CARBON ISOTOPE ANALYSES OF GRAPHITE IN ENSTATITE CHONDRITES AND UREILITES. J. Storz[1], T. Ludwig[2], A. Bischoff[1], W.H. Schwarz[2], M. Trieloff[2], [1]Institut für Planetologie, Universität Münster, Germany (j_stor06@uni-muenster.de). [2]Institut für Geowissenschaften, Klaus-Tschira-Labor für Kosmochemie, Universität Heidelberg, Germany.

Introduction: Carbon is of utmost importance for the volatile inventory of Earth. Although enriched in surface reservoirs as both organic and inorganic carbon, bulk Earth is highly depleted when compared to solar system abundances. Indeed, inner solar system material that eventually formed planetesimals and protoplanets accreting to Earth was subjected to high temperature processes causing loss of volatile carbon compounds [1,2]. A refractory phase that possibly survived high temperature processing is graphite which is present, e.g., in reduced assemblages of enstatite chondrites. These are considered as possible terrestrial building blocks, e.g., based on their isotopic similarity in oxygen, Cr and other isotopes [e.g., 3,4]. Isotopic analyses of carbon in graphite can provide important insights into the source materials involved in the accretion of terrestrial planets, as well as processes modifying primordial compositions by thermal processes in the solar nebula or on meteorite parent bodies. Previous graphite analyses yielded $\delta^{13}C$ values of –9‰ to +4‰ for enstatite chondrites [5] and –10‰ to 0‰ for ureilites [6,7]. Isotopic analyses of secondary ion mass spectrometry (SIMS) can provide additional insights by detecting variations at even smaller spatial scales.

Samples and techniques: Among 136 ureilites and 59 enstatite chondrites preliminarily studied by optical microscopy, we selected 33 polished thin sections, comprising 19 ureilites and 11 enstatite chondrites for SIMS analyses, using the Cameca ims 1280-HR at University of Heidelberg (HIP). We applied two slightly different setups (S1/S2), with a 20 keV Cs^+ primary ion beam of ~ 200 pA (S1) and ~ 400 pA (S2), and a raster size of 5 µm (7 µm during pre-sputtering). Negative secondary ions were accelerated to 10 keV. The secondary ion image was limited to 20 µm, with the dynamic transfer optical system (DTOS) being activated. ^{12}C, ^{13}C and $^{12}CH_2$ were detected simultaneously in two Faraday cups (10^{11} Ω) and one electron multiplier, respectively. The nominal mass resolving power was 5000 (S1) or 6000 (S2) for ^{13}C, and 2500 for ^{12}C and $^{12}CH_2$. Typical ^{12}C secondary ion intensities (normalised to the primary beam current) were $I_G = 6\times10^5$ cps/pA on graphite and $I_E = 3\times10^5$ cps/pA on epoxy. $^{12}CH_2/^{12}C$ ratios were used to discriminate and reject mixed analyses of epoxy and graphite and to correct for an instrumental mass bias

which depends on the CH_2/C ratio (Fig. 1). Including the time for beam centering, the analyses started after a total pre-sputtering time of ~190 s. Each analysis had 20 cycles with 7.5 s (S1) and 6 s (S2) integration time per cycle.

