Chapter 3

COSMOCHEMISTRY OF THE RARE EARTH ELEMENTS: METEORITE STUDIES

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3.1. Introduction

Study of the cosmochemistry of the REE can be said to have started with the early work of Noddack (1935), who determined the abundances of the REE in a composite mixture of meteorites using X-ray spectroscopy. No other work followed, however, until the pioneering work by Schmitt et al. (1960, 1963, 1964), who measured all fourteen REE plus Sc and Y in a wide variety of meteorites by neutron activation analysis. The early studies were aimed at determining the solar or cosmic abundances of the REE, but since that time numerous studies, both theoretical and experimental, have been undertaken to understand other aspects of the cosmochemistry of the REE.

Meteorites provide our best samples of primitive solar system materials. Many of them, particularly the chondrites, appear to have escaped igneous processing, and have preserved evidence of the earliest events responsible for the formation of the solar system. Other meteorites provide examples of igneous processing in systems different from those on the Earth and provide insight into the later processes that occurred on the meteorite parent bodies. This review will first provide a theoretical basis for our understanding of REE patterns related to nebular processes; it will then describe the evidence for such processes in the meteorites, comment on what the evidence may tell us about the formation of the solar system and finally describe the later parent body process.

Before discussing REE cosmochemistry we will very briefly describe current thoughts about the origin of the solar system, in order to provide a framework for considering the cosmochemical processes of interest. Our solar system is thought to have formed out of a large cloud of gas and dust (the pre-solar cloud). The cloud collapsed due to its internal gravity, perhaps initiated by shock waves from some source such as a nearby supernova. As it collapsed, the cloud flattened into a disk and became hot from the release of gravitational energy. Peak temperatures in the disk (the solar nebula) presumably increased with decreasing radial distance while the sun was forming at the center of the disk. The rise in temperature caused a considerable fraction of the dust to vaporize. The actual extent of the temperature rise is a subject of much debate and will be discussed below. Later the gas cooled, forming grains which agglomerated together. These agglomerations gradually grew by mutual accretion to form ever larger bodies, which eventually became planets, satellites, asteroids or comets.

Many of these bodies became warm enough to cause at least partial melting of the silicates, resulting in differentiated bodies. Differentiated bodies from which we have samples include the Earth, the Moon, and parent bodies of the achondrites and iron meteorites. The REE are very useful for studying igneous fractionation processes, such as partial melting and fractional crystallization. These studies can provide information about the petrogenesis of the sample studied, or they can be applied to large-scale planetary processes and properties. The study of REE in lunar samples has been reviewed by Taylor (1975, 1982) and will not be discussed in this review.

Most of the undifferentiated meteorites are referred to as chondrites, which are made up of metal, silicates and sulfides and contain abundances of non-volatile elements in nearly solar proportions. Because REE patterns are commonly normalized to chondrites, their classification will be briefly discussed. The classification into chemical groups, as proposed by Van Schmus and Wood (1967) and modified by Wasson (1974), is presented in Table 3.1. The designation consists of the chemical group, followed by a number referred to as the petrologic type, although the CI and CM meteorites are often cited without the number, since only one petrologic type is known. The CI chondrites are most nearly solar in composition and are generally used for normalization values in applications where one is concerned with the amount of an element in a sample relative to the solar nebula from

TABLE 3.1

Classification of chondrites into chemical groups

Common name	Group	Known petrologic types	Characteristics
Carbonaceous	CI	CI1	no chondrules, high carbon content, most nearly solar in composition
	CM	CM2	well-defined chondrules, high carbon content
	CO	CO3, CO4	small chondrules, Al/Si <0.11
	CV	CV2, CV3	large chondrules, Al/Si >0.11
Ordinary	LL	LL3—LL6	low total Fe, low metal
	L	L3—L6	low total Fe
	H	H3—H6	high total Fe
Enstatite	E	E4—E6	highly reduced silicates with nearly no oxidized Fe

which it formed. In most applications using REE, however, the important aspect of the normalization is the ratio between the REE. Traditionally, abundances in a mixture of chondrites from several classes are used (see section 3.5) and, except for when specifically designated otherwise, the average chondrite values of Wakita et al. (1971) will be used in this chapter.

3.2. Condensation theory

Condensation from a gas of solar composition

Several investigators have considered theoretical models for the condensation of elements from the solar nebula (Lord, 1965; Larimer, 1967; Grossman, 1972). These models have all assumed that the gas was initially at a sufficiently high temperature that all the elements were vaporized, that the gas had solar composition, and that the grains formed in thermodynamic equilibrium with the gas as it cooled. In a nebula of 10^{-3} atm total pressure, the first phase to condense is corundum, Al_2O_3, at 1758 K, followed by perovskite, $CaTiO_3$, at 1647 K; melilite, $Ca_2(Al_2,MgSi)SiO_7$, at 1625 K and spinel, $MgAl_2O_4$, at 1513 K. The most abundant phases, metallic iron and forsterite, Mg_2SiO_4, do not condense until 1473 K and 1444 K, respectively.

Grossman (1973) made similar calculations for a variety of refractory trace elements, assuming that they condensed as pure phases. Because refractory trace elements will condense at higher temperatures by forming solid solutions with major minerals, these calculations yield only a lower limit to the temperature at which the element will begin to condense from the gas. It was found that the trace elements which had condensation temperatures higher than 1473 K, the condensation temperature of iron, were enriched (relative to chondritic abundances) in Ca,Al-rich inclusions in the Allende meteorite. These inclusions will be discussed in more detail later, but for now it is sufficient to note that they have mineral and major element composition consistent with that expected of high-temperature condensates from the solar nebula. Although Grossman (1973) purposely ignored the condensation behavior of the REE, he noted that the REE were also enriched in the inclusions and suggested that they also condensed at high temperatures. Grossman and Ganapathy (1976a), however, calculated the condensation temperature at 10^{-3} atm total pressure for pure REE sesquioxides and found they ranged from 1590 K for Er to 1140 K for Eu. Only Dy, Ho, Er and Lu had condensation temperatures high enough to have started condensation at the point where the Allende Ca,Al-rich inclusions were presumably isolated from the gas. The fact that all of the REE are observed to be present in nearly their solar proportions in the inclusions demonstrates the inadequacy of pure-phase trace element condensation temperatures.

Because the REE will condense in solid solution with other elements, it is difficult to calculate an accurate condensation temperature. In addition, because at least a fraction of each of the REE will condense as soon as any host phase is present, the concept of a trace element condensation temperature that represents the onset of condensation has little significance. Generally, the temperature of 50% condensation, or the relative solid/gas distribution coefficient (discussed below), are better measures of the relative volatility of a trace element.

In order to calculate the amount of a REE condensed at a given temperature, it is necessary to first calculate the thermodynamic activity, a, of the element in some reference state, usually the oxide. Given sufficient thermodynamic data, the activity can be calculated from:

$$a_{\mathrm{LaO}_{1.5}} = K \cdot P_{\mathrm{LaO}} \left(\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}}\right)^{1/2} \tag{3.1}$$

where P is the partial pressure of the gaseous species and K is the equilibrium constant for the condensation reaction:

$$\mathrm{LaO}_{(g)} + \tfrac{1}{2}\,\mathrm{H_2O}_{(g)} \rightarrow \mathrm{LaO}_{1.5\,(s)} + \tfrac{1}{2}\,\mathrm{H}_{2(g)} \tag{3.2}$$

Then, to calculate the concentration of the element, it is necessary to know its activity coefficient in every phase present. The activity coefficient, γ, relates the thermodynamic activity of the element in the reference state to the mole fraction of the element, X, as:

$$a = \gamma \cdot X \tag{3.3}$$

The activity coefficient can be considered to be a measure of the ease with which the element can be accommodated by the host crystal lattice. For example, because of the similarity in size and valence, Ho_2O_3 is expected to be easily accommodated in Y_2O_3, and its activity coefficient in this phase should be near unity. However, in most common minerals the REE are considered incompatible elements and their activity coefficients in these minerals will be much greater than unity.

The difficulty in calculating the condensation temperature arises because the activity coefficients of the REE are unknown in any of the condensate phases. Grossman and Ganapathy (1976a) also calculated the fraction of REE condensed in the Ca,Al-rich inclusions, with the assumption that the REE condensed in perovskite with activity coefficients of unity. (This arbitrary assumption is often referred to as "ideal solid solution".) The result predicted that Eu still should not have been present in the Allende inclusions, contrary to observation. In an earlier work, however, Boynton (1975a) noted that much can be learned from studies of relative abundances of REE, even if the absolute abundances cannot be calculated at a given temperature. He noted that because the REE have very similar properties with respect to substitution in minerals, one could consider as a first approximation that the REE activity coefficients are identical; the absolute values are not required to calculate REE ratios. A second approximation was suggested, that the REE activity coefficient ratios vary as a smooth function of size, the variation being related to the mineral host. Boynton calculated relative solid/gas distribution coefficients at 1650 K, the approximate temperature of perovskite condensation at 10^{-3} atm. Perovskite is known to be a favorable host for REE (Borodin and Barinskii, 1960) and has been suggested as the most likely host of the REE in condensate minerals (Grossman, 1973). The activity coefficient ratios required to make a good fit between calculated REE abundances and abundances observed in a Ca,Al-rich inclusion by Tanaka and Masuda (1973) suggested that the host mineral showed a preference for light REE over heavy. This relationship was shown to be consistent with that expected for perovskite and was supported by subsequent measurements of perovskite/liquid distribution coefficients (Nagasawa et al., 1980a).

The relative solid/gas distribution coefficient, D_{M}, relates the element, M, to La ratio in the gas to the ratio in the solid according to:

$$\left(\frac{M}{\mathrm{La}}\right)_{(\mathrm{s})} = D_{\mathrm{M}} \left(\frac{M}{\mathrm{La}}\right)_{(\mathrm{g})} \tag{3.4}$$

The values for D_{M} can be calculated from thermodynamic data and knowledge of the oxygen fugacity. The latter can be readily calculated as a function of pressure and temperature with knowledge of the composition of the gas (which is usually assumed to be solar in composition). Most of the REE exist in the gas as monoxides, and for these elements the relative distribution coefficients are independent of oxygen fugacity. Condensation in gases of non-solar composition, which affect the oxygen fugacity, will be discussed in the next section.

Presentation of the thermodynamic data in the form of distribution coefficients is useful for calculating the REE patterns of condensates. The use of distribution coefficients allows the equations used for calculating REE patterns from partial melting or fractional crystallization to be used for their cosmochemical equivalents of partial vaporization or fractional condensation. By choosing the fractional amount condensed for one element, the amount condensed for each of the other REE can easily be determined. In addition, the distribution coefficients do not change much with temperature and can generally be considered constant over the temperature range of condensation. For example, at 10^{-3} atm total pressure in the nebula, significant condensation begins at about 1650 K, when perovskite appears, and ends at around 1500 K. Over this temperature range, the log of the D values change by only

10%. Thus, one unfamiliar with cosmochemical condensation calculations can easily calculate REE patterns in nebular condensates.

The distribution coefficients calculated by Boynton (1975a) are given in Table 3.2 and Fig. 3.1. The value for Ce is from Boynton (1978a) and reflects the contribution of CeO_2 in the gas which was ignored in the earlier work. Also given in Table 3.2 is the fraction of the gaseous element in the form of the monoxide, F_{MO}. The alternate gaseous form is the monatomic vapor except for Ce, which is CeO_2. As can be seen, the distribution coefficients span a very wide range, over 7 orders of magnitude. This range is much larger than that of conventional solid/liquid distribution coefficients, which seldom exceeds a factor of 100 and is generally less than a factor of 10. In addition, conventional solid/liquid distribution coefficients are always a smooth function of size, except for divalent Eu, but the solid/gas distribution coefficients show many irregularities. For example, one of the most volatile REE, Yb, differs by nearly a factor of 10^5 from the adjacent REE, Lu. As mentioned above, the relative amount of a REE that will condense is determined by both the intrinsic volatility of the element as measured by the solid/gas distribution coefficients, and by the ability of the element to substitute into the host crystal as measured by the activity coefficients. It should be noted that because the activity coefficient ratios are a smooth function of size, except for divalent Eu, the irregularities in the distribution coefficients may be seen in the REE pattern of a nebular condensate. It should also be noted here that Grossman and co-workers (Grossman and Ganapathy, 1976a; Davis and Grossman, 1979) have criticized this use of activity coefficients in the condensation calculations; a discussion of their

TABLE 3.2

Fraction of element present as gaseous monoxides and solid/gas distribution coefficients in the solar nebula at 1550 K

	F_{MO}	D
La	1.000	1.00
Ce	0.294	0.47
Pr	1.000	2.6
Nd	1.000	0.75
Sm	0.80	1.3
Eu	0.34	0.0014
Gd	1.000	65
Tb	1.000	200
Dy	0.954	350
Ho	0.975	380
Er	0.967	4300
Tm	0.51	640
Yb	$<1.5 \times 10^{-6}$	0.54
Lu	1.000	32,000

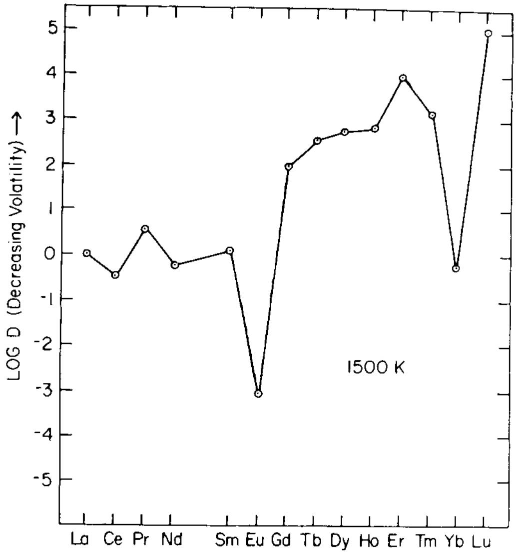


Fig. 3.1. REE solid/gas distribution coefficients; note greatly compressed logarithmic scale. These distribution coefficients determine the order in which the elements condense from the solar nebula and provide a very effective means of fractionating the REE in a way that is not a smooth function of size.

criticism will be deferred until the section on REE data in Ca,Al-rich inclusions.

