Meteoritics & Planetary Science 39, Nr 11, 1767–1779 (2004)
Abstract available online at http://meteoritics.org

Determination of parental magmas of HED cumulates: The effects of interstitial melts

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(Received 3 February 2004; revision accepted 10 June 2004)

Abstract–An evaluation of trapped melts effects during crystallization and subsolidus equilibration of cumulates is necessary to constrain the composition of their parental magmas. In this paper, a simple mass balance approach is described. It allows estimation of trace element abundances in these parental melts from phase compositions. It is used to discuss the genesis of cumulate eucrites and diogenites. The REE behavior is in full agreement with the view that cumulate eucrites formed from melts similar to noncumulate eucrites. Trapped melt fractions ranging from <10 wt% for Moama to ~30 wt% for Moore County were involved. The origin of diogenites is more complex. The assumption that eucrites and diogenites shared the same parental melts cannot satisfactorily explain the diversity of incompatible trace element ratios (e.g., Dy/Yb) observed in diogenitic orthopyroxenes, even if interstitial melt effects are taken into account. Moreover, some diogenites unambiguously crystallized from magmas displaying significant HREE (heavy rare earth elements) enrichments. More likely, diogenites formed from distinct batches of parental magmas, as previously proposed by Mittlefehldt (1994), Fowler et al. (1995), and Shearer (1997).

INTRODUCTION

The howardite, eucrite, and diogenite (HED) meteorites are believed to have originated on the same large asteroid, possibly 4 Vesta (Drake 2001). Eucrites are basaltic rocks composed mainly of plagioclase and pigeonite. Diogenites are essentially composed of orthopyroxene. Howardites are polymict breccias composed of both of these lithologies, and are considered examples of the regolith of their parent body.

For the last three decades, HED meteorites have been given considerable attention. These rocks are the remnants of one of the earliest crusts produced in the solar system (~4.5 Ga, e.g., Tera et al. 1997; Lugmair and Shukolyukov 1998; Quitté et al. 2000; Nyquist et al. 2003 and references therein) and offer a chance to understand the processes that triggered the differentiation of a small body. So far, no consensus on the genesis of HEDs exists. Some workers have proposed that the magmatic activity of the HED parent body was dominated by a large melting event which generated a global magma ocean. The crystallization of the latter has generated the whole range of eucrites and a variety of cumulates (e.g., Ikeda and Takeda 1985; Righter and Drake 1997; Ruzicka et al. 1997; Takeda 1997; Warren 1997; Barrat et al. 2000). An important implication of this model is that eucrites and diogenites shared the same parental melts. Such a point of view is not consensual. Others consider that the HED cumulates and lavas are not all cogenetic (e.g., Stolper 1977; Mittlefehldt 1994; Fowler et al. 1995; Shearer et al. 1997; Blichert-Toft et al. 2002). Therefore, the observed mineralogical and chemical diversities are partly a result of the various primary melts generated in the mantle of the parent body.

To evaluate these models, it is crucial to constrain the composition of parental melts of the HED cumulates (i.e., the diogenites and the cumulate eucrites) and to compare them with the noncumulate eucrites that are, in most cases, chemically close to the melts from which they have crystallized. The aim of this study is to examine the role of interstitial melts during the genesis of HED cumulates and to evaluate models for their origin.

THEORY

The approach developed in this paper is directly derived from the works of Bédart (1994, 2001), Cawthorn (1996), and Blundy (1997). The basis of the calculations are mass balance equations that reconstruct the composition of a cumulate rock at the point where the assemblage of cumulus phases +

trapped melt was sealed off from the main body of magma, and after the crystallization of the interstitial melt and equilibration of the phases.

Consider that the cumulate is made of *n* cumulus phases in equilibrium with the bulk liquid in the magma chamber (i.e., the crystals are homogeneous). When a mass fraction of liquid *f* is trapped in the framework of the cumulus crystals, the composition of the bulk rock $C_{B.R.}$ is:

$$C_{B.R.} = f\,C_L + \sum_{i=1}^{n} X_i D_i C_L = \left(f + \sum_{i=1}^{n} X_i D_i\right) C_L \qquad (1)$$

where X_i and D_i are the mass fraction of phase *i* in the system and the phase *i*-melt equilibrium partition coefficient, respectively, and C_L is the composition of the liquid. (Note that $f + \Sigma X_i = 1$.)

After crystallization of the trapped melt and equilibration of the phases, the rock contains homogeneous mineral phases *k*:

$$C_{B.R.} = \sum_{i=1}^{k} Y_i C_i = C_j \sum_{i=1}^{k} Y_i \frac{C_i}{C_j} \qquad (2)$$

where Y_i and C_i are the mass fraction and the composition of the phase *i* in the final system, repectively.

Hence, using these two equations, the effects of trapped melt and post-cumulus equilibration can be estimated using the apparent partition coefficient D_j':

$$D_j' = \frac{C_j}{C_L} = \frac{f + \sum_{i=1}^{n} X_i D_i}{\sum_{i=1}^{k} Y_i \frac{C_i}{C_j}} \qquad (3)$$

Thus, the apparent and equilibrium partition coefficients are not necessarily the same in a system undergoing crystallization of a trapped melt. The apparent partition coefficients are functions of the equilibrium partition coefficients and mass proportions of all cumulus phases, the mode and the compositions of the phases in the fully equilibrated rock, and of course, the mass fraction of trapped melt. Hence, estimating the composition of the trapped melt from the compositions of the phases is possible only if all these parameters are known or constrained.

Such a model for the genesis of cumulates is certainly oversimplified, because the cumulus phases + trapped melt system is assumed to be closed. If there was a significant movement of interstitial melt during the solidification of the rock (e.g., Irvine 1982; Tait et al. 1984), or in the case of metasomatic effects, the model is no longer valid. Despite these limitations, it still illustrates trapped melt effects reasonably well and can generate powerful constraints on the composition of cumulate parental melts.

In the following, the discussion has been limited to the rare earth elements (REEs), because their abundances have been repeatedly determined in the HED cumulate phases and because equilibrium partition coefficients between the cumulus phases (plagioclase, pigeonite, orthopyroxene) and the melt are established relatively well.

PARENTAL MELTS OF CUMULATE EUCRITES

Cumulate eucrites are a group of only a dozen meteorites with distinct chemical features. Compared with the other eucrites, they display higher Mg-numbers, lower abundances of incompatible trace elements, and their REE patterns exhibit pronounced positive Eu anomalies well explained by plagioclase accumulation. So far, two types of parental melts have been proposed for cumulate eucrites based on trace element data. Ma and Schmitt (1979), Pun and Papike (1995), Hsu and Crozaz (1997) have determined the composition of pyroxenes and plagioclases and, using various sets of mineral-melt partition coefficients, have calculated that the parental melts were unlike typical eucrites and were characterized by a strong LREE (light rare earth elements) enrichment. Schnetzler and Philpotts (1969) and Treiman (1996) suggested that subsolidus equilibration explains the LREE enrichments of the phases of the Moore County cumulate eucrite, which leads to erroneous calculations of parental melts. Subsequently, Pun et al. (1997) have shown that trace element contents for both pyroxenes and plagioclase have been altered by subsolidus exchange in these rocks. They suggested that the cumulate eucrites Binda, Moama, Moore County, and Serra de Magé might have re-equilibrated with different amounts of trapped melt. Treiman (1997) tested the involvement of a trapped melt fraction during the solidification of cumulate eucrites using a mass balance approach. Using major and rare earth element abundances in bulk rocks, Treiman showed that normal eucrites were plausible parental melts of cumulate eucrites. Recently, Barrat et al. (2000) and Saiki et al. (2001) confirmed Treiman's interpretation. To explain the composition of pyroxenes in cumulate eucrites, they used a new set of major and trace elements analyses and a liquid trapping model of fractional crystallization, respectively.

