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Trace element redistributions during metamorphism of E-chondrites: Implications for reduced bodies and the Earth

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ABSTRACT

We report on new trace element analyses of enstatite chondrites (ECs) to clarify their behavior during the metamorphism. During the transition from a type 3 to a type 5 or higher, silicates lose a large portion of their trace elements to sulfides. Our procedure allows us to obtain trace element abundances of the silicate fraction of an EC quite easily. The element patterns of these fractions (especially REE patterns) are quite different for EH and EL chondrites, and are furthermore dependent on the metamorphic grade. This procedure can be useful to classify meteorites, in particular when the sulfides are altered. Applied to anomalous ECs, it allows direct recognition of the EH affinity of QUE 94204, and suggests that Zaklodzie, NWA 4301, and NWA 4799 derive from the same EH-like body of previously unsampled composition.

We have used the concentrations obtained on the silicate fractions of the most metamorphosed chondrites to discuss the chemical characteristics of the primitive mantles of reduced bodies of EH or EL affinity (i.e., after core segregation). Our data indicate that these mantles are very depleted in refractory lithophile elements (RLEs), particularly in rare earth elements (REEs), and notably show significant positive anomalies in Sr, Zr, Hf, and Ti. These estimates imply that the cores contain most of the REEs, U and Th of these bodies. Interestingly, the inferred primitive mantles of these reduced bodies contrast with that of the Earth. If the Earth accreted essentially from ECs, one would expect similar signatures to be preserved, which is not the case. This mismatch can be explained either by a later homogenization of the bulk silicate Earth, or alternatively, that the materials that were accreted were isotopically similar to ECs, but mineralogically different (i.e., oldhamite-free).

1. Introduction

Among the 72,000 meteorites described at present, enstatite chondrites (EC) are remarkable for several reasons. First, these rocks were formed under the most reducing conditions of the solar system: their silicates are essentially iron-free, and many elements that have a lithophile behavior in all other meteorite groups, are strongly chalcophile in ECs. As a result, they contain a large number of mineral phases unknown or rare in other meteorites. The most characteristic one is oldhamite (CaS), which can be very rich in rare earth elements (REE), but other sulfides like niningerite (MgS), alabandite (MnS), and keilite [(Fe, Mg)S] can be also mentioned. These unusual sulfides are sometimes associated with sinoite (Si₂N₂O), osbornite (TiN), and nierite (Si₃N₄). Secondly,

these rocks have isotopic compositions of O, Cr, Ti, Mo and Ca, very close to terrestrial values (e.g., Javoy, 1995; Dauphas et al., 2002, 2014; Dauphas, 2017; Mougél et al., 2018; Zhang et al., 2012). These isotopic similarities have led many authors to consider that they were the main ingredients among the Earth's accreting materials, and therefore among the most abundant materials in the inner solar system. This may seem paradoxical since these rocks are rare. Today, we only know about 670 ECs, without taking into account the possibilities of pairing. Compared to the ~3000 carbonaceous chondrites and about 60,000 ordinary chondrites recorded in the Meteoritical Bulletin Database, enstatite meteorites are among the least well represented meteorites in the collections.

Enstatite chondrites are extremely diverse (e.g., Lin, 2022). All the

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intermediates between type-3 chondrites and rocks with achondritic textures have been described. Two main families of ECs have been defined: the niningerite-bearing EH chondrites and the alabandite-bearing EL chondrites (e.g., Sears et al., 1982). Both families display members of all metamorphic grades, from unequilibrated types 3 to highly metamorphosed types 6 or impact-melted rocks. Based on major differences in the sulfide and metal chemistry, Weyrauch et al. (2018) defined four distinct subgroups of ECs (EH_a, EH_b, EL_a, EL_b) that show full petrologic sequences. This suggests that ECs derived from at least four distinct bodies, and possibly eight, taken into account some anomalous chondrites. The situation may be more complex. Boyet et al. (2018) showed that EL3 and EL6 have slightly different ¹⁴²Nd/¹⁴⁴Nd ratios. If this result is confirmed, it could mean that these rocks are not genetically linked and originate from different parent bodies. In addition, there is a handful of meteorites that no longer contain chondrules, and whose classification is a matter of discussions. These ungrouped enstatite meteorites display particular textures, sometimes strongly recrystallized, or metal-rich. QUE 94204 (and other paired stones), Zakłodzie, Itqiy and NWA 2526 are the best known of these meteorites (Weisberg et al., 1997; Patzer et al., 2001; Keil and Bischoff, 2008; Van Niekerk et al., 2014; Krzesinska et al., 2019). Two groups can be simply defined based on mineralogy: some contain plagioclase (e.g., Zakłodzie, NWA 4301, NWA 4799, QUE 94204) and others do not (NWA 2526, Itqiy, Almahata Sitta clasts MS-MU-019, MS-MU-036, MS-245; Bischoff et al., 2022). The genesis of these rocks is still debated. They could be primitive enstatite achondrites, in other words rocks that result of partial melting of ECs, followed by the extraction of a small fraction of partial melts (e.g., Patzer et al., 2001; Keil and Bischoff, 2008; Izawa et al., 2011). These rocks could be analogs of the acapulcoites-lodranites that resulted from the partial melting of very different chondritic protoliths (e.g., Izawa et al., 2011). Alternatively, some of these rocks could be complex impact-melted ECs (e.g., Burbine et al., 2000), or new types of cumulates.

This paper is a continuation of a work undertaken a few years ago on the behavior of lithophile elements in ECs (Barrat et al., 2014) and aubrites (Barrat et al., 2016b). Our aim here is threefold. Firstly, minor and trace element abundances in silicates are modified during EC metamorphism (e.g., Keil, 1968; McKinley et al., 1984; Hsu and Crozaz, 1998). Barrat et al. (2014) showed that trace element abundances in bulk silicate fractions prepared with type 3 or 4 ECs are very different from those of more metamorphosed chondrites. Using a substantial additional sampling, the data we have obtained here allow us to describe the changes in the concentrations of many trace elements in silicate fractions during the metamorphism of enstatite chondrites. Secondly, we will use these results to discuss the possible EH or EL linkage of some of the ungrouped enstatite meteorites. Thirdly, we will use data obtained on the most metamorphosed chondrites to infer some chemical characteristics of primitive mantles of reduced bodies, and discuss potential implications for the Earth.

2. Samples and analytical procedures

We analyzed eighteen enstatite meteorites (Table S-1) including three EH3 (LAR 12001, LAR 12128, LAR 12252), one EH4 (EET 87746), one EH5 (EET 96135), one EH-IMB (Abee), one EH-IM (NWA 7324), two EL4 (NWA 4780 and MAC 02747), one EL5 (TIL 91714), two EL6 (LAP 10014 and NWA 3134), two impact-melted EL (Ilafegh 009 and Happy Canyon), and four anomalous enstatite meteorites (QUE 94204, Zakłodzie, NWA 4301, NWA 4799).

2.1. Whole rocks

Our analytical procedure is nearly the same as that used by Barrat et al. (2012, 2014, 2016a and 2016b) for chondrites and aubrites, and is summarized below. Powders were prepared using a boron-carbide mortar and pestle. Elemental abundances for most of the samples were

determined using a high-resolution ICP-MS spectrometer Thermo Element 2 at Institut Universitaire Européen de la Mer (IUEM), Plouzané, following well-established procedures (e.g., Barrat et al., 2012, 2014, 2016a). The only change we have made to this procedure concerns the determination of Zr concentrations. In some cases, when solutions were poor in Zr and very rich in Mn, an interference was detectable on the mass 91. Therefore, we no longer use both ⁹⁰Zr and ⁹¹Zr for the determination of Zr concentrations, but only ⁹⁰Zr. Results for international standards (BIR1, BCR2, JB2, WS-E, BE-N, UB-N, PCC1, Allende powder USNM 3529) have been reported previously (Barrat et al., 2012, 2014, 2016a and 2016b; Charles et al., 2021). Based on replicate standards and samples, the precision for abundances in powdered samples and residues is much better than 5%. The precision for trace element ratios (e.g., Y/Ho, Eu_n/Gd_n, Sm/Sm* and Yb/Yb*, where Sm* and Yb* are respectively the interpolated Sm and Yb concentrations for a smooth CI-normalized REE pattern, such that Sm*_n = (Nd_n × Gd_n)^{1/2} and Yb*_n = Er_n^{1/3} × Lu_n^{2/3}) is better than 2.5% (2 × relative standard deviation).

2.2. Leaching and preparation of bulk silicate fractions

A series of leaching experiments were undertaken to determine the trace element abundances of the insoluble silicate fraction. It is important to emphasize that, contrary to other types of chondrites, enstatite chondrites and achondrites are totally devoid of either apatite or merillite, phases which are usually important carriers of REEs or actinides in many other types of meteorites. Consequently, sulfides, and notably oldhamite, are here the sole REE-rich phases, and are easily dissolved in HCl (e.g., Lodders et al., 1993). Some of the meteorite powders (100–200 mg) were leached in hot 6 N HCl (1 h, 120 °C), to dissolve all the sulfides (including troilite) and the metallic FeNi, leaving residues composed essentially of insoluble phases (mainly enstatite and plagioclase). The residues were then rinsed five times in ultrapure water, dried and processed using the same methodology as employed for the other meteorite powders.

In order to demonstrate the efficiency of this protocol, we used 6 fractions of the same powder prepared from about 1 g of an EH3 (LAR 12001) and varied the leaching time from 10 to 85 min (Table S-1, Figs. 1 and 2). Co concentrations show that the FeNi metal is well removed after 45 min of leaching. The same is true for sulfides, as evidenced by changes in REEs and Sr concentrations.

The chondrules of LAR 12001 contain small quantities of olivine Fa₃ (Antarctic Meteorite Newsletters, 39 (1), 2016), and probably small amounts of glass for some of them. It is possible that hot HCl has at least partially attacked these phases. It is also possible that plagioclase or enstatite could also be partially attacked by HCl. The differential attack of some of the silicates could potentially bias the results. However, the homogeneity of the trace element contents of the residues obtained after 45 min of leaching shows that this is not the case (Figs. 1 and 2). In particular, such consistency of the REE patterns would not have been achieved if plagioclase or enstatite were dissolved preferentially by hot HCl. The effect of a preferential dissolution of olivine or traces of glass cannot be detected with these data either, suggesting that this possibility, if real, has no significant effect on the elements we have measured. We conclude that the residues obtained after 45–60 min of leaching provide a good picture of the composition of the silicate fraction of enstatite meteorites. However, these residues may contain traces of minerals insoluble in hot HCl. Traces of schreibersite are possible (Barrat et al., 2014). The higher Cu concentrations in the residues than in the unleached powders, as here for LAR 12001 (Fig. 1), can be explained by nuggets of native copper that are not attacked by HCl (see below). In any case, the possible occurrence of these accessory HCl-resistant phases should not be overestimated, and does not have a significant effect on the concentrations of most of the elements we have determined.