Condensation in non-solar environments

An interesting aspect of the condensation of REE is that the relative volatility of several of the REE is a function of the oxygen fugacity in the gas (Boynton, 1978a). The reason for this relationship can be seen by considering the following set of equations:

$$LaO_{(g)} + \tfrac{1}{4}\, O_{2(g)} \rightarrow LaO_{1.5(s)} \qquad (3.5)$$

$$CeO_{2(g)} \rightarrow CeO_{1.5(s)} + \tfrac{1}{4}O_{2\,(g)} \qquad (3.6)$$

$$Yb_{(g)} + \tfrac{3}{4}\, O_{2(g)} \rightarrow YbO_{1.5(s)} \qquad (3.7)$$

Most of the REE exist in the solar nebula as monoxides, and reaction (3.5) describes their condensation behavior; increasing the oxygen fugacity will drive the reaction to the right, making these elements more refractory. However, Ce, which is present in significant amounts in the form of gaseous CeO_2, will actually become more volatile if the oxygen fugacity is increased. For Yb, which is present almost exclusively as the monatomic vapor, an increase in oxygen has a much larger effect than it does for the other REE. Thus, when normalized to La, most of the REE have relative volatilities that are independent of oxygen fugacity, but Ce becomes much more volatile and Yb much less volatile with an increase in oxygen. From inspection of Table 3.2, it can be seen that Sm, Eu and Tm have significant amounts of monatomic vapor present, and they should behave like Yb. This is true for environments which are more reducing than the solar nebula, but in more oxidizing environments, the reaction:

$$Tm_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow TmO_{(g)} \qquad (3.8)$$

converts the monatomic vapor to monoxide and these elements then behave in the same way as La. Similarly, Ce will become much more volatile than La in an oxidizing environment, but it will be converted from CeO_2 to CeO in a reducing gas and will then behave like La.

The dependence of REE volatility on oxygen fugacity is important because several astrophysical environments with very different oxygen fugacities may have been important in creating grains that were present in our solar system. Several investigators (Hoyle and Wickramasinghe, 1970; Clayton, 1975; Lattimer et al., 1978) have suggested that grains can form in ejecta from a supernova. Such an environment can be highly oxidizing because the hydrogen, which is a strong reducing agent in a gas of solar composition, has been converted to helium, or beyond to carbon and oxygen. The large excess of oxygen over hydrogen yields a highly oxidizing gas. However, under certain conditions, more carbon than oxygen will be produced and the oxygen will be tied up as carbon monoxide, with the excess carbon present as graphite. Such an environment is much more reducing than is a gas of solar composition. Lattimer et al. (1978) give detailed calculations of the temperatures at which various minerals condense in a supernova. They find that the same minerals form in an oxidizing region of the supernova as during condensation in the solar nebula, e.g., perovskite, melilite, and corundum. Thus, these minerals, which are stable in the solar nebula, may have been preserved if peak nebular temperatures were not sufficient to vaporize them, and they may have preserved evidence of their formation in a highly oxidizing environment.

Even within our solar system, regions with variable oxygen fugacity have been proposed. Larimer (1975) has suggested that regions with high C/O ratios will yield the very low oxygen fugacities needed to explain the highly reduced enstatite chondrites. Herndon and Wilkening (1978) noted that oxidizing conditions can obtain if chondritic matter is vaporized after being removed from a large fraction of the gaseous components of the solar nebula. Such an environment has been suggested for the formation of chondrules, small spherical droplets present in chondritic meteorites.

3.3. REE abundances in Ca,Al-rich inclusions

By far the most work in recent years on REE abundances in chondrites has been with the Ca,Al-rich inclusions (CAI) found in carbonaceous chondrites. As mentioned earlier, they are thought to be early condensates from the solar nebula. Many of the inclusions are made up of the minerals expected, based on equilibrium thermodynamics, to be present in early condensates, but the most persuasive arguments for their origin as condensates come from studies of trace elements. In most of the inclusions a wide variety of refractory trace elements are enriched rather uniformly to abundances of approximately 17 times those in CI chondrites, suggesting that these inclusions represent the first 6% (= 100/17) of the elements to condense in the solar nebula (Grossman et al., 1977). The nearly uniform enrichment of the refractory trace elements, which include the REE, suggests that these elements are totally condensed; the enrichment factor is determined by the amount of dilution from major elements, which condense after the refractory elements. Although most investigators consider these inclusions to be early condensates, an equally plausible interpretation is that they are residues from incomplete vaporization of grains from the pre-solar cloud (Chou et al., 1976).

With only a few exceptions all of the CAI studied are from one meteorite, Allende, a member of the CV3 class of carbonaceous chondrites. Unless otherwise stated, all data in this section will refer to Allende CAI. The literature on the CAI is a little confusing because of various nomenclatures that have been used. The Allende inclusions can be grouped into two major types: coarse-grained chondrules and fine-grained aggregates (Clarke et al., 1971). Chondrules are rounded or subrounded, range in size from 3 to 25 mm and have grain sizes of the order of 1 mm. Aggregates are generally very fine-grained, highly irregular in shape and vary in size from 0.1 to 10 mm. Often the chondrules are referred to as coarse-grained inclusions, and the aggregates as fine-grained inclusions. Some of the confusion exists because some of the aggregates are somewhat coarser-grained than the others and some investigators group them with the coarse-grained inclusions, thus mixing aggregates and chondrules together. For example, the low-Rb aggregate of Gray et al. (1973) was re-classified as a coarse-grained inclusion by Grossman and Ganapathy (1975). Both the coarse-grained and the fine-grained inclusions can be sub-divided further. Grossman (1975) grouped the coarse-grained inclusions (including aggregates) into two types: type A have minor amounts of pyroxene, which occurs as diopside, whereas type B have major amounts of pyroxene ($>35\%$), which occurs as a Ti,Al-rich clinopyroxene called fassaite. The characteristics of the coarse-grained inclusions have recently been reviewed by Grossman (1980). The sub-divisions of the fine-grained aggregates are based on their REE patterns and will be discussed below.

Coarse-grained (Group I) inclusions

The abundances of REE in coarse-grained inclusions are generally enriched uniformly around 12 to 15 times chondrites; occasionally, samples have a small (20%) positive anomaly in Eu. Examples of this type have been analyzed for REE by many investigators (Gast et al., 1970; Grossman, 1973; Tanaka and Masuda, 1973; Martin and Mason, 1974; Osborn et al., 1974; Wänke et al., 1974; Grossman and Ganapathy, 1976b; Chou et al., 1976; Conard, 1976; Davis et al., 1978; Taylor and Mason, 1978; Nagasawa et al., 1981). A typical analysis from Tanaka and Masuda (1973) is plotted in Fig. 3.2. This type of REE pattern is referred to as Group I by Mason and co-workers (Martin and Mason, 1974; Mason and Martin, 1977; Taylor and Mason, 1978), who use REE patterns as major classification parameters.

The slight increase in chondrite-normalized abundance from La to Lu observed in the Group I REE patterns in Fig. 3.2 may represent a sampling

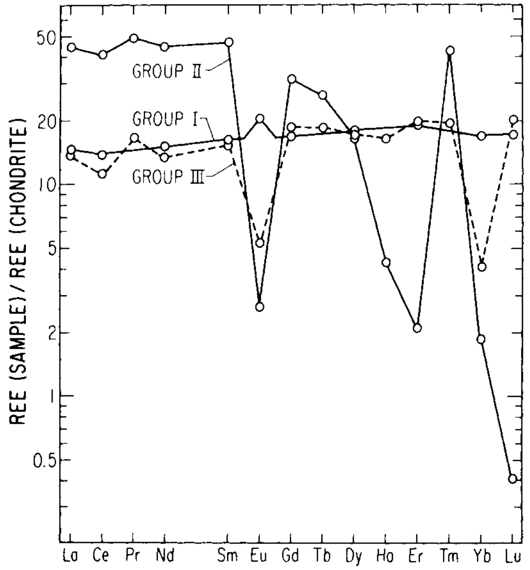


Fig. 3.2. Typical REE patterns found in Allende Ca,Al-rich inclusions. The Group I patterns are generally found in coarse-grained chondrules and represent nearly total condensation of REE; the enrichment to around 15 times chondritic abundances is due to the absence of Si, Mg and Fe, which condense at lower temperature and dilute the REE in chondrites. The Group II and Group III patterns are generally found in fine-grained aggregates. The Group III aggregates are deficient in the two most volatile REE, Eu and Yb, because they were isolated from the gas before Eu and Yb were fully condensed. The Group II aggregates are deficient in the highly refractory REE as well as in Eu and Yb. This material is thought to have condensed from a gas following the condensation of an ultra-refractory condensate which removed most of the refractory REE. Group I pattern from Tanaka and Masuda (1973); Groups II and III from Conard (1976).

problem, since the entire inclusion was almost certainly not analyzed. The enrichment cannot be caused by an incomplete condensation of the more volatile REE because Yb, which is more volatile than La, is enriched over La by the amount expected from interpolating between Er and Lu. Mason and Martin (1974), Onuma et al. (1974) and Nagasawa et al. (1977) have measured REE abundances in separated minerals from coarse-grained Allende inclusions, and both find similar results. Except for Eu, the REE are enriched in the pyroxene relative to the melilite, the enrichment increasing as a smooth function of size towards the HREE. The ratio of REE between the phases agrees very well with calculated pyroxene/melilite distribution coefficients, suggesting that the REE have equilibrated between the phases (Nagasawa et al., 1977). Thus, the enrichment in HREE could represent a preferential sampling of pyroxene over melilite in the material taken for analysis. However, as suggested by Grossman et al. (1977), various ratios of pyroxenes and melilite cannot account for the positive Eu anomaly, as the samples which are the most enriched in Eu are those most deficient in La, just the opposite of what would be expected from the addition of melilite, since melilite is enriched in both Eu and La.

Nagasawa et al. (1977) found that an anorthite separate contained about twice the Eu concentration of the bulk sample but negligible amounts of the other REE. Thus, anorthite can contribute Eu to the bulk sample without affecting the other REE. However, a 20% excess of Eu requires a 20% excess of anorthite, an amount that seems most unlikely considering that the inclusion studied by Nagasawa et al. (1977) had only 5% anorthite. In addition, the average of ten coarse-grained inclusions analyzed by Mason and Martin (1977) also show a positive anomaly, suggesting that sampling of the inclusions for analysis is not a likely explanation for the Eu excess. It should be noted that the average of ten inclusions also shows no significant slope from light to heavy REE, supporting the suggestion that a sampling problem is the explanation for the HREE enrichment shown in Fig. 3.2.

It is likely, therefore, that the positive Eu anomaly represents a real enrichment in the whole inclusion relative to the other REE. This result can be explained by condensation, since Eu is much more volatile than the other REE (Fig. 3.1). If some grains were removed from the nebula after most of the REE had condensed, the remaining gas would be over-abundant in Eu relative to the grains and continued condensation would yield an enrichment of the more volatile elements. It may seem rather ad hoc to invoke such a mechanism, but as we shall see from the following section, there is much evidence suggesting that there were multiple episodes of condensation and isolation of grains from the gas. There are also many examples of inclusions depleted in Eu, presumably because they were isolated from the gas before Eu had fully condensed, suggesting that, indeed, Eu-rich gases must have been present. However, these samples (the Group III inclusions) generally show Yb depleted to the same extent as Eu. If these materials were responsible for enriching the gas in Eu, they should also have enriched the gas in Yb, and Yb should also be enriched in the coarse-grained Group I inclusions, which is contrary to observations.

Another possible explanation of the positive Eu anomaly is that the whole inclusion was composed of various condensate grains which clumped together. The grains in the rounded coarse-grained inclusions probably partially melted during or after the aggregation. Different grains that may have been present in the gas may have contributed different amounts of the various trace elements. Grossman et al. (1977) tried to determine which elements may have been added simultaneously, and concluded that Ca, Sr and Eu were added together in the same phase, which is probably melilite. Although the abundances of refractory trace elements averaged over all the grains present would have uniform enrichments, variable amounts of different component grains could lead to variable enrichments of different elements. The implication of this model is that only a statistically small number of grains must have been sampled to make the inclusions. Because the anomalies are about 20%, no more than 100 grains of each type could be sampled. If many more grains had been aggregated together to form the inclusions, the grains would have been a good statistical sample of the grains present in the gas, and the inclusions would then have had uniform enrichments. Thus, according to this model, the centimeter-sized inclusions must have been made from millimeter-sized grains. It is doubtful that such large grains would form directly from the nebula.

Another difficulty of this model is that a mixture of a small number of condensate grains should contribute other volatility-related irregularities. If several different minerals contain REE, it is unlikely that they started condensing at exactly the same time. The grains which started to condense later would be deficient in the most refractory REE, such as Lu and Er, and enriched in more volatile REE, such as Yb. Non-representative sampling of these grains would be expected to provide volatility-related anomalies between Yb and Lu, which is again contrary to observation.

