpha}{\partial P}\right)_X = -\frac{1}{\alpha K_X}\left(\frac{\partial K_X}{\alpha T}\right)_P \tag{1}$$

where $X = T$ or S (temperature or entropy) P is pressure, and K_X is the isothermal or adiabatic bulk modulus. These quantities relate laboratory data to the density, ρ, and seismic parameter, $\Phi = K_S/\rho$, at pressure-temperature conditions of the lower mantle (*3*, *4*). For the purpose of illustration, we assume that δ_X is independent of P and T, yielding

$$\rho(P,T) = \rho(P,T_0)\exp[-\overline{\alpha}\Delta T] \tag{2}$$

$$\Phi(P,T) = \Phi(P,T_0)\exp[\overline{\alpha}(1 - \delta_S)\Delta \mathrm{T}] \tag{3}$$

where $\Delta T = T - T_0$, and $\overline{\alpha} = \overline{\alpha}_0[\rho(0,T_0)/\rho(P,T_0)]^{\delta_T}$ is the mean value of $\alpha(P,T)$ from T_0 to T. There have been no earlier measurements of δ_T or δ_S of perovskite, and the pressure and temperature dependence of these quantities is not known. Several groups have measured the thermal expansivity of perovskite (*5*–*8*) but two of these studies disagree severely with each other (*5*, *8*). Workers analyzing lower mantle composition, relying on contradictory measurements or estimates of these crucial properties, have come to opposite conclusions. Some have argued for homogeneous mantle compositions (*8*–*10*) while others have proposed that the lower mantle is enriched in silica or iron, or both (*5*, *11*, *12*). Model calculations for a range of plausible values have indicated that values of $\overline{\alpha}_0$ greater than 2.5×10^{-5} to 4×10^{-5} K^{-1} and δ_T larger than 4 require that the lower mantle has a nearly pure perovskite composition (*9*, *13*).

Recently, the equations of state of (Mg$_{0.9}$,Fe$_{0.1}$)SiO$_3$ perovskite and (Mg$_{0.6}$,Fe$_{0.4}$)O magnesiowüstite were measured at combined high pressures and temperatures (*1*, *2*) (Fig. 1). The measurements were performed in externally heated diamond cells with the use of synchrotron x-ray diffraction. These data place experimental constraints on the thermal expansivity of perovskite at high pressures; that is to within the stability field of the material (P > 23 GPa). Such data are particularly important for perovskite because of problems associated with its metastability at low pressure (*14*, *15*). The data show that thermal expansivity decreases strongly with pressure and increases strongly with temperature, so that $\overline{\alpha}_0$ (300 to 2000 K) is significantly larger than 4×10^{-5} K^{-1}. The value of δ_T (≈7) was found to be substantially greater than earlier estimates (*1*), whereas the results for magnesiowüstite were consistent with earlier predictions (*2*, *16*). Detailed comparison with seismic determinations of ρ and Φ requires analysis of these quantities at lower mantle conditions.

We extract from the data the Debye temperature, θ_0, the Grüneisen parameter, γ_0, and q (*17*). These quantities are used to characterize the thermodynamic Helmholtz potential, $F(\rho,T)$, which yields complete thermodynamic information through its density and temperature derivatives (*18*). This approach allows us to calculate self-consistent equations of state and adiabatic temperature profiles, which are appropriate for a convecting system (Fig. 2). Possible systematic errors in the extrapolation of ρ and Φ to mantle conditions, due to the assumed form of $F(\rho,T)$, are expected to be small. Indeed, density and seismic parameter profiles determined from $F(\rho,T)$ with either Einstein or Debye models of the vibrational density of states are identical to Eqs. 2 and 3 with

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