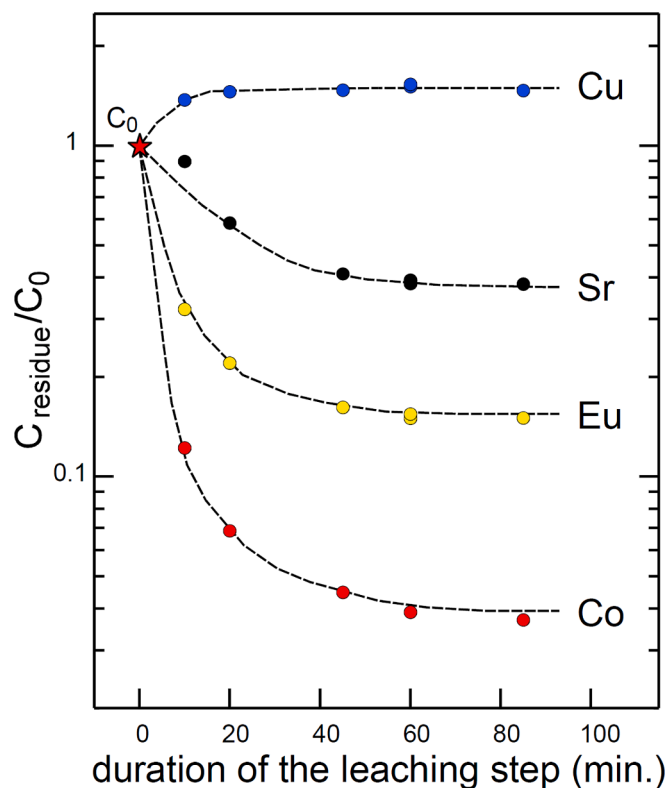


Fig. 1. Evolution of Cu, Sr, Eu, and Co concentrations in the residues of an EH3 chondrite powder (LAR 12001) leached with hydrochloric acid (6 N) at 120 °C as a function of time.

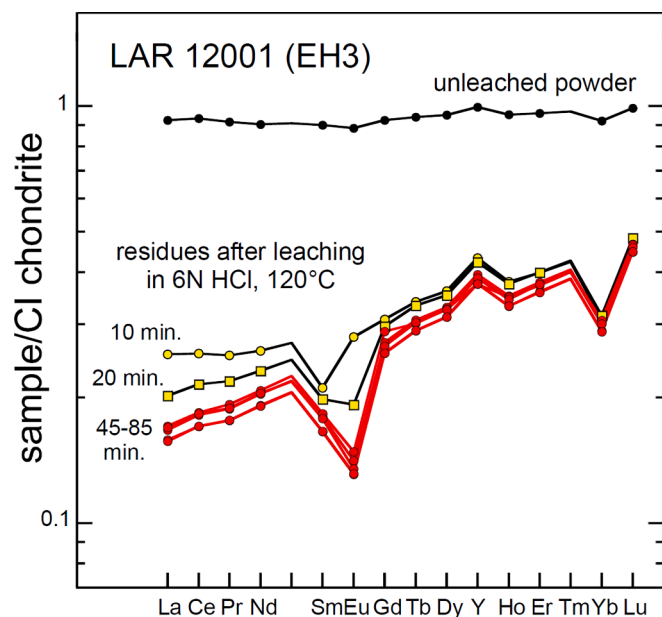


Fig. 2. CI-normalized REE patterns of the EH3 chondrite LAR 12001, and its residues obtained after leaching with hydrochloric acid (6 N) at 120 °C. The patterns of the residues obtained after 45 min or more are similar.

3. Results

Our new data complement the series of twenty-four enstatite chondrites previously analyzed in Grenoble (Université Joseph Fourier, Laboratoire de Géodynamique des Chaînes Alpines) or in Brest (Institut Universitaire Européen de la Mer, Plouzané) using the same

methodology, including the leaching step for determining the trace element abundances in silicate fractions (Barrat et al., 2014). Barrat et al. (2014) reported only concentrations for selected elements (Sc, Rb, Sr, Y, Zr, Nb, Ba, REEs, Hf, Th, U). Here, all the data obtained by Barrat et al. (2014), including revised Zr abundances calculated using ^{90}Zr only, and concentrations of other elements not reported in the previous paper (Be, K, Ti, V, Mn, Co, Cu, Zn, Ta...), are reported and allows the discussion of an analytically homogeneous database obtained on 41 enstatite meteorites. The number of new analyses being large, the results are given in Table S-1.

4. Discussion

4.1. Enstatite chondrites

4.1.1. Whole rock analyses

The geochemistry of trace elements in ECs has been the subject of numerous publications (e.g., Sears et al., 1982; Kallemeyn and Wasson, 1986; Zhang et al., 1995; Kong et al., 1997; Rubin et al., 2009; Rubin and Wasson, 2011; Barrat et al., 2014; Dauphas and Pourmand, 2015; Boyet et al., 2018 and reference therein). The data we have obtained here confirm and complement these previous studies. To enable comparisons between EL and EH chondrites, we have represented the trace element patterns normalized to CI and Sc abundances (Fig. 3). We have deliberately excluded from this figure some abnormal or altered meteorites (e.g., Galim (b), EET 92063, Al Haggounia 001) whose unusual characteristics have already been reported (e.g., Barrat et al., 2014; Rubin, 2016).

EH3 and EH4 chondrites display flat trace element patterns with noticeable enrichments in some moderately volatile elements such as Cu, Ga, Rb, and limited depletions in Zn. Excepted for these few moderately volatile elements, the patterns do not display significant variability. This is not the case for the more metamorphosed EH chondrites, whose patterns are similar in shape to that of the previous ones, but show more dispersions. Cu and Ga enrichments relative to CI are still present, but some samples such as Saint Marks (EH5) or LAP 02225 (EH-IM) show marked depletions in the most volatile elements such as Rb, Cs and Zn. Significant anomalies also appear as exemplified by Ti, Nb and V depletions in our Abee sample (EH4-5 IMB) or Ba in NWA 7324.

EL3 and EL4 chondrites have trace element patterns that differ clearly from those of EH3 and EH4 chondrites with no Cu or Ga enrichments, and with marked depletions in Rb, Cs and Zn. EL6 chondrites are well known for their low LREE and Nb depletion compared to most other chondrites. These particularities explain most of the differences observed between the patterns of EL6 and EL3 (and EL4) chondrites. In addition to these, EL6 display low Zn abundances, which are certainly related to the thermal history of these rocks (e.g., Moynier et al., 2011). We analyzed only one EL5 chondrite (TIL 91714), and its trace element concentrations are identical to those of EL6.

We did not distinguish in our diagrams the chondrites according to the subgroups EH_a , EH_b , EL_a , EL_b proposed by Weyrauch et al. (2018), because not all our meteorites were classified by these authors. We note that the dispersions we obtained for the different types (Fig. 2) are quite limited, and do not allow us to distinguish different subgroups among them. This observation does not rule out the conclusions made by Weyrauch et al. (2018), but shows the limits of trace elements to classify EC.

4.1.2. Trace element abundances in silicate fractions and redistribution during metamorphism of EC.

Barrat et al. (2014) prepared silicate fractions to discuss the contribution of sulfides in the budget of lithophile elements in EC. Indeed, the concentrations of a given element in the residues give a good idea of its chemical affinity. An element that would be strictly chalcophile or siderophile, would be totally absent in our residues. On the other hand, the leaching step concentrates in the residues all the elements contained

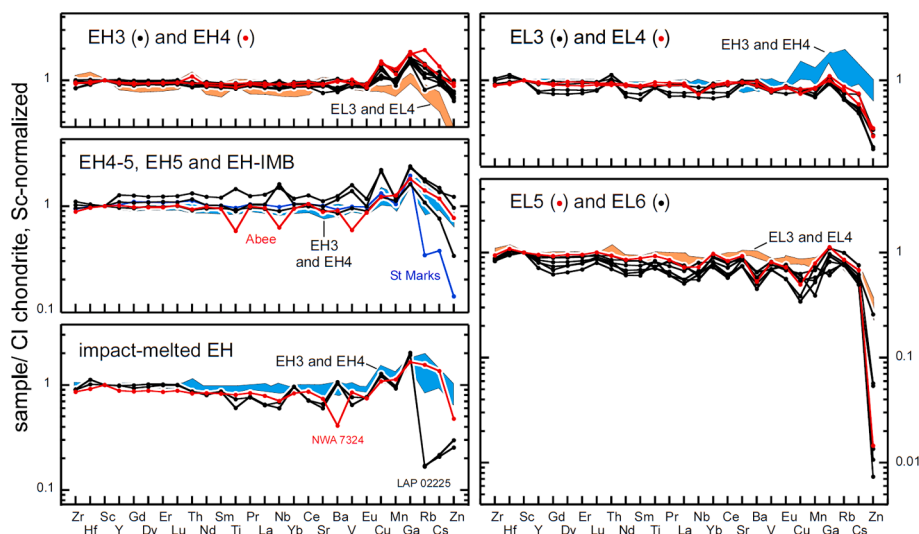


Fig. 3. CI-normalized abundances (Sc-normalized) for ECs. The reference CI chondrite is from Barrat et al. (2012).

in the phases insoluble in hot HCl (essentially the silicates). Using the typical modal compositions of EH or EL chondrites (Weisberg and Kimura, 2012), the concentrations of perfectly lithophile elements in residues are $1.5\text{--}1.6 \times$ higher than in the unleached samples (Barrat et al., 2014). Barrat et al. (2014) showed that these concentrations were diverse, distinct for EL and EH and dependent on the metamorphic grade. With the additional 14 samples we have leached here, we now have data for 31 chondrites, including some rare types 4 or 5 and impact-melted chondrites.

The compositions of the residues show considerable ranges of abundance compared to those of the host chondrites. To take just a few examples, Ti abundances in the residues range from 14 to 448 $\mu\text{g/g}$, from 0.25 to 34 $\mu\text{g/g}$ for V and from 2.6 to 68 ng/g for La.