A solution to this difficulty is to suggest that the coarse-grained chondrules are secondary objects formed from pre-existing coarse-grained material. If equilibration between phases had occurred in the pre-existing material, then the components which mixed together to form the inclusions would have contributed REE and other trace elements according to mineral preference effects rather than volatility effects. The bulk composition of the pre-existing material would, of course, be determined by the volatility of the elements. Several of the models for the formation of ordinary chondrules are based on pre-existing material (Wasson, 1974, p. 198f; Kieffer, 1975; Dodd, 1978). A serious constraint on this model is the presence of ^{26}Al ($t_{1/2} = 7.4 \times 10^5$ years) in the Allende inclusions (Lee et al., 1976), which requires that the inclusions must have formed within a few million years of the last nucleosynthetic event.

Fine-grained (Groups II and III) inclusions

Most of the fine-grained Ca,Al-rich aggregates in Allende can be divided into two groups, called Group II and Group III by Martin and Mason (1974). Typical examples of the REE patterns in these groups are plotted in Fig. 3.2. Analyses of REE in fine-grained aggregates have been reported by many groups (Tanaka and Masuda, 1973; Nagasawa et al., 1977; Conard, 1976; Grossman and Ganapathy, 1976b; Mason and Martin, 1977; Taylor and Mason, 1978). The Group II patterns are characterized by strong enrichment of light REE relative to heavy, accompanied by large anomalies at Eu, Tm and Yb. In addition, smaller anomalies among the LREE are often observed. It was noted by Tanaka and Masuda (1973), who first discovered these peculiar inclusions, that although the Eu and Yb anomalies are in the opposite direction, their chondrite-normalized abundances are similar. Subsequent analyses have shown this observation to be generally true. The Group III REE patterns are quite flat except for depletions at Eu and Yb; again, the chondrite-normalized abundances of Eu and Yb are usually identical in a given sample, but the depletion relative to the other REE can vary widely between various samples.

Models for the formation of these REE patterns have been discussed by several workers. Boynton (1975a) and Davis and Grossman (1979) discussed detailed thermodynamic calculations and applied them mainly to the Group II inclusions, while Boynton (1978b) gave a less rigorous discussion of both Group II and III. The Group III patterns are a bit easier to understand and will be discussed first. The uniform enrichment of most of the REE suggests that these elements are totally condensed, while Eu and Yb are volatile enough to have only partially condensed. Examination of Fig. 3.1 shows that Eu and Yb are indeed the most volatile REE, which is consistent with the above suggestion. However, in detail, there are problems with the model because Yb is only slightly more volatile than the LREE, and Eu is much more volatile than Yb. Yet in the Group III (and Group II) inclusions the Eu/Yb ratio is generally chondritic (Taylor and Mason, 1978; Davis and Grossman, 1979), suggesting that these elements have equal volatility. In addition, La/Yb ratios as large as 50 have been found (Nagasawa et al., 1977), suggesting that Yb is much more volatile than La.

As mentioned above, the activity coefficients indicate that the early condensates show a preference for the light REE relative to the heavy. This preference will tend to increase the volatility of Yb relative to La. Davis and Grossman (1979) made an alternative suggestion to increase the volatility of Yb relative to the LREE by proposing that the condensation took place in a more highly reduced region of the nebula. In section 3.1 it was shown that Yb will indeed become more volatile in a reducing environment, but Sm shows a similar effect, and one would expect a significant Sm depletion in those samples with a large Yb depletion. The Sm depletions are not observed, suggesting that only slightly more reducing conditions can be tolerated. It is possible that a combination of activity coefficient effects and reducing conditions are responsible for the enhanced volatility of Yb.

It is unlikely, however, that these effects would be such that Yb would have a volatility precisely equal to that of Eu. A more reasonable suggestion is that Eu and Yb are sufficiently more volatile than the other REE so that they will not have condensed significantly when the remaining REE have totally condensed. At this time, if the grains are partially separated from the gas (e.g. by settling to the median plane of the nebula) and condensation continues, Eu and Yb can condense totally and maintain their solar proportions. They will be depleted relative to the other REE to the extent that a portion of the original gas was lost. An alternative mechanism in which Eu and Yb were added with a later volatile-rich component was suggested by Davis and Grossman (1979). In either case a rather abrupt separation of grains from gas seems to be required.

The Group II inclusions have an even more complicated history. The REE pattern is unlike any previous pattern found from studies of terrestrial, lunar or meteoritic samples. Patterns generated by igneous processes often yield familiar Eu abundance anomalies due to the stability of Eu in the divalent state. Although one could argue that under sufficiently reducing conditions Yb could also become divalent, it is not possible to reduce Tm to the divalent state without reducing several other REE. Clearly, the Tm anomaly in the Group II inclusions cannot be made by igneous fractionation.

If these inclusions were the first condensates to form from the solar nebula, the REE solid/gas distribution coefficients (Fig. 3.1) would suggest that Lu and Er, the two most refractory REE, would be the first REE to condense and would be the most enriched. This suggestion is contrary to observation; in fact, the opposite appears to be the case. The more refractory elements are the most depleted and the more volatile elements are the most enriched; the only exceptions to this observation are Eu and Yb, which will be discussed later. Boynton (1975a) noted this effect and suggested that the Group II inclusions may have formed from the gas remaining after an earlier, more-refractory condensate formed and depleted the gas in the most refractory REE. A plot of REE in a typical Group II inclusion is shown in Fig. 3.3, with calculated values based on the REE solid/gas distribution coefficients. The calculations assume that the initial condensate has an activity coefficient relationship which shows a preference for light REE relative to heavy. The calculated values shown are not for the initial highly-refractory condensate, but rather for the gas remaining after the initial condensate formed and was isolated from the solar nebula. It can be seen that within the errors in the distribution coefficients (approximately a factor of two to three) the theoretical REE pattern agrees well with the observed pattern; even the peculiar Tm anomaly is explained. Davis and Grossman (1979) present plots of REE data from twenty individual Group II REE

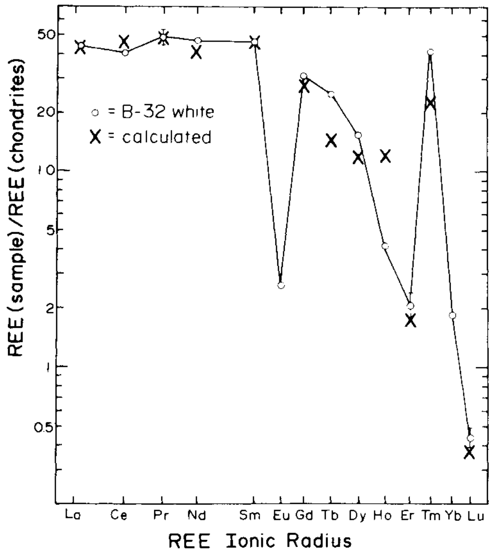


Fig. 3.3. A Group II REE pattern with calculated REE abundances. The values calculated based on REE volatility account very well for the peculiar fractionation pattern. The Tm anomaly is expected in a gas/solid fractionation, but not in any igneous, or parent body, fractionations; it provides strong evidence that this material condensed from the solar nebula.

patterns with calculated values shown as in Fig. 3.3. It is remarkable how well the calculations fit the variety of observed Group II REE patterns.

Calculated values for Eu and Yb have not been plotted in Fig. 3.3 because these elements are so volatile that they did not condense into the Group II inclusions. They are presumably depleted in these inclusions by a mechanism similar to that suggested for the Group III inclusions. Thus, the REE in the Group II inclusions represent the middle of the REE condensation sequence; the more refractory REE were removed by an initial condensate that was isolated from the gas, and the more volatile REE were left behind in the gas from which the Group II inclusion was isolated.

Boynton (1978b) discussed the implications of these REE patterns. He noted that they gave strong evidence for multiple episodes of condensation and isolation from the gas. The isolation mechanism must have been very efficient; it is quite common for Lu to be depleted by a factor of 100 relative to La. This depletion requires that 99% of the Lu was removed and isolated from the solar nebula before the second condensation episode, the one which produced the grains that made the Group II inclusions. The Lu must have remained isolated throughout the entire formation period of the Group II inclusions.

The Group II inclusions are also significant in that they are the only samples which are unequivocally condensates. As mentioned earlier, many of the Ca,Al-rich inclusions have a trace element pattern that is consistent with having an origin from either condensation or partial vaporization. If the formation process occurs at equilibrium, the results will be identical. The Group II inclusions, with their strange abundance anomalies, require a gas/solid fractionation process to generate their REE patterns. Furthermore, because of the inverse relationship between abundance and volatility, the Group II inclusions must have been made from material that was originally the gas component of the fractionation. The fact that these REE were in the gas phase places strong constraints on the temperature reached in the region of the solar nebula where these inclusions formed.

Without knowing the amount of the various host phases and the REE activity coefficient in these phases, one cannot calculate the temperature precisely. However, a lower limit to the temperature can be calculated by assuming that the REE condense as pure phases; condensation in solution with other phases can only raise the temperature. The calculations for the Group II patterns require that essentially all the LREE are in the gas phase. Grossman and Ganapathy (1976a) calculated condensation temperatures of pure REE oxides in a solar nebula of 10^{-3} atm and found that the LREE began to condense at temperatures from 1312 to 1353 K. Thus, 1300 K can be taken as a lower temperature limit if the nebula was at 10^{-3} atm. At 10^{-6} atm, about the lowest pressure possible to account for the mass of the planets in the solar system, this temperature limit will drop to about 1150 K.

This temperature of 1150 K is a very rigorous limit. The REE will almost certainly condense out at higher temperatures by forming solutions with other phases. Wasson (1978) suggested that if the REE condensed in perovskite, the limit at 10^{-6} atm is 1440 K. This temperature is a reasonable, although less rigorous, estimate to the lower limit of the peak temperatures achieved in this part of the solar nebula.

The temperature of 1440 K is difficult to understand in terms of proposed models for the formation of the solar nebula (e.g., Cameron, 1978). Although there is sufficient gravitational energy to heat the solar nebula during the collapse, the process is generally thought to be slow enough that the heat is quickly radiated away. Currently, the evidence for high temperatures in parts of the solar nebula is very strong; finding a physical environment in which these high temperatures can occur still remains a problem.

Other models for the solar nebula, in which the gas of the nebula is very hot but the grains are very cool, have been suggested (e.g., Arrhenius and Alfven, 1971; Alfven and Arrhenius, 1976). Under these conditions the gas is hot enough that most elements are ionized; the elements are thought to condense in the order in which they became neutral, which is determined largely by their ionization potentials. Boynton (1975b) noted that the ionization potentials of the REE vary as a smooth function of size except for large anomalies at Gd and Lu. Condensation under such non-thermal conditions as proposed by Arrhenius and co-workers should result in samples with large abundance anomalies at Gd and Lu. Such samples have not been found. The Group II inclusions argue strongly for condensation under conditions near or at thermodynamic equilibrium.

Grossman and Ganapathy (1976b) have proposed another model for the Group II and Group III inclusions. They suggested that Group II and Group III inclusions all belonged to the same class of aggregates with similar condensation temperatures. They suggested that the different inclusions could be formed by incorporating different proportions of several phases, each of which preferentially accepted different REE into its structure during condensation. The gas from which these grains condensed was thought to have a composition intermediate between the Group II and Group III compositions. This gas was that which remained after the coarse-grained inclusions condensed and were isolated from the solar nebula. The amount of a given element left behind in the gas was determined not by thermodynamic properties of the element but by a property called the accretion efficiency of the element. No explanation for different accretion efficiencies of individual REE was suggested. The model has difficulty explaining how an assemblage of many fine grains, with a composition determined by non-equilibrium processes, can be sampled to produce an assemblage with solar abundances of REE (the Group III inclusions), and an assemblage that mimics an equilibrium fractionation (the Group II inclusions).

Davis and Grossman (1979) agreed with the model of Boynton (1975a) for the formation of the Group II REE patterns, but suggested two changes in the method of calculations. They did not allow for non-ideal solid solution, but preferred to assume that the activity coefficients were equal to unity. (Such values are not excluded in the original Boynton (1975a) model, of course; it was simply shown that, with the inclusion studied, the fit was better with non-ideal solutions.) Davis and Grossman also allowed for a second REE component with chondritic abundance ratios in the Group II inclusions, as suggested by Tanaka and Masuda (1973). The chondritic component can often account for a large fraction of Lu, the most depleted element, but generally contributes a negligible amount of the LREE. The two-component, ideal-solution model was found to have a slightly better fit than the one-component, non-ideal solution model (a mean deviation of 8.0% vs. 11.4%) when only the elements Gd, Tb, Dy, Ho, Er and Lu were considered in twenty Group II inclusions. The ideal model, however, did not provide a good fit for Tm.

Davis and Grossman (1979) noted that the non-ideal, one-component model required large differences in the ratio of the activity coefficients between Lu and Sm. The ratio was found to vary from unity to 2093. Such a variation is not expected if only one mineral phase, such as perovskite, is the host for the REE. Even if, as now seems likely, other phases such as hibonite, with a different activity coefficient versus size relationship, were an additional host for REE, such a change in the activity ratio seems large.

Davis and Grossman (1979) concluded that such a variable ratio argued strongly against non-ideal solid solutions and they preferred their two-component, ideal-solution model. However, because they changed two parameters between the models (ideal vs. non-ideal and one vs. two components), they had no way to determine which parameter accounted for the slight improvement in the fit for the subset of REE which they considered. They failed to realize that all of the variability in the activity coefficient ratio can be attributed to the absence of the chondritic component in the test of the non-ideal calculations. Clearly, a two-component, non-ideal model would give a better fit to the data than would the two-component, ideal model, even if the Lu/Sm activity ratio were fixed at some value. The ideal model is simply a special case of the non-ideal model in which the ratio is fixed at unity.

