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Geochemistry of CI chondrites: Major and trace elements, and Cu and Zn Isotopes.

By

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Abstract

In order to check the heterogeneity of the CI chondrites and determine the average composition of this group of meteorites, we analyzed a series of 6 large chips (weighing between 0.6 and 1.2 g) of Orgueil prepared from 5 different stones. In addition, one sample from each of Ivuna and Alais were analyzed. Although the sizes of the chips used in this study were “large”, our results show evidence for minor chemical heterogeneity in Orgueil, particularly for alkali elements and U. After removal of one outlier sample, the spread of the results is considerably reduced. For most of the 46 elements analyzed in this study, the average composition calculated for Orgueil is in very good agreement with previous CI estimates. This average, obtained with a “large” mass of samples, is analytically homogeneous and is suitable for normalization purposes.

Finally, the Cu and Zn isotopic ratios are homogeneously distributed within the CI parent body with a spread of less than 100 ppm per atomic mass unit (amu).

“What is pride? A whizzing rocket that would emulate a star.”*

William Wordsworth (1770-1850)

(*: English translation of the French word “orgueil”)

1. Introduction

Carbonaceous chondrites are rare types of meteorites that comprise less than 5 % of the meteorite falls. These rocks display a wide range of petrographical, chemical and O-isotopic features, and are classified in 8 main groups (CI, CM, CO, CV, CK, CR, CH and CB) derived from very diverse asteroids. The CI chondrite group is small: it comprises only 5 falls (Alais (6 kg), Ivuna (0.7 kg), Orgueil (14 kg), Revelstoke (1 g), Tonk (10 g)) and possibly a few finds from Antarctica (Yamato (Y) 86029 (11.8 g), Y-86737 (2.81 g), Y-980115 (772 g), 980134 (12.2 g)). Unlike other chondrites, these rocks are essentially devoid of chondrules and other high temperature components. They have undergone the highest degree of aqueous alteration of all the meteorite classes (Scott and Krot, 2007). Despite the scarcity of such chondrites, they have been the center of a large number of studies. They are generally considered to be among the most primitive rock types in the Solar System from a chemical point of view. Indeed, their bulk compositions are similar to that of the solar photosphere excepted for volatiles such as H, C, N and O. Thus, because they mirror the composition of the Sun, their compositions are widely used to estimate the abundances of almost all the elements in the Solar System (e.g., Cameron, 1982; Anders and Ebihara, 1982; Anders and Grevesse, 1989; Lodders et al., 2009).

Over the years, a huge amount of chemical data has been obtained on CI chondrites (e.g., Lodders et al., 2009). Taken as whole, the results show noticeable spreads for many elements including the refractory ones (i.e., the REEs). Determining an average composition is not straightforward. First, these rocks are extremely rare, and samples from only two of them (i.e., Orgueil and Ivuna) can be usually obtained from institutional collections. Therefore, the great majority of the chemical and isotopic data available for CI chondrites was obtained from the analysis of Orgueil, the largest one, and to a lesser extent of Ivuna (Lodders, 2003). Second, chemical analyses have been performed generally on small samples by different analysts, using different analytical procedures, different calibration strategies, different standards, and finally, with different accuracy and analytical precision. Hence, part of the spread of the results is most probably explained by analytical biases or artifacts.

Moreover, some CI-chondrite analyses are based on samples < 100 mg, which Morlok et al. (2006) showed to be mineralogically and chemically heterogeneous. An additional part of the spread of the results could hence be explained by the possible lack of representativeness of these small samples. To overcome these problems, the database for CI chondrites was filtered with the aim of eliminating any anomalous data prior to calculating average compositions (e.g., see Lodders et al. (2009) for the details of the calculations). Although it is widely accepted that the average CI composition is at present reasonably well constrained for most of the elements, adjustments or improvements are possible for some elements.

In this study, we present new major, trace element, and Cu and Zn isotopic compositions obtained on six “large” chips (from 0.6 to 1.2 g each) prepared from five different stones of Orgueil. Our aim was to evaluate the chemical heterogeneity of Orgueil at this scale of sampling. In addition, we analyzed samples of Alais and Ivuna. These data will be used to calculate and discuss an improved average for the chemical composition of CI chondrites.

2. Samples and Analytical Procedures

2.1. Samples

Six chips of Orgueil prepared from five different stones, and one chip of Alais and Ivuna were provided by the Muséum National d’Histoire Naturelle, Paris (Table 1). CI are extremely friable and most samples are partly or totally disintegrated into chips within the clear polystyrene boxes or glass jars in which they are stored. Fusion-crust free chips of the appropriate sizes were selected under a binocular microscope with the help of plastic tweezers.

2.2. Bulk rock compositions

Chips were totally powdered using a boron carbide mortar and pestle. Typically 120 mg of the powder were dissolved in closed screw-top teflon vessels (Savillex) at about 130 °C for three days using 5 ml of concentrated HF, and 2 ml of concentrated HNO₃. The vessels were then opened. After evaporation to dryness of the acid mixture, approximately 2 ml of HNO₃ was added, and the vessels were capped and placed back on the hot plate and left overnight. The samples were then dried again, and taken up in about 20 g of 6 M HCl (“mother solutions”). No residual grains were observed in the mother solutions excepted in a couple of

Orgueil solutions which contained some “fine black dust” (insoluble carbon?) with apparently no impact on the results. Only reagents double-distilled in quartz or teflon sub-boilers were used. Abundances of both major and trace elements were analyzed using aliquots of the same mother solutions for all samples at the Institut Universitaire Européen de la Mer (IUEM), Plouzané.

The concentrations of Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, P, Co and Ni were determined by ICP-AES (inductively coupled plasma-atomic emission spectrometry) using a Horiba Jobin Yvon Ultima 2 spectrometer following the procedure of Cotten et al. (1995). Aliquots of mother solutions containing the equivalent of 50 mg of samples were used for the determination of the concentrations of these elements.

The concentrations of trace elements were determined by ICP-SFMS (inductively coupled plasma-sector field mass spectrometry) using a Thermo Element 2 spectrometer following the procedures described by Barrat et al. (2007, 2008). Two aliquots of each mother solutions containing the equivalent of 15 mg of sample were weighted in dry screw-top Teflon vessels. One was spiked with a solution of pure Tm, and the other not. After evaporation to dryness, the residues were taken up at 130°C with 5 drops of conc HNO₃, and subsequently diluted with 15 ml of ultrapure water containing traces of HF, to ensure the stability in solution of high field strength elements (especially Nb and Ta). The solutions were transferred to vials and analyzed at least twice. The concentrations were determined using the unspiked solutions (determination of the Tm/Yb and Tm/Er ratios in order to calculate the Tm abundances) and the spiked solutions (all the other elements), following calculations adapted from Barrat et al. (1996). Notice that the results obtained with the unspiked solutions were used to control the quality of the reported analyzes but were not averaged with the final results. Two procedural blanks were processed in parallel in each series of analyses. The contributions of the blanks were insignificant for all the elements.

The precision and the accuracy of the results were estimated using well characterized standards and sample duplicates. The results obtained for a series of standards (WS-E, JB2, BIR1) and for the Allende chondrite (USNM 3529, Jarosewich et al., 1987) are reported in Tables 2 to 4. For ICP-AES results, the accuracy is better than 7 % for Na and P, and probably much better than 3 % for the other elements.

The trace element concentrations obtained by ICP-SFMS are given relative to our revised working values for the USGS basalt BHVO-2 (Table 3), which are based on our own measurements and values from the literature (see Table 3). These working values are identical to those given by Barrat et al. (2007), excepted for a few elements. Our previous working value for Cs is not correct, because it generates results which are systematically about 15 % higher than the recommended values for all the well-characterized rock standards, and thus has been corrected accordingly. For Zr, Hf, Nb, and Ta, we have adopted the values obtained by Pfänder et al. (2007) which are among the most accurate available at present for this group of elements. Finally, we have redetermined the W abundance in BHVO2 and our new results were significantly lower than our previous estimation by a factor of about 23 %, and indistinguishable of the W abundance determined in BHVO2g (a glass standard prepared with the BHVO2 powder) by isotope dilution (König et al., 2008). In the event of future change to these BHVO-2 values, the data need only to be corrected by the ratio of the new and old values. Moreover, these working values can be used to evaluate possible interlaboratory bias. A correction can be made accordingly if necessary.

The trace element concentrations obtained for the basalts BIR-1, JB2 and WS-E are reported in Table 3. The concentration reproducibility is generally much better than 5 %. The results are in very good to excellent agreement with various literature values (see the GEOREM database (<http://georem.mpch-mainz.gwdg.de>) for a more extensive compilation of literature values). One of the most significant differences is for Y in the JB2 basalt, for which the concentration measured by Makishima and Nakamura (2006) is not correct (as suggested by the non-chondritic Y/Ho (=23) they have obtained for this standard). In order to validate our procedure for chondrites, we obtained 3 splits of the Allende powder standard USNM 3529 from the Smithsonian Institution (14/2, 14/22, and 15/3). Each split was analyzed twice and 125 to 162 mg were used per analysis. The results are given in Table 4. The relative standard deviations (RSD) for the six analyses are 9 % for W, 4 % for Pb and much less than 3 % for all the other elements. Again, the concentrations are in excellent agreement with literature data. This Allende powder is known to be heterogeneous for lead and the concentrations we obtained are in the range of the reported values (Jarosewich et al., 1987). The good reproducibility of our analyses is illustrated by the results obtained on the rare earth elements (REE). The Allende powder USNM 3529 displays an unusual REE pattern displaying a prominent Tm positive anomaly, and small negative Ce and Eu anomalies (Fig. 1). These unusual features are certainly inherited from some Ca, Al-rich inclusions which are

frequent in Allende and display the same anomalies (e.g., McPherson, 2004). Notice that the spread of our results is more restricted than the spread of the literature data (e.g., Jarosewich et al., 1987; Pourmand et al., 2011). The powder could be slightly heterogeneous for the refractory elements. The fact that we dissolved more powder than most other analysts could explain the good reproducibility we achieved for the REEs.