Ti is strongly chalcophile in ECs, and is largely controlled by troilite, which contains between 0.17 and 1% Ti in these rocks (e.g. Weyrauch et al., 2018). Troilites in types 5 and 6 tend to be richer in Ti than in type 3 ones. To the opposite, enstatites in highly metamorphosed EC are strongly Ti-depleted compared to those in unequilibrated ECs (e.g., Hsu and Crozaz, 1998). Among EC silicates, enstatite is the only phase that contains Ti. Thus, Ti abundances in the residues are function of their enstatite contents, and Ti concentrations in this phase. Since enstatite is by far the most abundant silicate in ECs, Ti content in residues is a possible index of the importance of exchanges between phases during metamorphism of ECs, particularly between enstatite and sulfides. Ti concentrations in residues are highly dependent on the metamorphic grade: all the residues prepared from types 3 or 4 have Ti concentrations above 175 $\mu\text{g/g}$ while those prepared from more metamorphosed chondrites have concentrations below 145 $\mu\text{g/g}$, and can drop to 14 $\mu\text{g/g}$. Thus, we selected Ti abundances in the residues to describe the chemical evolutions during metamorphism. We will first examine below the behavior of siderophile elements (Ga, Co), chalcophile elements (Cu, Zn, Pb), some transition metals (Sc, Mn, V), and finally usual lithophile elements, including alkali metals, alkaline earth elements, high field strength elements, lanthanides, and actinides.

Gallium and Co (Fig. 4a and b). These two elements are strongly siderophile and their concentrations are largely controlled by metal that contains Ga-rich sphalerite inclusions (e.g., Kong et al., 1997). Not surprisingly, their concentrations in our silicate fractions are much lower than in the unleached chondrites. Residues prepared with types 3 or 4 tend to have higher concentrations for these elements than those obtained with more metamorphosed chondrites. However, the data are quite scattered, and part of this spread could be explained by minute amounts of metal that would not have been dissolved by hot HCl. In any case, it can be noted that EL5 and EL6 residues have generally lower Ga

and Co concentrations than those prepared from strongly-metamorphosed EHs.

Copper (Fig. 4c). EHs are slightly richer in Cu than EL chondrites (see above). This difference is also found with residues. A few phases can potentially control Cu abundances in ECs (e.g., Weisberg and Kimura, 2012). The most obvious are chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), djferfisherite $[(\text{K},\text{Na})_6(\text{Cu},\text{Fe},\text{Ni})_{25}\text{S}_{26}\text{Cl}]$, and of course native copper (Cu). Hot HCl easily attacks Cu-sulfides but not native copper, and this phase can be present in many samples. This is clearly the case for LAR 12001 (EH3) used to perform leaching tests (Fig. 2). The residues obtained with this meteorite have concentrations 1.4–1.5 times higher than that of the original sample. This indicates that most of the Cu contained by this meteorite is insoluble in hot HCl; thus, it is in its native form (Cu^0). The spread observed for the Cu content of the residues is most probably due to a nugget effect.

Lead and Zn (Fig. 4d and e). The concentrations of these two chalcophile elements in residues prepared from type 3 or 4 chondrites are not very different from those of chondrites before leaching, which suggests that they are not only contained by sulfides. Their concentrations in the residues of the more metamorphosed chondrites generally appear to be lower, but trends show a wide dispersion. In the case of Zn, evaporation during metamorphism may partially explain the dispersions of residues (Ikramuddin et al., 1976; Moynier et al., 2011). However, we cannot rule out the possibility that the dispersion observed is due to the presence of an HCl-resistant phase (which we have not identified) in some residues (nugget effects).

Scandium, Mn and V (Fig. 5): these three elements are not hosted by the same phases and thus, diversely chalcophile. Scandium is chalcophile in EH but not in most EL chondrites (Barrat et al., 2014). This marked difference is the fingerprint of niningerite that contains significant amounts of Sc (Frazier and Boynton, 1985; Lehner et al., 2013). The abundances of Sc in the residues allow distinguishing quite easily most EL from EH chondrites. All residues prepared from EH chondrites have Sc concentrations below 8 ppm, well correlated with Ti abundances. For residues prepared with EL chondrites, Sc concentrations are around 10 $\mu\text{g/g}$ and do not change at all with metamorphism. However, the residues prepared with two metamorphosed chondrites, NWA 3134 (EL6) and Happy Canyon (impact-melted EL) have abnormally low Sc concentrations, suggesting that sulfidation can affect occasionally this element during EL metamorphism. Manganese is strongly controlled by sulfides (e.g., Rubin, 2008; Weyrauch et al., 2018). Residues prepared with the most metamorphosed ECs are depleted in Mn. Low Mn abundances were previously noticed in enstatites from these meteorites and it is well accepted that metamorphism and simultaneous sulfidation of Mn,

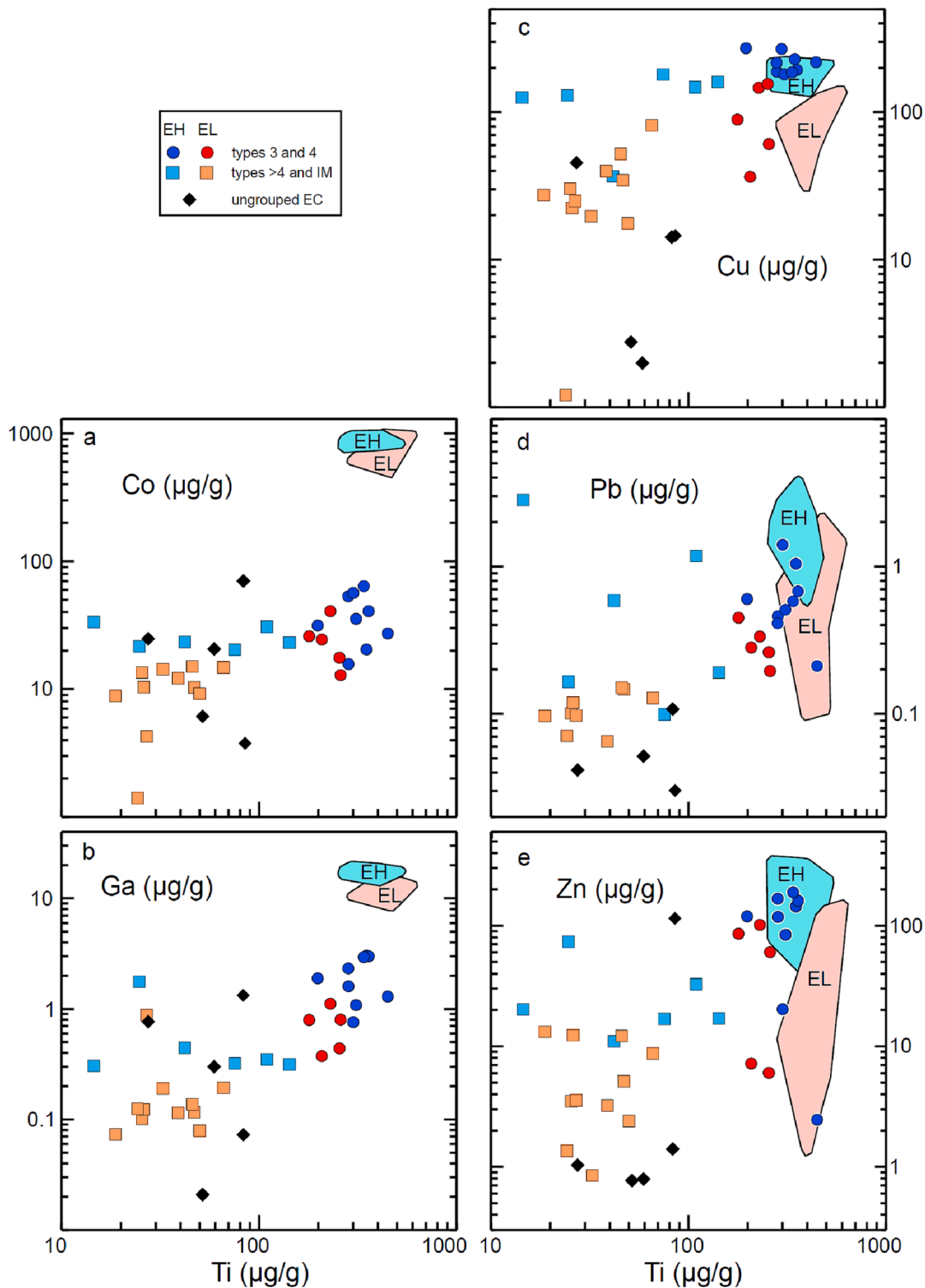


Fig. 4. Co, Ga, Cu, Pb, Zn vs. Ti plots for E-chondrites (blue and red fields) and their residues after leaching with hot HCl (6 N, 120 °C).

explains the Mn-depletion in enstatite (e.g., Rubin, 2008). Troilite can be rich in V (Yoshizaki et al., 2021) and it is not surprising that Ti and V concentrations are well correlated in residues. As for Ti, the residues obtained with the most metamorphosed chondrites display the lowest concentrations. There is no difference between EH and EL chondrites to be reported with this element.

Potassium, Rb and Cs (Fig. 6a–c). Alkali metals are not the most chalcophile elements in ECs. Djerfisherite can host part of these alkali metals in these chondrites, and the occurrence of such sulfides can

explain the deviation of their behaviors from strictly lithophile (e.g., Barrat et al., 2014). With the exception of NWA 3134 (EL6) and Happy Canyon (impact melted EL) with low Cs concentrations, all residues have alkali abundances similar to those of unleached ECs.