USGS24 graphite powder (pressed at 0.5 GPa in a closed Al-capsule) was used as a primary standard ($\delta^{13}C_{VPDB}$ = –16.049‰ ± 0.035 [8]. During S2 a second reference material GR961 was added, which is a solid natural graphite sample from Sri Lanka ($\delta^{13}C_{VPDB}$ = –6.62‰ ± 0.04), in order to correct for a systematic bias induced by the presence of CH_2 (Fig. 1) The typical repeatability of bias-corrected analyses was ± 0.6 ‰ (1sd) for USGS24 and ± 0.4 ‰ for GR961. The internal precision of an analysis (1sd) was typically < 0.15 ‰.
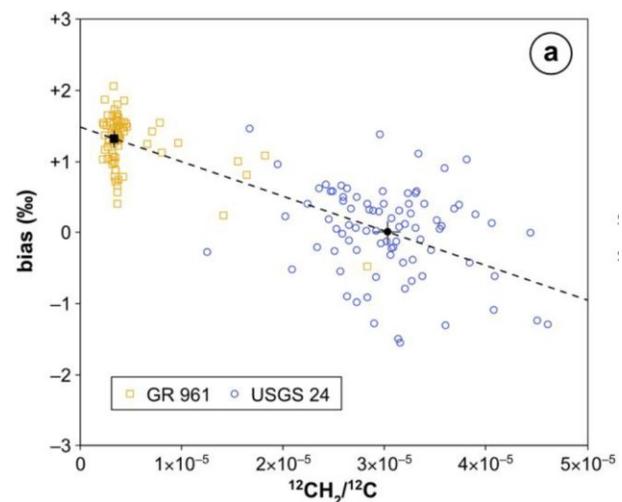

Fig. 1 Bias of measured carbon isotopic composition of graphite standards depending on presence of CH_2.

Results and discussion: Graphite in enstatite chondrites shows remarkably distinct isotopic compositions (Fig. 2) between silicate-associated graphite (SAG) with a restricted compositional range of $\delta^{13}C_{VPDB}$ = –4 to +2‰, and metal-associated graphite (MAG) with a more diverse $\delta^{13}C_{VPDB}$ ranging between –20‰ and +14‰. While we cannot exclude parent body processes, we rather relate the diversity of carbon isotopic compositions of MAG to precursor solar nebula material [9].

Isotopic composition of graphite in ureilites is shown in Fig. 3: Graphite in coarse-grained ureilites is within previously reported ranges between –9‰ and 0‰ [6,7] and shows relatively small intra-sample variations. Fig. 4 confirms the correlation of isotopic composition and Fa content of olivine (oxygen fugacity) previously noticed by [7]. On the other hand, graphite in fine-grained ureilites extends the $\delta^{13}C_{VPDB}$ range to +11‰, with significant isotopic intra-sample heterogeneity (up to +14‰, see Fig. 3). Our new data follow a trend assumed to be caused by smelting [e.g., 7], a more detailed discussion is in preparation [10].
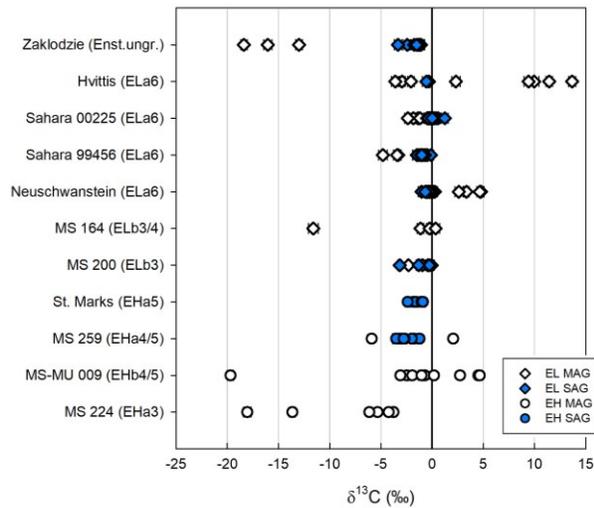

Fig. 4 Correlation of carbon isotopic and olivine composition in ureilites: While graphite of coarse-grained ureilites falls onto a trend recognized by [7], graphite in fine-grained ureilites could be explained by smelting.