2.3. Cu and Zn isotopes

The Zn and Cu isotopic composition were analyzed following the procedure described in Maréchal et al. (1999) and Moynier et al. (2010a and b). Zn was first purified on AG1X8 anion-exchange resin in HBr/HNO₃. Cu was further purified on AGMP-1 anion-exchange resin in HCl. For both Zn and Cu chemical purifications, the yield was found to be better than 99 % and the blanks of <10 ng for Zn and <5 ng for Cu are negligible (<0.05%) with respect to the total amounts of Zn and Cu in the samples, which are >20 µg. Isotopic ratios of Zn and Cu in all samples were analyzed with the MC-ICP-MS Thermo-Finnigan Neptune Plus at Washington University in St Louis as described in Herzog et al. (2009). Isotope ratios are expressed as permil relative deviations from the standards NIST 976 for Cu ($\delta^{65/63}\text{Cu}$), and JMC-Lyon for Zn ($\delta^{66/64}\text{Zn}$, $\delta^{67/64}\text{Zn}$ and $\delta^{68/64}\text{Zn}$). Replicate analyses of the same samples carried out during different analytical sessions define an external reproducibility of ± 0.09 ‰ for $\delta^{66}\text{Zn}$, ± 0.26 ‰ for $\delta^{67}\text{Zn}$, ± 0.27 ‰ for $\delta^{68}\text{Zn}$ and ± 0.10 ‰ for $\delta^{65}\text{Cu}$ (see Herzog et al. (2009) for extensive discussion of our analytical precision).

3. Results

3.1. Major and trace elements

Orgueil

At first glance, the six samples of Orgueil display a limited range of abundances for most major and trace elements (Tables 5 and 6). This is well shown by the relative standard deviations (RSD), which are around or below 5 % for most elements. Only four elements exhibit RSD > 10 %: Na (22 %), K (20 %), Rb (13 %), U (13 %). These variations are much larger than the analytical reproducibility, and can be explained by the heterogeneity of the meteorite at the 0.6-1 g scale. Indeed, Na and K concentrations, respectively determined by ICP-AES and ICP-SFMS, are strongly correlated ($r = 0.990$), and it can be noticed that our six samples display very similar Na/K ratios close to 8.6. In the case of Rb and U, the high RSD

are due by sample ORG6, which displays Rb and U abundances significantly lower and higher respectively than the five other samples.

Elements displaying lower RSD, display ranges that could still reflect a real, although limited, heterogeneity of the meteorite. For example, Mn and P abundances range respectively from 0.178 to 0.210 wt% and from 0.094 to 0.108 wt% as determined by ICP-AES. These ranges were nicely confirmed by the ICP-SFMS analyses. Interestingly, the sample ORG6 is again significantly distinct from the other samples, and shows the lowest Zn abundance, and somewhat unusual REE abundances (slight LREE enrichment compared to the 5 other samples, Fig. 2). Similar light REE enrichments were recently observed in a few other Orgueil fragments much smaller in size by Pourmand et al. (2011). In agreement with these authors, such a feature is more likely explained by a local redistribution of the REEs from phosphates (merrillite or apatite) by aqueous fluids on the CI-parent body. We thus consider the sample ORG6 as an outlier, and we have excluded it in the Orgueil average that we discuss in this paper. We will use this average composition for normalization purposes. It is in agreement with literature results for most elements (e.g., Kallemeyn and Wasson, 1981; Anders and Ebihara, 1982; Beer et al., 1984; Anders and Grevesse, 1989; Lodders et al., 1989), and differences will be extensively described later.

Alais and Ivuna

Previous analyses obtained on these two chondrites have shown that their compositions are close to that of Orgueil (e.g., Kallemeyn and Wasson, 1981; Rocholl and Jochum, 1993; Lodders, 2003). The results obtained here on Ivuna are in agreement with literature data, and are in the range defined by our five “normal” Orgueil samples for most elements, with the exception of K (Tables 5 and 6). The fragment of Alais analyzed here was small (327 mg), and probably not representative of the meteorite. Indeed, its composition deviates slightly from the other CIs, as shown by its unusual convex REE pattern (Fig. 2).

3.2. Cu and Zn isotopes

The Cu and Zn isotopic compositions of Orgueil and Ivuna have been previously determined by Luck et al. (2003, 2005). Because the sample of Orgueil used by these authors was an aliquot of the powder made with the anomalous chip ORG6 (see above), we analyzed our 8 samples of CI chondrites in order to refine the Zn and Cu isotopic composition of CI and detect possible heterogeneities. The results are in agreement with the previous studies

(Table 7). The samples display narrow ranges of Cu and Zn isotopic compositions, including the Alais and ORG6, the two anomalous chips. These ranges are of the same order as the external reproducibility of the analyses for Zn isotopic compositions, and twice the external reproducibility for the $\delta^{65}\text{Cu}$ values. Thus, all these data can be used to define an average CI composition (Table 7).

4. Discussion

4.1. How heterogeneous is Orgueil really?

The heterogeneity of the CI-chondrites is well known for the major elements at the mm scale (e.g., Morlok et al., 2006). Furthermore, trace element analyses made on samples smaller than 200 mg give results that can deviate substantially from canonical CI-compositions (e.g., Evensen et al., 1978; Ebihara et al., 1982; Rocholl and Jochum, 1993; Mittlefehldt, 2002; Pourmand et al., 2011). Although the ranges of major and trace element abundances observed in this study are relatively narrow for most elements, the spread of concentrations displayed by some of them suggests that heterogeneity is still detectable using a series of $\sim 0.5 - 1\text{g}$ size samples prepared from different stones. Alternatively, it can be argued that the chips used in this study were all lower than the threshold mass for chemical heterogeneity of Orgueil. We are confident that the ranges obtained reflect a real heterogeneity among the different stones collected. If the limited spread shown by our data were explained solely by the size of the samples, we should observe variations for a number of elements whatever their geochemical behaviors (e.g., Mittlefehldt, 2002). In fact, the elements exhibiting the highest relative standard deviations (Na, K, Rb, Cs, U) are notoriously known for their mobility with aqueous fluids. Thus, these ranges are more likely the result of the complex aqueous alteration suffered by the Orgueil parent body. Although some chemical variations can be detected in Orgueil, these heterogeneities are not strong and should not be overemphasized. Indeed, as pointed out by Lodders et al. (2009), the secondary processes that this meteorite has suffered, must have been essentially isochemical on a cm-scale, otherwise its chemical composition, and certainly its Zn isotopic composition, which can be modified by aqueous alteration (Cloquet et al., 2011), would be much more heterogeneous.

4.2. Cu and Zn isotopic compositions of CI chondrites

The lack of isotopic anomalies (i.e. $\delta^{68/64}\text{Zn}/2 \sim \delta^{67/64}\text{Zn}/1.5 \sim \delta^{66/64}\text{Zn}$) confirms the conclusions from Luck et al. (2005) and Moynier et al. (2009) that despite different

nucleosynthetic origins Zn isotopes were well mixed in the solar nebula. By combining our data with those of Luck et al. (2003, 2005), we calculate an average of $\delta^{66/64}\text{Zn} = 0.46 \pm 0.08$ and $\delta^{65/63}\text{Cu} = 0.05 \pm 0.16$ for CI chondrites. These results show that Zn and Cu isotopes are homogenized within the CI chondrite group and represent the best estimate for the Cu and Zn isotopic composition of solar system so far. Other groups of chondrites are isotopically distinct from CI for both Cu and Zn (see Figure 3). These variations have been suggested to represent a mixing between two or more sources of Zn in the early solar system (Luck et al., 2003, 2005). The isotopic composition of terrestrial mantle rocks overlap within error with the average reported in this study (see Albarède (2004), Ben Othman et al. (2006), Cloquet et al. (2008) for average composition of terrestrial igneous rocks) and suggest that the bulk silicate Earth is CI-chondritic for Cu and Zn isotopes (see Figure 3).

Using a different technique (double spike-TIMS), Ghidan and Loss (2011) analyzed the Zn isotopic composition of Orgueil. Our results are similar to theirs within analytical uncertainty, but with a much smaller analytical uncertainty (± 0.30 on $\delta^{66/64}\text{Zn}$ in Ghidan and Loss vs. ± 0.10 in the present study).

4.3. Orgueil and the CI average composition

The vast majority of the chemical data available at present on CI chondrites were determined on Orgueil (e.g., Lodders, 2003; Lodders et al., 2009). In view of the available masses of the 5 CI falls in the institutional collections, the situation will undoubtedly not change in the near future, unless a new large fall of this type is recovered. The average composition of the CI-chondrites has been calculated using a weighted average of all the CI-chondrites (e.g., Lodders, 2003) or using only Orgueil (e.g., Palme and Beer, 1993). Because the compositional differences among CI-chondrites are probably limited (e.g., Kallemeyn and Wasson, 1981; Lodders, 2003), and because Orgueil is by far the most analyzed one, the two approaches converge to very similar results. Here, we will consider the average composition of Orgueil using the major and trace element abundances obtained on the five “regular” chips (ORG1 to ORG5). We will compare it with the CI-chondrite average calculated by Anders and Grevesse (1989), one of the most used CI-chondrite averages, and with the values calculated by Lodders et al. (2009), this time the most recently updated Orgueil composition (Table 8). The convergence of our average composition with both of these compositions is excellent, with differences less than $\pm 5\%$ for most of the elements (Fig. 4). Thus, only a limited number of elements need to be discussed here.

Beryllium: This element has been rarely determined in CI chondrites (Vilcsek and Lohmann, 1978; Makishima and Nakamura, 2006). Our new analyses for Orgueil are in agreement with the literature data. Note that our average value is very similar to the results obtained for Alais and Ivuna. Our data confirm the good agreement between the photospheric (Grevesse et al., 2010) and meteoritic Be abundances, suggesting that the destruction of this element has not occurred over the Sun's lifetime contrary to most solar Li which has been burned (Lodders, 2003; Lodders et al., 2009).

Sodium and potassium: The ranges displayed by the Na and K abundances in Orgueil are significant and reflect a real heterogeneity of the samples. The average reported in Table 5 has been calculated without an outlier (ORG6) that displays low K and Na abundances. It can be emphasized that the results are very close to those calculated by Lodders et al. (2009) based on a large compilation of literature data (n=20 for Na, n=17 for K). Although we believe these average compositions to be correct, it is possible that the results were slightly biased by the filtering of the data.

Aluminum and calcium: our Al and Ca concentrations are about 10 % lower than those obtained by Anders and Grevesse (1989) and Lodders et al. (2009). We suspect a slight underestimation of the Al and Ca abundances during the course of our study. However, these differences are not highly significant.

Phosphorus: The average abundance obtained for P is 1010 $\mu\text{g/g}$. It is in agreement with the XRF data of Wolf and Palme (2001), and the ICP-MS data of Makishima and Nakamura (2006). The P abundance in CI chondrites given by Anders and Grevesse (1989) is overestimated (1220 $\mu\text{g/g}$) and should not be used in future studies.