Beryllium, Sr and Ba (Fig. 6d–f). Beryllium concentrations in the residues are chondritic or slightly higher, showing a rather lithophile behavior, with no marked difference between EL and EH residues, and no metamorphic effects. Strontium is more chalcophile in EH than in EL chondrites, whatever their metamorphic type. The behavior of Ba is

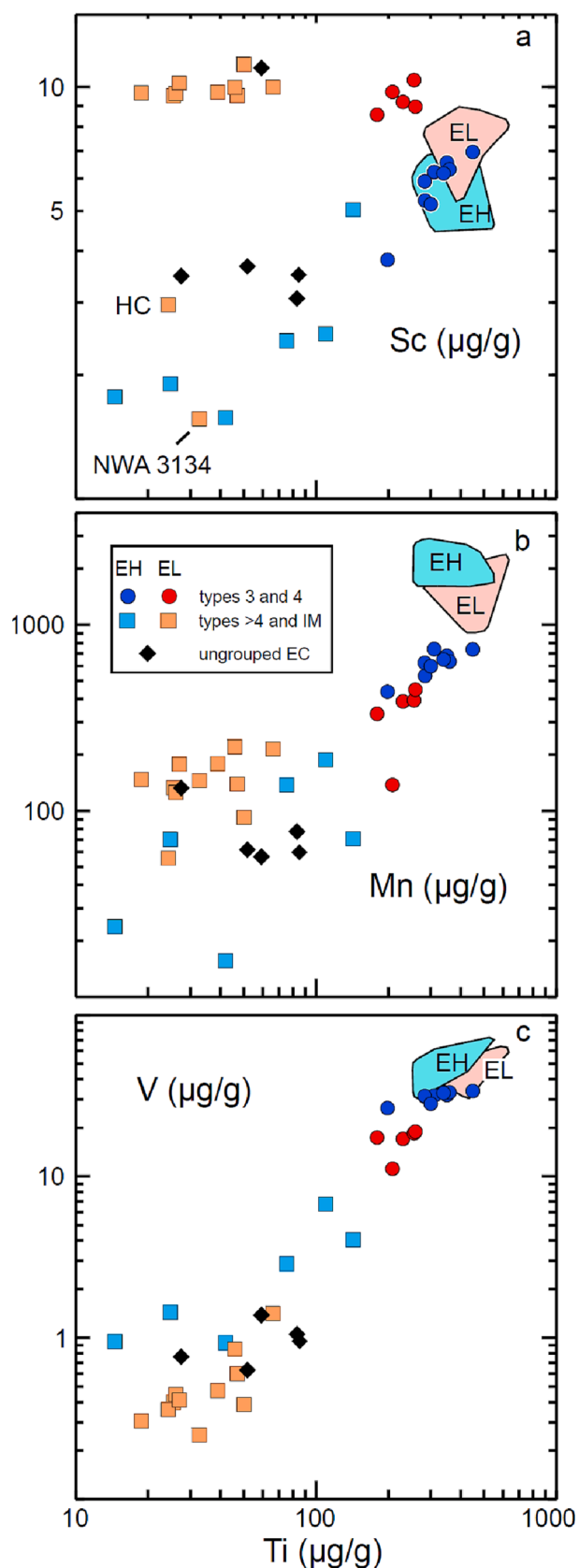


Fig. 5. Sc, V, Mn vs. Ti plots for E-chondrites (blue and red fields) and their residues after leaching with hot HCl (6 N, 120 °C).

more complex. Barium is clearly chalcophile in EH3 and EH4 chondrites: the residues obtained with these chondrites display always Ba abundances lower than in whole rocks. Residues prepared with more metamorphosed EH chondrites have higher Ba abundance pointing to a more lithophile behavior during metamorphism (plagioclase involvement?). EL3 and EL4 residues are richer in Ba than EH3 and EH4 residues, which indicates a more lithophile behavior of this element in these chondrites (Barrat et al., 2014). Ba abundances in EL5 and EL6 residues show some dispersion but are in the same level as EL3 and EL4 ones, indicating limited metamorphic redistributions with sulfides for these chondrites.

Niobium and Ta (Fig. 7a–c). The chalcophile affinities of Nb in ECs were suggested by Barrat et al. (2014). Münker et al. (2017) experimentally showed that at low oxygen fugacity, Nb is chalcophile and can be easily decoupled from Ta, its geochemical twin. Residues prepared with type 3 chondrites have Nb abundances similar to those of the whole rocks, but their Ta abundances tend to be higher. The concentrations of these two elements are correlated with those of Ti, the residues prepared with the most metamorphosed chondrites displaying the lowest abundances. The Nb/Ta ratios are similar or slightly lower than those of total rocks for residues prepared with types 3 and 4 and significantly lower for those prepared with the most metamorphosed chondrites. There is no marked difference between EH and EL chondrites. The lithophile affinities of these two elements decrease during the metamorphism of these rocks and confirm that segregation of sulfides can significantly modify the Nb/Ta ratios in agreement with Münker et al. (2017).

Zirconium and Hf (Fig. 7d–e). Oldhamite in EH chondrites contain significant amounts of Zr (Croaz and Lundberg, 1995; Lehner et al., 2013). Sulfides contain <20% of Zr and Hf in types 3–4, and this proportion reaches >60% in EL6 chondrites (Barrat et al., 2014). The abundances of Zr and Ti residues are well correlated while those of Hf show more dispersion. Zirconium being less chalcophile than Hf, the Zr/Hf ratios of the residues and total rocks are similar for type 3 or 4 chondrites, but can be very low and lower than 20 for residues prepared with the most metamorphosed rocks. As for Nb and Ta, there are no significant differences between EH and EL chondrites.

Lanthanides and Y (Figs. 8 and 9). Oldhamite largely controls the budget for these elements in EC (e.g., Larimer and Ganapathy, 1987; Croaz and Lundberg, 1995; Gannoun et al., 2011; Barrat et al., 2014). The residues show a very wide range of concentrations for REE and Y, and depending on the metamorphic type. All residues are on the same trend in the La vs. Ti diagram (Fig. 8a), with slight differences between EH and EL. Very marked differences between EH and EL chondrites appear for heavy REEs and Y, but also for Eu (Fig. 8b–e). These elements are much less chalcophile in EL during metamorphism, leading among other things to Y/Ho ratios much higher than 45 in EL5 and EL6 and impact melted EL chondrites. The differences are very well highlighted by the REE patterns (Fig. 9).

The patterns of EH3 and EH4 residues show highly variable REE abundances (from 0.03 to $0.8 \times \text{CI}$) and marked negative anomalies in Sm ($\text{Sm}/\text{Sm}^* = 0.56\text{--}0.86$) and Yb ($\text{Yb}/\text{Yb}^* = 0.56\text{--}0.75$). Such anomalies have already been measured in the phases of these chondrites (Hsu and Croaz, 1998; Jacquet et al., 2015) and are certainly inherited from early nebular condensation processes. The patterns are also enriched in heavy REEs ($\text{Gd}_n/\text{Lu}_n = 0.37\text{--}0.66$), with depletions to slight enrichments in light REEs ($\text{La}_n/\text{Nd}_n = 0.77\text{--}1.09$). They also have variable Eu anomalies ($\text{Eu}_n/\text{Gd}_n = 0.42\text{--}1.27$) that are inversely correlated with REE abundances (not shown). Residues prepared with more metamorphosed EH chondrites display very different patterns. Firstly, all the samples display much lower heavy REE abundances with $\text{Lu}_n < 0.1 \times \text{CI}$, light REE enrichments ($\text{La}_n/\text{Nd}_n = 1.20\text{--}2.19$), and large positive Eu anomalies ($\text{Eu}_n/\text{Gd}_n = 2.56\text{--}17.2$). The residue obtained with LAP 02225 (EH impact melt) is unusual, with a lower positive Eu anomaly ($\text{Eu}_n/\text{Gd}_n = 1.73$) and a small light REE depletion ($\text{La}_n/\text{Nd}_n = 0.79$). The patterns of the residues of these chondrites no longer show negative Sm and Yb anomalies typical for the EH3 and EH4 residues. It is possible that such anomalies are still present, as for NWA 7324 (impact-melted EH), but

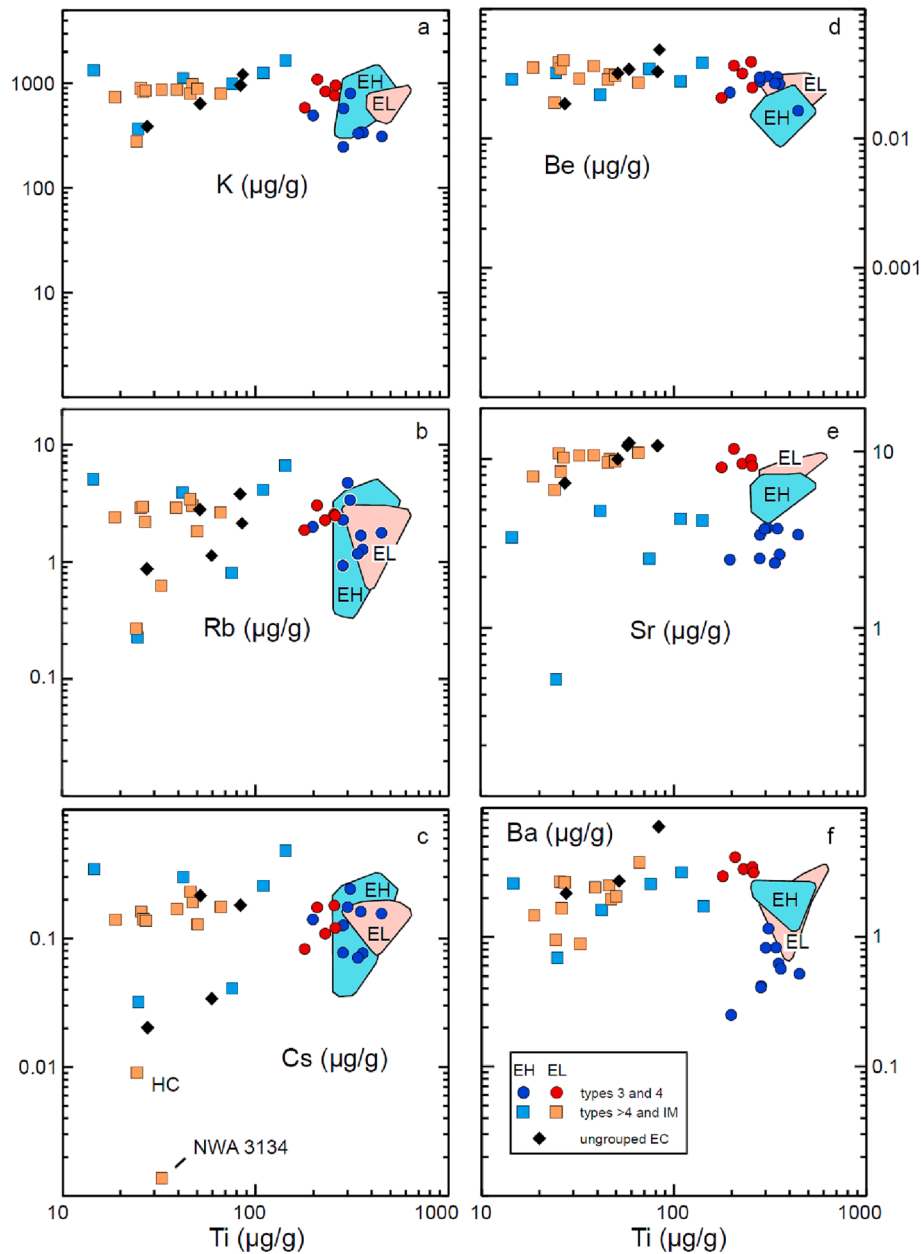


Fig. 6. K, Rb, Cs, Be, Sr, Ba vs. Ti plots for E-chondrites (blue and red fields) and their residues after leaching with hot HCl (6 N, 120 °C).

they are at best ambiguous, and difficult to quantify. It is important to note that there is a clear dichotomy in these REE patterns: those obtained with types 3 and 4 and those obtained with the most metamorphosed chondrites are very different, without transitional samples between these two groups.