Over the last thirty five years, the major and trace element abundances in bulk rocks and mineral phases for four cumulate eucrites (Moore County, Moama, Serra de Magé, and Binda) were determined repeatedly and they illustrate the approach described earlier. Here, I will only discuss the nature of the parental melts of Moore County and Moama. I have not selected Serra de Magé because it contains an accessory phase (possibly zircon) which affects the HREE budget of the rock (Barrat et al. 2000). I have not selected Binda because the available REE analyses of the phases are incomplete (Pun and Papike 1995; Pun et al. 1997).

Table 1. Partition coefficients and data used for the calculation of the Moore County and the Moama parental melts.[a]

	Equilibrium partition coefficients		Moore County			Moama		
	plagioclase/melt	pigeonite/ melt	plagioclase (µg/g)	pigeonite (µg/g)	pigeonite/ plagioclase	plagioclase (µg/g)	pigeonite (µg/g)	pigeonite/ plagioclase
La	0.036	**0.0015**	–	–	**0.17**	0.455	0.082	0.18
Ce	0.031	**0.003**	6.91	2.24	0.32	0.980	0.255	0.26
Nd	**0.026**	0.01	2.47	2.96	1.20	0.423	0.339	0.80
Sm	0.02	0.02	0.388	1.33	3.43	0.077	0.189	2.47
Eu	1.15	0.009	1.26	0.031	0.025	0.978	0.016	0.016
Gd	0.016	0.033	0.344	2.00	5.81	0.0656	0.376	5.73
Dy	**0.013**	**0.057**	0.123	2.82	23.0	0.0324	0.652	20.12
Er	**0.01**	**0.089**	0.039	1.70	43.2	0.0087	0.532	61.14
Yb	0.007	0.15	0.031	1.96	63.3	0.0104	0.582	56.23

[a] The values in bold are interpolated graphically from experimentally determined values. The plagioclase/melt partition coefficients are from Phinney and Morrison (1990) except for Eu, taken from Jones (1995). The pigeonite/melt partition coefficients are from McKay et al. (1991), determined for wollastonite content of 8%. The Moore County and Moama data are from Schnetzler and Philpotts (1969) and Hamet et al. (1978), respectively. The abundances of the plagioclase fractions are corrected for a slight pigeonite contribution (2.75% for Moore County, 3% for Moama).

The Moore County Eucrite

To calculate the apparent partition coefficients between phases and possible parental melts, a series of parameters needs to be estimated or hypothesized: the mode of the rock after the full crystallization of the interstitial melt, the composition of the phases after sub-solidus equilibration, the mineral assemblage crystallized from the trapped melt, and finally, the nature of the cumulus phases in equilibrium with the parental melt and their equilibrium partition coefficients.

Moore County is an unbrecciated stone made of homogeneous plagioclase crystals, pigeonite inverted to orthopyroxene and augite, accessory chromite, silica, troilite, and metal. Based on the major element composition of the phases (Pun and Papike 1995; Pun et al. 1997) and the average composition of the bulk rock (e.g., Kitts and Lodders 1998; Barrat et al. 2000), it can be estimated that Moore County contains about 59 wt% inverted pigeonite, 39 wt% plagioclase, and 2 wt% other phases. Since chromite, silica troilite, and metal are nearly devoid of REEs, and since all the REEs in this meteorite reside in plagioclase and pyroxene with no significant contribution of accessory phosphate (Barrat et al. 2000), the involvement of all the accessory phases can be neglected in the calculations.

The REE abundances in the Moore County phases were determined on separate fractions by neutron activation or isotope dilution (Schnetzler and Philpotts 1969; Laul and Schmitt 1973), or in situ by SIMS (Pun and Papike 1995; Pun et al. 1997; Hsu and Crozaz 1997). In situ measurements are less prone to contributions from impurities, but the estimation of the composition of the bulk pyroxene is not straightforward from this kind of analyses because the pigeonites are inverted. Moreover, the elements with the lowest concentrations (e.g., LREEs in low-Ca pyroxene or HREEs in plagioclase) are not always accurately determined, and the uncertainties obtained for the $C_{\text{plagioclase}}/C_{\text{pigeonite}}$ ratios are very high, particularly for the HREEs. Thus, I preferred the phase compositions obtained by isotope dilution which are more accurate (Schnetzler and Philpotts 1969). As pointed out by Pun et al. (1997), the plagioclase fraction analyzed by Schnetzler and Philpotts contained about 2.75% pigeonite. The data have been corrected accordingly. However, these corrections did not change the conclusions.

For calculation purposes, I will assume that Moore County contained initially cumulus pigeonite and plagioclase crystals and a trapped basaltic melt. The mineral assemblage crystallized from this melt was 49.5 wt% plagioclase, 49.5 wt% pigeonite, and 1 wt% minor phases devoid of REEs. One may argue that these proportions are approximate. Even then, a several-percent deviation in the amounts of plagioclase or pigeonite is not critical. The equilibrium partition coefficients pigeonite/melt and plagioclase/melt used here (Table 1) are the same as those selected by Pun et al. (1997).

Using these parameters, it is possible to calculate the mass fraction of cumulus crystals at a given trapped melt fraction, and then the apparent partition coefficients for plagioclase and pigeonite (Fig. 1). Three important observations emerge from these calculations, and they can be applied to gabbroic cumulates:

1. The apparent partition coefficients calculated for $f = 0$ (no trapped melt) and the equilibrium partition coefficients are different. These differences are a consequence of subsolidus re-equilibration, and are explained by the fact that the $C_{\text{plagioclase}}/C_{\text{pigeonite}}$ and $D_{\text{plagioclase}}/D_{\text{pigeonite}}$ ratios are not the same in an equilibrated gabbroic cumulate.
2. The apparent partition coefficients are strongly correlated with the amount of interstitial melt involved during the cooling of the cumulate, and a wide range of values are obtained. The most noticeable effects are obtained for the most incompatible elements. For example, the apparent partition coefficients of plagioclase and pigeonite vary by a factor of 30 in the case of La when f increases from 0 to 0.5.

