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High field strength elements in chondrites and their refractory components

C. Münker, M. Pfeifer, V. Krisponeit, F. Wombacher

Supplementary Information

The Supplementary Information includes:

- Sample Digestion and Ion Exchange Separation
- Mass Spectrometry for HFSEs, Lu-Hf and Sm-Nd Measurements
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Sample Digestion and Ion Exchange Separation

Both the various isotope dilution measurements and quadrupole ICPMS measurements of REE in CAIs were performed on the same, ca. 100 mg-sized sample powder split (some refractory inclusions as low as 14 mg). Prior to digestion, the chondrite samples were spiked with mixed ^{149}Sm-^{150}Nd, mixed ^{229}Th-^{233}U-^{236}U and mixed ^{183}W-^{180}Ta-^{180}Hf-^{176}Lu-^{94}Zr tracers that were calibrated against >99.9% pure metal standards. During the course of our measurements, the same isotope traces were used throughout, thus ensuring consistency of the isotope dilution data reported. Typically, sample digestion was performed on hotplates in HF-HNO_3 at 120°C using Savillex vials, followed by an additional 24 hr Parr bomb step at 180°C in HF-HNO_3. For carbon-rich samples such as some CI and CM chondrites one additional 24 hr Parr bomb step in concentrated HNO_3 at 180°C was performed to oxidize residual compounds, mostly carbon. For bombing, only vials with low W blanks, as tested during pre-bombing steps in concentrated HF, were used. After repeated drydown in ca. 2-5 ml HNO_3, complete sample dissolution and sample-spike equilibration was achieved in a visibly clean solution of ca. 10 ml of 6N HCl-0.01N HF. From this sample solution, different aliquots were prepared, these different aliquots were taken for most HFSE, U-Th and Hf-Nd isotopes (ca. 80%) and W-isotope dilution (ca. 20%). In contrast to the chondrite samples, the refractory inclusions were first dissolved and only a ca. 10% aliquot was spiked with the different mixed tracers and a ca. 5% unspiked aliquot was used for conventional trace element measurements, the remaining ca. 85% were used elsewhere for measurements of nucleosynthetic isotope variations (e.g., Peters *et al.*, 2017; Pfeifer, 2017).

A Lu-rich HREE fraction, Ta, Hf, a quantitative Zr-Nb cut, a U-Th-rich fraction and a matrix cut containing the LREE were each separated by a three-stage ion exchange procedure from the HFSE cut, employing Eichrom (now Triskem) Ln Spec resin and AG1-X8 anion resin (Münker *et al.*, 2001; Münker, 2010; Thiemens *et al.*, 2019). Samarium and Nd were further purified from the matrix cut using AG 50W-X8 and Ln Spec resins in HCl (Pin and Santos Zaldegui, 1997). Separation of a W fraction from the 20% W-isotope dilution aliquot was achieved using micro-columns filled with AG1x8 anion resin (Kleine *et al.*, 2004; Münker, 2010). Purification of U and Th cuts from the U-Th-rich fraction was achieved using Triskem Tru resin (modified technique after Luo *et al.*, 1997). Typical procedural blanks

during the course of the measurements were better than 35 pg for W, 15 pg for Nb, 20 pg for Ta, 800 pg for Zr, 80 pg for Hf, 12 pg for Lu, 5 pg for Th, 6 pg for U, and <20 pg for Sm-Nd. These blanks were negligible, and propagated errors from blank uncertainties were always smaller than 1%.

Mass Spectrometry and Measurements of HFSEs, Lu-Hf and Sm-Nd Abundances

For HFSE and Lu concentration measurements, the isotope compositions of spiked Lu, Zr, Ta and W were analyzed by mass bias correction to isotope compositions of doped Re (Ta, W) and Sr (Zr) and with Yb in the Lu cut using the Neptune MC-ICPMS at the joint Cologne-Bonn laboratory (see also Weyer *et al.*, 2002; Lagos *et al.*, 2007). Abundances of Nb were measured as Zr/Nb against a Zr/Nb standard prepared from >99.9% pure Ames Laboratory metals. The Nb abundance is calculated from the measured Zr/Nb using the Zr abundances obtained by isotope dilution (Weyer *et al.*, 2002).