The EL-residues display different features, with again a marked dichotomy between the residues obtained from EL3 and EL4 chondrites and those obtained with more metamorphosed types. The patterns of the five EL3 and EL4 residues we analyzed are very similar in abundances and shapes. They are slightly enriched in heavy REEs ($Gd_n/Lu_n = 0.42\text{--}0.60$) and flat for light REEs ($La_n/Nd_n = 0.98\text{--}1.16$) with positive anomalies in Eu ($Eu_n/Gd_n = 2.16\text{--}4.29$), Y ($Y/Ho = 30.3\text{--}31.6$), and especially marked negative anomalies in Sm ($Sm/Sm^* = 0.45\text{--}0.71$) and Yb ($Yb/Yb^* = 0.52\text{--}0.67$). All the residues prepared from the more metamorphosed EL chondrites are poor in light REEs, show enrichments from Nd to La ($La_n/Nd_n = 1.20\text{--}2.74$), and from Nd to Lu ($Nd_n/Lu_n = 0.015\text{--}0.08$) with striking positive anomalies in Eu ($Eu_n/Gd_n = 10.4\text{--}39.3$) and Y ($Y/Ho = 46.9\text{--}60.4$). Again, these patterns no longer

show negative anomalies in Sm and Yb (it is important to note that the calculation of Sm^* with the formula given in Section 1 is not correct for these patterns due to their concavities, and can induce wrong Sm/Sm^* ratios).

Thorium and U (Fig. 10). Oldhamite contains both elements (e.g., Murrell and Burnett, 1982). However, Th is rather lithophile in EL3 and EL4 and clearly chalcophile in EH3 and EH4. They are largely chalcophile in the more metamorphosed chondrites, in which sulfides contain well over 70% of the U and Th of these rocks (Barrat et al., 2014). The concentrations of these two elements appear to be correlated with those of Ti in the residues, but the spreads are significant. The Th/U ratios in the residues are variable, but values higher than 8 were measured in all the silicate fractions prepared with the most metamorphosed EL chondrites (EL5, EL6 and impact-melted EL).

Important conclusions emerge from the previous observations. First, none of the elements we have analyzed is perfectly lithophile during the formation of ECs (type 3), or during their metamorphism. This is particularly striking for elements such as alkalis, REEs, Zr, Hf, Th and U,

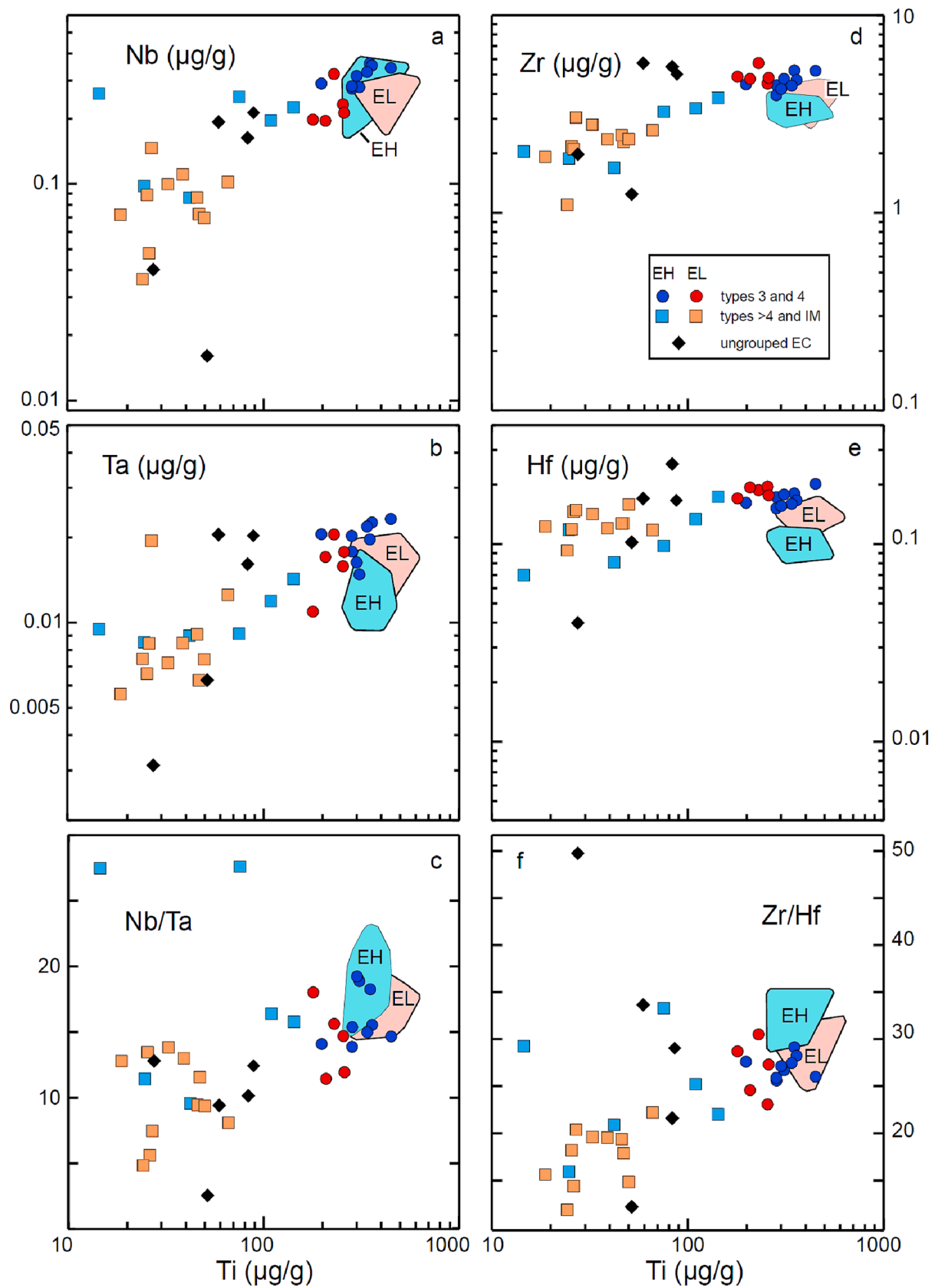


Fig. 7. Nb, Ta, Nb/Ta, Zr, Hf, Zr/Hf vs. Ti plots for E-chondrites (blue and red fields) and their residues after leaching with hot HCl (6 N, 120 °C).

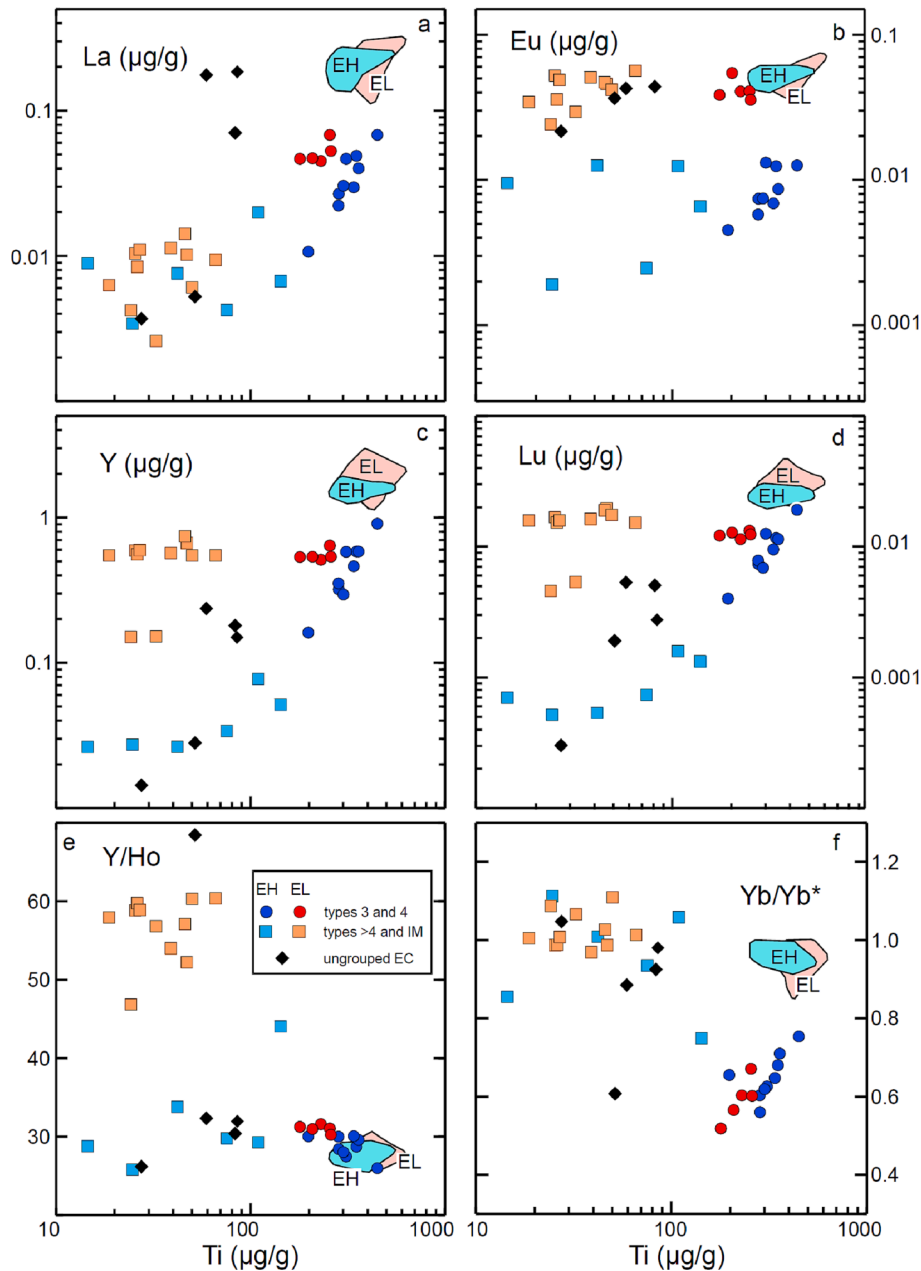


Fig. 8. La, Eu, Y, Lu, Y/Ho, Yb/Yb* vs. Ti plots for E-chondrites (blue and red fields) and their residues after leaching with hot HCl (6 N, 120 °C).