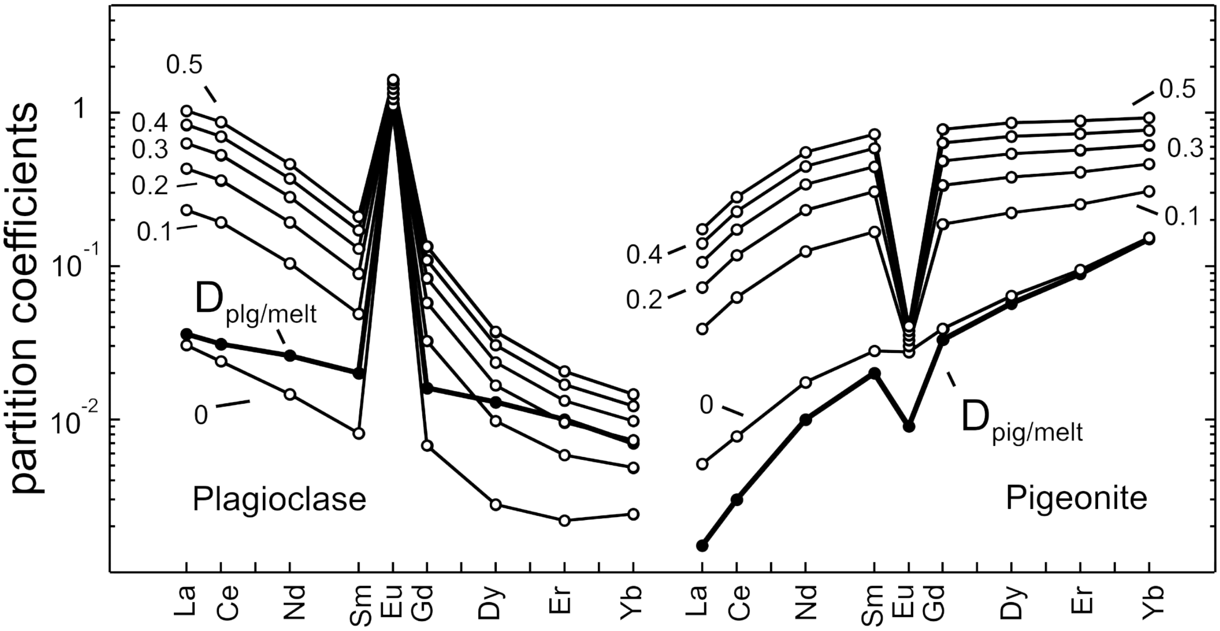

Fig. 1. The apparent partition coefficients of pigeonite and plagioclase for the Moore County cumulate eucrite. The partition coefficients are calculated for mass fraction of trapped melt ranging from 0 to 0.5. See text for details.

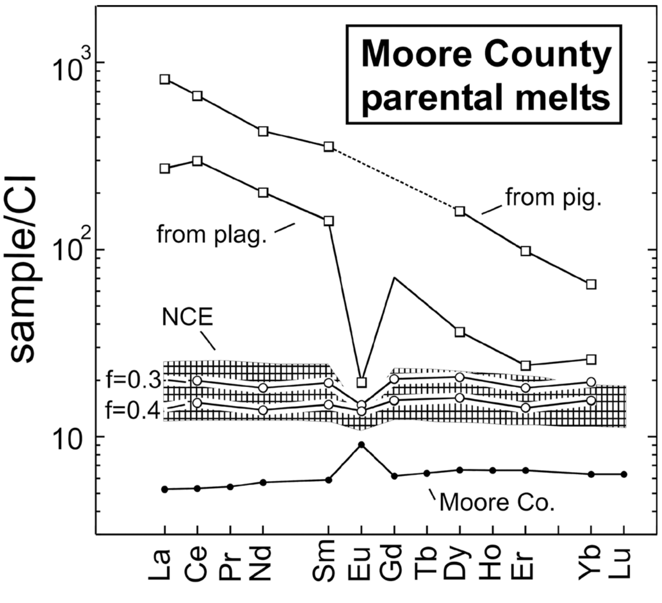

Fig. 2. The calculated Moore County parental melts using apparent partition coefficients estimated for $f = 0.3$ and $f = 0.4$. The parental melts, estimated from the REE abundances in plagioclase and pigeonite, and assuming no trapped melt effects, are indicated. The REE pattern of the bulk meteorite and the range of noncumulate eucrites (NCE) are shown for comparison (Shimizu and Masuda 1986; Barrat et al. 2000, 2003). The reference chondrite is from Evensen et al. (1978).

3. Because the behavior of Eu is strongly controlled by plagioclase, the ranges of D'_{Eu} for plagioclase and pigeonite are more limited as those of D'_{Sm} and D'_{Gd}. Thus, the involvement of interstitial melt has a strong effect on the $D'_{\mathrm{Eu}}/D'_{\mathrm{Eu*}}$ ratios. This observation is important because it implies that the Eu anomalies of the phases of an equilibrated gabbroic cumulate are not necessarily magmatic but may be strongly affected by late-stage processes. Eu anomalies in pyroxenes and plagioclases have been used in the case of angrites and shergottites to infer the oxygen fugacity conditions during the crystallization of volcanics (McKay et al. 1994; Wadhwa 2001). This method should not be extended to equilibrated cumulates. In such a case, it is illusive to look after magmatic Eu/Eu* ratios from the chemistry of the phases because these kind of ratios are too dependent of subsolidus equilibration.

The mass fraction of an interstitial melt that was involved during the crystallization of Moore County is very difficult to estimate. According to mass balance calculations, f values ranging from 0.3 to 0.4 are realistic if it is assumed that this melt was eucritic (Treiman 1997; Barrat et al. 2000). The apparent partition coefficients allow an independent check of this hypothesis. The parental melts calculated for $f = 0.3$ and $f = 0.4$ are not strongly enriched in LREEs. Their REE patterns plot nicely in the range defined by the noncumulate eucrites (Fig. 2). This strongly supports the inference that Moore County crystallized from such a liquid.

The Moama Eucrite

Moama is an unbrecciated eucrite that displays the same mineralogy as Moore County. The major elements of the bulk sample (Lovering 1975) is well determined to be a mixture of 62 wt% inverted pigeonite, 37 wt% plagioclase, and 1 wt%

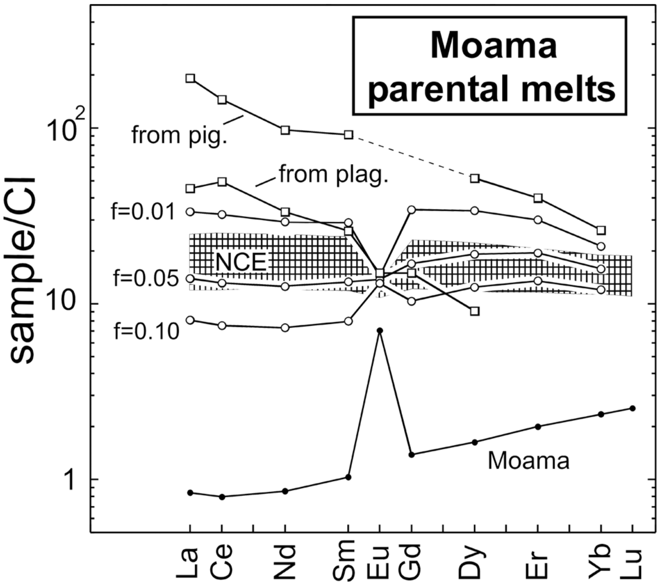

Fig. 3. The calculated Moama parental melts using apparent partition coefficients estimated for *f* = 0.01, 0.05, and 0.1. The parental melts estimated from the REE abundances in plagioclase and pigeonite assuming no trapped melt effects, are indicated. The REE pattern of the bulk meteorite (Hamet et al. 1978) and the range of noncumulate eucrites (NCE) are shown for comparison (Shimizu and Masuda 1986; Barrat et al. 2000, 2003).

accessory phases (chromite, metal, etc.), again using the phase compositions given by Pun and Papike (1995) and Pun et al. (1997). Hamet et al. (1978) obtained the most precise REE analyses on Moama phases by isotope dilution. Unfortunately, their results for plagioclase are certainly hampered by traces of pigeonite because the HREE abundances they have measured in their fraction are much higher than those determined in situ by SIMS (e.g., Dy = 51 ng/g by ID-TIMS and 30 ng/g by SIMS; Pun et al. 1997). The discrepancy between the two data sets is not significant if 3 wt% of pigeonite are removed from the plagioclase fraction (Table 1).