Zirconium and hafnium: The range of Hf abundances obtained here for Orgueil is tight (0.104-0.109 $\mu\text{g/g}$), and consequently the average concentration is well determined. The concentrations measured for Ivuna and Alais are identical to the Orgueil average value. Unsurprisingly, our new Hf average is in good agreement with the Anders and Grevesse (1989) and Lodders et al. (2009) values. Furthermore, our Zr concentration (3.52 $\mu\text{g/g}$) confirms the value calculated by Lodders et al. (2009) (3.62 $\mu\text{g/g}$), and suggests that of Anders and Grevesse (1989), 3.94 $\mu\text{g/g}$, is overestimated. The Zr/Hf ratio we have obtained

(32.8) is only 2 % lower than the CI-chondrite average (33.4) obtained by Lu et al. (2007), and 4 % lower than the chondritic value (34.3) proposed by Münker et al. (2003), both obtained by isotope dilution. These differences are small and should not be overemphasized.

Niobium and tantalum: Nb and particularly Ta are notoriously difficult to determine accurately in carbonaceous chondrites. Our Orgueil average displays a Nb abundance markedly higher than the estimation made by Anders and Grevesse (1989), and similar to the average proposed by Lodders et al. (2009) (Fig. 2 and Table 5), which are based on a limited number of analyses (e.g., Rocholl and Jochum, 1993; Jochum et al., 2000; Münker et al., 2003; Lu et al., 2007), or have been inferred from the Zr/Nb ratios of carbonaceous chondrites. The Nb/Ta ratios we obtained for Orgueil (Nb/Ta=19.4) are similar to the chondritic value (Nb/Ta=19.9) obtained by Münker et al. (2003) using an accurate isotope dilution procedure. (Notice that the Nb and Ta abundances that we have previously reported (Bollinger et al., 2011) were systematically overestimated due to a loss of these elements in one of our standard solutions).

Rare earth elements: These elements received considerable attention during the last forty years, and the REE abundances in chondrites have been determined not only for cosmochemical purposes, but also for the normalization and presentation of geochemical data. Many sets of chondritic values have been proposed, some of which became very popular in the geochemical literature. It is beyond the scope of our work to review and compare each reference chondrite and discuss how the concentrations have been measured and/or calculated. Here, we selected some of them (Evensen et al., 1978; Beer et al., 1984; Anders and Grevesse, 1989; Sun and McDonough, 1989; McDonough and Sun, 1995; Lodders et al., 2009; Pourmand et al., 2011), and compare them with our Orgueil average in Figure 5. The patterns show that the new Orgueil average is in good agreement with all these reference values. Interestingly, our average is analytically undistinguishable from the results obtained by isotope dilution on a “large” sample (> 3 g) of Orgueil (Beer et al., 1984). The other chondrites (except for the values given by Sun and McDonough (1989), which are largely derived from the previous analysis) appear somewhat slightly more light REE enriched, but this is at most marginally significant. More importantly, some scatter is apparent for monoisotopic REEs, which is explained by the fact that their concentrations are in most cases, an assemblage of results obtained by different methods, often on different samples. In any case, the use of each of these reference chondrites produces a REE pattern with a very similar

shape, and the differences are subtle especially when a logarithmic scale is used. Nevertheless, the use of the Anders and Grevesse (1989) values should be made with caution when Tm is determined and when Yb anomalies are discussed. We suggest that our Orgueil values are among the best currently obtained, especially when REE are compared with other lithophile refractory elements, in order to avoid the use of reference concentrations obtained on different samples.

Yttrium: The Y/Ho ratio of Orgueil is well constrained and close to 27.6 (Table 6). This value is undistinguishable from that obtained in the course of our study on CM-chondrites (Y/Ho=27.5, RSD=0.9%, n=6), and on the terrestrial standards BIR-1 and BHVO-2 (respectively 27.8 and 27.6). These analyses confirm that terrestrial basalts and carbonaceous chondrites exhibit similar Y/Ho ratios (Pack et al., 2007). Although the difference is small, our CI-value is slightly higher than the result reported by Pack et al. (2007), who obtained a ratio close to 25.9 for the carbonaceous chondrites. This slight discrepancy is probably explained by a calibration effect, as shown by the results obtained by these authors on the BCR2-G standard (Y/Ho=26.3). Our results on BCR2 (the powder used to make BCR2-G) is consistently slightly different (Y/Ho=29.03, RSD=1.2 %, n=30) and identical to the well known BCR1 standard (Y/Ho=29.18 , RSD=1.1 %, n=6) from the same quarry.

Tungsten: W has not often been measured on Orgueil. Recent analyses reported in the literature display a significant range (e.g., 0.078 to 0.117 $\mu\text{g/g}$, Friedrich et al., 2002; Kleine et al., 2004; Babechuk et al., 2007). The W abundances obtained here on CI-chondrites (including Alais and Ivuna) are between 0.10 and 0.12 $\mu\text{g/g}$ (Table 3). Thus, the W abundance in Orgueil is well determined here (0.11 $\mu\text{g/g}$), a value about 15 % higher than those reported in the compilations made by Anders and Grevesse (1989) and Lodders et al. (2009). Our values (W abundance, and W/Hf ratio) are in perfect agreement with the results obtained by Kleine et al. (2004) by isotope dilution using a 400 mg chip.

Thorium and uranium: our average concentrations for these two elements are slightly lower than the values reported by Anders and Grevesse (1989) and Lodders et al. (2009). Rocholl and Jochum (1993) have shown that U and Th are heterogeneously distributed in CIs at a low scale, and that some small samples display a noticeable U enrichment. This enrichment could be explained by a local redistribution of U from phosphates by aqueous fluids. Although the databases used for the estimations of the abundances of U and Th were

filtered to avoid the anomalous samples, the results could be slightly hampered by this redistribution. Nevertheless, the differences between our Orgueil average composition and the literature ones are very limited for both elements and should not be considered very significant.

4. Conclusions

- (1) It is well known from previous studies that Orgueil and other CI-chondrites are significantly heterogeneous at a scale of 100 mg (Morlok et al., 2006). In this study, we show that significant heterogeneity can occasionally be detected using chips ranging in mass from 0.6 to 1.2 g, particularly for elements mobile during aqueous alteration (alkali elements and U). This result is important because it is generally believed that Orgueil is rather homogeneous at this level of sampling. Thus, a single chip, even if its mass is in the order of 1 g, is not necessarily representative of this famous fall, nor of the CI-chondrite group.
- (2) In our sampling, a 1 g chip was chemically distinct for many elements, including some refractory ones such the REEs. Despite this anomalous sample, no significant heterogeneity has been detected for Cu and Zn isotopes. Our results obtained on Orgueil and on two other falls give a definitive characterization of the CI-chondritic reservoir for these isotopes.
- (3) The average chemical composition calculated with the “regular” Orgueil samples is very close to the previous estimates, which were calculated from a compilation of literature results. Although the agreement is excellent for most elements, our results show that only measured concentrations for W depart significantly from compiled values. We strongly recommend the use of our average composition for normalization purposes, because 1) it has been calculated using results obtained on “large” samples, and 2) the concentrations have been determined using the same sample digestions.

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References

- Albarède F. (2004) The stable isotope geochemistry of copper and zinc. In: Johnson, C. M., Beard, B. L., and Albarède, F. (Eds.), *Geochemistry Of Non-Traditional Stable Isotopes*. Mineralogical Society of America. **55**, 409-425.
- Anders E. and Ebihara M. (1982) Solar-system abundances of the elements. *Geochim. Cosmochim. Acta* **46**, 2363-2380.
- Anders E. and Grevesse N. (1989) Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197-214.
- Babechuk M.G., Kamber B.S., Greig A., Canil D., Kodolanyi J. (2010) The behaviour of tungsten during mantle melting revisited with implications for planetary differentiation time scales. *Geochim. Cosmochim. Acta* **74**, 1448-1470.
- Barrat J. A., Keller F., Amosse J., Taylor R. N., Nesbitt R. W. and Hirata T. (1996) Determination of rare earth elements in sixteen silicate reference samples by ICP-MS using a Tm addition and an ion exchange chromatography procedure. *Geostand. Newsl.* **20**, 133-139.
- Barrat J.A., Yamaguchi A., Greenwood R.C., Bohn M., Cotten J., Benoit M., Franchi I.A. (2007) The Stannern trend eucrites: Contamination of Main-Group eucritic magmas by crustal partial melts. *Geochim. Cosmochim. Acta* **71**, 4108-4124.
- Barrat J.A., Yamaguchi A., Benoit M., Cotten J. and Bohn M. (2008) Geochemistry of diogenites : Still more diversity in their parental melts. *Meteoritics Planet. Sci.* **43**, 1759-1775.
- Beer H., Walter G., Macklin R.L., Patchett P.J. (1984) Neutron capture cross sections and solar abundances of $^{160,161}\text{Dy}$, $^{170,171}\text{Yb}$, $^{175,176}\text{Lu}$, and $^{176,177}\text{Hf}$ for the s-process analysis of the radionuclide ^{176}Lu . *Phys. Rev.* **30**, 464-478.
- Ben Othman, D., Luck, J. M., Bodinier, J. L., Arndt, N. T., and Albarède, F. (2006) Cu-Zn isotopic variations in the Earth's mantle. *Geochim. Cosmochim. Acta* **70**, A46 (abstract).
- Bollinger C., Zanda B., Moynier F., Barrat J.A., Liorzou C. (2011) How heterogeneous is Orgueil really? *Meteoritics Planet. Sci.* **46**, Special issue 1, A24 (abstract).
- Cameron A. G. W. (1982) Elemental and nucleonic abundances in the solar system. In *Essays in Nuclear Astrophysics* (eds. C. A. Barnes, D. D. Clamon, D. N. Schramm), pp. 23-43. Cambridge Univ. Press.
- Cloquet, C., Carignan, J., Lehmann, M. F., and Vanhaecke, F. (2008) Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: a review. *Anal. Bio. Chem.* **390**, 451-463.
- Cloquet C., Carignan J., France-Lanord C. (2011) Zn mobility during oceanic crust alteration inferred by its isotopic composition. *Goldschmidt Conference Abstracts, Mineralogical Magazine*, **75** (3), P683.
- Cotten J., Ledez A., Bau M., Caroff M., Maury R. C., Dulski P., Fourcade S., Bohn M. and Brousse R. (1995) Origin of anomalous Rare-Earth Element and Yttrium enrichments in subaerially exposed basalts—evidence from French-Polynesia. *Chem. Geol.* **119**, 115-138.
- Dauphas N., Pourmand A. (2011) Hf-W-Th evidence for rapid growth of Mars and its status as a planetary embryo. *Nature* **473**, 489-492.
- Ebihara M., Wolf R., Anders E. (1982) Are C1 chondrites chemically fractionated? A trace element study. *Geochim. Cosmochim. Acta* **46**, 1849-1861.
- Evensen, N.M., Hamilton, P.J., O'Nions, R.K. (1978) Rare-earth abundances in chondritic meteorites. *Geochim. Cosmochim. Acta* **42**, 1199-1212.
- Friedrich J.M., Wang M.S., Lipschutz M.E. (2002) Comparison of the trace element composition of Tagish Lake with other primitive carbonaceous chondrites. *Meteoritics Planet. Science* **37**, 677-686.
- Ghidan O.Y., Loss R.D. (2011) Isotope fractionation and concentration measurements of Zn in meteorites determined by the double spike, IDMS-TIMS techniques. *Meteoritics Planet. Science* **46**, 830-842.
- Govindaraju K. (1994) 1994 compilation of working values and sample description for 383 geostandards, *Geostandards newsletter*, **18**, Special issue, 1-158.
- Grevesse N., Asplund M., Sauval A.J., Scott P. (2010) The composition of the Sun. *Astrophys. Space Sci.* **328**, 179-183.