The presence of the chondritic component was first suggested by Tanaka and Masuda (1973), who showed that the REE abundances in one of their inclusions could be duplicated almost exactly by a mixture of 55% of another inclusion and 45% chondritic material. How this chondritic component, which Davis and Grossman (1978) show to be present in most Group II aggregates, came to be mixed into the inclusions is still a mystery. It provides one more example of how complicated was the formation of the solar system.

Mason and Martin (1977) have suggested a few other groups of Ca,Al-rich inclusions in Allende. They designate Group V inclusions as those inclusions which have flat REE patterns with no significant anomalies. The Group VI inclusions are those with flat REE patterns, except for positive Eu and Yb anomalies. Apparently the Eu and Yb fractionation that occurs relative to the other REE in the Group III inclusions can be either enrichments or depletions. There does not appear to be enough data in the literature to determine whether these groups are statistically significant, or whether they represent a continuum from Group III though Group V to Group VI.

The Group IV inclusions of Mason and Martin (1977) are not Ca,Al-rich inclusions. They generally have fairly flat chondrite-normalized REE patterns at values of about 3—4. The patterns are similar to the amoeboid olivine aggregates of Grossman et al. (1979), who also measured REE abundances. The Group IV inclusions may represent later stages in the condensation sequence after olivine condensed and diluted the refractory trace elements.

None of the inclusions discussed so far have the REE pattern which is complementary to that of the Group II inclusions. In fact, the author is aware of 96 analyses of Allende Ca,Al-rich inclusions (including 11 unpublished analyses by H. Palme), in which at least a partial REE pattern was determined, and none of them contains the REE pattern expected of the hypothetical initial condensate that is complementary to the Group II pattern.

Inclusions from other carbonaceous chondrites: ultra-refractory condensates

Relatively few Ca,Al-rich inclusions from carbonaceous chondrites other than Allende have been studied for REE abundances. Examples of the ultra-refractory component apparently missing from Allende have been observed, however. The only fairly complete REE pattern available is of an inclusion, MH-115, from the Murchison meteorite, a member of the CM class of carbonaceous chondrites (Boynton et al., 1980). The REE pattern is given in Fig. 3.4. The sample is strongly enriched in the heavy REE, but the enrichment is clearly not a smooth function of size. The most volatile elements, Yb and Eu, are strongly depleted, while Ce and Tm are moderately depleted relative to their neighbors. As can be seen from Fig. 3.4, the abundances agree well with those calculated using the solid/gas distribution coefficients. The abundances of Eu and Yb are higher than expected based on the solid/gas distribution coefficients and, as with the Allende fine-grained aggregates, the elements are present in their solar ratios. As was noted for Allende aggregates, this observation suggests that either the grains may have settled or otherwise become partially isolated from the gas, or Eu and Yb may have been added later by an additional component.

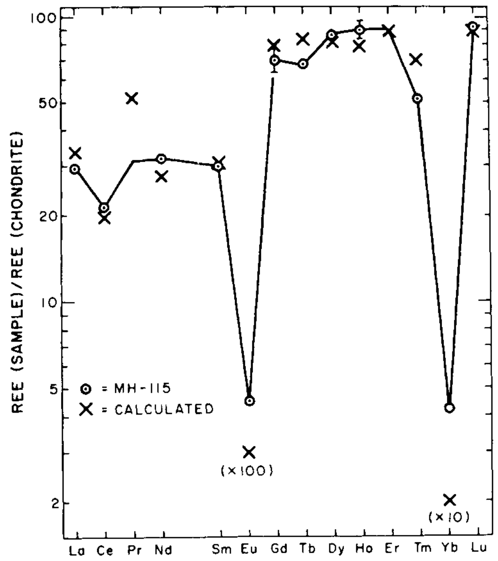


Fig. 3.4. The missing ultra-refractory component has not been found in Allende, but an example has been found in Murchison (Boynton et al., 1980). It is similar to that which may have depleted the gas from which the Group II Allende inclusions formed. This inclusion may represent the first 1% of the solid matter to condense from the solar nebula. Again, the anomalies are expected from a nebula fractionation but not from a planetary fractionation.

Although inclusion MH-115 is not exactly complementary to the Group II inclusions, it has all of the right properties. It is enriched in the highly refractory REE, those depleted in the Group II inclusions, and is depleted in the LREE and Tm. Similar material, isolated at a slightly earlier stage in the condensation sequence, would be a very good example of the Group II complementary material.

The Ca,Al-rich inclusions in Murchison have been the subject of several mineralogical investigations and consist mainly of spinel and hibonite, with small amounts of perovskite (Fuchs et al., 1973; Macdougall, 1979; MacPherson et al., 1980). These minerals are more refractory than those found in the Allende inclusions; this fact supports the conclusion that MH-115 is made of ultra-refractory materials. The enrichment of about a factor of 100 in the most refractory REE, Dy, Ho and Lu, suggests that MH-115 may represent the first 1% of the total condensation sequence.

Tanaka et al. (1980) have analyzed similar inclusions from Murchison but found different REE patterns. One inclusion has a typical Group III REE pattern with the REE enriched to 17 times chondritic abundances except for Eu and Yb, which are enriched to only 11 and 14 times chondritic abundances, respectively. Another sample, actually two inclusions that were mixed together, had a typical Group II pattern. The only exception is that Gd was nearly as depleted as Eu. This result was found by instrumental neutron activation analysis (Grossman et al., 1977), and confirmed in the above work by radiochemical analysis. The possibility that the result was due to a variation in the isotopic ratio of Gd (Gd was the only element determined via a *p*-process nuclide, ^{153}Gd) was dismissed. They concluded that the Gd anomaly was due to chemical processes. Another possibility not considered by Tanaka et al. (1980) is that a reaction interference in the high flux reactor used for the analysis tends to make large amounts of ^{153}Gd from ^{151}Eu (Kramar, 1980; Boynton, 1979); this interference would make ^{153}Gd a measure of Eu in the sample and would account for the apparent Gd depletion.

Kurat (1975) determined Y, Dy and Gd with an electron microprobe in perovskite from a Ca,Al-rich inclusion from Lancé, a carbonaceous chondrite from the class CO3. The chondrite-normalized enrichments range from 3000 to about 6000. These data are too incomplete to tell much about the origin of the inclusion, but they do indicate that perovskite is a favorable host for REE. Noonan et al. (1977) measured the REE with an ion microprobe in a Zr-Y oxide found in an inclusion from Ornans, also a CO3 chondrite. The LREE were undetectable (<100 times chondritic), but the HREE had enrichment factors from 5000 times chondritic abundances for Gd to 35,000 for Er. The more volatile elements Tm and Yb are enriched by factors of 9000 and <2000, respectively. Except for the most refractory REE, Lu, which had an enrichment factor of 9000, all these abundances are in direct proportion to their solid/gas distribution coefficients. This sample may also be an example of an early ultra-refractory condensate. Why Lu is not the most enriched REE is not clear; it may be due to an even more refractory condensate scavenging a significant fraction of the Lu or it may be simply a mineral preference effect tending to exclude Lu from the Zr-Y oxide.

Recently, Palme and Wlotzka (1981) found a Ca,Al-rich phase, also from Ornans, in which Dy, Ho, Er and Lu are progressively enriched from about 1500 to 10,000 times chondritic abundances. The more volatile REE, La, Sm, Eu and Yb, could not be detected; their upper limits are less than 100 times chondritic abundances except for Yb, for which the limit is about 1000. The abundances of the four REE, as well as the four upper limits, are consistent with an origin of the inclusion as an ultra-refractory condensate from the nebula. The observed abundances agree quite well with those predicted based on the REE solid/gas distribution coefficients. However, Palme and Wlotzka (1981) prefer an origin as a refractory residue from a partial vaporization event. Although an equilibrium configuration should be identical regardless of whether equilibrium is approached from above or below, a refractory residue can form in a hydrogen-poor environment. Under such conditions, the vaporized gas becomes oxidizing, and relative volatilities of the trace elements will change (see section 3.2). Although none of the REE determined by Palme and Wlotzka (1981) are sensitive to this effect, they found that W, which is sensitive to oxygen, was more depleted than expected from a reduced, hydrogen-rich gas. It is for this reason that they consider the inclusion to be an evaporation residue rather than a condensate. A determination of the LREE abundances, including Ce, would give further support to the hypothesis that, if the inclusion is a residue, Ce would be highly depleted relative to the other LREE. The Murchison inclusion studied by Boynton et al. (1980) has no large negative Ce anomaly and must therefore have formed under reducing conditions.

The presence of these inclusions indicates that materials can be isolated from the nebula at very early stages in the condensation sequence. The chondrite-normalized Lu value of 100 in MH-115 suggests that this inclusion represents the first 1% of the solid matter to condense; the Ornans inclusion, with a chondrite-normalized Lu value of 10,000, may be the first 0.01% to condense. Alternatively, of course, the inclusions could be the last 1% and last 0.01% that remained after partial vaporization.

In any event, it is clear that very efficient, very high-temperature fractionation events occurred early in the history of the solar system. Finding a plausible mechanism for such events remains a problem.

FUN inclusions

There is another group of Allende inclusions, consisting of three members, that have been very actively studied. The three samples, designated C1, EK 1-4-1 and HAL, are referred to as FUN inclusions because the isotopic abundances of several elements are Fractionated relative to terrestrial ratios and also have a component of Unknown Nuclear origin (Wasserburg et al., 1977). Although all Ca,Al-rich inclusions have oxygen isotopic abundances that are distinct from terrestrial values in a way that cannot be due to chemical fractionation effects (Clayton et al., 1977), the FUN inclusions have isotopic abundance anomalies in nearly all of the elements studied. These abundance anomalies require incomplete mixing of material from a variety of nucleosynthetic sources (e.g., different supernovae). The whole topic of isotopic anomalies has received much attention and a detailed discussion is beyond the scope of this chapter. The interested reader is referred to a review by Lee (1979).

Analyses of Sm and Nd isotopic composition in C1 and EK 1-4-1 (McCulloch and Wasserburg, 1978a,b; Lugmair et al., 1978) have figured prominently in the interpretation of the nucleosynthetic components present. Inclusion EK 1-4-1 has an excess of *r*-process and *p*-process components relative to *s*-process. (The processes designate rapid neutron capture, formation of proton-rich nuclides, and slow neutron capture, respectively.) Inclusion C1 has only an excess of the *p*-process component. The excesses are small, on the order of 0.1% or less. These components are thought to come from an injection of material from a supernova (Cameron and Truran, 1977; McCulloch and Wasserburg, 1978a), but incomplete mixing of material from many past events has also been suggested (Lugmair et al., 1978; Clayton, 1979).

In addition to their peculiar isotopic composition, at least two of the FUN inclusions have another unique aspect; they apparently formed under highly oxidizing conditions. This suggestion was first made by Boynton (1978a), who noted that inclusion C1 had a large negative Ce anomaly, unaccompanied by a negative Eu anomaly, indicating this oxidizing condition. Inclusion HAL was later shown to also have a large negative Ce anomaly (Tanaka et al., 1979). It was also shown that these inclusions have low abundances of other trace elements that, like Ce, become more volatile in an oxidized environment (Boynton and Cunningham, 1981). Most recently, however, the REE pattern of the third FUN inclusion, EK 1-4-1, was found to have normal Ce abundances (Nagassawa et al., 1981).

The REE patterns of these inclusions are shown in Fig. 3.5. Inclusion C1 appears to have a normal Group I REE pattern except for the Ce depletion. Because Ce is slightly more volatile than the other LREE, even in a reducing environment, the small Ce anomaly by itself does not require highly oxidizing conditions. However, the fact that Ce is depleted less than Eu, which is normally more volatile than Ce, does require a highly oxidizing environment. The REE pattern of HAL, both the core and the bulk inclusions, show a very large Ce anomaly requiring the highly oxidized conditions independent of consideration of the Eu abundance. The bulk HAL has a fairly flat pattern except for Ce and smaller depletions of Eu and possibly Gd. The core, on the other hand, except for Ce, has a REE pattern like the Group II inclusions

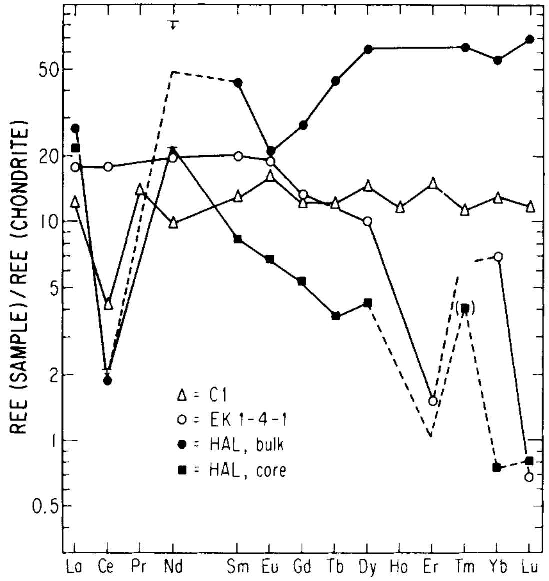


Fig. 3.5. REE patterns from three FUN inclusions in Allende, C1 (Conard, 1976), HAL (Tanaka et al., 1979) and EK 1-4-1 (Nagasawa et al., 1981). The large Ce anomalies in HAL and C1 indicate that each inclusion was made from grains which were found in a highly oxidizing environment. The lack of a Ce depletion in EK 1-4-1 does not rule out an oxidizing environment because Eu is also not depleted and the material may have equilibrated with an oxidized gas to lower temperatures. The isotopic anomalies and the Ce anomalies found in the FUN inclusions suggest that the grains may have formed in an oxidized zone of a supernova, but there are difficulties with this suggestion. The Tm anomaly in the HAL core may be an analytical error (A.M. Davis, private communication).

with the strong depletions of the HREE and the positive Tm anomaly. It was noticed that Tm was not so enriched relative to the LREE as it is in the Group II inclusions; this result also was thought to be indicative of a change in Tm volatility due to the oxidized conditions (Tanaka et al., 1979). (Tm becomes more refractory in oxidizing conditions; hence it will be more strongly depleted in Group II type material.) More recent data, however, indicate that the Tm anomaly may have been due to analytical error, and that the HREE are smoothly depleted, probably due to mineral preference effects (A.M. Davis, private communication, 1981).