To estimate the composition of parental melts, the other parameters needed for the calculations are of course the same as those taken for Moore County (i.e., the equilibrium partition coefficients and the nature of the interstitial melt), except for the mass fraction of interstitial melt. Once again, the estimation of the latter is a difficult task. Moama is poor in incompatible trace elements such as LREEs and U (e.g., Hamet et al. 1978). Therefore, the mass fraction of interstitial melt involved during the crystallization of this gabbroic cumulate was very low, and certainly less than 0.1, in agreement with mass balance calculations (Treiman 1997). I have calculated hypothetical parental melts for *f* = 0.01, *f* = 0.05, and *f* = 0.1 (Fig. 3). The results are unlike the LREE enriched parental melt inferred from the composition of pigeonite (Pun and Papike 1995). For *f* = 0.01, the REE pattern of the calculated liquid displays a large negative Eu anomaly (Eu/Eu* = 0.44). At first glance, it resembles those of the most evolved noncumulate eucrites (i.e., Bouvante, Nuevo Laredo), but the REE abundances (excepted for Eu) are much higher. For *f* = 0.05, the REE pattern of the calculated liquid plots in the field of the noncumulate eucrites. For greater *f* values, as exemplified by *f* = 0.1, the calculated parental melts are poorer in LREE than non-cumulate eucrites and exhibit significant positive Eu anomalies suggesting that these results are unrealistic for true magmatic liquids. Clearly, these calculations indicate that the Moama parental melt displayed REE abundances of the same order as non-cumulate eucrites, but it fails to reconstruct perfectly a typical eucritic pattern. Assuming the parental melt of Moama was eucritic, two hypotheses can explain the differences between eucrites and the calculated parental melts: 1) it has been assumed that the system cumulus phases + trapped melt was closed during the formation of Moama, and this assumption may not be valid; unfortunately, it is not possible to determine if a given cumulate rock behaves as a closed system or not when the parental melt is unknown; hence, this hypothesis cannot be tested; 2) because Moama is very poor in incompatible elements, only a very limited amount of trapped melt was involved during its crystallization; thus, the incompatible trace element contributions from the cumulus minerals come to dominate the bulk rock abundances and the choice of REE equilibrium partition coefficients is here more critical than for Moore County, as already pointed out by Treiman (1997); the equilibrium partition coefficients for pigeonite and plagioclase that I have used are, without any doubt, among the most appropriate available for eucrites, but they have not been determined in the same system. In view of the uncertainties on these coefficients, the discrepancies are rather limited and should not be overemphasized. The parental melt of Moama was probably a eucritic melt.

PARENTAL MELTS OF DIOGENITES

With more than 100 kg available, diogenites constitute one of the largest groups of achondrites. In terms of their mineralogical compositions, these rocks are rather uniform. They are nearly exclusively composed of equilibrated orthopyroxene crystals, the compositions of which range between $En_{79}Wo_1Fs_{20}$ to about $En_{65}Wo_5Fs_{30}$ with minor chromite, silica, troilite, metal, and occasionally olivine, diopside, plagioclase, and rare phosphate (e.g., Mittlefehldt 1994, 2000; Fowler et al. 1994). Chemically, diogenites and their orthopyroxene crystals display a limited range of abundances for major elements. By contrast, their abundances for minor and trace elements (especially the incompatible ones) are highly variable (e.g., Fukuoka et al. 1977; Masuda et al. 1979; Wolf et al. 1983; Mittlefehldt 1994; Fowler et al. 1994, 1995). For example, Fowler et al. (1995) measured the concentrations of Y in several orthopyroxene crystals by

SIMS, and obtained an impressive range (from 0.012 μg/g in Ellemeet to ~4.7 μg/g in Roda).

Were diogenites and eucrites genetically linked? The compositions of diogenitic orthopyroxenes imply that they formed from melts, the Fe/Mg ratios of which were lower than those of noncumulate eucrites. Therefore, assuming that eucrites and diogenites are co-magmatic, it has been suggested that eucrites crystallized from residual melts formed after the extraction of diogenites (e.g., Mason 1967; Grove and Bartels 1992). This assumption is critical for all models of magma oceans proposed so far for the differentiation of 4 Vesta (e.g., Ikeda and Takeda 1985; Righter and Drake 1997; Ruzicka et al. 1997; Warren 1997; Barrat et al. 2000; Drake 2001), and this point is not unanimously accepted. Stolper (1977) proposed that diogenites and eucrites are not directly linked. He suggested that their parental melts derived from a partial melting of sources that were already depleted by the removal of eucritic magmas. Mittlefehldt (1994) analyzed most of the diogenites known at that time and documented precisely the wide trace element ranges displayed by diogenites. He suggested that these variations do not confirm simple co-genetic relationship between eucritic melts and diogenites and that diogenites did not all share the same parental melts. These melts were probably not basaltic but rather ultramafic (orthopyroxenitic in composition). The huge incompatible element variations were subsequently confirmed by the extensive SIMS analytical work of Fowler et al. (1994, 1995) on orthopyroxenes. Following their point of view (Shearer et al. 1997), trace element systematics in orthopyroxenes indicate that diogenites cannot be produced by extensive fractionation of a single basaltic or ultramafic magma, but formed from distinct batches of basaltic melts (not necessarily related to eucrites) that crystallized in shallow layered intrusions.

In previous discussions on trace element systematics in diogenites, it has been assumed that their crystals, or at least their cores, have preserved part of their pristine igneous features. Fowler et al. (1995) and Shearer et al. (1997) have used the REE concentrations in orthopyroxenes to constrain the origin of diogenites because these elements have lower diffusivities in orthopyroxene than Fe and Mg. On the other hand, the initial distributions of trace element in the crystals may be partly erased by re-equilibration with interstitial melts (e.g., Mittlefehldt 1994; Papike et al. 2000). These effects were always neglected, and no attempts were undertaken to estimate the trapped melt effects in diogenites. Obviously, the lack of discussion of these effects strongly weakens the conclusions of the previous studies. In the following, I will review the main evidences of trapped melts in diogenites and evaluate their effects on parental melt reconstructions.

Evidence of Trapped Melts in Diogenites

Most diogenites are breccias made of fragments of orthopyroxene crystals set in a fine-grained matrix. Therefore, the contacts between crystals are barely preserved. The remnants of phases, which have crystallized from interstitial melts (plagioclase, phosphates, etc.), can only be expected in the matrix. Furthermore, because some of these breccias are ejecta products (e.g., McLeish and Treiman 2003), they sometimes contain foreign fragments like eucritic or chondritic clasts (e.g., Lomena et al. 1976; Mittlefehldt 1994) which can make it difficult to identify pristine interstitial material.

Two diogenites are unbrecciated: Tatahouine (Lacroix 1932) and Grosvenor Mountains (GRO) 95555 (Papike et al. 2000). Tatahouine is a highly shocked stone (Benzerara et al. 2002), the crystals of which are very large (1–5 cm). Unfortunately, this meteorite broke up along grain boundaries in the Earth's atmosphere and upon impact. Most of the available samples are gram-size debris of single crystals. Hence, contacts between crystals are rarely observed in polished sections. Until now, chromite, troilite and metal are the only interstitial phases observed in this stone. GRO 95555 essentially displays a polygonal-granular aggregate of orthopyroxene crystals smaller than in Tatahouine (~2 mm) and no interstitial olivine, plagioclase, or phosphate are reported (Papike et al. 2000). The lack of observed interstitial silicate phases suggests that the melts were efficiently expelled during the crystallization of these two unbrecciated diogenites.