- Herzog G.F., Moynier F., Albarède F., Berezhnoy A.A. (2009). Isotopic and elemental abundances of copper and zinc in lunar samples, Zagami, Pele's hairs, and a terrestrial basalt. *Geochim. Cosmochim. Acta* **73**, 5884–5904.
- Jarosewich, E., Clarke, R.S.J., Barrows, J.N.E. (1987) The Allende Meteorite Reference Sample. *Smithsonian Contributions to the Earth Sciences* **27**(1).
- Jochum K.P., Stolz J., McOrist G. (2000) Niobium and tantalum in carbonaceous chondrites : constraints on the Solar System and primitive mantle niobium/tantalum, zirconium/niobium, and niobium/uranium ratios. *Meteoritics Planet. Sci.* **35**, 229-235.
- Kallemeyn G.W., Wasson J.T. (1981) The compositional classification of chondrites –1. The carbonaceous chondrite groups. *Geochim. Cosmochim. Acta* **45**, 1217-1230.
- Kleine T., Mezger K., Münker C., Palme H., Bischoff A. (2004) ^{182}Hf - ^{182}W isotope systematics of chondrites, eucrites, and martian meteorites: Chronology of core formation and early mantle differentiation in Vesta and Mars. *Geochim. Cosmochim. Acta* **68**, 2935-2946.
- König S., Münker C, Schuth S., Garbe-Schönberg D. (2008) Mobility of tungsten in subduction zones. *Earth Planet. Sci. Lett.* **274**, 82-92.
- Lu Y., Makishima A., Nakamura E. (2007) Coprecipitation of Ti, Mo, Sn and Sb with fluorides and application to determination of B, Ti, Zr, Nb, Mo, Sn, Sb, Hf and Ta by ICP-MS. *Chemical Geol.* **236**, 13-26.
- Lodders K. (2003) Solar system abundances and condensation temperatures of the elements. *Astrophys. J.*, **591**, 1220–1247.
- Lodders K., Palme H., Gail, H.P. (2009) Abundances of the elements in the solar system. In Landolt- Bornstein, New Series, Vol. VI/4B, Chap. 4.4, J.E. Trumper (ed.), Berlin, Heidelberg, New York: Springer-Verlag, p. 560-630.
- Luck J.M., Ben Othman D., Barrat J.A., and Albarède F (2003). Coupled ^{63}Cu and ^{16}O excesses in chondrites. *Geochim. Cosmochim. Acta* **67**, 143-151.
- Luck, J.M., Othman, D.B., Albarède, F. (2005) Zn and Cu isotopic variations in chondrites and iron meteorites: early solar nebula reservoirs and parent-body processes. *Geochim. Cosmochim. Acta* **69**, 5351–5363.
- MacPherson, G. J. (2004) Calcium-aluminum-rich inclusions in chondritic meteorites. In *Treatise on Geochemistry*, **No. 1** (ed. Davis, A. M.). Elsevier, 201-246.
- Makishima, A., Nakamura, E. (1999) Determination of molybdenum, antimony and tungsten at sub $\mu\text{g}\cdot\text{g}^{-1}$ levels in geological materials by ID-FI-ICP-MS. *Geostandards Newsletter* **23**, 137-148.
- Makishima A, Kobayashi K., Nakamura E. (2002) Determination of chromium, nickel, copper and zinc in milligram samples of geological materials using isotope dilution high resolution inductively coupled plasma-mass spectrometry. *Geostandards Newsletter* **26**, 41-51.
- Makishima, A., Nakamura, E. (2006) Determination of major, minor and trace elements in silicate samples by ICP-QMS and ICP-SF-MS applying isotope dilution-internal standardisation (ID-IS) and multi-stage internal standardisation. *Geostandards and Geoanalytical Research* **30**, 245-271.
- Maréchal, C. N., Telouk P., and Albarède F. (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source spectrometry. *Chem. Geol.* **156**, 251–273.
- McDonough W.F. and Sun S.S. (1995) The composition of the Earth. *Chem. Geol.* **120**, 223-253.
- Mittlefehldt, D.W. (2002) Geochemistry of the ungrouped carbonaceous chondrite Tagish Lake, the anomalous CM chondrite Bells, and comparison with CI and CM chondrites. *Meteoritics Planetary Science* **37**,703-712.
- Moynier, F, Beck P., Yin Q.Z., Ferroir T., Barrat J.A., Paniello R., Telouk P., Gillet P. (2010a) Volatilization induced by impacts recorded in Zn isotope composition of ureilites. *Chem. Geol.* **276**, 374-379.
- Moynier F., Koeberl C., Beck P., Jourdan F., Telouk P. (2010b) Isotopic fractionation of Cu in tektites. *Geochim. Cosmochim. Acta* **74**, 799–807.
- Moynier F., Dauphas N., and Podosek F. A. (2009) Search for ^{70}Zn anomalies in meteorites. *Astrophys. J.* **700**, L92-L95.
- Morlok A., Bischoff A., Stephan T., Floss C., Zinner E., Jessberger E.K. (2006) Brecciation and chemical heterogeneities of CI chondrites *Geochim. Cosmochim. Acta* **70**, 5371–5394.

- Münker C., Pfänder J.A., Weyer S., Büchl A., Kleine T., Mezger K., 2003. Evolution of planetary cores and the Earth-Moon system from Nb/Ta systematics. *Science* **301**, 84-87.
- Nakamura N. (1974) Determination of REE, Ba, Fe, Mg, Na and K in carbonaceous and ordinary chondrites. *Geochim. Cosmochim. Acta* **38**, 757-775.
- Pack A., Russell S.S., Shelley J.M.G., van Zuilen M. (2007) Geo- and cosmochemistry of the twin elements yttrium and holmium. *Geochim. Cosmochim. Acta* **71**, 4592-4608.
- Palme H. and Beer H. (1993) Abundances of the elements in the solar system. In *Astronomy and Astrophysics, Landolt Börnstein Group VI* (ed. H. H. Voigt), pp 196-221. Springer-Verlag, Berlin, Germany.
- Pfänder J.A., Münker C., Stracke A., Mezger K. (2007) Nb/Ta and Zr/Hf in ocean island basalts - Implications for crust-mantle differentiation and the fate of Niobium. *Earth Planet. Sci. Lett.* **254**, 158-172.
- Pourmand A., Dauphas N., Ireland T.J. (2011) A novel extraction chromatography and MC-ICPMS technique for rapid analysis of REE, Sc and Y: Revising CI-chondrite abundances and Post-Archean Australian Shale (PAAS). *Chemical Geology*, doi: 10.1016/j.chemgeo.2011.08.011.
- Raczek I., Stoll B., Hofmann A.W. and Jochum K.P. (2001) High-precision trace element data for the USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, DTS-1, DTS-2, GSP-1 and GSP-2 by ID-TIMS and MIC SSMS. *Geostandards Newsletter* **25**, 77-86.
- Rocholl A., Jochum K.P. (1993) Th, U and other trace elements in carbonaceous chondrites: Implications for the terrestrial and solar-system Th/U ratios. *Earth Planet. Sci. Lett.* **117**, 265-278.
- Shinotsuka K., Hidaka H., Ebihara M. (1995) Detailed abundances of rare earth elements, thorium and uranium in chondritic meteorites : an ICP-MS study. *Meteoritics* **30**, 694-699.
- Scott E.R.D., Krot A.N. (2007) Chondrites and their components. *Treatise on Geochemistry, chapter 1.07*, pp1-72.
- Sun S.S., and McDonough W.F. (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In *Magmatism in the Ocean Basins* (eds. A. D. Saunders and M. J. Norry, vol. 42.). The Geological Society, pp. 313-345.
- Tomascak P.P., Langmuir C.H., Le Roux P.J., Shirey S.B. (2008) Lithium isotopes in global mid-ocean ridge basalts. *Geochimica Cosmochimica Acta* **72**, 1626-1637.
- Vilcsek E., Lohmann G. (1978) Bestimmung von Beryllium in extraterrestrischer Materie mit Hilfe der Flammenlosen Atomabsorbtiionspektroskopie. *Z. Anal. Chem.* **293**, 410-411.
- Wolf D., Palme H. (2001) The solar system abundances of phosphorus and titanium and the nebular volatility of phosphorus. *Meteoritics Planetary Science* **36**, 559-571.

Table 1. Details of samples studied

	MNHN n°	mass (g)
Orgueil		
ORG1	219239	1.00
ORG2	222	0.62
ORG3	222	0.61
ORG4	234	0.84
ORG5	250	0.86
ORG6	237	1.02
Ivuna	3578	0.71
Alais	24	0.33

Table 2. Major element, Cr, Ni and Co abundances in the BIR1 and JB2 basalts and in the Allende standard determined by ICP-AES and compared with literature values (a: GEOREM preferred values, b: Gavindaraju (1994), and c: Jarosewich et al. (1987)).

		BIR 1		RSD% reference ^a	JB2		RSD% reference ^b	USN3529		RSD% reference ^c
n		5			4			3		
TiO ₂	wt%	0.91	1	0.97	1.10	1	1.19	0.13	6	0.15
Al ₂ O ₃	wt%	15.25	1	15.4	14.36	0.4	14.67	3.52	1	3.28
Fe ₂ O ₃	wt%	11.83	1	11.3	14.84	0.3	14.34	33.40	0.3	33.7
MnO	wt%	0.17	1	0.176	0.22	1	0.22	0.18	8	0.19
MgO	wt%	9.76	0.5	9.70	4.77	1	4.66	24.09	0	24.59
CaO	wt%	13.16	1	13.4	9.68	1	9.89	2.62	0	2.58
Na ₂ O	wt%	1.85	6	1.81	2.07	6	2.03	0.48	2	0.45
K ₂ O	wt%	< 0.05		0.03	0.38	2	0.42	< 0.05		0.04
P ₂ O ₅	wt%	0.07	4	0.027	0.13	7	0.12	0.26	2	0.24
Cr	µg/g	409	2	391	16	11	27	3623	0.2	3630
Co	µg/g	54	4	52	38	5	33	659	1	600
Ni	µg/g	190	1	166	12	18	17	14758	1	14200

Table 3. Trace element abundances (in $\mu\text{g/g}$) selected for the international standard BHVO2 (B : our lab, P : Pfänder et al. (2007), R : Raczek et al. (2001), T : Tomascak et al. (2008) ; U : US geological survey, certificate of analysis ;), and results obtained by ICP-SFMS for BIR1, JB2 and WD-E compared with reference values (G : GEOREM preferred values; L: Lu et al. (2007); M: Makishima and Nakamura (1999, 2006) and Makishima et al. (2002)). Because of the use of a Tm-spike, we did not determine the abundances of this element in these standards.