Abundances of Sm and Nd were measured using a ^{149}Sm-^{150}Nd mixed tracer and the Neptune MC-ICPMS at the joint Cologne-Bonn laboratory. Measured ^{143}Nd/^{144}Nd values were normalized relative to a ^{146}Nd/^{144}Nd of 0.7219 using the exponential law. All Nd isotope data are given relative to a ^{143}Nd/^{144}Nd of 0.511859 for the La Jolla standard, at an external precision of ±0.3 ε-units (2 s.d.). Measured ^{176}Hf/^{177}Hf values were normalized relative to a ^{179}Hf/^{177}Hf of 0.7325 using the exponential law. All Hf data are given relative to a ^{176}Hf/^{177}Hf of 0.282160 for the Münster AMES standard that is analytically indistinguishable from JMC-475 (Münker *et al.*, 2001). The external precision for Hf isotope measurements was ±0.3 ε-units (2 s.d.). External precision and accuracy as determined by multiple digestions of different rock matrices were typically better than ±4% for Nb/Ta, ±0.6% for Zr/Hf, ±0.2% for Lu/Hf, ±0.2% for Sm/Nd and ±1% for Ta/W (all 2 r.s.d.; Münker *et al.*, 2001, 2003; König *et al.*, 2008).

Uranium-Th measurements were performed using the Neptune MC-ICPMS at Cologne and Bonn (see Thiemens *et al.*, 2019; Obert *et al.*, 2022). The measured Th cuts were doped with the NBL CRM 112A U standard for mass bias correction of measured ^{229}Th/^{232}Th, and concentration-matched IRM-035 and IRM 036 standards were used at equal count rates to ensure ion counter yield corrections. For ^{238}U/^{236}U and ^{238}U/^{233}U measurements, mass bias correction was performed using the measured ^{233}U/^{236}U or ^{238}U/^{235}U of the spiked U cuts and the certified ^{233}U/^{236}U from Richter *et al.* (2010) for the doped IRM-3636 double spike that was used for preparation of the mixed U-Th tracer. If combined with HFSE measurements by isotope dilution, our external precision and accuracy for elemental ratios determined by isotope dilution involving U and Th typically is better than ±1% for U/Th, U/W and Th/W (2 r.s.d.).

Mass Spectrometry for Additional Trace Element Measurements by Quadrupole ICPMS (REEs in Refractory Inclusions)

To better characterize the refractory inclusions, additional REE data (Table S-4) were obtained by quadrupole ICPMS and instrumental neutron activation analysis (only data for CAI A-33 and A-44 are from Jacobsen *et al.*, 2008). The majority of REE data were obtained using the iCAPQ at Universität zu Köln in KED mode. Three matrix matched external calibration solutions ranging from CV chondritic to CAI compositions were prepared from existing multi-element solutions (Braukmüller *et al.*, 2018, 2020). However, samples CAI-12 and CAI-15 were analyzed earlier in the STD mode (no collision-reaction cell) relative to a solution of Allende (Allende CAI host in Table S-4) and assuming REE abundances as published by Braukmüller *et al.* (2018) for the Allende Smithsonian powder and by Stracke *et al.* (2012) for Ho. Finally, the data for CAI-1 and CAI-4 were analyzed by ICPMS at the Universität Kiel/Germany (Garbe-Schönberg, 1993). As no internal standard was added before the CAI analyses, Hf abundances were determined along with the REE by ICPMS and the REE data were corrected to match the Hf abundances determined by isotope dilution. The Lu data agree to within 16% with that obtained by isotope dilution (Table S-4), except for CAI-1 (49%), CAI-14 (+26%) and CAI A-33 (-25%).

Supplementary Tables

Table S-1 High precision isotope dilution and isotope composition data obtained for carbonaceous chondrites. Weights for Orgueil, Ivuna and Alais are from Barrat *et al.* (2012), where also trace element data are given for the same powder aliquots. Data sources/powder sources We02, Mü03, Ba2012, Be2014 and Br2018 refer to Weyer *et al.* (2002), Münker *et al.* (2003), Barrat *et al.* (2012), Bendel (2014) and Braukmüller *et al.* (2018), respectively. The USN Allende reference powder is further described in Jarosewich *et al.* (1987), different powder aliquots provided by the Smithsonian Museum to different studies were analysed here.

Table S-2 High precision isotope dilution and isotope composition data obtained for enstatite chondrites. Samples marked with asterisks are the subset with unfractionated Zr/Nb (12.8-17.2) that was used for calculation of the average values in Table 1. Data sources as in Table S-1.

Table S-3 High precision isotope dilution and isotope composition data obtained for ordinary chondrites. Data sources as in Table S-1.