Evidence of interstitial melts is found in a few diogenitic breccias. The evidence is both mineralogical and chemical, and it is best exemplified in Johnstown, Roda, and Bilanga:

- In Johnstown, minor plagioclase and olivine crystals occur between the orthopyroxene crystals of the large clasts (Floran et al. 1981). Furthermore, the range of trace element abundances displayed by various bulk samples indicates involvement of a interstitial LREE-rich, alkali-rich component that has been interpreted to be a trapped melt (Floran et al. 1981).
- Plagioclase and olivine are also present in Roda. Moreover, Mittlefehldt (1994) observed an orthopyroxene crystal containing two grains of REE-rich phosphate and an inclusion of Si-Al-K-Ba rich glass, the composition of which is unique in diogenites but resembles inclusions analyzed in Bluewing 001 eucrite (Warren and Gessler 2001). These phases testify to the participation of a trapped melt during the crystallization of this diogenite. Furthermore, many bulk analyses of Roda (e.g., Takahashi and Masuda 1990; Mittlefehldt 1994) are more LREE enriched than in situ analyses of orthopyroxene crystals (Papike et al. 1994; Fowler et al. 1995, 1997) and indicate once again the participation of a LREE enriched component.
- In Bilanga, aggregates of diopside, plagioclase, silica, troilite, and chromite, are seen as remnants of trapped melts (Kolar et al. 2002; Domanik et al. 2003). No systematic study has been undertaken yet to detect the effects of this trapped melt component on the chemistry of the bulk rock. I have determined the REE abundances

of a 3.4 g subsample of Bilanga. The results (Table 2) are similar to the SIMS analyses of orthopyroxene (Domanik et al. 2003). This suggests that the trapped melt is probably heterogeneously distributed inside Bilanga and has been efficiently expelled (at least for my sample).

Thus, diogenites are not an exception among cumulates: disseminated trapped melts were involved during their crystallization. The modal compositions of diogenites imply that the proportions of trapped melt were rather limited and ranged between nearly 0 (as in Tatahouine and GRO 95555) and probably no more than a few percent (as in Johnstown and Roda).

Chemical Effects of Interstitial Melts in Diogenites

One of the most severe obstacles for modeling the effects of interstitial melts during the cooling of diogenites is the lack of strong constraints on the nature of their parental melts. Were they pyroxenitic in composition, similar to some kind of Mg-rich basalts or Mg-rich andesites? The problem is still not resolved and has important consequences for calculations. Here, I have chosen two types of parental melts with contrasting crystallizing assemblages: a hypothetical ultramafic melt that crystallizes only orthopyroxene, and liquids that crystallize orthopyroxene (45 wt%), plagioclase (49 wt%), clinopyroxene (5 wt%), and various amounts of merrillite (0, 0.1 wt%, and 1 wt%). I have neglected the contribution of chromite or olivine because these phases have insignificant effects on the REE budget of the rock.

A good knowledge of orthopyroxene-melt equilibrium partition coefficients is required for modeling the chemical evolution of the parental melts of diogenites. Schwandt and McKay (1998) accurately determined these parameters for REEs. One could argue that their *D* values might not be suitable for diogenites because these parameters are strongly dependent on melt compositions, temperatures, and oxygen fugacity. However, this case is less critical if ratios of partition coefficients are used in the discussion because they are less sensitive to melt compositions. This is well demonstrated by the $D_{\mathrm{Dy}}/D_{\mathrm{Yb}}$ ratios which are close to 0.5 for ultrabasic, basaltic or andesitic liquids (e.g., Rollinson 1993; Kennedy et al. 1993; Schwandt and McKay 1998).

Unfortunately, available trace element abundances for interstitial phases are scarce and are insufficient to allow satisfactory modeling. Hence, I have used the equilibrium partition coefficients to estimate the required phase abundance ratios (Table 2) and assumed that C_i/C_j was close to D_i/D_j. This assumption is probably correct for the HREEs, but certainly not for the LREEs, as exemplified by the exsolved pyroxenes analyzed in terrestrial orthopyroxenites (Papike et al. 1995). Nevertheless, these approximations will not change the conclusions drawn from the models.

Assuming that orthopyroxene was the only cumulus phase in diogenites, it is possible to calculate the mineralogical composition of the rock for a given trapped melt fraction. The apparent partition coefficients were calculated for a series of parental melts using Equation 3, and selected results are shown in Figs. 4 and 5. As for cumulate eucrites, a restricted amount of trapped melt in an orthopyroxenite can drastically move the apparent partition coefficients of the pyroxene away from the equilibrium partition coefficients. The differences are more pronounced for the most incompatible elements and are strongly dependent not only on the proportions of trapped melt, but also on the nature and proportions of the interstitial phases (i.e., the composition of the trapped melt).

Figure 5 illustrates how the proportions and compositions of trapped melt affect the ratios of the apparent

Table 2. Partition coefficients and data used for the calculation of diogenite parental melts.[a]

	Equilibrium partition coefficients				Bilanga	Tatahouine	Johnstown	Roda
	Opx/melt	Cpx/melt	Plagio/melt	Mer/melt	(ng/g)	(ng/g)	(ng/g)	(ng/g)
La	0.0004	0.025	0.036	20	9.7	2.21	10	11
Ce	0.00106	0.04	0.031	19	40.8	5.10	63	36
Pr	–	–	–	–	9.9	0.74	–	–
Nd	0.00393	0.09	0.026	17	67.1	3.96	83	88
Sm	0.0113	0.17	0.02	15	41.4	2.05	32	83
Eu	0.00421	0.11	1.15	(11)	3.3	0.24	<2	<4
Gd	0.0238	0.2	0.016	14	84.3	6.95	–	–
Tb	–	–	–	–	17.1	2.36	–	–
Dy	0.0501	0.24	0.013	13	131.4	24.54	93	440
Ho	–	–	–	–	32.2	8.06	–	–
Er	0.0896	0.27	0.01	12	104.1	33.95	85	342
Yb	0.103	0.29	0.007	11	123.9	63.64	115	391
Lu	–	–	–	–	20.7	12.64	–	–

[a] The orthopyroxene/melt and clinopyroxene/melt partition coefficients are from Schwandt and McKay (1998) and McKay et al. (1986), respectively. The plagioclase/melt partition coefficients are from Phinney and Morrison (1990) except for Eu, taken from Jones (1995). The merrillite/melt partition coefficients are estimated from Treiman (1996) and from various analyses obtained on the Shergotty meteorite. The average compositions of orthopyroxenes from Johnstown and Roda (Fowler et al. 1995) and the bulk analyses of Tatahouine (Barrat et al. 1999) and Bilanga (Barrat, unpublished data) have been used to estimate the composition of parental melts (Fig. 7). The REE abundances in the orthopyroxenes and the bulk analyses of these two meteorites are indistinguishable.

