IN SITU MEASUREMENTS OF SULFUR ISOTOPIC COMPOSITION OF SULFIDES IN ENSTATITE CHONDRITES. J. Hopp[1], M. Böhm[1], T. Ludwig[1], A. Varychev[1], M. Trieloff[1], [1]Institut für Geowissenschaften, Klaus-Tschira-Labor für Kosmochemie, Universität Heidelberg (Im Neuenheimer Feld 234-236, 69120 Heidelberg, Germany; jens.hopp@geow.uni-heidelberg.de).

Introduction: Enstatite chondrites formed at highly reducing conditions, leading to rather exotic mineral assemblages, for example, phosphides (e.g. schreibersite), halogenides (e.g. djerfisherite and lawrencite), Fe-Ni-metal with alloyed Si, and also various sulfides such as Cr-Ti-bearing troilite (FeS), niningerite (Mg,Fe,Mn)S, alabandite (Mn,Fe,Mg)S, daubréelite ($FeCr_2S_4$), and oldhamite CaS (e.g., [1,2]). The isotopic compositions of the different sulfides may have recorded a variety of processes, e.g., formation in the solar nebula and/or on the enstatite chondrite parent bodies, or subsequent thermal metamorphism, or impact-induced thermal events.

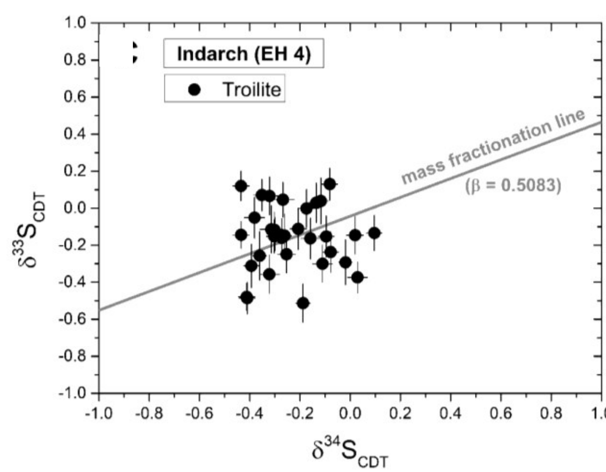
Sulfur isotope compositions of whole rock samples reported for various chondrite classes (e.g., [3-5]) reveal only very small intra-group variations (less than 1‰), with carbonaceous chondrites showing the highest $\delta^{34}S_{CDT}$-values (+0.1 to +0.6 ‰) and largest variation. The enstatite chondrites display the lowest $\delta^{34}S_{CDT}$-values (-0.4 to -0.2 ‰; [4]). The latter values are compatible with recent TIMS analyses of water-insoluble sulfide fractions of enstatite chondrites, except for some EL 6 with more negative $\delta^{33,34}S_{V\text{-}CDT}$-values down to -1.02 ‰ [5]. These values refer to bulk analyses, and nothing is known about potential heterogeneities at mineral scales, which may relate to e.g., solar nebula processes.

Samples and techniques:

We applied SIMS analyses (using a Cameca ims 1280-HR at University of Heidelberg; HIP) to various sulfides of EH chondrites Sahara 97072 and Sahara 97096 (both EH3, paired), Indarch (EH4), Abee 2,2,0 (EH4 / EH impact melt breccia), EET 96135 (EH4/5), EH impact melt LAP 02225, and the EL-chondrites MAC 88136 (EL3), Grein 002 (EL4/5), TIL 91714 (EL5), LON 94100, Neuschwanstein and NWA 974 (all EL6). As troilite standard we used Canyon Diablo Troilite (CDT), although whole rock studies noticed some heterogeneity in sulfur isotopic composition (e.g., [6]). As SIMS analyses require homogeneity at small spatial scales, we checked CDT by SEM and found ubiquitous micrometer-sized daubréelite inclusions scattered within troilite (Fig. 1). Analyses compromised by such inclusions were identified by elevated count rates and discarded, resulting in reproducibility of CDT analyses of better than 0.2 ‰ for both $\delta^{33}S$ and $\delta^{34}S$. We applied a ~250 pA, 20 keV Cs^+-primary ion beam with a raster size of 10 µm (20 µm during pre-sputtering). Negative secondary ions were accelerated to 10 keV. The secondary ion image was limited to ~18 µm, with the dynamic transfer optical system (DTOS) being activated. NEG was activated for charge compensation, nominal mass resolving power (MRP) was 5000 for all detectors, sulfur isotopes were measured in multi-collection mode on Faraday cups L'2, C' and the axial FC (all 10^{11} Ω). Each analysis comprised 20 cycles with an integration time of 10 s/cycle.

Results:

In diagrams showing $\delta^{33}S$ versus $\delta^{34}S$ (Fig. 1), troilite isotopic data either indicate homogeneous composition of troilite scattering around mean values (e.g., Indarch: $\delta^{33}S$ = (-0.16 ± 0.17) ‰ and $\delta^{34}S$ = (-0.23 ± 0.14) ‰), or follow a mass dependent fractionation line (e.g., EET96135). When compared to troilite, other sulfides (niningerite in EET96135, alabandite in MAC 88136, daubréelite in Neuschwanstein, oldhamite in Grein 002 and Sahara 97072) display significantly larger intra-sample variations, of up to 12‰ for oldhamite in Sahara 97072 (Fig. 1 bottom).