The lack of a Ce anomaly in EK 1-4-1, which could be expected from the data for the other FUN inclusions, does not necessarily argue against an oxidized environment. Because Eu is also not depleted, it is possible that EK 1-4-1 could have formed in an oxidizing environment but was isolated from the gas at low enough temperatures that all the Ce condensed, even though Ce may have been more volatile than Eu. The pattern of EK 1-4-1 is like that of the Group II inclusions, but Tm was not analyzed. An analysis of Tm, showing it to be depleted relative to the LREE, would be indicative of the oxidizing conditions, for reasons discussed above with respect HAL (Tanaka et al., 1979).

Boynton (1978a) suggested that the grains which aggregated to form inclusion C1 condensed in an oxidizing environment that may have been in the ejecta of a supernova. Such an environment was shown to be highly oxidizing (because H has been fused to form He), and could be conducive to grain formation (Lattimer et al., 1978). However, a problem with this model is that to preserve such a large Ce anomaly, the inclusions must be made of a large fraction of supernova grains, and one would expect much larger isotopic anomalies in Sm and Nd than are observed. Although it is possible to generate oxidizing conditions in a supernova with only a minimum of nucleosynthesis, very special conditions appear to be required (Dearborn and Boynton, 1981). Finding other astrophysical environments with oxidizing conditions is difficult because of the ubiquity of hydrogen. A partial vaporization event generating a gas that displaces the hydrogen, as suggested by Palme and Wlotzka (1981) for the Ornans inclusion, is certainly possible.

3.4. REE in other components of chondrites

Chondrules and other inclusions

Graham et al. (1976) analyzed REE in a Ca,Al-rich glass inclusion from the Bovedy (L3) chondrite. Although this glass is Ca,Al-rich, it has little in common with the inclusions discussed above. It has major element abundances similar to a plagioclase of composition An_{85}, and is thought to have formed by shock from a pre-existing plagioclase. The chondrite-normalized REE abundances in the glass inclusion decrease smoothly from 0.73 at La to 0.20 at Lu, with a large positive Eu anomaly of a factor of 30. This Eu anomaly was compared to plagioclases from basaltic achondrites (eucrites) and lunar mare basalts and was found to be much larger. The size of the Eu anomaly could be matched only by lunar anorthosites. Graham et al. (1976) suggested that the Bovedy glass was actually a shocked fragment of an anorthosite. If this suggestion is true, igneous rocks needed to be present before the material in the Bovedy chondrite accreted to form the stone.

Tanaka et al. (1975) determined the REE abundances in a large (7 mm) olivine chondrule from Allende (Fig. 3.6). These abundances were much lower than those previously found in a smaller Allende olivine chondrule analyzed by Tanaka and Masuda (1973). The smaller chondrule has a flat REE pattern at about 1.8 times chondritic abundances with no significant anomalies. The large chondrule is about a factor of 40 lower in REE abundances, with a chondrite-normalized pattern which decreases from 0.06 at La to 0.045 at Lu. In addition, this chondrule has a positive Eu anomaly of a

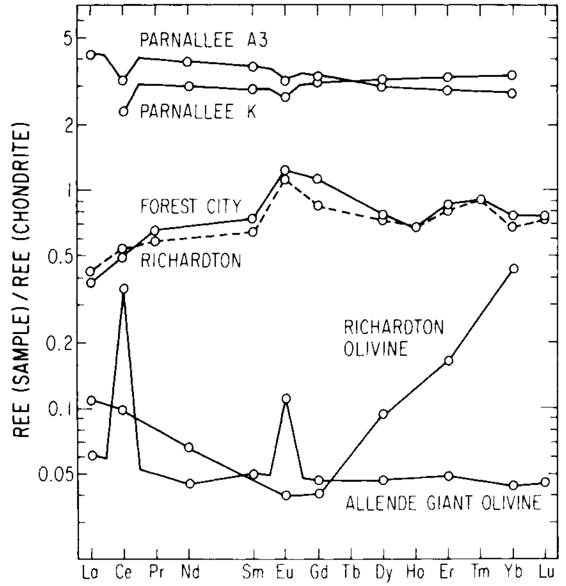


Fig. 3.6. REE patterns in chondrules. The olivine chondrule from Allende (Tanaka et al., 1975) has large positive Ce and Eu anomalies, perhaps due to addition of late condensing REE in an oxidizing environment. An olivine chondrule from Richardton (Evensen et al., 1979a) has an unusual shape similar to olivine in pallasites. A composite of many chondrules from the equilibrated chondrites Richardton and Forest City (Schmitt et al., 1968) show a linear fractionation and positive Eu anomaly thought to be due to migration of trivalent REE from the chondrules to the matrix. The chondrules from the unequilibrated chondrite Parnallee (Hamilton et al., 1979) show a linear fractionation with Ce and Eu anomalies perhaps indicative of partial vaporization under oxidizing conditions.

factor of 2.3 and a large positive Ce anomaly of a factor of 6.2. The chondrule is also remarkable in that its chondrite-normalized Ba abundance is about 4.5. The authors suggested that this large chondrule may have sampled some of the late condensing refractory elements from the solar nebula. They noted that even though Eu is expected to be more volatile than Ce in the solar nebula, the volatility of the pure oxides decreases in the order Ba > Ce > Eu. Although this order of volatilities is not expected in the solar nebula, it is exactly the order expected under oxidizing conditions (Boynton and Cunningham, 1981). It is possible, therefore, that this chondrule received some extra component, containing Ba, Ce and Eu, which condensed from a gas generated by a partial vaporization event. As discussed above, a partial vaporization event, either after the hydrogen-rich nebula had dissipated, or if rapid enough to displace the hydrogen, can generate the necessary oxidizing conditions.

Schmitt et al. (1968) determined the REE in 30 combined chondrules from Mokoia (CV2), 30 from Chainpur (LL3), 35 from Forest City (H5) and 50 from Richardton (H5). They found that the Mokoia chondrules were enriched to about twice the whole-rock values and showed a slight increase from La to Lu of about 20% with no anomalies. The Chainpur chondrules had unfractionated abundances at chondritic levels. Chondrules from the two equilibrated chondrites, Forest City and Richardton, had significant linear fractionations showing about a factor of 1.9 increase from light to heavy REE (Fig. 3.6). The absolute amounts of REE were lower in these chondrules (La = 0.40 times chondritic abundances), but positive anomalies were observed with Eu being present at nearly chondritic levels. The authors noted that the fractionated pattern is found only in the chondrules from the two equilibrated, H5, chondrites, and suggested that during the period of metamorphism, the LREE preferentially migrated into the matrix. The positive Eu anomalies resulted from a lack of mobilization of divalent Eu.

Evensen et al. (1979a) determined the REE in nine individual chondrules from Richardton. Their average result agreed quite well with the values found by Schmitt et al. (1968), but the individual analyses differed widely. Five of the chondrules had positive Eu anomalies, two showed no anomalies, and one had a negative Eu anomaly; the abundances of LREE ranged over a factor of 7.5. The remaining chondrule (Fig. 3.6) had low REE abundances and an unusual U-shape, similar to that found for olivine in the Brenham pallasite (Masuda, 1968). Hamilton et al. (1979) analyzed four individual chondrules from the unequilibrated chondrite, Parnallee (LL-3). Two of the chondrules, J and E, have patterns similar to those from Richardton, although the absolute abundances are higher. One chondrite-normalized pattern is flat at about 2.5, and the other is fractionated with Ce at 1.0 and Yb at 1.5. Both chondrules have small positive Eu anomalies. The other two chondrules, A3 and K, each have negative Ce and Eu anomalies (Fig. 3.6) and chondrule K also shows a significant linear fractionation with the LREE enriched.

Because Parnallee is an unequilibrated chondrite, the non-chondritic REE patterns cannot easily be explained by metamorphism, as suggested for the Richardton and Forest City chondrules. Hamilton et al. (1979) suggested that the Ce and Eu anomalies in chondrules A3 and K are related and reflect a partition of REE between a gas phase and a solid or liquid. As discussed above, such Ce anomalies could be expected if the gas were oxidizing. Loss of Ce and Eu by partial vaporization could generate the necessary oxidizing conditions, leaving the chondrules as the residue. Such a process, however, cannot explain the presence of the linear REE fractionations observed in the chondrules. If the vaporization event were rapid enough to be controlled by diffusion, a linear fractionation could result, but such a mechanism does not explain why both positive and negative slopes are observed. Because each of the individual chondrules were split and only a portion analyzed, some of the fractionation and anomalies may represent non-random sampling of the phases in the chondrule.

The origin of chondrules is still a mystery, but the ability of the REE to distinguish, in principle, nebular fractionations (gas/solid or gas/liquid) from planetary fractionations (solid/solid or solid/liquid) may eventually shed some light on the problem.

Mineral separates

Several investigators have studied REE abundances in mineral separates of chondrites. The techniques used for generating the separates were selective dissolution (Honda and Shima, 1967; Shima and Honda, 1967) and heavy liquid separation (Schnetzler and Bottino, 1971; Allen and Mason, 1973; Curtis and Schmitt, 1979). With the exception of Shima and Honda, who studied Abee (E4), all investigators studied equilibrated, type 6 chondrites. The minerals in the equilibrated meteorites presumably have lost any record of primitive REE distributions, so such studies will mainly address questions related to metamorphism.

The most detailed work on REE abundances in mineral separates is that of Curtis and Schmitt (1979), who studied three L6 chondrites and determined the REE in olivine, orthopyroxene, clinopyroxene, feldspar and phosphates; metal and troilite separates were prepared, but the REE were so low in abundance that the analyzed quantity was due largely to incomplete separation from other minerals. They found that the REE patterns are as expected for closed system equilibration between minerals. Based on mineral/liquid distributions, the absolute abundances of REE were found to be about a factor of ten higher than those expected if the minerals had equilibrated with a liquid having chondritic REE abundances. Curtis and Schmitt also found that the REE abundance ratios between phosphates and pyroxenes differed by a factor of four in two of the meteorites. Because they found that the mineral compositions were virtually identical between the two meteorites, they attributed this difference in abundance ratio to metamorphic temperature or pressure effects.

3.5. Whole-rock chondrite analyses

Solar abundances

The early work on REE analyses was concerned exclusively with whole rock measurements (Schmitt et al., 1960, 1963, 1964). Most of the samples studied were chondrites. It was known at that time that the chondrites were relatively unfractionated samples of solar system material. In order to test models of nucleosynthesis, one needs to know the solar abundances, in at least relative quantities, over a wide range of mass and atomic number. The REE, which span a range of atomic number from 57 to 71 and a range of mass from 138 to 176, are ideally suited for such studies. Since the REE were known to migrate as a group (Goldschmidt, 1954), it was thought that in chondrites they would very precisely reproduce solar ratios. As is well known, the abundances of REE in chondrites are indeed quite similar, but it will be shown in this section that, at levels on the order of 10%, the REE abundances in chondrites are in fact quite variable, both in absolute abundances and in ratios of elements. The early REE studies provided considerable input to theories of nucleosynthesis (Suess and Urey, 1956). The solar abundances of REE are still providing input for such models. Recently, for example, Steinberg and Wilkens (1978) suggested that the smooth peak in abundances in the REE region near mass 165 was most likely due to the fission of a superheavy element at the termination of *r*-process nucleosynthesis, and that this termination must have occurred beyond mass 300.

The early measurements of the REE abundances in chondrites cited above were made using neutron activation analysis (NAA). Most of the more recent measurements (Masuda et al., 1973; Nakamura and Masuda, 1973; Nakamura, 1974; Evensen et al., 1978) have been made using isotope dilution mass spectrometry (IDMS). The latter technique produces higher precision, about 2—3%, than the older NAA data, which has a precision of 10—15%, although newer NAA techniques are capable of precision comparable to that of IDMS. In an excellent review of whole-rock chondrite REE analyses, Evensen et al. (1978) found that of 77 analyses of 50 chondrites, 55 were found to have one or more abundance anomalies. (An anomaly was defined as an abundance which differed by more than 3% (IDMS) or 20% (NAA) from a smooth curve through the remaining REE.) Even when Eu anomalies are excluded, half of the samples still have abundance anomalies. It is clear that chondrites with ‘‘chondritic’’ REE abundances are the exception rather than the rule.