Table S-4 High precision isotope dilution and isotope composition data as well as REE data obtained for refractory inclusions (CAIs and AOAs). "Allende CAI host" is the remaining bulk Allende powder that hosted the inclusions, "Allende USN" is the Allende USN 3529 powder analysed alongside with the refractory inclusions. Data source/powder source St2012 refers to Stracke *et al.* (2012).

Tables S-1 to S-4 are available for download (.xlsx) from the online version of this article at https://doi.org/10.7185/geochemlet.2533.

Supplementary Figures

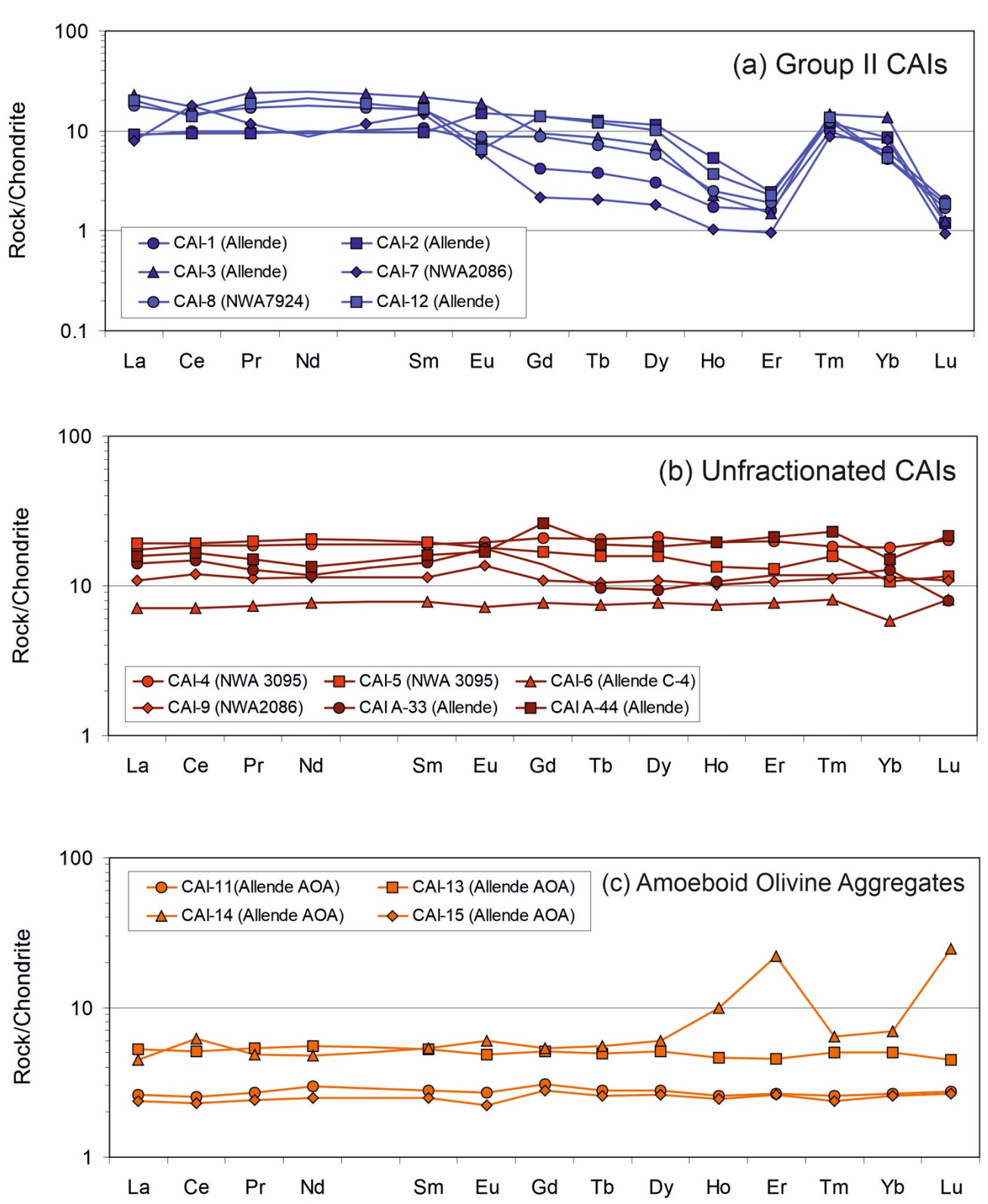

Figure S-1 Normalized Rare Earth Element (REE) patterns of refractory inclusions, analysed by quadrupole ICPMS.