	BHVO2	BIR1	RSD% reference		JB2	RSD% reference		WS-E	RSD% reference	
	W.V.		G			M, L			G	
n		10			14			5		
Li	4.7^T	3.26	4	3.2	8.67	2	7.74	14.31	1	13.7
Be	1.1^B	0.08	8	0.12	0.245	4	0.228	1.15	3	1.14
P	1178^U	104	5	118	415	4	389	1353	1	1309
K	4317^U	198	1	230	3492	2	3490	8329	1	8302
Sc	32.3^U	44.2	3	43	56.6	2	53.3	28.87	2	28
Ti	16364^U	5802	2	5814	7137	3	6950 ^L	15353	1	14386
V	317^U	329	4	319	600	3	613	352	1	329
Cr	280^U	385	1	391	23.60	3	25	91.87	2	99
Mn	1290^U	1290	5	1363	1641	2	1620	1328	1	1317
Co	45^U	51.5	4	52	36.15	2	33	46.23	2	44
Ni	121^B	171	2	166	12.55	3	15.4	54.43	2	54
Cu	123^B	111	3	119	203	4	219	61.40	3	67
Zn	101^B	63	6	72	99.0	5	107	118	2	113
Ga	20.6^B	14.8	3	15.3	15.90	2	17.6	21.89	1	21.7
Rb	9.08^R	0.19	5	0.20	6.22	2	6.12	25.99	2	26
Sr	396^R	110	4	109	178	2	177	418	1	407
Y	27.6^B	16.29	2	15.6	25.07	1	(20)	33.70	1	31
Zr	164.9^P	13.9	2	14	44.78	1	42.9 ^L	202	1	204
Nb	16.82^P	0.555	2	0.55	0.463	5	0.459 ^L	16.98	1	18.2
Cs	0.096^B	0.004	6	0.007	0.778	2	0.768	0.468	2	0.47
Ba	131^R	6.26	2	7.14	217	2	215	346	1	334
La	15.2^R	0.591	2	0.615	2.21	1	2.14	27.40	1	26.8
Ce	37.5^R	1.84	2	1.92	6.47	2	6.39	61.26	1	61
Pr	5.31^B	0.363	2	0.37	1.12	2	1.1	8.01	1	7.7
Nd	24.5^R	2.35	3	2.38	6.26	2	6.32	34.03	1	32.8
Sm	6.07^R	1.09	2	1.12	2.24	2	2.19	8.90	1	8.8
Eu	2.07^R	0.526	2	0.53	0.828	2	0.818	2.29	1	2.2
Gd	6.24^R	1.84	2	1.87	3.14	3	3.20	7.39	1	7.1
Tb	0.94^B	0.365	3	0.36	0.581	2	0.579	1.11	1	1.08
Dy	5.31^R	2.58	2	2.51	3.95	2	4.01	6.31	1	6.06
Ho	1.00^B	0.585	2	0.56	0.882	2	0.868	1.22	2	1.18
Er	2.54^R	1.72	3	1.66	2.59	2	2.58	3.20	2	3.07
Tm	0.34^B	*		0.25	*		0.376	*		0.43
Yb	2.00^R	1.66	3	1.65	2.51	2	2.49	2.61	1	2.49
Lu	0.27^B	0.244	2	0.25	0.377	2	0.386	0.363	2	0.35
Hf	4.474^P	0.591	2	0.582	1.51	2	1.45 ^L	5.51	2	5.20
Ta	1.10^P	0.0372	3	0.0357	0.0396	8	0.0307 ^L	1.08	2	1.14
W	0.22^B	0.02	8	0.07	0.286	11	0.299	0.473	6	0.50
Pb	1.51^B	2.78	4	3.1	5.02	6	4.88	14.54	5	12.8
Th	1.21^B	0.0300	2	0.032	0.253	2	0.261	3.14	2	3.00
U	0.41^B	0.0098	3	0.010	0.148	2	0.156	0.64	2	0.62

Table 4. Trace element abundances (in $\mu\text{g/g}$) obtained by ICP-SFMS for the Allende powder USNM 3529 and compared with literature values (1 : Jarosevich et al. (1987), 2 : Makishima and Nakamura (2006), 3 : Lu et al. (2007), 4 : Dauphas et al. (2011) for U, Th , Hf and Pourmand et al. (2011) for the other elements, 5 : Shinotsuka et al. (1995), and 6 : Nakamura (1974).

	Split 14/2		Split 14/22		Split 15/3		average	RSD%	1	2	3	4	5	6
	A	B	A	B	A	B								
mass (g)	0.16228	0.15083	0.1325	0.13535	0.12532	0.15975								
Li	1.89	1.82	1.79	1.83	1.73	1.79	1.81	3		1.48				
Be	0.0461	0.0429	0.0461	0.0451	0.0436	0.0465	0.0450	3	0.03	0.0445				
P	1181	1169	1154	1153	1175	1205	1173	2	1047	1163				
K	274	276	273	277	282	279	277	1	330	295				
Sc	10.57	11.50	11.49	11.12	11.54	11.47	11.28	3	11	11.35		11.33		
Ti	866	873	878	863	889	897	878	1	899		896			
V	93.9	94.2	95.1	92.7	96.5	98.6	95.2	2	92	99.5				
Mn	1422	1408	1407	1393	1426	1464	1420	2	1471	1506				
Co	623	622	609	605	616	623	616	1	600	717				
Cu	99.7	100	96.8	96.6	99.1	101.4	99.0	2	119	118				
Zn	116	118	118	119	120	122	119	2	110	139				
Ga	5.71	5.70	5.57	5.52	5.72	5.85	5.68	2	6	6.79				
Rb	1.18	1.17	1.15	1.17	1.19	1.20	1.18	1	1.2	1.29				
Sr	14.75	14.56	14.67	14.46	14.84	15.05	14.72	1	12	16.1				
Y	2.84	2.86	2.86	2.82	2.95	2.93	2.88	2	3	2.83		2.70	2.47	
Zr	6.48	6.57	6.56	6.51	6.80	6.76	6.61	2	9		6.60			
Nb	0.559	0.579	0.570	0.565	0.576	0.591	0.573	2			0.561			
Cs	0.0890	0.0885	0.0872	0.0861	0.0877	0.0903	0.0881	2		0.0911				

Table 4 (continue)

	Split 14/2		Split 14/22		Split 15/3		average	RSD%	1	2	3	4	5	6
	A	B	A	B	A	B								
Ba	4.55	4.50	4.54	4.47	4.53	4.59	4.53	1	4	4.51				4.85
La	0.516	0.517	0.517	0.503	0.518	0.525	0.516	1	0.52	0.534		0.548	0.503	0.507
Ce	1.28	1.27	1.29	1.26	1.31	1.31	1.29	2	1.33	1.32		1.37	1.26	1.33
Pr	0.200	0.200	0.202	0.197	0.203	0.204	0.201	1	0.21	0.206		0.212	0.197	
Nd	1.02	1.03	1.03	1.00	1.03	1.04	1.02	1	0.99	1.06		1.09	0.968	1.004
Sm	0.327	0.328	0.330	0.324	0.332	0.334	0.329	1	0.34	0.338		0.346	0.323	0.330
Eu	0.113	0.114	0.114	0.112	0.115	0.116	0.114	1	0.11	0.111		0.118	0.104	0.113
Gd	0.427	0.421	0.422	0.404	0.419	0.410	0.417	2	0.42	0.411		0.447	0.393	0.414
Tb	0.0776	0.0760	0.0774	0.0746	0.0768	0.0750	0.0762	2	0.081	0.0735		0.0807	0.069	
Dy	0.510	0.507	0.516	0.496	0.511	0.508	0.508	1	0.42	0.491		0.544	0.466	0.504
Ho	0.107	0.108	0.108	0.104	0.108	0.107	0.107	1	0.1	0.106		0.109	0.0954	
Er	0.309	0.314	0.310	0.303	0.313	0.310	0.310	1	0.29	0.284		0.317	0.288	0.303
Tm	0.0554	0.0562	0.0563	0.0552	0.0565	0.0556	0.0559	1	0.055	0.0518		0.0551	0.0496	
Yb	0.322	0.323	0.325	0.323	0.328	0.330	0.325	1	0.3	0.317		0.328	0.311	0.315
Lu	0.0455	0.0461	0.0457	0.0454	0.0468	0.0459	0.0459	1	0.052	0.0451		0.0460	0.0456	0.0465
Hf	0.197	0.202	0.201	0.199	0.206	0.205	0.202	2	0.21		0.201	0.1939		
Ta	0.0347	0.0352	0.0343	0.0338	0.0334	0.0340	0.0342	2			0.0314			
W	0.206	0.232	0.192	0.204	0.186	0.184	0.200	9	0.2					
Pb	1.26	1.33	1.34	1.21	1.23	1.22	1.27	4	1.39	1.09				
Th	0.0587	0.0593	0.0607	0.0582	0.0599	0.0597	0.0594	2		0.0551		0.05864	0.061	
U	0.0149	0.0152	0.0151	0.0148	0.0156	0.0156	0.0152	2		0.0154		0.01554	0.0154	

Table 5. Major and minor element abundances in Alais, Ivuna and Orgueil obtained by ICP-AES.