Evensen et al. (1978) compiled a table of average REE abundances in CI chondrites for normalization purposes. The values, reproduced in Table 3.3, are based on IDMS data for the multi-isotopic elements and NAA data for the mono-isotopic elements; the NAA data are normalized based on elements analyzed in common by the two techniques. As mentioned in section 3.1, CI normalization values are the best estimates of solar abundances and are recommended for cosmochemists concerned with condensation of the elements. For others interested in igneous fractionation processes, whether in terrestrial or extraterrestrial materials, the absolute values of the REE used for normalization purposes are less important than the ratios. In the past most investigators have chosen to normalize to ‘‘average chondrites’’ rather than to CI chondrites. For this reason the normalizations in this book have been made to the chondrite composite NAA values of Wakita et al. (1971) or Haskin et al. (1968), which are also given in Table 3.3. These normalization values, as well as a few others that have been commonly used, are plotted in Fig. 3.7. It can be seen that the older NAA data do scatter quite

TABLE 3.3

Rare earth element normalization values

	CI average[a]	Wakita et al. composite[b]	Haskin et al. composite[c]	Recommended chondrite
La	0.2446	0.34	0.330	0.310
Ce	0.6379	0.91	0.88	0.808
Pr	0.09637	0.121	0.112	0.122
Nd	0.4738	0.64	0.60	0.600
Sm	0.1540	0.195	0.181	0.195
Eu	0.05802	0.073	0.069	0.0735
Gd	0.2043	0.26	0.249	0.259
Tb	0.03745	0.047	0.047	0.0474
Dy	0.2541	0.30	—	0.322
Ho	0.05670	0.078	0.070	0.0718
Er	0.1660	0.20	0.200	0.210
Tm	0.02561	0.032	0.030	0.0324
Yb	0.1651	0.22	0.20	0.209
Lu	0.02539	0.034	0.034	0.0322

[a] Evensen et al. (1978).
[b] Wakita et al. (1971).
[c] Haskin et al. (1968).

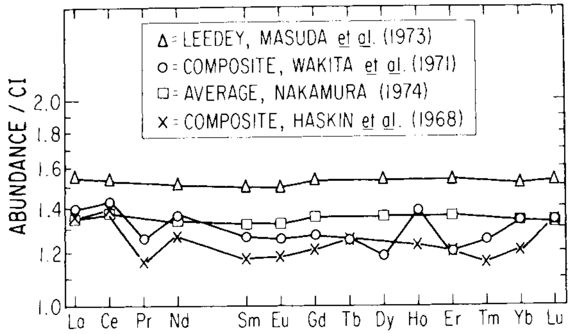


Fig. 3.7. Commonly used chondrite normalization values relative to CI chondrite values from Evensen et al. (1978). The older data scatter more than the more recent data but include data on the mono-isotopic REE. Recommended chondrite normalization values (Table 2) are based on the CI values of Evensen et al. adjusted to the difference between CI chondrites and average chondrites.

badly compared to the IDMS data or the more recent NAA data on which the CI normalization values are in part based. For the future, this author has calculated a "recommended" set of chondrite normalization values derived from the CI normalization values of Evensen et al. (1978) by multiplying by the factor of 1.267, the average of the Wakita et al. (1971) and Haskin et al. (1968) normalization values.

The absolute abundances of REE clearly vary between the different groups of chondrites. Evensen et al. (1978) plotted median abundances in the various chondrite groups and showed that the abundances ranged from about CI abundance levels (in CI and E chondrites) to about 2.3 times CI levels for the CV chondrites. These abundance differences have two origins. One simply relates a dilution by different amounts of volatile components, and the other represents a nebula-wide fractionation of refractory elements. The conventional way of expressing chondritic abundances to eliminate the effect of variable amounts of volatiles is to normalize to Si. Nakamura (1974) normalized his data for the various chondritic classes in this manner and found that abundances decreased in the order $CV > CM \approx CI > L \approx H > E$. This order is the same as that found for a variety of refractory elements and is generally thought to be caused by a nebula-wide fractionation of refractory elements (Larimer and Anders, 1970; Wasson 1978). The REE appear to be typical refractory elements in this regard.

In spite of all of the high-temperature fractionations observed in the Ca,Al-rich inclusions of the carbonaceous chondrites, the average REE patterns of the various classes are quite flat, suggesting that this large-scale nebular fractionation of refractory elements took place after the REE were totally condensed. Exceptions to this lack of flatness are evident only in the CV group (represented by Allende and Mokoia), which appears to have an excess of Group II type material, as discussed in section 3.3, and possibly the CO group, which may have an excess of the ultra-refractory condensates. Sampling uncertainties, however, prohibit a firm conclusion regarding the CO group fractionation. Enough analyses of Allende have been performed to ensure adequate sampling of that meteorite, but it is not clear that Allende is an adequate sample of its parent body. Allende is known to be heterogeneous on a scale of tens of centimeters and it is certainly possible that its parent body is heterogeneous on a scale of meters or more. If these analyses are indicative of the meteorite parent body composition, then apparently the higher-temperature refractory element fractionations, as discussed in section 3.3, operated over a region of the solar nebula comparable in size to the zone which accreted to form the CV parent body.

Chondrites with anomalous REE patterns

It was noted above that the majority of chondrite analyses have one or more abundance anomalies at a level of 4% or more. The fact that average or median abundances are quite regular suggests that much of the problem may be due to inadequate sampling. Considering the wide range of REE patterns in individual chondrules (section 3.4), it should not be surprising that small samples would yield variable results. In fact, Keil (1962) suggested that typically 10—70 g would be required for most chondrites, but Dodd and Jarosewich (1980) suggest that 10 g is an adequate amount in most cases.

Typically, analyses are made on less than a gram; six of the eighteen analyses made by Evensen et al. (1978) were on samples under 0.1 g. Thus many of the anomalies suggested by Evensen et al. may just be indicative of the heterogeneity of the meteorites.

Some meteorites have very large anomalies that appear to be far beyond those reported from sampling of chondrules. Nakamura and Masuda (1973) published several such analyses. For example, two pieces of Kohar (L3) weighing 0.9 and 0.2 g, each had a positive Ce anomaly of around a factor of four and a positive Gd anomaly of about 10% in an otherwise flat pattern. They also analyzed two chips of Abee (E4); a 0.2-g chip had a flat REE pattern, but a 0.75-g chip had a "zig-zag" pattern with alternating enrichments and depletions of about 20% (only multi-isotopic REE were determined) and a large positive Yb anomaly of nearly a factor of three. Two samples of Atlanta (E5) were analyzed and found to have Eu and Ce anomalies on a curved pattern which appeared to be smoothly partitioned as a function of size, suggesting an igneous fractionation.

Some of these anomalies are very difficult to understand. The large Ce anomalies in Kohar can be explained by consideration of solid/gas fractionations in an oxidizing atmosphere, but the Gd anomaly would not be expected under such conditions. Neither nebular nor planetary fractionations appear to offer an easy way to fractionate Gd from the other REE. The apparent igneous fractionation of Atlanta is difficult to understand except that Atlanta is a find. Frazier and Boynton (1981) found a substantial amount of REE in Abee to be water leachable, presumably from oldhamite, CaS. The smooth pattern in Atlanta could be a weathering phenomenon.

The Abee pattern, with its large Yb anomaly and alternating anomalies in the other REE, is probably the most difficult to understand. In preliminary work Frazier and Boynton (1980, 1981) found no large Yb anomalies in four clasts or mineral separates of matrix material from Abee. The Abee enstatite chondrite is composed of clasts which are internally equilibrated (Rubin and Keil, 1980), but based on magnetic measurements, the clasts have not equilibrated with each other (Sugiura and Strangway, 1981). Perhaps the larger sample analyzed by Nakamura and Masuda came from a rare clast with peculiar REE abundances. Again, these abundances are not easily explained. Perhaps because the highly reduced nature of the enstatite chondrite allows the REE to go into phases such as sulfides (or phosphides?), the REE partitioning between phases would permit such irregularities. (Our experience of terrestrial rocks is mainly with fractionation between oxides. When sulfides or phosphides are involved, the difference in affinity of the individual REE for sulfur or phosphorous may be important.) It is also possible that the REE condensation from the nebula into phosphides or sulfides may generate such peculiar patterns. Unfortunately sufficient thermodynamic data to permit calculation of solid/gas distribution coefficients for phosphides or sulfides are lacking.

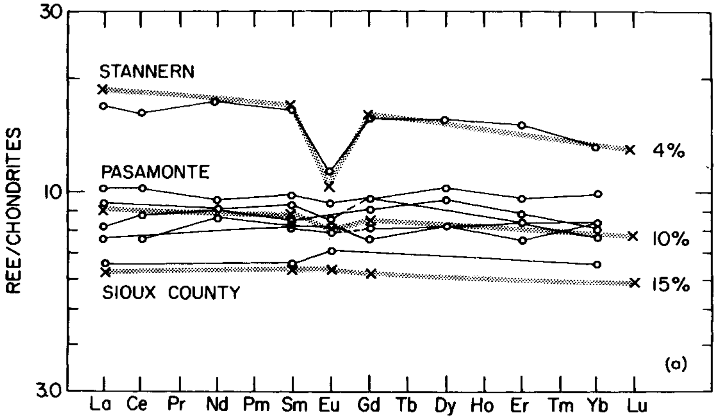
It is clear in any event that the REE abundances in chondrites are not as featureless as once thought. With recent developments in analytical capability to measure REE with high precision on small samples, it is hoped that future work will shed some light on the detailed processes that were operating when our solar system formed.

3.6. Analyses of achondrites

Eucrites, howardites and diogenites

The eucrites, howardites, and diogenites are discussed as a group because they are considered by many investigators to be genetically related. Analyses of REE in this group have been published by Schmitt et al. (1963, 1964), Haskin et al. (1966), Schnetzler and Philpotts (1969), Gast et al. (1970), Gast and Hubbard (1970), Jérome (1970), Fukuoka et al. (1977), Palme et al. (1978), Hamet et al. (1978), Ma and Schmitt (1979), Mittlefehldt (1979), Mittlefehldt et al. (1979) and Grossman et al. (1981). These meteorites, like all achondrites, appear to have formed by igneous processes. The eucrites and howardites have been called the pyroxene-plagioclase achondrites after their dominant minerals. The eucrites have been distinguished from the howardites by several criteria. Prior (1920) classified them on the type of pyroxene present; eucrites were those meteorites in which pigeonite was dominant over hypersthene, whereas howardites had hypersthene dominant over clinopyroxene. Mason (1962) showed that the howardites and eucrites plotted in different fields on a plot of CaO vs. FeO/(FeO + MgO); eucrites had higher values of both parameters. Duke and Silver (1967) defined eucrites as monomict breccias (made from material with a common origin) and howardites as polymict breccias. Grossman et al. (1981) showed that the Mason (1962) chemical criterion and the Prior (1920) mineralogical criterion were consistent. From fig. 1 in Grossman et al. (1981) it can be seen that the FeO/(FeO + MgO) parameter is not required, since the CaO content of all eucrites is greater than 9% and in all howardites it is less than 9%. There are no unbrecciated or monomict howardites but there are five polymict eucrites.

Most of the eucrites have REE patterns which are flat and enriched from 6 to 10 times chondritic abundances, within the range shown for Pasamonte and Sioux County in Fig. 3.8. A few eucrites have greater enrichments of REE and have negative Eu anomalies, while a few have lower REE abundances and positive Eu anomalies (Fig. 3.8). Stolper (1977) suggested, on the basis of experimental petrology, that most of the eucrites could be formed as partial melts of primitive chondritic material. A few of the eucrites, of which Moore County and Serra de Magé are examples, could have formed as cumulates from the same partial melt liquid. Consolmagno and Drake



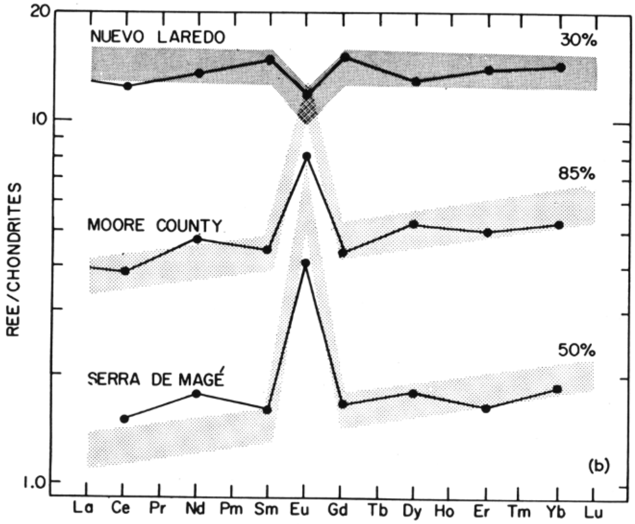


Fig. 3.8. REE data on eucrites with calculated values from Consolmagno and Drake (1977). (a) Most of the eucrites fall within the range defined by Pasamonte and Sioux County and represent 6—10% partial melting. (b) The cumulate eucrites Moore County and Serra de Magé could have formed after 85% or 50% fractional crystallization of a Pasamonte-like partial melt, although other constraints argue against this hypothesis (see text). Nuevo Laredo could have formed as the residual liquid after 30% crystallization. Note that these degrees of melting or crystallization are a function of the assumed initial REE concentration, here taken to be 1.0 times chondritic abundances. Ma and Schmitt (1979) have noted some difficulty with the Consolmagno and Drake model (see text).

(1977) calculated REE patterns for this model using REE mineral/liquid distribution coefficients. They noted that the REE pattern in partial melts is a sensitive indicator of the nature of the source region. Various minerals leave a "signature" in the melt REE pattern; for example, pyroxenes in the source yield an enrichment in LREE, and plagioclase yields a negative Eu anomaly. Consolmagno and Drake found that the model proposed by Stolper (1977) does indeed account for the observed REE patterns. Most of the eucrites could form as a partial melt of material with chondritic REE abundances. Most of the eucrites require 10% melting of the source, but others require less (e.g., Stannern — 4%) or more (e.g., Sioux County — 15%). Calculated REE patterns from Consolmagno and Drake (1977) are also shown in Fig. 3.8. The negative Eu anomaly with 4% partial melting results from the presence of plagioclase which has been consumed in the source after 4% but before 10% partial melting.