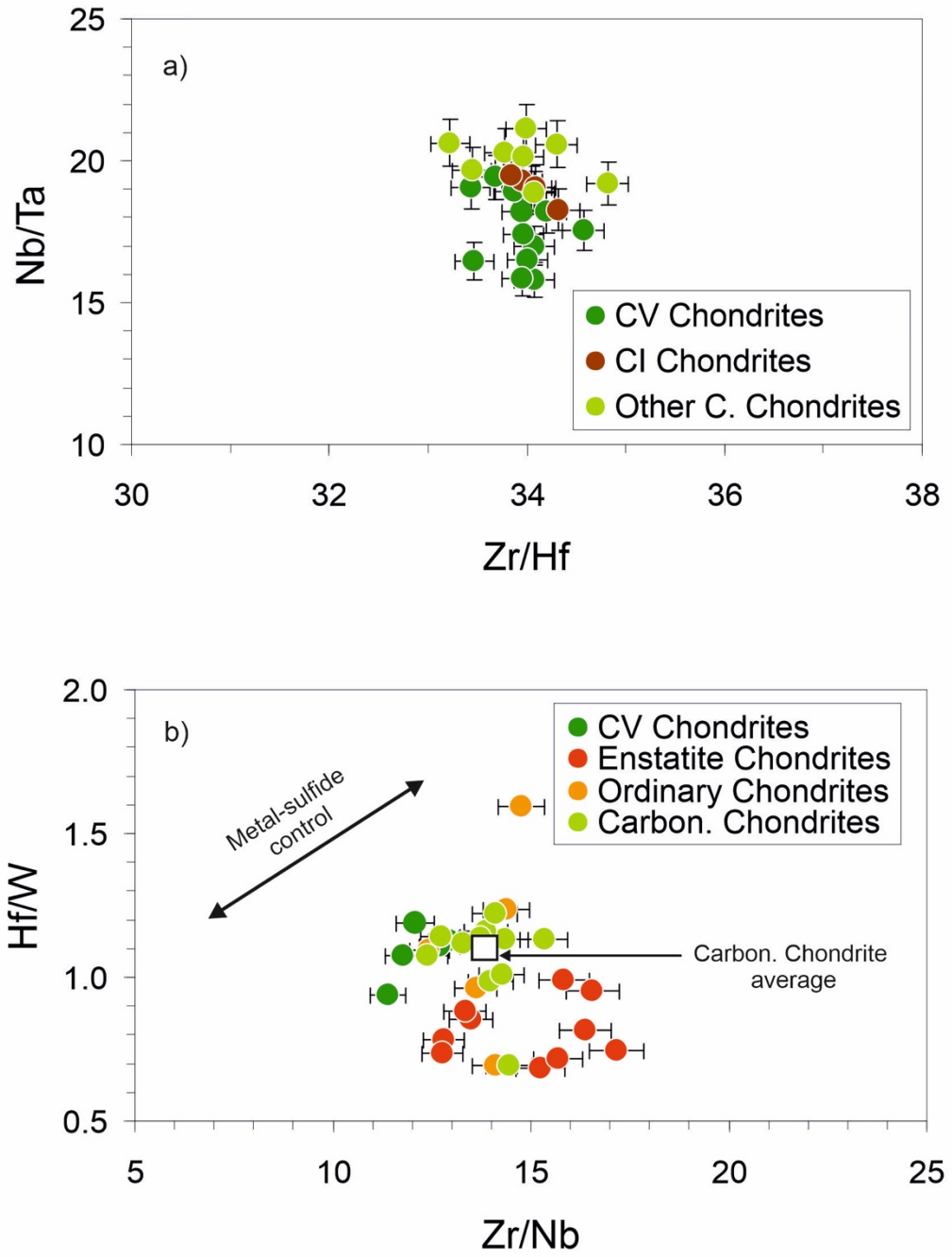

Figure S-2 Supplementary plots (a) Plot of Nb/Ta vs. Zr/Hf, illustrating the composition of CI chondrites relative to other groups of carbonaceous chondrites. There is no systematic difference between CI chondrites and other carbonaceous chondrites (except for CV chondrites). (b) Plot of Hf/W vs. Zr/Nb for all classes of studied chondrites, illustrating the possibly combined effects of metal or sulfides on sample heterogeneity. As both ratios are not positively correlated, it is likely that only the Nb abundances in enstatite chondrites are controlled by sulfides (*cf.* Fig. 1a), but not the Hf/W patterns that are rather controlled by nebular processes.

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