		Alais	Ivuna	Orgueil									
				ORG1	ORG2	ORG3	ORG4	ORG5	ORG6	av. 1-6	RSD(%)	av. 1-5	RSD(%)
mass	mg	120.62	133.40	119.60	111.33	124.76	118.62	104.50	106.60				
Ti	wt%	0.043	0.043	0.044	0.043	0.042	0.045	0.044	0.042	0.043	2.6	0.044	2.3
Al	wt%	0.776	0.784	0.778	0.798	0.789	0.806	0.788	0.760	0.786	2.0	0.792	1.3
Fe	wt%	18.64	18.88	18.97	19.15	20.92	19.36	19.19	18.73	19.39	4.0	19.52	4.1
Mn	wt%	0.218	0.202	0.186	0.194	0.209	0.188	0.210	0.178	0.194	6.5	0.197	5.7
Mg	wt%	9.41	9.55	9.17	9.38	9.55	9.48	9.52	9.03	9.36	2.3	9.42	1.6
Ca	wt%	0.860	0.921	0.782	0.808	0.964	0.778	0.890	0.810	0.839	8.8	0.844	9.5
Na	wt%	0.422	0.490	0.485	0.423	0.442	0.453	0.596	0.291	0.448	22.0	0.480	14.3
P	wt%	0.101	0.102	0.094	0.098	0.104	0.104	0.108	0.096	0.101	5.6	0.102	5.6
Cr	wt%	0.263	0.257	0.257	0.264	0.263	0.268	0.262	0.257	0.262	1.6	0.263	1.5
Ni	wt%	1.08	1.20	1.23	1.12	1.08	1.12	1.12	1.15	1.14	4.7	1.13	5.2
Co	µg/g	494	531	535	519	502	529	510	520	519	2.3	519	2.6

Table 6. Trace and minor element abundances in Alais, Ivuna and Orgueil obtained by ICP-SFMS (in µg/g).

	Alais	Ivuna	Orgueil									
			ORG1	ORG2	ORG3	ORG4	ORG5	ORG6	av. 1-6	RSD%	av. 1-5	RSD%
Li	1.38	1.44	1.39	1.42	1.46	1.48	1.46	1.43	1.44	2	1.44	3
Be	0.0232	0.0232	0.0223	0.0227	0.0235	0.0237	0.0210	0.0219	0.0225	5	0.0226	5
P	979	1061	952	965	1024	1038	1069	886	989	7	1010	5
K	608	432	546	483	498	547	677	365	519	20	550	14
Sc	5.75	6.08	5.77	5.78	5.88	6.04	5.77	5.57	5.80	3	5.85	2
Ti	450	466	442	436	445	461	459	438	447	3	449	3
V	53.0	54.0	51.2	51.7	51.8	53.6	54.0	51.5	52.3	2	52.4	2
Mn	2062	2003	1801	1866	2014	1813	2057	1715	1878	7	1910	6
Co	491	554	533	523	496	533	506	523	519	3	518	3
Cu	136	138	125	124	122	139	124	128	127	5	127	6
Zn	277	330	307	303	303	311	291	272	298	5	303	2
Ga	9.04	9.67	9.39	9.43	9.34	9.75	9.50	9.13	9.42	2	9.48	2
Rb	2.16	2.23	2.44	2.35	2.25	2.47	2.16	1.68	2.23	13	2.33	6
Sr	8.09	8.04	7.36	7.14	8.28	7.50	8.40	6.99	7.61	8	7.73	7
Y	1.67	1.60	1.46	1.62	1.50	1.60	1.62	1.47	1.54	5	1.56	5
Zr	3.26	3.48	3.57	3.50	3.49	3.60	3.42	3.39	3.49	2	3.52	2
Nb	0.314	0.298	0.268	0.282	0.282	0.303	0.308	0.306	0.292	6	0.289	6
Cs	0.177	0.192	0.190	0.192	0.177	0.203	0.180	0.154	0.182	9	0.189	5
Ba	2.71	2.57	2.43	2.35	2.44	2.46	2.65	2.57	2.48	4	2.46	5

Table 6. (continue)

	Alais	Ivuna	Orgueil						av. 1-6	RSD%	av. 1-5	RSD%
			ORG1	ORG2	ORG3	ORG4	ORG5	ORG6				
La	0.255	0.241	0.227	0.243	0.228	0.238	0.239	0.262	0.240	5	0.235	3
Ce	0.660	0.614	0.581	0.621	0.585	0.607	0.603	0.660	0.610	5	0.600	3
Pr	0.103	0.0920	0.0881	0.0947	0.0889	0.0918	0.0917	0.0938	0.0915	3	0.0910	3
Nd	0.534	0.471	0.447	0.486	0.453	0.469	0.466	0.467	0.465	3	0.464	3
Sm	0.177	0.155	0.147	0.161	0.149	0.153	0.154	0.150	0.152	3	0.153	4
Eu	0.0688	0.0597	0.0556	0.0617	0.0574	0.0595	0.0588	0.0568	0.0583	4	0.0586	4
Gd	0.239	0.213	0.198	0.216	0.201	0.208	0.209	0.200	0.205	3	0.206	3
Tb	0.0430	0.0388	0.0359	0.0394	0.0359	0.0380	0.0385	0.0362	0.0373	4	0.0375	4
Dy	0.285	0.260	0.243	0.264	0.248	0.260	0.257	0.241	0.252	4	0.254	3
Ho	0.0621	0.0579	0.0537	0.0589	0.0549	0.0575	0.0579	0.0531	0.0560	4	0.0566	4
Er	0.178	0.170	0.159	0.172	0.160	0.169	0.172	0.157	0.165	4	0.166	4
Tm	0.0276	0.0271	0.0249	0.0266	0.0254	0.0266	0.0273	0.0244	0.0259	4	0.0262	4
Yb	0.173	0.171	0.160	0.171	0.163	0.171	0.176	0.156	0.166	5	0.168	4
Lu	0.0252	0.0248	0.0231	0.0256	0.0240	0.0248	0.0256	0.0230	0.0243	5	0.0246	4
Hf	0.106	0.107	0.108	0.107	0.108	0.109	0.104	0.104	0.107	2	0.107	2
Ta	0.0155	0.0149	0.0140	0.0142	0.0146	0.0155	0.0159	0.0158	0.0150	6	0.0148	6
W	0.12	0.10	0.10	0.10	0.10	0.12	0.12	0.11	0.11	10	0.11	10
Pb	3.13	2.65	2.56	2.99	2.59	2.66	2.65	2.78	2.70	6	2.69	6
Th	0.0295	0.0289	0.0274	0.0282	0.0278	0.0287	0.0292	0.0314	0.0288	5	0.0283	3
U	0.0100	0.00749	0.00750	0.00763	0.00735	0.00781	0.00833	0.0102	0.00813	13	0.00772	5
(La/Sm) _n	0.94	1.01	1.01	0.98	0.99	1.01	1.01	1.14	1.02	6	1.00	1
(La/Lu) _n	1.06	1.02	1.03	1.00	1.00	1.00	0.98	1.19	1.03	8	1.00	2
Eu/Eu*	1.01	1.00	0.99	1.00	1.00	1.01	0.99	1.00	1.00	1	1.00	1
Y/Ho	26.8	27.6	27.1	27.5	27.4	27.8	27.9	27.6	27.6	1	27.6	1
Nb/Ta	20.3	20.0	19.2	19.8	19.3	19.5	19.3	19.4	19.4	1	19.4	1
Zr/Hf	30.9	32.4	33.0	32.8	32.3	33.0	32.8	32.5	32.7	1	32.8	1
Th/U	2.95	3.86	3.66	3.70	3.78	3.68	3.50	3.08	3.54	7	3.66	3

Table 7. Isotopic compositions of Cu and Zn in CI chondrites. The isotopic compositions are represented using the δ notation (parts per 1000 deviation from terrestrial Cu standard NIST 976 or Zn standard JMC-Lyon respectively).

	$\delta^{65}\text{Cu}$	$\delta^{66}\text{Zn}$	$\delta^{67}\text{Zn}$	$\delta^{68}\text{Zn}$
Alais	0.02	0.46	0.61	0.85
Ivuna	0.00	0.54	0.83	1.06
Luck et al. (2005):				
Chunk 1		0.49	0.60	0.92
Chunk 2		0.46	0.48	0.86
Orgueil				
ORG1	0.13	0.42	0.60	0.79
ORG2	-0.01	0.45	0.68	0.88
ORG3	-0.03	0.43	0.57	0.79
ORG4	0.19	0.43	0.60	0.80
ORG5	0.11	0.51	0.75	1.02
ORG6	0.04	0.45	0.60	0.87
Luck et al. (2003, 2005):				
Chunk 1 (ORG6)	-0.09	0.46	0.71	0.90
Chunk 2		0.52	0.75	1.01
Mean CI (this work)	0.05	0.46	0.66	0.88
2 σ	0.16	0.08	0.18	0.21

Table 8. Abundances in CI-chondrites based on the Orgueil meteorite. (*Si has been estimated using the same Si/Mg ratio as Lodders et al. (2009)).

Element	unit	this work	RSD %	Lodders et al. (2009)	Anders and Grevesse (1989)	atoms per 10 ⁶ Si atoms (this work)	
3	Li	μg/g	1.44	3	1.47	1.5	55.5
4	Be	μg/g	0.0226	5	0.021	0.0249	0.671
11	Na	wt%	0.480	14	0.499	0.5	55700
12	Mg	wt%	9.42	2	9.58	9.89	1.03 10 ⁶
13	Al	wt%	0.79	1	0.85	0.868	78340
14	Si	wt%	10.52*		10.7	10.64	10 ⁶
15	P	μg/g	1010	5	967	1220	8710
19	K	μg/g	550	14	544	558	3760
20	Ca	wt%	0.84	10	0.922	0.928	56240
21	Sc	μg/g	5.85	2	5.9	5.82	34.7
22	Ti	μg/g	449	3	451	436	2502
23	V	μg/g	52.4	2	54.3	56.5	275
24	Cr	μg/g	2627	2	2650	2660	13490
25	Mn	μg/g	1910	6	1930	1990	9280
26	Fe	wt%	19.52	4	18.5	19.04	9.33 10 ⁵
27	Co	μg/g	519	3	506	502	2350
28	Ni	wt%	1.13	5	1.08	1.1	51560
29	Cu	μg/g	127	6	131	126	534
30	Zn	μg/g	303	2	323	312	1236
31	Ga	μg/g	9.48	2	9.71	10	36.3
37	Rb	μg/g	2.33	6	2.31	2.3	7.29
38	Sr	μg/g	7.73	7	7.81	7.8	23.6
39	Y	μg/g	1.56	5	1.53	1.56	4.68
40	Zr	μg/g	3.52	2	3.62	3.94	10.3
41	Nb	μg/g	0.289	6	0.279	0.246	0.83
55	Cs	μg/g	0.189	5	0.188	0.187	0.38
56	Ba	μg/g	2.46	5	2.41	2.34	4.79
57	La	μg/g	0.235	3	0.242	0.2347	0.452
58	Ce	μg/g	0.600	3	0.622	0.6032	1.142
59	Pr	μg/g	0.0910	3	0.0946	0.0891	0.173
60	Nd	μg/g	0.464	3	0.471	0.4524	0.859
62	Sm	μg/g	0.153	4	0.152	0.1471	0.272
63	Eu	μg/g	0.0586	4	0.0578	0.056	0.103
64	Gd	μg/g	0.206	3	0.205	0.1966	0.350
65	Tb	μg/g	0.0375	4	0.0384	0.0363	0.0630
66	Dy	μg/g	0.254	3	0.255	0.2427	0.418
67	Ho	μg/g	0.0566	4	0.0572	0.0556	0.0916
68	Er	μg/g	0.166	4	0.163	0.1589	0.266
69	Tm	μg/g	0.0262	4	0.0261	0.0242	0.042
70	Yb	μg/g	0.168	4	0.169	0.1625	0.259
71	Lu	μg/g	0.0246	4	0.0253	0.0243	0.0376
72	Hf	μg/g	0.107	2	0.106	0.104	0.160
73	Ta	μg/g	0.0148	6	0.0145	0.0142	0.0218
74	W	μg/g	0.11	10	0.096	0.0926	0.15
82	Pb	μg/g	2.69	6	2.63	2.47	3.47
90	Th	μg/g	0.0283	2	0.031	0.0294	0.0325
92	U	μg/g	0.0077	5	0.0081	0.00893	0.00866