The REE in the cumulate eucrites, Moore County and Serra de Magé, are also consistent with the Stolper (1977) model. The calculated REE patterns agree quite well with the observations (Fig. 3.8). These patterns are generated in a pyroxene-plagioclase cumulate which formed from a starting liquid similar in composition to that of typical eucrites, 8—10 times chondritic REE abundances. The pattern of Serra de Magé formed after 50% fractional crystallization of this liquid and Moore County after 85%. The pattern of Nueveo Laredo represents the residual liquid after 30% fractional crystallization has occurred.

Consolmagno and Drake (1977) noted that the age of the eucrites is similar to the age of the solar system and thus the eucrites may be interpreted as having formed in a single-stage melting event. Because they were able to determine the composition of the source of this melting event, they concluded that they had actually determined the bulk composition of the eucrite parent body, assuming the body was homogeneous. They compared their inferred composition of the eucrite parent body with others determined by largely independent means and found good agreement. They noted that the disappearance of plagioclase in the source put a tight constraint on the amount of this mineral present in the parent body. They could not distinguish olivine from metal in the source (both have very low REE distribution coefficients), but the sum of these two components was reasonably well-known. The amount of pyroxene was constrained by the sum of the other components.

Fukuoka et al. (1977), however, pointed out the difficulty in modeling the composition of the source materials by such a technique. They noted that the composition is dependent on the assumed absolute concentration of REE in the starting materials. Depending on assumed initial chondrite-normalized concentrations from 1 to 3, they found a wide range of partial melting and mineral compositions that would be consistent with the observed REE abundances in the non-cumulate eucrites. Apparently of the three parameters — initial abundance, degree of fractionation, and composition of the source — the REE patterns of the melt allow any two to be determined.

Ma and Schmitt (1979) performed a detailed study of REE and other elemental abundances in two cumulate eucrites, Serra de Magé and Moore County. They used REE data on plagioclase separates to calculate the REE abundances in the equilibrium magmas, the liquids from which each of the eucrites formed. They noted that it is difficult to calculate the REE pattern of the parental magma, the liquid present before a fractional crystallization had occurred, unless an independent estimate of the degree of fractional crystallization is available. The estimates made by Consolmagno and Drake (1977) are not useful because they *assumed* that the parental magma was 8—10 times chondritic abundances in order to calculate the degree of crystallization. The problem is similar to that noted by Fukuoka et al. (1977) for the non-cumulate eucrites. In particular, Fukuoka et al. noted that although the Consolmagno and Drake (1977) calculations for the origin of the cumulate eucrites were internally consistent, the model could not explain the observed FeO/(FeO + MgO) ratios. Following fractional crystallization the FeO/(FeO + MgO) ratio would reach higher values. They concluded that there was no means to generate Serra de Magé and Moore County by a fractional crystallization process from a common parent magma. A possible relationship between the two meteorites was suggested in which their formation involved a difference, by a factor of about six, in the degree of partial melting of the same source. (The process of partial melting has only a small effect on FeO/(FeO + MgO) ratios and makes this parameter easier to model.) Fukuoka et al. concluded that the source material must contain >30% high-Ca pyroxene and have a chondrite-normalized La/Yb ratio about 3; this material is quite different from that proposed for the non-cumulate eucrites. The two meteorites could then form as cumulates from these two different partial melt liquids. If such a model is correct, the relationship between the cumulate eucrites and non-cumulate eucrites must be distant at best.

It can be seen from this discussion of eucrite genesis that the REE can provide strong constraints on models of petrogenesis. Like all studies on samples, the REE data can often easily be used to eliminate a model but cannot be used to choose between a variety of models that may all be consistent with the observations. Ma and Schmitt (1979) argued that the Consolmagno and Drake (1977) model for the cumulate eucrites is not consistent with all the available data, but they left us with a complicated model that requires many steps in order to account for the data. It appears that the work of the model makers will be to use their ingenuity to find the simplest model that is consistent with the data, but to recognize that Mother Nature may not have felt compelled to be simple.

The diogenites are nearly monomineralic meteorites composed almost entirely of hypersthene. With the exception of Tatahouine, all are brecciated. They have been studied in detail by Fukuoka et al. (1977). The REE in the diogenites, except for Roda, are highly fractionated; the patterns show strong enrichments from LREE to HREE and negative Eu anomalies ranging from

2 to 4. The chondrite-normalized Lu/Sm ratio ranges from over 100 in Tatahouine to 6 in Johnstown; Lu is at nearly chondritic abundance. Roda, on the other hand, has a much flatter chondrite-normalized REE pattern with Sm = 1.4 and Lu = 2.3. Fukuoka et al. suggested that the diogenites are cumulates formed from a melt having nearly chondritic-relative REE abundances, but with chondrite-normalized abundances between 2 and 10; the mineral/liquid distribution coefficients were not known well enough to determine the absolute amount with high precision. The high LREE abundances in Roda, compared to the other diogenites, were thought to be due to mixing of eucrite material or the presence of trapped intercumulus liquid. The latter hypothesis was preferred, since no eucrites were known with a large enough negative Eu anomaly to account for that observed in Roda. A separation of Johnstown, into coarse pyroxene crystals and a fine fraction which would presumably contain any mesostasis, indicated that the LREE were present in significant amounts in accessory phases. The highly fractionated REE pattern in Tatahouine led Fukuoka et al. (1977) to suggest that this meteorite must have crystallized from a melt which was already highly fractionated. A melt derived from other diogenites was suggested.

Consolmagno (1979) attempted a more detailed modelling of the diogenites with the hope that they could be related to the eucrites by a simple means. He was unable to devise a simple genetic mechanism and had particular difficulty in trying to account for the large Eu anomalies if the diogenites formed from material related to the eucrites.

Although the REE data do not suggest a simple relationship between the eucrites and diogenites, there is one group of meteorites that indirectly suggests a relationship. This group is the howardites. The howardites are generally considered to represent mechanical mixtures between diogenites and eucrites, presumably in a parent body regolith (Jérome, 1970; Jérome and Goles, 1971; McCarthy et al., 1972; Dreibus et al., 1977; Fukuoka et al., 1977). Fukuoka et al. (1977) showed that only two components, diogenites and eucrites, could account for the major, minor and trace elements of the howardites, except for siderophile elements; the siderophile elements required a few percent of a chondritic component. Recent REE analyses of howardites are reported by Fukuoka et al. (1977) and Mittlefehldt et al. (1979). The chondrite-normalized REE patterns are typically flat at between 2 and 8. Mittlefehldt et al. (1979) found one sample of Malvern with a flat pattern and another sample with a negative Eu anomaly of a factor of two. They emphasized the problem of sampling these polymict meteorites.

Jérome (1970) and Jérome and Goles (1971) first suggested that a compositional and textural continuum exists from diogenites through howardites to eucrites. Mittlefehldt (1979) found a large (~4 mm) plagioclase clast in the diogenite Johnstown and using REE analyses and mineral/liquid partition coefficients, concluded that the clast could not have formed from the same liquid as the Johnstown pyroxene. The presence of a foreign clast indicates that Johnstown is polymict and thus shares some characteristics with the howardites. Fukuoka et al. (1977) noted that siderophile elements in Johnstown were also higher than in other diogenites, which further supports the idea of a continuum. With this evidence linking eucrites, diogenites, and howardites, it is perhaps surprising that a simple igneous model cannot account for the REE patterns in the diogenites and eucrites. It may be that because our sample of the eucrite parent body is probably non-representative, other unsampled meteorite types may exist which contain other pieces to the puzzle.

Angra dos Reis

Angra dos Reis is a unique achondrite which has been the subject of a detailed consortium study by a number of investigators (Keil, 1977). The REE were studied by Ma et al. (1977), who measured whole-rock samples and olivine, pyroxene, and whitlockite mineral separates. This meteorite consists mainly of pyroxene (fassaite) and is thought to have formed as a cumulate (Prinz et al., 1977). Ma et al. (1977) found that the whole-rock REE pattern and the clinopyroxene REE pattern were virtually identical. The patterns are enriched to 20—30 times chondritic abundances, are concave downwards, and have a small negative Eu anomaly. The whitlockite separate is highly enriched in REE, with chondrite-normalized values decreasing from La = 1100 to Lu = 70. Two olivine separates were made; in each the chondrite-normalized value for Lu is about 9, but for La the values are 0.12 and 0.67 in the different separates. This difference was attributed to the presence of variable amounts of kirschsteinite ($CaFeSiO_4$) in the olivine.

Using the clinopyroxene REE data and mineral/liquid distribution coefficients, Ma et al. (1977) calculated the composition of the magma from which Angra dos Reis could have crystallized. They found it to be enriched in REE and fractionated linearly with chondrite-normalized values from La = 200 to Lu = 35. Using these data, they considered various models to relate Angra dos Reis to other known meteorite types, but all their models were unsuccessful. Angra dos Reis could not easily be related to the non-cumulate eucrites because its highly fractionated magma could not be generated from the eucrites without extensive fractional crystallization. The fractional crystallization would raise the $FeO/(FeO + MgO)$ ratio above that observed in the eucrites, but Angra dos Reis requires a lower ratio. Ma et al. also considered the formation of Angra dos Reis from nakhlites but, for a similar reason, found it to be unlikely. The formation of Angra dos Reis from the cumulate eucrites or by a process similar to that which formed the cumulate eucrites was also dismissed mainly on the basis of major element data. They concluded that Angra dos Reis was unrelated to any other achondrites.

Ma et al. proposed a model for the origin of Angra dos Reis but cautioned that, as discussed above with respect to the eucrites, the model is a function of the assumed initial REE abundances. Their preferred model is as follows: Angra dos Reis crystallized following 70% fractional crystallization of a melt generated from 7 to 10% partial melting of source materials with REE abundances between 3.5 and 4.7 times chondrites. They note that estimates of the initial chondrite-normalized REE abundances for the Moon are between 3 and 5, and thus a high initial REE abundance is not unreasonable.

Ureilites

The ureilites are a group of achondrites with very low REE abundances. They have been analyzed for REE by Wänke et al. (1972b) and Boynton et al. (1976). They are composed mainly of olivine and pigeonite and are thought by Berkley et al. (1976) to have formed as cumulates. The REE data, however, argue against an origin as a cumulate and suggest an origin as a residue of partial melting. The REE patterns of the ureilites are plotted in Fig. 3.9. They are all V-shaped, or, in the case of Haverö, U-shaped. From Kenna, both an acid-treated and an untreated sample were analyzed. It was

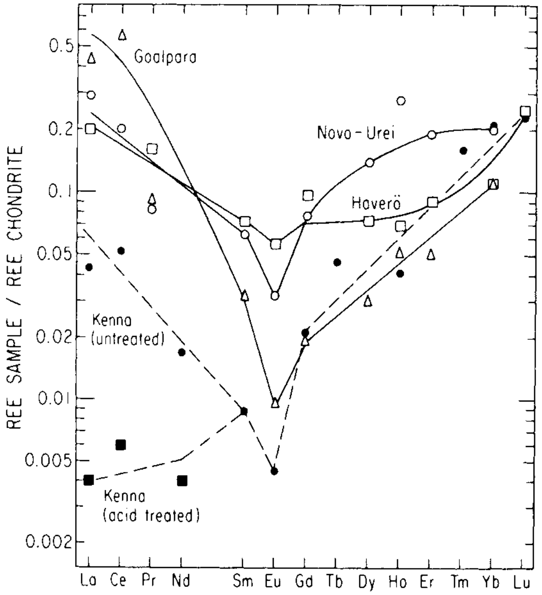


Fig. 3.9. REE patterns of ureilites from Boynton et al. (1976) and Wänke et al. (1972b). The peculiar V-shaped patterns require addition of two components. The HREE component is thought to be present in the olivine and pyroxene, which was a residue of a fractional partial melting event. The LREE are thought to have been added later, but the source of the material and the mechanism for this addition are unclear.

found that the LREE were removed in the acid treatment (15 minutes in concentrated HNO_3), suggesting that they are located in a phase different from the HREE. As noted by Boynton et al. (1976), however, one would not expect such a sharp V-shaped REE pattern to be made from REE in one phase, since minerals are expected to have REE distribution coefficients which are a smooth function of ionic size, without sharp discontinuities.

Boynton et al. (1976) considered both fractional crystallization and partial melting to model the observed REE patterns. They expressed the calculated REE pattern in terms of the chondrite-normalized Lu/Sm ratio. The quantity is equal to 27 in Kenna, which has the most fractionated pattern. Boynton et al. found that because the REE distribution coefficients are much less than unity for olivine and pigeonite, the dominant minerals in the ureilites, the liquid did not change much in Lu/Sm ratio during fractional crystallization. Over a wide range of crystallization, from 10% to 90%, the chondrite-normalized Lu/Sm ratio in the solid ranged between 3.6 and 6.3, considering both fractional crystallization, with continuous removal of crystals, or equilibrium crystallization, with removal at the end of the process. The process of partial melting provided the desired chondrite-normalized Lu/Sm ratio of 27 with only 7% melting, provided the liquid was removed from the solid as soon as it formed. They noted that complete removal of liquid as soon as it formed was unreasonable and cited 7% as a strict lower limit. They suggested, therefore, that a more extensive partial melting with a less efficient loss of liquid was responsible for the formation of the ureilites. The partial melting event could only explain the HREE. They suggested that the LREE were added by some later event although the nature of the event is obscure.

Because the REE pattern is so highly fractionated in the ureilites, it provides a strong constraint on the origin of these stones. The conclusion of an origin by partial melting seems very sound, but a more elaborate mechanism cannot be excluded. The petrographic studies, however, show crystals oriented as expected in a cumulate which has experienced flow (Berkley et al., 1976). This discrepancy between cumulate or partial melt residue can be resolved if the partial melting residue is allowed to flow, e.g., by extrusion or convection, and then solidify as proposed for the cumulate. Such a mechanism can account for the petrographic observations as well as the trace element data.