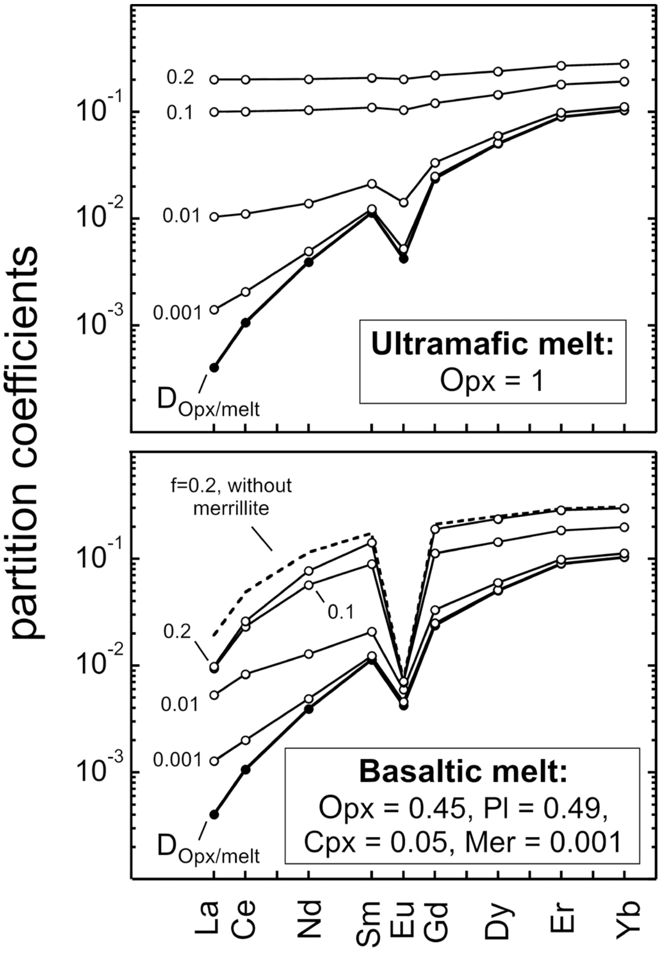

Fig. 4. The apparent partition coefficients for orthopyroxene assuming different trapped melt compositions. They are calculated for mass fractions of trapped melt ranging from 0 to 0.2. Note that the involvement of trace amount of merrillite does not change the REE behavior significantly. See the text for details.

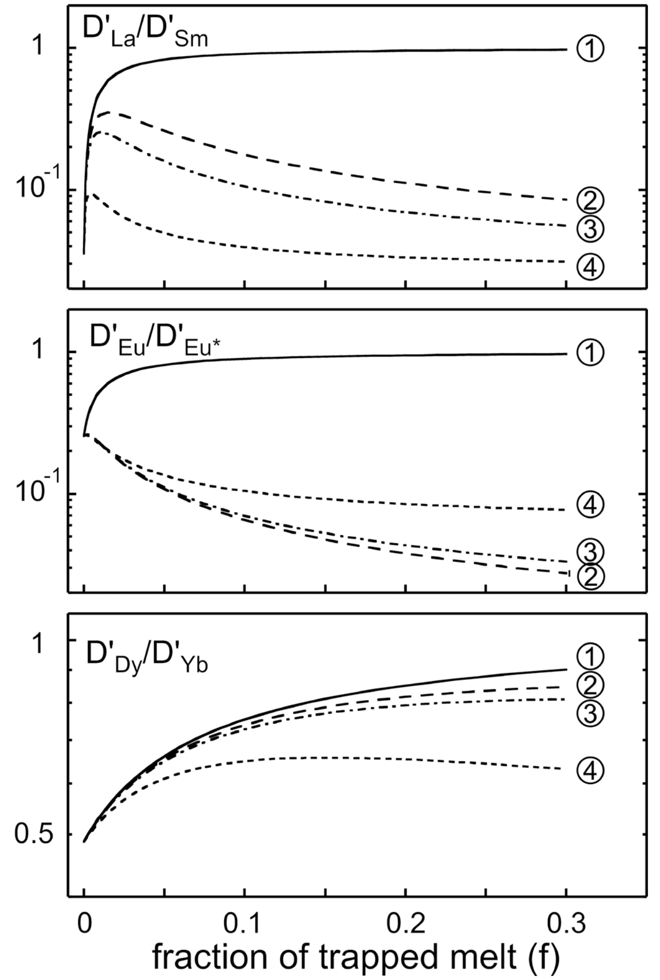

Fig. 5. The apparent partition coefficient ratios as a function of trapped melt fraction. Four different compositions of trapped melts are considered: 1) a hypothetical ultramafic magma crystallizing only orthopyroxene; 2) a magma crystallizing 45 wt% orthopyroxene, 49 wt% plagioclase, and 5 wt% clinopyroxene; 3) the same melt as model 2, but with 0.1 wt% merrillite in the crystallizing assemblage; 4) the same melt as model 2, but with 1 wt% merrillite in the crystallizing assemblage. The equilibrium partition coefficients used in the calculations are given in Table 2.

partition coefficients of orthopyroxene. LREEs are extremely sensitive to a limited participation of interstitial melt, as illustrated by the D'_{La}/D'_{Sm} ratios. Less than 3 wt% of trapped melt can raise by a factor of 10 (or more) the La/Sm ratio of orthopyroxene crystals.

Similarly, the behavior of Eu is strongly dependent on the proportions of trapped melt and on the nature of the post-cumulus phases. For a plagioclase-free system (such as the hypothetical orthopyroxenitic melt), the trapped melt fraction will enhance the Eu/Eu* ratios displayed by the orthopyroxene crystals after equilibration. If plagioclase is a post-cumulus phase in the system (i.e., the trapped melt is basaltic), the model predicts just the opposite effect. Therefore, the Eu/Eu* ratios displayed by the orthopyroxene crystals can hardly be used to constrain the oxygen fugacity during crystallization of an equilibrated orthopyroxenite.

HREEs are less model-dependent than the middle or light REEs, as shown by the behavior of the D'_{Dy}/D'_{Yb} ratios (Fig. 5). Involvement of a trapped melt fraction will increase the Dy/Yb ratios of the orthopyroxene crystals. This effect will be much less pronounced than the modifications expected for LREE ratios and, above all, less sensitive to the proportions of post-cumulus plagioclase, pyroxenes, and traces of merrillite. If the trapped melt crystallizes significant amounts of phases rich in REEs and characterized by very high Dy/Yb ratios, re-equilibration can theoretically decrease the Dy/Yb ratios of the orthopyroxene crystals. At least four diogenites contain REE-rich minerals (Aïoun el Atrouss, Johnstown, Roda [Mittlefehldt 1979, 1994]; and Bilanga [Domanik et al. 2003]), but not enough to produce such an effect. Consequently, this possibility has not been further investigated.

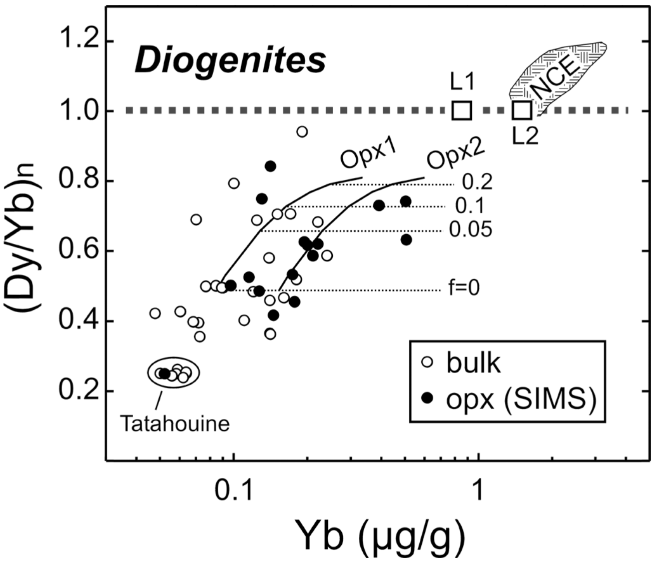

Fig. 6. $(Dy/Yb)_n$ versus Yb for diogenites. NCE, the field for noncumulate eucrites (Shimizu and Masuda 1986; Barrat et al. 2000, 2003) and the composition of orthopyroxene (Opx1 and Opx2) re-equilibrated with two different liquid compositions (L1 and L2, respectively; 5× CI and 9× CI) are shown for comparison. The calculations were done using the crystallizing assemblage of model 3 in Fig. 5 (Opx 0.45, Pl 0.49, Cpx 0.05, Mer .001). Data are from Fukuoka et al. (1977), Masuda et al. (1979), Mittlefehldt (1994, 2000), Papike et al. (1994, 2000), Fowler et al. (1995, 1997), and Barrat et al. (1999). When not determined, Dy abundance has been interpolated using Tb and Yb.