which are classically considered to be among the most lithophile ones in other chondrites (OC, CC). The chalcophile behavior of many elements (e.g. Ti, Mn, V, HFSE, light REEs, actinides) is amplified during metamorphism, resulting in important redistributions between silicates and sulfides, and particularly lower concentrations for types 5 and 6 than in types 3 and 4 silicate fractions. Many sulfides are present in ECs and can contribute to this effect. However, in agreement with in-situ analyses (e.g., Crozaz and Lundberg, 1995; Lehner et al., 2013), oldhamite, troilite and Mn-sulfides (e.g., alabandite, keilite...) mainly control the observed evolutions. Although these phases control different elements, the fact that the concentrations of light REEs, Ti and Mn are generally well correlated in the silicate fractions is a noteworthy point. The differences in the composition of silicate fractions between EL and EH chondrites, and between types 3, 4 and >4 are also remarkably sharp. The most metamorphosed ECs have undoubtedly had various and probably complex thermal histories (Rubin et al., 2009; Rubin and Wasson, 2011), sometimes involving shock reheating and local melting. In addition to

the previous study (Barrat et al., 2014), we analyzed additional ECs of types 4 and 5 (EET 87746 (EH4, S3), EET 96135 (EH5, S4), MAC 02747 (EL4, S4), NWA 4780 (EL4, S3), TIL 91714 (EL5, S2), shock stage after Rubin (2015)), some of which do not show fingerprints of impact melting of silicates. Thus, if this process could be invoked for impact-melted ECs, it is certainly not the sole cause of redistributions between silicates and sulfides. Residues only provide information on the composition of bulk silicates in a given chondrite. The mechanisms of the decrease in concentrations of these elements cannot be addressed in depth with this kind of data. Detailed in-situ studies are needed to assess the possible roles of diffusion or sulfidation during metamorphism and are beyond the scope of this study.

4.2. Ungrouped enstatite meteorites

4.2.1. Trace element abundances in whole rocks

The trace element and REE + Y patterns of the anomalous enstatite

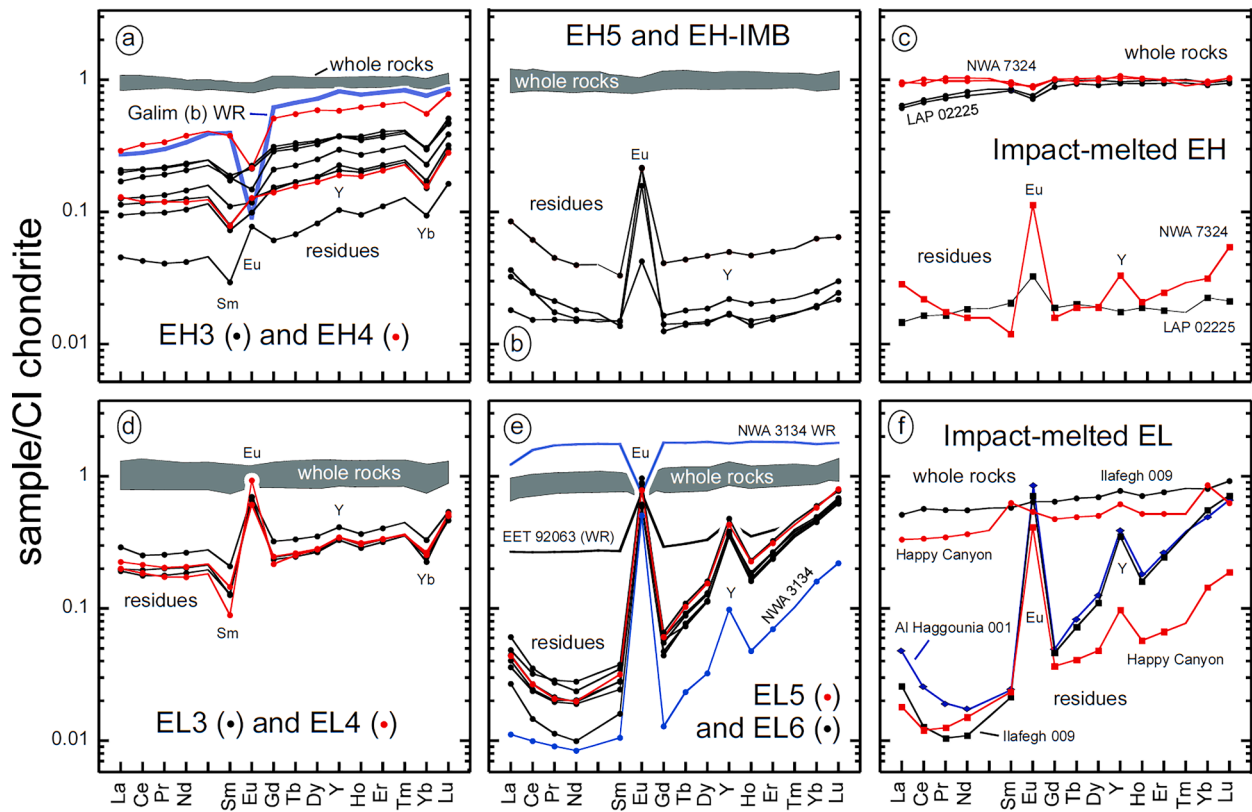


Fig. 9. CI-normalized REE patterns of EH and EL chondrites and their residues obtained after leaching with hydrochloric acid (6 N) at 120 °C.

meteorites are given in Figs. 11 and 12. Zakłodzie, NWA 4301, NWA 4799, and QUE 94204 have Zr, Hf and Sc contents that are chondritic, but the abundances of the other elements show much more variability than ECs, as shown by their REE patterns that are different from those of typical chondrites. Those obtained for Zakłodzie are flat or enriched in LREE, with positive Eu and Y anomalies, while NWA 4301 shows a pronounced negative Eu anomaly. The pattern of QUE 94204 resembles at first glance to that of an EL6 exceptionally rich in REE (even richer than NWA 3134, see Fig. 8e), but shows a negative anomaly in Eu, and an unusual marked light REE depletion.

These meteorites were weathered, in the soil of Poland (Zakłodzie), on the surface of the Sahara or in the ice of Antarctica. Trace element concentrations are very sensitive to these processes (e.g., Ba and Sr enrichment in hot desert finds, e.g., Stelzner et al., 1999; Barrat et al., 1999, 2003). This problem is much more critical for enstatite meteorites than for other chondrites or achondrites, since a large proportion of the trace elements of interest are contained in sulfides which are among the first phases being destroyed by weathering. Trace element patterns of altered enstatite meteorites may no longer have anything in common with those of falls or fresh finds (e.g., Barrat et al., 2014; Rubin, 2016; Udry et al., 2019). Therefore, these data will not be discussed further.

4.2.2. Trace element abundances in silicate fractions.

Residues prepared with anomalous enstatite meteorites have low Ti concentrations similar to those of chondritic residues, and ranging between 20 and 215 $\mu\text{g/g}$.

For most of the elements we have determined, their residues display abundances always in the range of those obtained with strongly metamorphosed ECs (Figs. 4–8 and 10). Apart from one sample of Zakłodzie, all of these residues have Y/Ho ratios < 45, similar to those of EH residues (Fig. 8e). All of them also have Th/U < 6, comparable to those of EH residues (Fig. 10c), suggesting an EH parentage for all these meteorites. On the other hand, they all have Eu and Sr concentrations similar to those obtained with EL5 to EL7 residues (Figs. 6e and 8b).

Silicate fractions in Zakłodzie display variable REE contents (Fig. 12a). The sample with the lowest abundances exhibits both pronounced light REE and heavy REE enrichments ($\text{La}_n/\text{Nd}_n = 5.71$, $\text{Gd}_n/\text{Lu}_n = 0.031$) with a huge positive Eu anomaly ($\text{Eu}_n/\text{Gd}_n = 264$), and a large positive Y anomaly ($\text{Y}/\text{Ho} = 68.4$). The same features are observed in the other sample but are less pronounced ($\text{La}_n/\text{Nd}_n = 2.38$, $\text{Gd}_n/\text{Lu}_n = 0.39$, $\text{Eu}_n/\text{Gd}_n = 9.20$, $\text{Y}/\text{Ho} = 30.4$). The residues obtained from NWA 4301 and 4799 are similar to the Zakłodzie residue displaying the highest REE abundances, and show like the latter, in addition to a large positive Eu anomaly, marked light REE enrichments. All these patterns are different from those obtained for EH and EL chondrites. It could be proposed that these differences result from silicate/sulfide exchanges related to a different thermal history than those of the most metamorphic ECs. However, it seems more probable that Zakłodzie, NWA 4301 and 4799 derive from the same EH-like body of previously unsampled composition.

The residue obtained with QUE 94204 differ from the previous ones. Its REE pattern is rather flat with very low REE abundances, between 0.01 and $0.02 \times \text{CI}$, except for Eu, and shows a large positive Eu anomaly ($\text{Eu}_n/\text{Gd}_n = 30.93$). Such a pattern is very similar to that of EH5 and EH-IM residues. This meteorite was initially classified as anomalous E7, then as an EH chondrite melted rock (Weisberg et al., 1997), as EH-impact melt breccia (Rubin et al., 1997; Rubin, 2015), as partially melted E-chondrite with an achondrite primitive texture (Izawa et al., 2011), or as impact-melted E chondrite whose EH or EL parentage could not be specified (van Niekerk et al., 2014). The REE pattern of the residue clearly indicates that this meteorite is an impact-melted EH chondrite.