Chassignites and nakhlites

The Chassigny meteorite is composed mainly of an iron-rich (92 vol.%, Fa_{31}) olivine with minor pyroxene feldspar, chromite and melt inclusions, and is thought to be a cumulate (Prinz et al., 1974). Its REE pattern has been determined by Mason et al. (1976) and Boynton et al. (1976). The chondrite-normalized pattern found by Mason et al. is fractionated from 1.3

at La to 0.5 at Yb, with a minimum of 0.39 at Dy. Only five REE were determined by Boynton et al., but they showed a progressively greater enrichment toward the LREE, suggesting sampling heterogeneity. Boynton et al. noted that if the trend were real, it could not be due to differences in amount of trapped liquid in the two samples, since the ratio of LREE to HREE is unaffected by the ratio of olivine to trapped liquid, as olivine is expected to contain negligible amounts of REE. They suggested that a significant fraction of the clinopyroxene may be a cumulus phase.

The nakhlites are composed mainly of augite (79 wt.%) and olivine (15.5 wt.%), with minor plagioclase, magnetite, and K-feldspar; they are also thought to be cumulates, with the olivine being an intercumulus phase (Bunch and Reid, 1975). Schmitt and Smith (1963) determined the REE patterns in Nakhla and Lafayette. The patterns are fractionated with chondrite-normalized values of La = 5, Ce = 6, followed by a linear decrease to Lu = 1.

Boynton et al. (1976) calculated the chondrite-normalized REE abundances in the liquid from which the nakhlites could have formed and found a decrease from La = 16 to Lu = 2.2. They found that even with 15% trapped liquid in the nakhlites, the cumulus phase, augite, contains a significant fraction of the HREE. They noted the similar enrichment in LREE relative to HREE in the liquids from which Chassigny and the nakhlites formed and suggested that similar processes may have been responsible for generation of the liquid. They did not suggest a mechanism for this enrichment, but did indicate that Chassigny and the nakhlites could not have formed from the same source, because of differences in their oxygen isotope ratios.

Shergottites

The shergottites are volatile-rich achondrites composed mainly of pyroxene (pigeonite plus augite = 70%) and maskelynite (23%); the pyroxenes are thought to be cumulus phases (Stolper and McSween, 1979). They have been studied for REE abundances by Schnetzler and Philpotts (1969), A.J. Irving (unpublished data; in Stolper and McSween, 1979), Ma et al. (1981a, b), and Shih et al. (1981). The two shergottites, Shergotty and Zagami, and the related meteorite, Allan Hills 77005, have similar REE patterns. They are concave downwards with the maximum near Dy. In Shergotty and Zagami, the chondrite-normalized REE are at about 5—10, but in Allan Hills 77005 they range from 1 to 4.

Ma et al. (1981b) noted that it would be difficult to produce this type of pattern if the meteorite is either a cumulate from a melt with chondritic or LREE-enriched liquids, or a residue from partial melting. They suggested that the LREE part of the pattern was not caused by igneous differentiation but may represent an episode of metasomatism with a volatile-rich fluid.

Ma et al. were unable to model this process quantitatively, however. Shih et al. noted that Nd isotope ratios preclude Allan Hills 77005 and Shergotty from being co-magnetic.

3.7. REE in other differentiated meteorites

As expected, most studies of REE in meteorites have been concerned with the stony meteorites; chondrites provide information about early solar system formation processes and achondrites provide information about later planetary fractionation events. A few studies have been made of stony-irons, irons and a few unique meteorite types. These studies have generally been aimed at trying to understand the origin of the silicate component in the meteorite, although a few investigations have been concerned with silicate-free meteorites.

Mesosiderites

Mesosiderites are meteorites composed of approximately equal parts of silicates and metal. The silicates are considered to be igneous in origin and are similar to the silicates of eucrites and howardites (Prior, 1920). The silicate portion of the mesosiderite has been analyzed for REE by Schmitt et al. (1963, 1964), Wänke et al. (1972a), Mittlefehldt (1979), and Mittlefehldt et al. (1979). In particular, Mittlefehldt and co-workers were comparing the silicates of mesosiderites to those of howardites.

Mittlefehldt et al. (1979) analyzed six mesosiderites and found that in all but one of them, the LREE were enriched relative to the HREE by a factor of about 2, and only small or non-existent Eu anomalies were observed. In Morristown, however, La was depleted relative to Lu by a factor of 3, and a large positive Eu anomaly of a factor of 3 was observed. They noted that it was difficult to get the LREE enrichment with a fractional crystallization model and proposed several models to form the mesosiderite silicates via partial melting. They chose a small degree of partial melting, 2.5—4%, of a source depleted to about 0.3—0.4 times chondritic abundances. The source needed to have a flat REE pattern, and they claimed that this was expected of a eucrite residue if it contained some trapped liquid. Thus, according to their model, the eucrite source material, after losing its liquid to form the eucrites, melted a few percent more to generate a liquid from which the mesosiderite silicates formed.

The Mittlefehldt et al. (1979) data on Morristown is similar to the Wänke et al. (1972a) data on three other mesosiderites and suggests a cumulative origin. They calculated that 80% equilibrium crystallization from a melt, which was enriched to 3.3 times chondritic abundances, gave a good fit to the data. Mittlefehldt et al. (1979) concluded that the REE data from the mesosiderites indicate that these meteorites are not closely related to the howardites or eucrites. Most of the howardites and eucrites have flat REE patterns, whereas the mesosiderites have patterns indicative of a more extensive igneous history. Although the models for the formation of the REE patterns in the mesosiderites may not necessarily be correct, the conclusion of, at best, a distant relationship between these mesosiderites and the eucrites or howardites seems quite reasonable.

Pallasites

The pallasites are stony-iron meteorites with about equal amounts of metal and olivine. They are generally thought to have formed at the core-mantle interface in the interior of the parent body. Only two pallasites have been studied for REE, Brenham and Thiel Mountains by Schmitt et al. (1964), and Brenham by Masuda (1968). Both patterns show a U-shape, though it is much more pronounced in Brenham. The REE in Thiel Mountains are more abundant that in Brenham by factors of 2—10.

Consolmagno (1979) attempted to model the REE patterns in the pallasites with little success. He concluded that these meteorites probably did not come from the eucrite parent body, but this conclusion was based more on petrographic evidence, and the idea that the eucrite parent body is still intact so that its core-mantle interface could not have been sampled.

Irons

Several classes of iron meteorites have silicate inclusions. Bild (1977) determined REE abundances in four IAB iron meteorites. In two of the meteorites, Copiapo and Landes, the HREE were flat at chondritic levels with no Eu anomaly, but La was depleted by about a factor of 2. Woodbine had a pattern that was slightly concave down, was enriched from about 1.5 to 2.5 times chondritic abundances and had a negative Eu anomaly of about a factor of 2. Masuda (1969) also analyzed silicates from Woodbine and found a similar pattern. The shape was better determined by Masuda, who analyzed ten REE compared to five by Bild. Based on a variety of other trace elements, Bild concluded that the silicates were chondritic; the cause of the LREE depletion was not clear, but a loss of a small amount of partial melt was suggested as a possibility.

Fukuoka et al. (1978) determined the REE in silicates from Lodran, a unique meteorite containing nearly equal amounts of metal, olivine and pyroxene. They found a chondrite-normalized pattern with the LREE being flat at about 0.5, a negative Eu anomaly of a factor of 2.7 and a monotonic increase in HREE to 1.2. They also interpreted the pattern as being due to the loss of a small amount of partial melt from chondritic parent material.

Two inclusions from Campo del Cielo, an IA iron meteorite with inclusions of silicate, graphite and troilite, have REE patterns which are concave upwards with large positive Eu anomalies (Bild, 1977). The average chondrite-normalized pattern has La = 0.1, Sm = 0.07, Eu = 1, and Lu = 0.7. The pattern was attributed to a mixture of plagioclase and diopside (The sample contained 57% orthopyroxene, 27% olivine, 16% plagioclase and 0.3% diopside.)

Evensen et al. (1979b) measured REE abundances in five inclusions from Weekeroo Station, a IIE iron meteorite. The five inclusions have very different chondrite-normalized REE patterns. Two are fairly flat at values of 0.2 and 5, with positive Eu anomalies of a factor of 10 and 2, respectively. Three others show the HREE enriched relative to the LREE by a factor of 2—5, with both positive and negative Eu anomalies. Evensen et al. claimed that to a first approximation four of the five patterns could be related to a single parent liquid but that this liquid was highly evolved and fractionated relative to chondritic material. They did not give any further details on the nature of the fractionations. It is clear, however, that Weekeroo Station silicates are not at all chondritic and are quite different from those studied by Bild (1977) in the IAB irons.

Abundances of REE in iron meteorites without silicate inclusions have also been studied and, as expected, are found to be very low. Schmitt et al. (1963) measured REE in Odessa and Yardymly (= Aroos) and found chondrite-normalized abundances at about 10^{-4}. Because this value, although quite low, was about a factor of 10^3 higher than that predicted from thermodynamic data, they attributed the REE concentrations to contamination or to a small silicate inclusion. The thermodynamic calculations, however, did not include effects of non-ideal solution, either in the silicates or the metal, so the calculations could easily be in error by a factor of 10^3.

Kaiser et al. (1981) and Nozette and Boynton (1981) measured REE in iron meteorites for another reason. They were looking for a possible decay product of an extinct siderophile superheavy element. The superheavy element is expected to decay by spontaneous fission and would contribute neutron-rich isotopes of the REE to the meteorite. Kaiser et al. measured Sm and Nd in Santa Clara, Cañon Diablo, and Piñon by mass spectrometry and found abundances of the various isotopes on the order of $5\text{—}100 \times 10^8$ atoms per gram. This value translates to about 2×10^{-12} grams of Sm per gram, or 10^{-5} times chondritic abundance. Nozette and Boynton (1981) found $(10.8 \pm 1.8) \times 10^8$ atoms of ^{152}Sm per gram (10^{-12} g/g, or 5×10^{-6} times chondritic abundance) in Santa Clara. These meteorites were selected because studies of Ag isotopic ratios showed an excess of ^{107}Ag, presumably due to the decay of ^{107}Pd ($t_{1/2} = 6.5 \times 10^6$ years), suggesting that the meteorites are very old and may preserve a record of other extinct radionuclides (Kelly and Wasserburg, 1978). Values or upper limits for heavier REE were determined in Santa Clara by Nozette and Boynton (1981) and ranged from 42 for Eu to 0.39 for Lu in units of 10^8 atoms per gram.

Neither group found any evidence for a significant amount of a superheavy element.

3.8. Summary of REE cosmochemistry and future directions

As in studies of terrestrial samples, the analysis of REE in extraterrestrial materials provides a powerful tool in understanding the processes that were active in forming the sample. In studies of material formed at the very beginning of our solar system the REE provide a unique set of elements which are highly sensitive to the condensation process, but only moderately sensitive to mineral preference effects. Any later planetary fractionation cannot erase abundance anomalies that are imprinted during condensation. The REE have provided certain evidence of very efficient gas/solid fractionation mechanisms which occurred in the early history of solar system formation. Studies of individual chondrules have shown that their REE patterns are fractionated in a way unlike that expected for gas/solid fractionation and strongly suggest that the chondrules received their REE pattern as signatures of pre-existing minerals.

In the achondrites, which have undergone processes familiar to geochemists, the REE patterns provide strong constraints on the processes that formed the rocks. For example, the non-cumulate eucrites (Fig. 3.8a) must certainly represent partial melt liquids, even if the exact extent of partial melting or the initial concentrations in the source are not tightly constrained. Likewise, the cumulate eucrites (Fig. 3.8b) must, indeed, be cumulates, even if the exact origin of the magma from which they formed is unclear. In studies of these planetary fractionation processes, the constraints provided by REE studies can be particularly important because we necessarily do not have the field data that can provide constraints in studies of terrestrial systems. Interpreting REE data on clasts and inclusions from rare meteorites is more difficult, of course, because only a few samples are available for comparison, but nevertheless, constraints on the origin of the material can usually be provided.

Future directions in REE studies of meteorites are difficult to predict. In the area of Ca,Al-rich inclusions, it seems clear that much of the future work will be done on inclusions from meteorites other than Allende. It seems certain that a variety of different REE patterns will be found which will provide much information on early nebula-fractionation processes. The origin of chondrules has always intrigued cosmochemists and it is likely that more work in this area will provide constraints on chondrule formation processes.

Advances in techniques are opening up new areas of study. The study of milligram-sized chondrules by isotope dilution mass spectrometry would not have been possible a few years ago. New radiochemical neutron activation analysis techniques permit studies of microgram-sized inclusions with precisions for most elements of 1—2%, comparable to those achieved by mass spectrometry. These improvements, and ones which will certainly follow, will permit more detailed examination of smaller samples. It is now possible, for example, to extract a 30-μm-sized grain from a thin section and determine its REE pattern.

For studies of achondrites, programs sponsored by both the United States and Japan to find meteorites in Antarctica are providing much-needed new material. At least two meteorites similar to the shergottites have been found (doubling the world's inventory) and promise to aid our understanding of this important group of meteorites. Several polymict eucrites have been found. The clasts in these eucrites may provide new types of material with different relationships to the igneous fractionation processes which occurred on the eucrite parent body. These new materials may help to compensate for what currently seems to be the limited sampling of the parent body.

The prospect for REE cosmochemistry in the coming decade looks good. We can all look forward to significant advances in our understanding of the origin and evolution of the solar system. These advances will certainly come in part from REE studies.

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