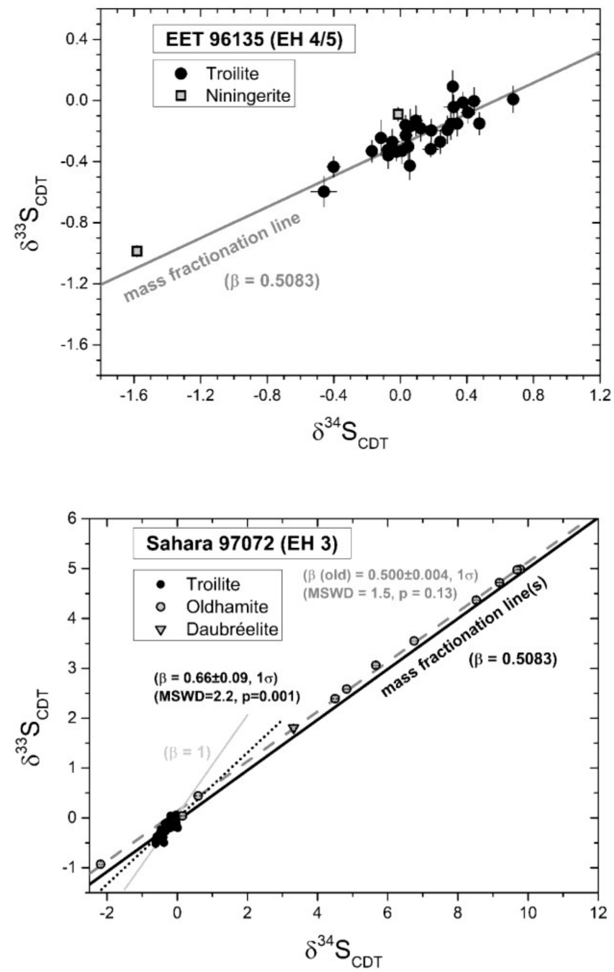


Fig. 1 Troilite, niningerite, daubréelite and oldhamite sulfur isotopic variations for Indarch, EET 96135 and Sahara 97072

Oldhamite compositional variations follow kinetic mass fractionation lines and are significant. As oldhamite standards were lacking, there may be an uncorrected systematic shift of all oldhamite data along the mass fractionation line, however, the large scatter indicates true compositional differences and requires further explanations, such as inheritage from solar nebula compositions of other fractionation processes during formation, or subsequent alteration.

Our troilite data agree with TIMS data [5] of non-soluble sulfides (comprising all sulfides except for oldhamite), except for some EL6 samples with apparently lower TIMS values, a discrepancy that cannot yet be readily explained.

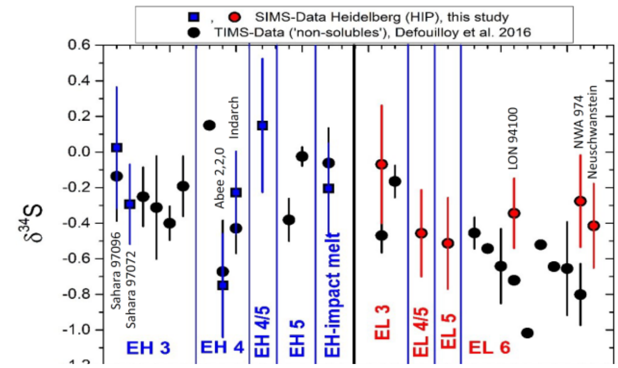


Fig. 2 Troilite average data (SIMS, this study) compared with TIMS (non water soluble sulfides).

The average compositions of our samples are $\delta^{33}S$ = (-0.30 ± 0.05) ‰ and $\delta^{34}S$ = (-0.35 ± 0.15) ‰ for EH and $\delta^{33}S$ = (-0.21 ± 0.04) ‰ and $\delta^{34}S$ = (-0.22 ± 0.28) ‰, for EL chondrites, i.e. indistinguishable within errors. Consistent with previous bulk measurements, these values are lower than carbonaceous or ordinary chondrite compositions [3,4]. If enstatite chondrites are representative of Earth's building blocks, the bulk Earth value should have a $\delta^{34}S$-value of about -0.3 ± 0.2‰, quite different to estimates of the bulk silicate Earth of about -1.28 ± 0.33‰ [7]. However, this could be reconciled with an appropriate amount of sulfur counterbalanced by the core. According to [7], if the core has a composition of $\delta^{34}S$ = +0.07‰, a fraction of sulfur in the core of about 60-85% of total terrestrial sulfur would yield a bulk Earth value consistent with enstatite chondrite composition.

References:

[1] Mason B. (1966) *Geochim. Cosmochim. Acta 30*, 23-39. [2] Keil K. (1968) *J. Geophys. Res. 73*, 6945-4976. [3] Gao X. and Thiemens M.H. (1993) *Geochim. Cosmochim.Acta 57*, 3171-3176. [4] Gao X. and Thiemens M.H. (1993). *Geochim. Cosmochim. Acta 57*, 3159-3169. [5] Defouilloy C., Cartigny P., Assayag N., Moynier F. and Barrat J.-A. (2016) *Geochim. Cosmochim. Acta 172*, 393-409. [6] Beaudoin G., Taylor B.E., Rumble III D. and Thiemens M. (1994) *Geochim. Cosmochim. Acta 58*, 4253-4255. [7] Labidi J., Cartigny P., and Moreira M. (2013). *Nature 501*, 208-211.