Using high-quality procedures, the HREE abundances in several diogenites and their orthopyroxene crystals have been determined (e.g., Fukuoka et al. 1977; Masuda et al. 1979; Floran et al. 1981; Wolf et al. 1983; Mittlefehldt 1979, 1994, 2000; Papike et al. 1994; Fowler et al. 1995, 1997; Barrat et al. 1999) and have the potential to give straightforward constraints on diogenite petrogenesis. Diogenites and their orthopyroxene crystals show a considerable range of Dy/Yb ratios and Yb abundances (Fig. 6). These variations can clarify the relationships between eucrites and diogenites.

If diogenites were pure cumulates that formed successively from the same parental magma, they should have homogeneous $(Dy/Yb)_n$ ratios, the values of which can be directly estimated from the orthopyroxene equilibrium partition coefficients. Assume that eucrites and diogenites crystallized from the same parental melts. Since Dy and Yb are incompatible during the crystallization of an ultramafic or a basaltic liquid, the parental melts of diogenites should display the same $(Dy/Yb)_n$ ratios as noncumulate eucrites which are uniform and range from 1 to 1.2. Consequently, based on the experimental partition coefficients, orthopyroxenes in equilibrium with parental magma should have well-constrained and close to 0.5 $(Dy/Yb)_n$ ratios (Kennedy et al. 1993; Schwandt and McKay 1998). Only a few diogenites fulfill this condition, and the spread of the data in Fig. 6 negates the general model for diogenites that is based on a simplistic explanation, which is in agreement with Fowler et al. (1995).

Are trapped melts responsible for the wide range of $(Dy/Yb)_n$ ratios in diogenites? The apparent partition coefficients calculated above allow an estimation of the effects of trapped melt on equilibrated orthopyroxene compositions. I have chosen two basaltic melts crystallizing pyroxenes, plagioclase, minor merrillite (Fig. 4 and model 3 in Fig. 5), and characterized by a flat HREE pattern, respectively, at 5× and 9× the CI abundances (L1 and L2 in Fig. 6). At first glance, the orthopyroxene compositions generated by trapped melt fractions ranging from 0 to 0.25, can explain an important part of the scatter defined by the diogenitic orthopyroxenes (curves Opx1 and Opx2 in Fig. 6). One may suggest that most diogenites formed from parental melts characterized by flat HREE patterns and that a re-equilibration of diogenites with trapped melt accounts for the variety of Dy/Yb ratios. In fact, this model fails to explain the database as a whole:

- The fractions of trapped melt calculated are high, especially for pyroxenes that have the highest Dy/Yb ratios (e.g., Manegaon, GRO 95555). These results can hardly be reconciled with the lack or scarcity of interstitial phases such as plagioclase. The disagreement disappears if parental melts characterized by $(Dy/Yb)_n > 1$ were involved.
- A parental magma containing as much HREEs as eucrites is required to account for the orthopyroxenes displaying the highest HREE abundances (e.g., Roda). Eucrites are unlike this melt: they are too ferroan to be in equilibrium with diogenitic pyroxenes and orthopyroxene is never at their liquidus (e.g., Stolper 1977).
- Among diogenites, Tatahouine displays the most fractionated HREE pattern ($[Dy/Yb]_n = 0.25$). As shown above, even if trapped melts were involved, they would have shifted the $(Dy/Yb)_n$ ratios to higher values, not to the lower ones. Thus, such a low ratio (much under 0.5) implies that Tatahouine has not crystallized from a parental melt characterized by a chondritic Dy/Yb ratio. Mittlefehldt (1994) reached a similar conclusion using Sm/Yb ratios. A few other diogenites are characterized by $(Dy/Yb)_n$ ratios lower than 0.5 (e.g., Yamato-74) (Masuda et al. 1979) and suggest the involvement of parental magmas similar to the Tatahouine one.

The REE patterns of parental melts of selected diogenites were calculated (Fig. 7). A basaltic composition was assumed, but similar results are obtained for low-trapped melt fractions using a hypothetical orthopyroxenitic melt (not shown). The calculations point out that the parental melts of diogenites were characterized by various HREE fractionations, as shown in Fig. 7. Moreover, some diogenites unequivocally crystallized from a melt displaying a very low