4.3. Implications for the trace element abundances in primitive mantles of reduced bodies.

For a body made of ECs, our results show that before melting, many trace elements will have been strongly redistributed between phases by metamorphic processes, and in particular in favor of sulfides. Silicates

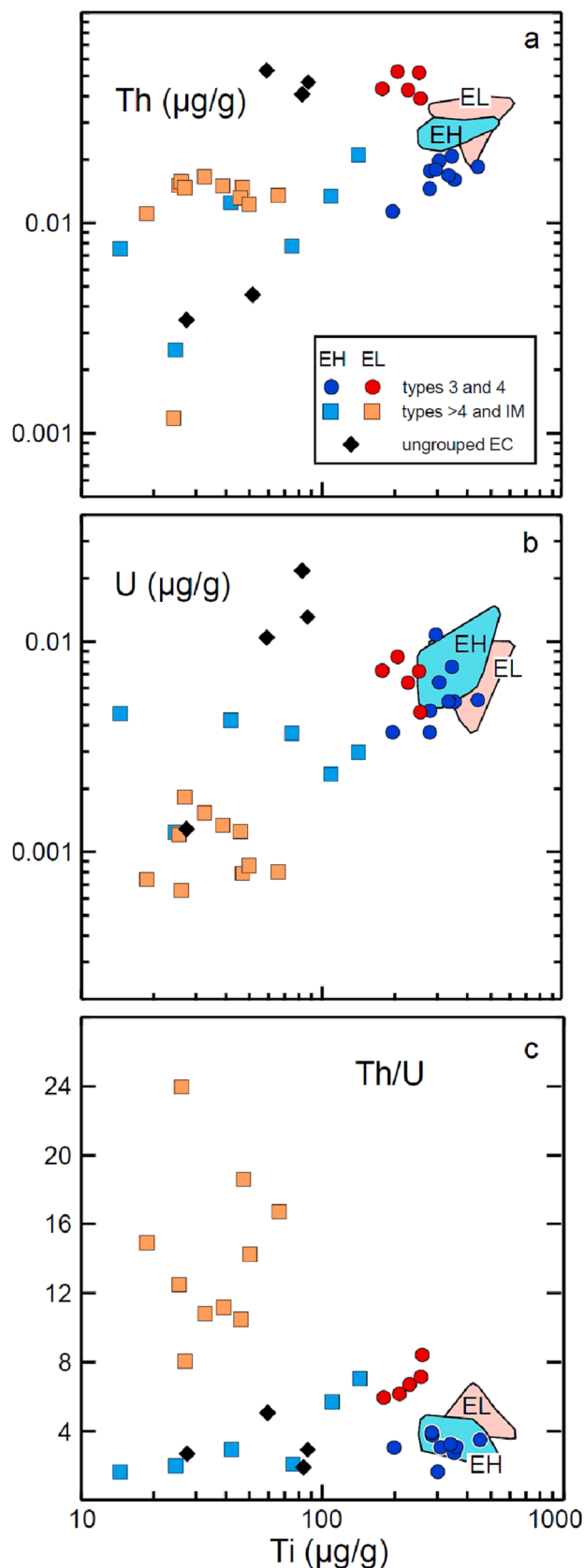


Fig. 10. Th, U, Th/U vs. Ti plots for E-chondrites (blue and red fields) and their residues after leaching with hot HCl (6 N, 120 °C).

will have been largely depleted in REE, for example. By analogy with other chondritic materials, the first phases to be melted will be troilite and metal at temperatures below 1000 °C. Isotopic data obtained on both iron meteorites and some achondrites show that percolation of sulfide-rich melts produced at these temperatures occurred (e.g., [Kruijer et al., 2014](#); [Barrat et al., 2015](#) and references therein). There is a general agreement that the segregation of these sulfide liquids can potentially fractionate at least some refractory lithophile elements. [Münker et al. \(2017\)](#) experimentally showed that under highly reducing conditions, Nb is more chalcophile than Ta, and that sulfide liquids mobilize Nb and reduce the Nb/Ta ratios of residual materials. The same is true for Ti, since this element is mainly contained in troilite in ECs ([Yoshizaki et al., 2021](#)). However, ECs do not only contain Fe-sulfides. Experiments made on Indarch (EH4) by [McCoy et al \(1999\)](#) showed that all sulfides, including oldhamite, participate in melting along the Fe-FeS cotectic. All sulfides and metal have melted at 1000 °C, and that three immiscible melts coexist at this temperature: FeNiSi metallic, Fe-sulfide, and Fe,Ca, Mg,Cr,Mn-sulfide melts. Silicate melting begins around 1100 °C ([McCoy et al., 1999](#)).

Fe-rich sulfide liquids may contain U and REEs (e.g., [Wohlens and Wood, 2017](#)), and Fe,Ca,Mg,Cr,Mn-sulfide liquids are probably a major carrier of refractory lithophile elements suggesting that both sulfide melts mobilize part of these elements during the early stages of melting of an EC. Therefore, it is likely that, after the segregation of sulfide melts, the resulting melting residue displays abundances of many refractory lithophile elements significantly lower than chondrites, and that these elements are no longer in chondritic proportions. Partition coefficients are lacking to directly model the trace element concentrations of this residue. Among other things, determination of trace element concentrations in Fe,Ca,Mg,Cr,Mn-sulfide liquids produced during EC melting experiments would be particularly useful in this respect.

In spite of the lack of these data and additional experimental works, one can however try to deduce some of the chemical features of the bulk silicate reservoir (=“primitive mantle”) formed in a reduced body of EH or EL composition, after segregation of the core. The closest analogues of the rocks of such a body before the extraction of the sulfide melts and metal, are obviously the most metamorphic ECs. After the extraction of this core component, and before the beginning of the partial melting of the silicates, we can suppose that the composition of the remaining solid is close to that of its bulk silicate fraction for some elements at least, like the REEs and the actinides for example. We have therefore estimated the composition of the bulk silicate reservoir by averaging the compositions of the residues obtained after leaching from the most metamorphic ECs. This approach may be considered simplistic, but it is very unlikely that the formation and subsequent segregation of sulfide melts would change all their element distributions in any significant way ([Ingrao et al., 2019](#)), e.g. by re-enrichment of the silicates in some trace elements, largely or totally erasing the anomalies produced during metamorphism. We have limited our estimates to REEs, HFSEs, and a few other elements such as U, Th, Ti, and Sr whose concentrations are not modified by small amounts of metal ([Kong et al., 1997](#)). These calculations show that the primitive mantles of the reduced bodies have concentrations for these elements, much lower than those of the chondrites, with patterns showing striking anomalies. (Table S-1, and Fig. 13). Whether the starting materials are EL or EH chondrites, they are very poor in light REE ($\approx 2\text{--}4 \cdot 10^{-2} \times \text{CI}$) and display huge positive anomalies in Sr, actinides, and HFSE. Differences in chalcophile affinities of these elements explain these anomalies ([Barrat et al., 2014](#)). The element patterns of the primitive mantles calculated for EH or EL chondrites are quite similar. The EL primitive mantle is distinguished from the EH one by much larger Eu and Y anomalies, and significant heavy REE enrichment. The Sr and Eu anomalies are related to the presence of feldspar in the mantle, which is potentially the case for planetesimals. For larger bodies, where feldspars are not the dominant Al-rich phase, these two anomalies would not necessarily be as prominent. We have not attempted to estimate concentrations in sulfide melts, but previous calculations have shown that

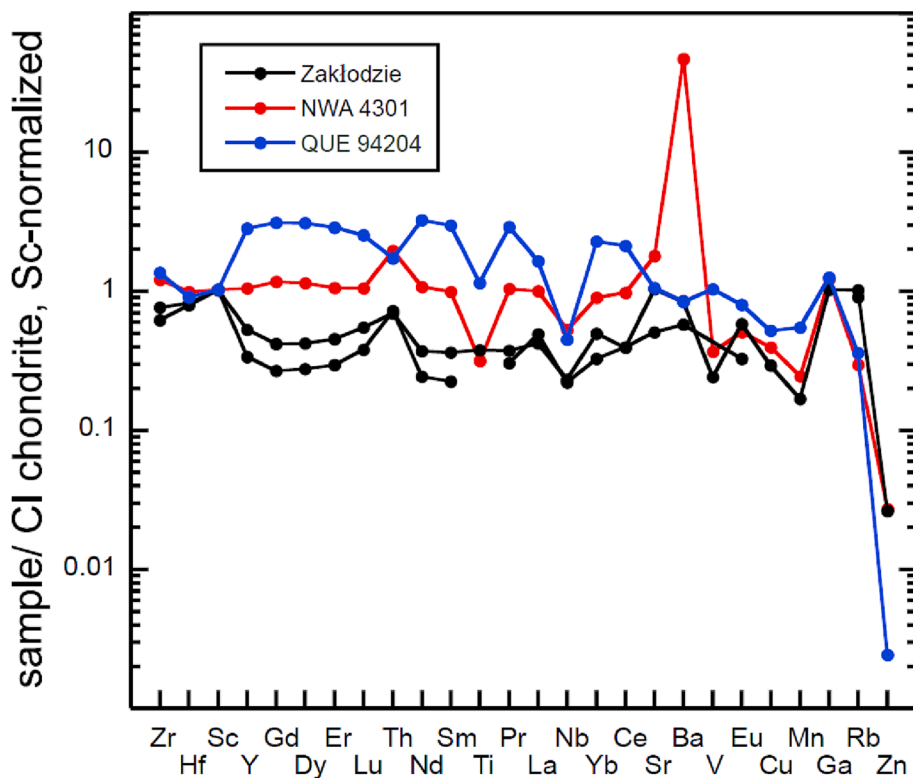


Fig. 11. CI-normalized abundances (Sc-normalized) for ungrouped enstatite achondrites.

sulfides contain over 60% of Th and U, and over 90% of REEs in the most metamorphosed ECs (Barrat et al., 2014). Therefore, we suggest that the cores that sulfide melts contributed to build, could be the dominant reservoirs for these elements in differentiated reduced bodies. Experimental work carried out a few years ago, moreover, demonstrated the capability of Fe-sulfide melts to incorporate under reducing conditions U, Th, and traces of REE. They suggested the presence of these elements in the outer core of the Earth (Wheeler et al., 2006), and in a possible Fe-sulfide layer located between the mantle and the core of Mercury (Wohlert and Wood, 2015, 2017; Boujibar et al., 2019). However, the partitioning of U, Th, and REE in Fe,Ca,Mg,Cr,Mn-sulfide liquids has not yet been studied. One can speculate that these liquids could be major carriers of REE and actinides, which would even allow to envisage much higher concentrations of these elements in the cores of differentiated reduced bodies than those considered with only Fe-sulfide melts.

4.4. Implications for the Earth

The nature and composition of the building blocks that formed our planet is a topic that has been widely debated over the last decades. A variety of models has been put forward, ranging from an Earth whose composition is derived from a carbonaceous chondrite (e.g., Allègre et al., 1995), to an Earth whose composition is close to an EC (Javoy, 1995; Javoy et al., 2010), or explained by assemblages of different types of chondrites dominated by ECs (e.g., Lodders, 2000; Warren, 2011; Dauphas, 2017). It is not our goal here to discuss all these models in details. The history of the accretion of our planet is particularly complex, with multiple impacts, including a cataclysmic one at the origin of the Moon. In spite of this certainly very eventful history, the similarity of the isotopic compositions of the Earth for many elements (e.g., O, Cr, Ti, Ca...) with those of the enstatite chondrites is more than spectacular, and cannot be a coincidence. It legitimizes the view that Earth accreted essentially from this type of chondrites, or from other primitive materials not yet discovered, and formed from the same reservoir.