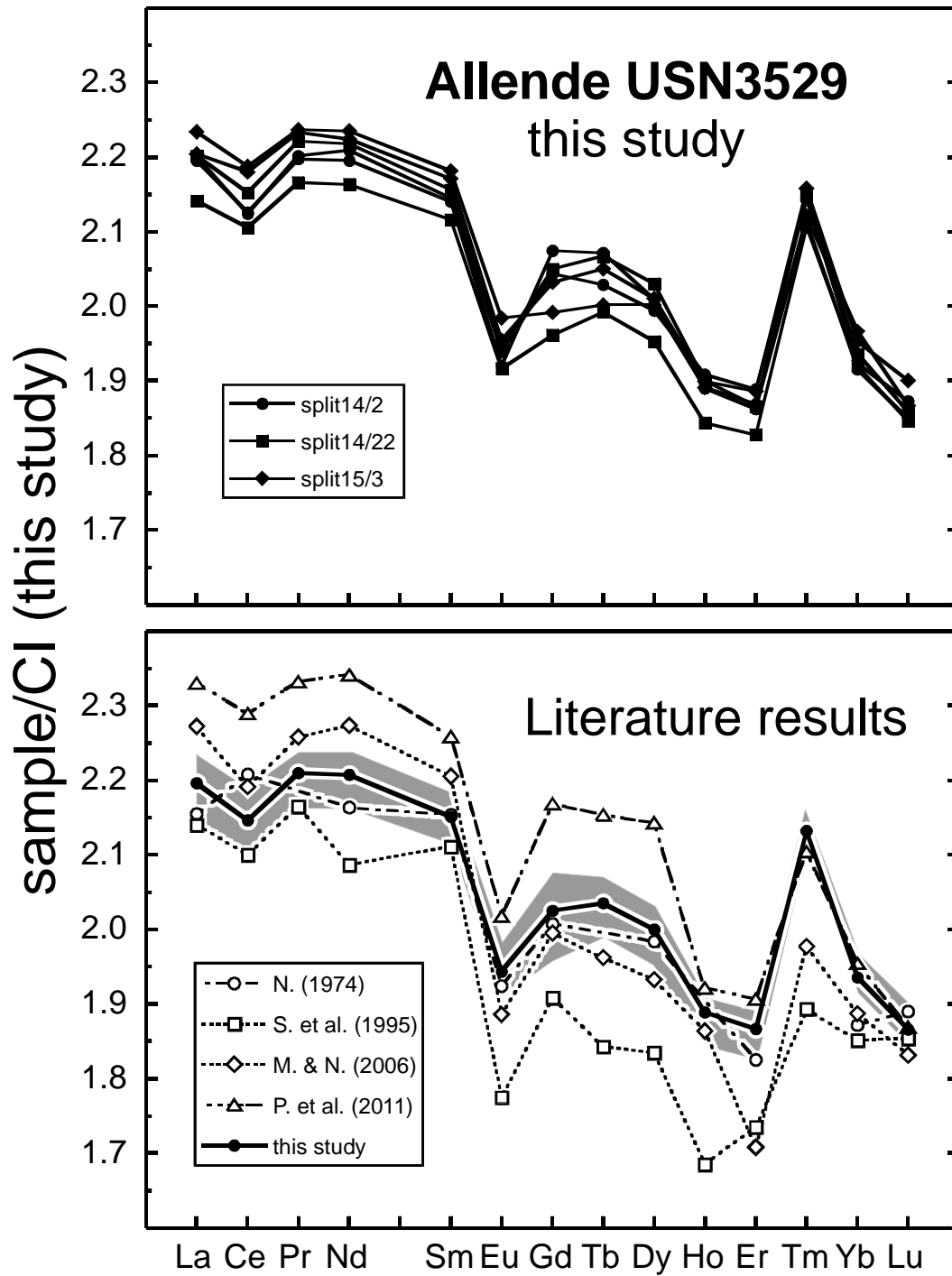


Figure 1. REE patterns of the Allende standard normalized to the average Orgueil composition calculated in this study (literature results from Nakamura (1974), Shinotsuka and Ebihara (1995), Makishima and Nakamura (2006), and Pourmand et al. (2011)).

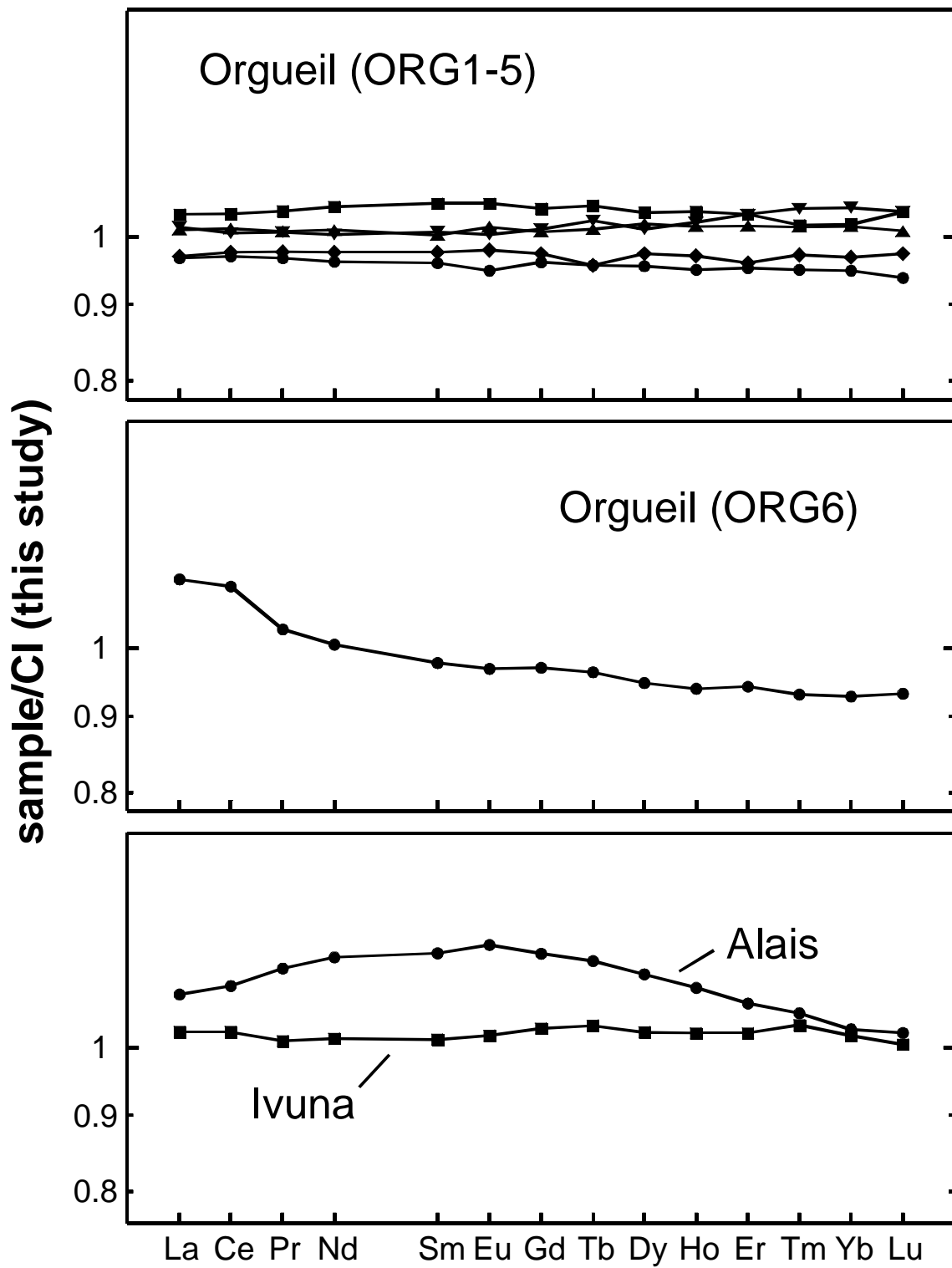


Figure 2. REE patterns of the chips of CI chondrites normalized to the average Orgueil composition calculated in this study