Fig. 2 $\delta^{13}C_{VPDB}$ of metal- and silicate-associated graphite (MAG, SAG) in enstatite chondrites. Error bars are 2σ, mostly smaller than symbol size.
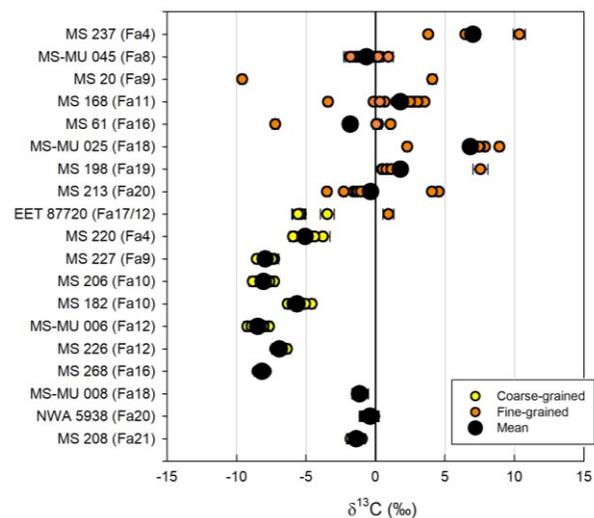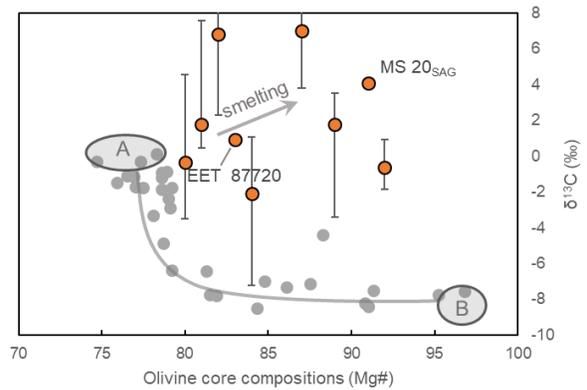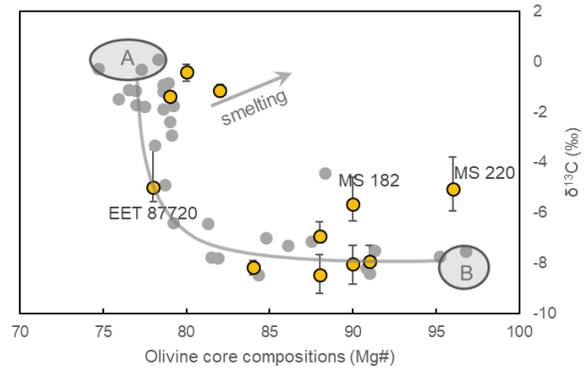

Fig. 3 Carbon isotopic composition of graphite in coarse- and fine-grained ureilites. Fayalite content of olivine is also indicated.

References:
[1] Gail H.-P. and Trieloff M. (2017) *Astronomy & Astrophysics 606*, A16 [2] Marty B., Alexander C. M. O. and Raymond S. N. (2013) *Reviews in Mineralogy and Geochemistry 75*, 149–181 [3] Dauphas N., Chen J. H., Zhang J., Papanastassiou D. A., Davis A. M. and Travaglio C. (2014) *Earth and Planetary Science Letters 407*, 96–108 [4] Fischer-Gödde M. and Kleine T. (2017) *Nature 541*, 525–527 [5] Grady M. M., Wright I. P., Carr L. P. and Pillinger C. T. (1986). *Geochimica et Cosmochimica Acta 50*, 2799–2813 [6] Grady M. M. and Wright I. P. (2003) *Space Science Reviews 106*, 231–248 [7] Barrat J.-A., Sansjofre P., Yamaguchi A., Greenwood R. C. and Gillet P. (2017) *Earth and Planetary Science Letters 478*, 143–149 [8] Coplen T. B., Brand W. A., Gehre M., Gröning M., Meijer H. A. J., Toman B. and Verkouteren R. M. (2006) *Analytical chemistry 78*, 2439–2441. [9] Horstmann M., Humayun M. and Bischoff A. (2014) *Geochimica et Cosmochimica Acta 140*, 720–744 [10] J. Storz, T. Ludwig, A. Bischoff, W.H. Schwarz, M. Trieloff (2021) in prep.