If ECs were major or even essential ingredients during the accretion

of the Earth, an immediate question arises: can the fingerprint of sulfides present in ECs be found in present-day terrestrial reservoirs? The concentrations of refractory lithophile elements (RLE) in primitive mantle (or Bulk Silicate Earth (BSE)) have been calculated since the 1980s (e.g., Anderson, 1983; Hofmann, 1988; Sun and McDonough, 1989), and the values are now quite consensual, and based on various approaches including geochemistry of mantle rocks, mantle derived volcanics (e.g., Palme and O'Neill, 2014 among others) and experimental data (Faure et al., 2021). Indeed, all authors agree in deriving the concentrations of most RLEs by multiplying an average CI chondrite composition by a constant. In Fig. 13, we have plotted the value of the primitive mantle calculated by Palme and O'Neill (2014) as an example. Obviously, this approach is not going to show any significant anomaly. Here, only two anomalies are visible: for Y and for Nb. Palme and O'Neill (2014) chose a slightly different Y/Ho ratio for their chondritic reference than that measured by Barrat et al. (2012) which is explained by a difference in calibration between laboratories. The anomaly for Nb, on the other hand, is real, and its origin has been the subject of an extensive literature (e.g., Rudnick et al., 2000; Wade and Wood, 2001; Münker et al., 2017 among others), and will not be discussed here. This estimate of the concentrations of the other RLEs is perfectly justified, and there is no reason to imagine the existence of other significant anomalies for the elements selected in Fig. 13. As an illustration, consider Sm, Hf, and Ti that are similarly incompatible during the genesis of ocean floor basalts as long as the Fe-Ti oxides are not on the liquidus. We used Jenner and O'Neill's (2012) database of over 600 analyses of basalts of all types (N-MORB to E-MORB) from all oceans, and calculated Ti/Sm and Hf/Sm ratios for the least evolved of them ($MgO > 5.5\%$). The obtained ratios are chondritic: $(Ti/Sm)_n = 0.91$ ($\sigma = 0.06$) and $(Hf/Sm)_n = 0.99$ ($\sigma = 0.07$), $n = 597$. Therefore, the behavior of RLEs in the BSE can be estimated by assuming that these elements are perfectly lithophile.

Earth's primitive mantle is considerably richer in RLEs than those of the reduced differentiated bodies we have estimated (Fig. 13). If EC-like sulfides were involved during the differentiation of the Earth, inevitably much lower concentrations of RLEs but also marked decoupling between

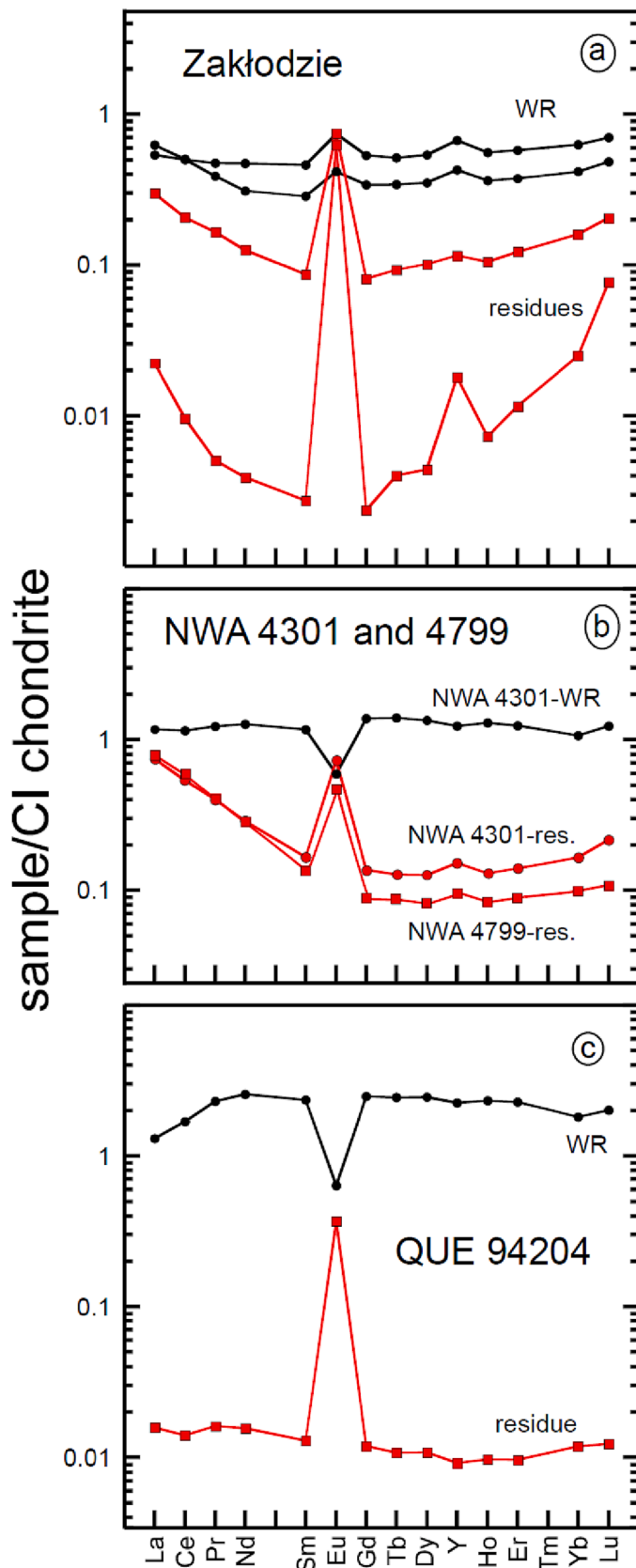


Fig. 12. CI-normalized REE patterns of the ungrouped enstatite Zakłodzie, NWA 4301, NWA 4799, QUE 94204, and their residues obtained after leaching with hydrochloric acid (6 N) at 120 °C.

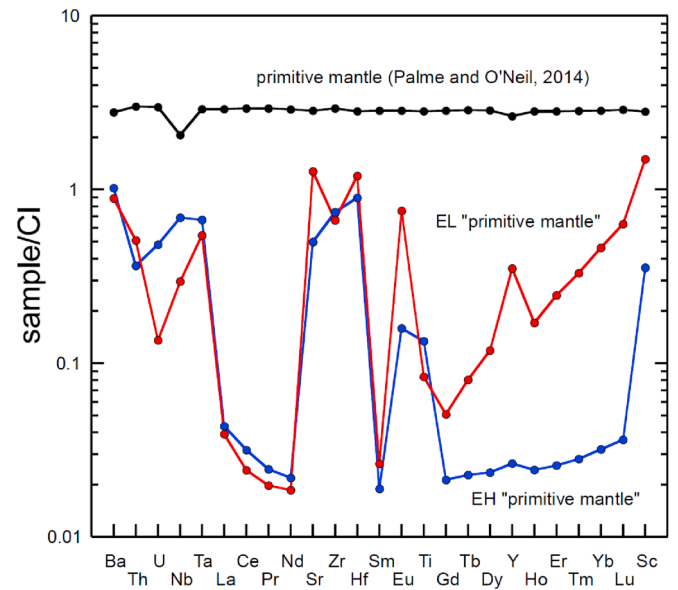


Fig. 13. CI-normalized RLE patterns of the terrestrial primitive mantle (Palme and O'Neill, 2014) and the proposed primitive mantles calculated for EH and EL-like differentiated bodies (this work). These primitive mantles are estimated from the average silicate fractions of the most metamorphic ECs. The different chalcophile behaviors of the elements explain the anomalies.

certain elements (e.g. between Zr or Hf with REEs) would have been expected, as in the case of reduced bodies. This is not the case at all. Either the EC-like sulfide signatures were totally erased during the Earth differentiation, or EC-like sulfides were never in sufficient proportion in the Earth building blocks to leave their chemical fingerprints. Both possibilities have to be tested now. Indeed, we cannot exclude that the loss of these signatures is a consequence of the Giant Impact (but this would imply a total homogenization of the whole mantle with the fraction of the core containing sulfides). It can also be proposed that most of the Earth's parent materials were formed from the same reservoir as ECs but under less reducing conditions. This hypothesis would explain the isotopic compositions of many elements in the BSE, but would also be a parameter to take into account to explain its oxidation state.

5. Conclusions

- The analyses we obtained (this work and Barrat et al., 2014) on the ECs as well as on their silicate fractions (the residues after leaching) provide a detailed view on the behavior of trace elements during the metamorphism of these rocks. Among the elements we measured, none shows a perfect lithophile behavior. During metamorphism, silicates are considerably depleted in some of these elements, such as REEs.
- The trace element depletion of silicates is different for EH and EL chondrites. Therefore, it is possible to determine the EH or EL affinity of an EC by analyzing the composition of its silicate fraction. This is well illustrated by the REE patterns, which also allow the less metamorphic types to be distinguished from the more metamorphic. We suggest that analysis of the silicate fraction of an EC can help to classify it, especially if it is highly altered.
- We also analyzed the silicate fractions of four anomalous ECs that show achondritic textures, and whose formation is still debated. The data obtained on one of them (QUE 94204) clearly indicate strong similarities with the most metamorphosed EHs we analyzed. The other three (Zakłodzie, NWA 4301 and 4799) have different silicate fractions than the regular ECs. We suggest that they derive from the same EH-like body of previously unsampled composition.

In the lack of sufficient experimental data, and of partition coefficients for the different sulfide melts produced during EC melting, we have attempted to constrain the chemical features of the primitive mantles of reduced bodies of EH or EL affinity using the compositions of the silicate fractions of the most metamorphic samples. These are poor in REEs, U and Th, implying that the cores of these objects contain most of these elements.

The primitive mantle of the Earth is very different from the previous ones because of its much higher abundances in RLEs, which are in chondritic proportions unlike the reduced bodies. This observation is very important, because it has often been proposed on the basis of the isotopic compositions of many stable elements, that the Earth was formed by accretion essentially of ECs. If this was indeed the case, one would expect that element ratios modified by melting and segregation of sulfides present in ECs (e.g. Zr/Sm or Hf/Sm) during differentiation would be at least partially preserved in the Earth's mantle. The chondritic proportions of RLEs in the primitive mantle indicate either that materials comparable to ECs had only a limited contribution during terrestrial accretion, or that the signatures they generated were completely erased (e.g., by the giant impact). A third possibility could of course be that the Earth could have been accreted from primitive materials with isotopic compositions similar to those of the ECs, but formed under less reducing conditions (i.e., without oldhamite and the other unusual sulfides that accompany it). The possibility that the true "building blocks" of the Earth are still absent from meteorite collections today is a hypothesis that cannot be ruled out (e.g., Drake and Righter, 2002).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Table S-1 contains all the trace element data obtained during the course of this study. Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2023.07.003>.

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