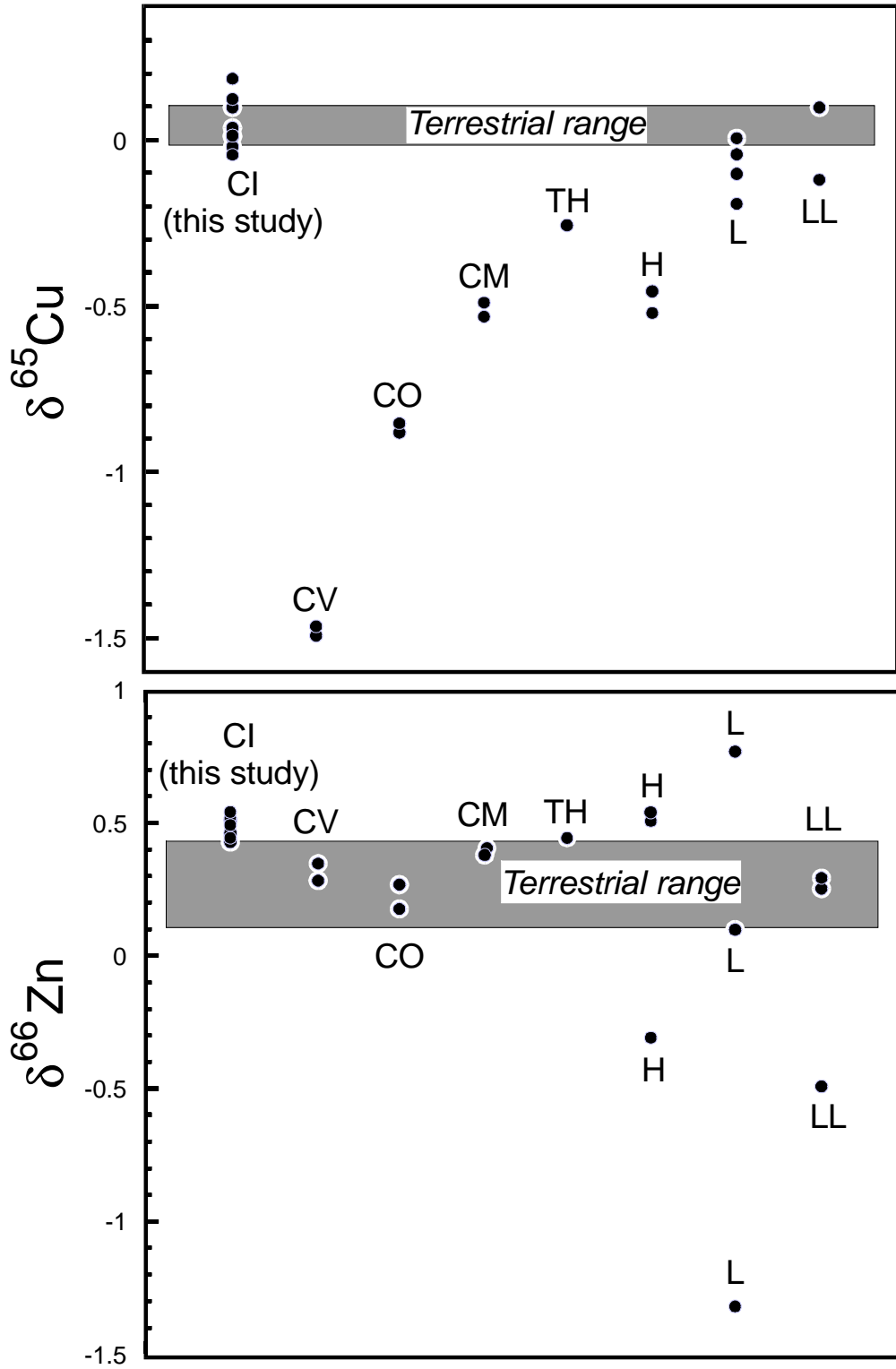


Figure 3. Isotopic compositions of Cu and Zn in chondritic meteorites (Luck et al., 2003, 2005, and this study).

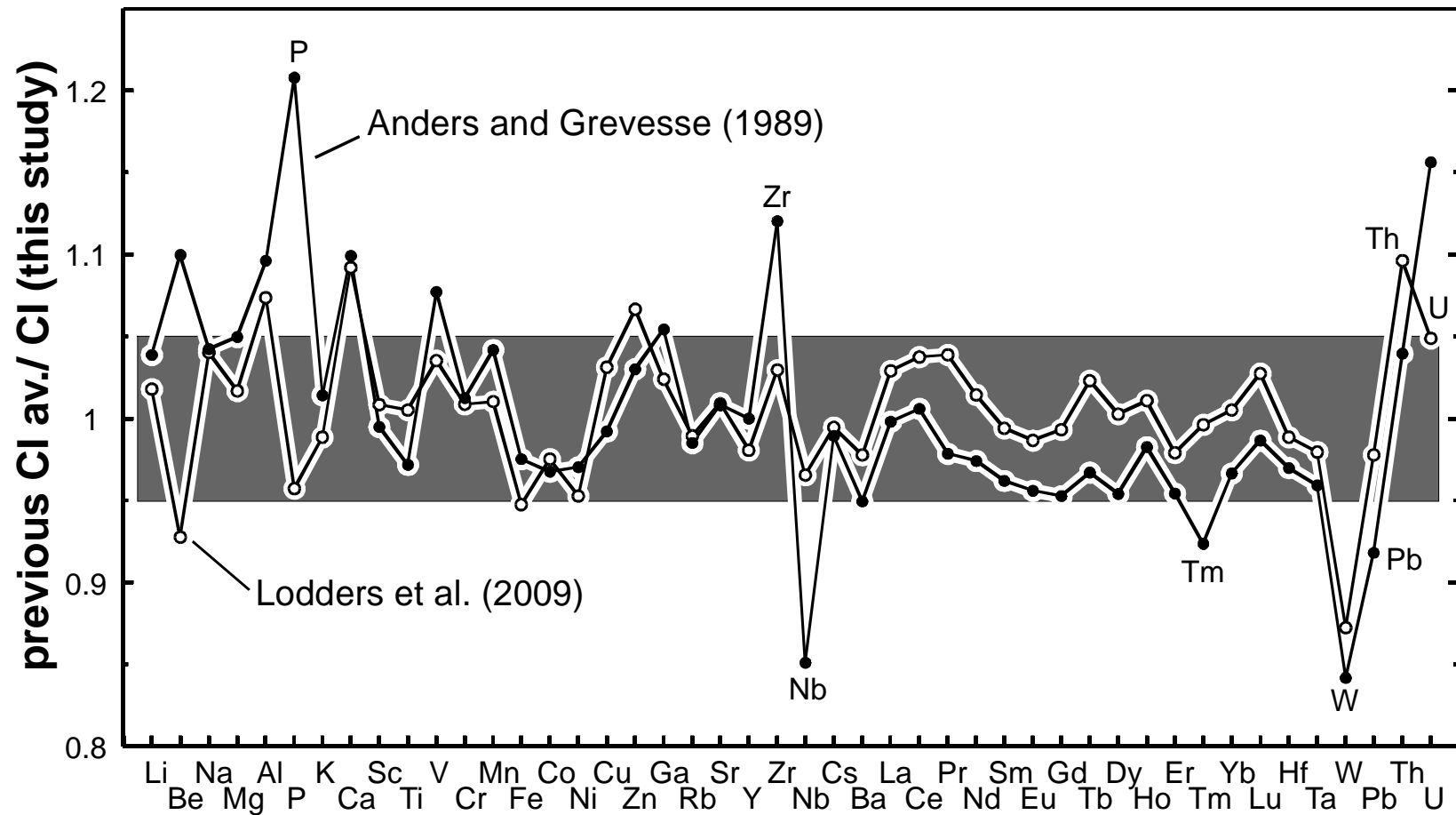


Figure 4. Average compositions of CI chondrites (Anders and Grevesse, 1989 ; Lodders et al., 2009) normalized to the average Orgueuil composition calculated in this study (Table 8).

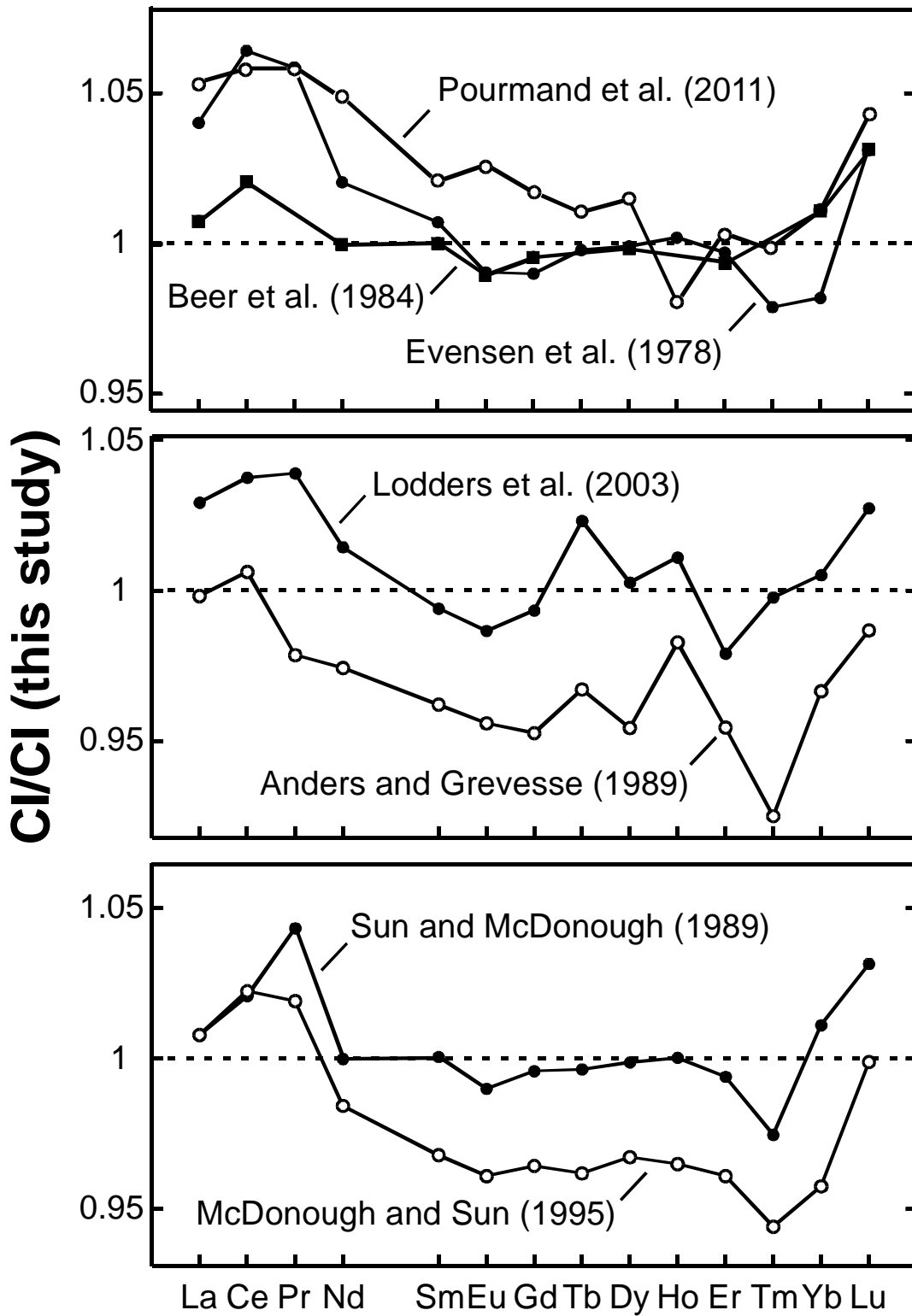


Figure 5. Selected CI chondrite reference compositions normalized to the average Orgueil composition calculated in this study (Table 8)