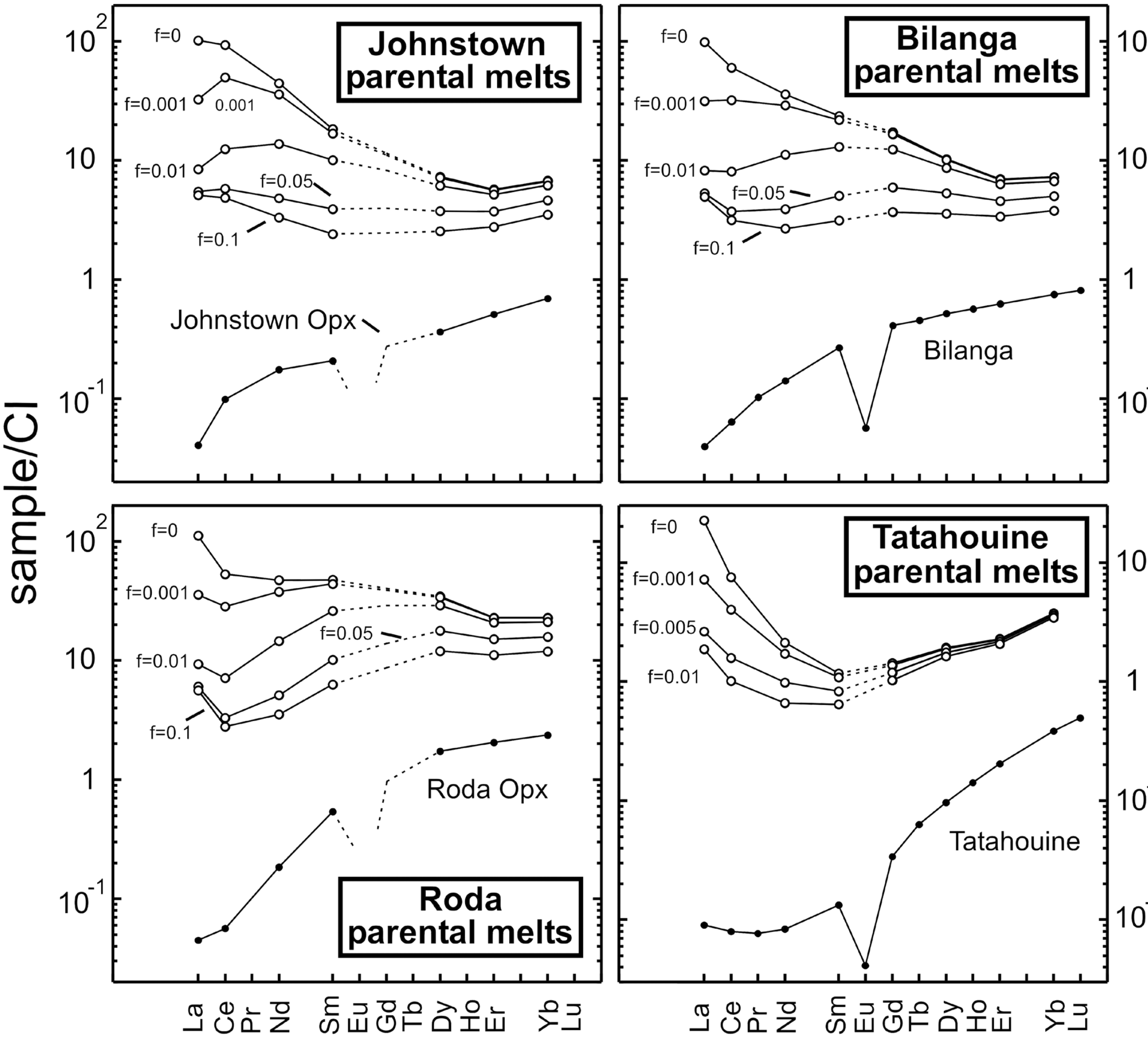

Fig. 7. The calculated parental melts of selected diogenites obtained by assuming a basaltic trapped melt (model 3 of Fig. 5) and using apparent partition coefficients estimated for *f* values ranging from 0 to 0.1. the results are just indicative (see text for details and Table 2 for the data sources).

$(Dy/Yb)_n$ ratio (e.g., ~0.5 for Tatahouine, or less if a significant amount of trapped melt was involved).

If diogenites contained very low amounts of trapped melt fractions, a pronounced LREE enrichment was characteristic of their parental melts (Fig. 7). But such a conclusion is questionable. It is a consequence of the high incompatibility of LREEs in orthopyroxene, and very low *D* values are extremely difficult to assess. In addition, apparent partition coefficients for LREEs are not firmly constrained and are highly model-dependent (Figs. 4 and 5). However, the involvement of LREE enriched components has been already observed for Johnstown, Roda, and Aïoun el Atrouss (Floran et al. 1981; Mittlefehldt 1994).

Therefore, the wide range of $(Dy/Yb)_n$ ratios and possibly the behavior of LREEs recorded in diogenites reflect chiefly the diversity of their parental magmas in agreement with Mittlefehldt (1994) and Fowler et al. (1995). These calculations strongly suggest that maybe none of the diogenites were genetically linked to eucrites.

SUMMARY AND IMPLICATIONS FOR THE MAGMATIC ACTIVITY ON 4 VESTA

The involvement of trapped melts during the crystallization of equilibrated HED cumulates cannot be neglected in estimating the trace element abundances in their parental liquids. The models developed in this study are in agreement with the view that the cumulate eucrites formed from melts similar to noncumulate eucrites (e.g., Treiman 1997; Barrat et al. 2000; Saiki et al. 2001). The trapped melt fractions range between <10 wt% for Moama to ~30 wt% for Moore County. The genesis of diogenites is more complex. It was previously inferred that distinct batches of parental melts were needed to account for the range of trace element abundances in these orthopyroxenites (Mittlefehldt 1994 2000; Fowler et al. 1995; Shearer et al. 1997). This study shows that the same conclusion is reached when the involvement of trapped melt is not neglected. Furthermore, the models developed in this study indicate that many diogenites did not share the same parental liquids with the noncumulate eucrites. The most obvious example of such a diogenite is Tatahouine which crystallized from a melt characterized by a strong HREE enrichment (i.e., by a $(Dy/Yb)_n$ ratio significantly lower than 1).

The presence of cumulates that crystallized from HREE-enriched melts in HED meteorites is important for understanding the differentiation history of 4 Vesta. Magmas characterized by $(Dy/Yb)_n$ ratios less than 1 are uncommon. On the Moon, HREE enrichments have been described only in some Apollo 17 VLT basalts (Wentworth et al. 1979) and among the Apollo 15 pyroclastic green glasses (Galbreath et al. 1990). On Earth, low $(Dy/Yb)_n$ ratios are known in some komatiites (e.g., Sproule et al. 2002) and are typically observed in boninites, some high-Mg andesitic lavas found in forearc terrains (e.g., Taylor et al. 1994). HREE enrichments in melts are necessarily inherited from their sources (e.g., Wentworth et al. 1979; Taylor et al. 1994) and suggest a complex history. Two contrasting scenarios can be put forward for the 4 Vesta case. Since a number of assumptions are involved, the scenarios briefly described below are only speculative.

Re-Melting of Residual Source

Assuming a chondritic pattern for the initial source, REE patterns of mantle residues after partial melting and extraction of a large fraction of magma can display a significant HREE enrichment. Re-melting of these residual sources produces liquids characterized by $(Dy/Yb)_n$ ratios <1. Stolper (1977) proposed this kind of model for the genesis of diogenites. He suggested that their parental magmas were extracted from source regions in the mantle of 4 Vesta that were already depleted in basaltic component by the removal of eucritic melts. This model seems unlikely because the second generation melts would have HREE concentrations that are too low to be in equilibrium with diogenitic orthopyroxenes (Mittlefehldt 1994).

Melting of Cumulates

The formation of reservoirs displaying a HREE enrichment can be produced during the crystallization of basic melts characterized by chondritic HREE distributions. Partition coefficients indicate that olivine and low-Ca pyroxenes in equilibrium with this type of magmas are strongly HREE enriched (e.g., McKay 1986; Schwandt and McKay 1998 among others). Therefore, cumulates dominated by these two phases (harzburgitic cumulates and olivine pyroxenites) can be characterized by low $(Dy/Yb)_n$ ratios depending on the amount of trapped melts they contain. If a magma ocean drove the differentiation of 4 Vesta, then such rocks will be common below the eucritic crust (e.g., Righter and Drake 1997; Ruzicka et al. 1997) and would be serious candidates for the sources of many (if not all) diogenites. Interestingly, the melting of a harzburgitic cumulate at low pressure will not generate classical basaltic melts, but Mg-rich andesitic magmas akin to boninites (Klingenberg and Kushiro 1996). These melts can crystallize a large fraction of Mg-rich orthopyroxene and limited amounts of other phases (olivine, chromite, or plagioclase) as required for diogenites.

Both models are difficult to test rigorously but have the same implications. Obviously, HREE enriched magmas cannot be the early products of the asteroidal magmatic activity. Hence, the immediate questions are: Do eucrites and diogenites have the same crystallization age? Are diogenites (or at least some of them) younger than eucrites? If such is the case, what are the heat sources and the reasons for diogenitic magmatism? These questions are not simple, and more geochronological studies (especially with short-lived radionuclides) are needed to resolve these issues.

Acknowledgments–I thank Randy Korotev for the editorial handling, Takahashi Mikouchi and Noboru Nakamura for constructive comments, Ramon Capdevilla, Laure Dosso, Albert Jambon, Violaine Sautter for a review of an early draft of this paper, and Pascale Barrat for her help. I gratefully acknowledge the Programme National de Planétologie (CNRS-INSU) for financial support. This research has made use of NASA's Astrophysics Data System Abstract Service. This paper is dedicated to the memory of Jean Hartmann, who died in the summer of 2003. Jean was not only a friend, but also a great humanist. This work is I.U.E.M. contribution #919.

Editorial Handling—Dr. Randy Korotev

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