A coordinated in situ NanoSIMS, HR-SEM and TEM search for presolar grains in an ALHA77307 chondrule rim

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Only recently, fine-grained rims around chondrules (FGRs) have been reported to contain presolar grains [e.g.,1, 2]. Competing hypotheses explaining formation history of FGRs are namely formation in the solar nebula or as a result of meteorite parent-body alteration processes [3]. FGRs and interchondrule matrix material do not differ chemically or mineralogically except for the grain size of the respective constituent minerals [4]. From the primitive CO3.0 chondrite ALHA 77307 containing a 390 μm x 300 μm large porphyritic chondrule surrounded by a FGR of 30 μm - 75 μm thickness, a transparent thin film suitable for TEM studies was prepared with a new preparation technique, ArIS [5]. Subsequently, 2,200 μm^2 of the FGR part of the thin film was analyzed with the NanoSIMS 50 ion probe in Mainz to search for O-rich presolar grains. Obtained isotope images, HR SEM images and TEM images of the same area were superimposed to unambiguously relocate the presolar grains among the surrounding solar material in the TEM. We detected 4 oxygen anomalous grains (3 silicates and one oxide), showing excesses in their $^{17}O/^{16}O$ ratio relative to the solar value. These grains represent relative abundances of ~ 70ppm and ~ 33ppm for the silicates and oxides, respectively. All grains are Group I which to date constitute the bulk of identified presolar O-rich species forming around low mass RGB/AGB stars. One presolar silicate is a crystalline fayalitic olivine, 180 nm x 40 nm in size. The grain is embedded in a groundmass comprising fine-grained Fe-rich silicates, refractory silicates, sulfides and Fe-Ni metal. There is no microscopically observable evidence of equilibration and this absence more likely favours the solar nebula accretion hypothesis rather than parent body alteration, a conclusion previously obtained only by SEM and NanoSIMS studies in the case of ALHA 77307 [e.g., 6].

[1] Haenecour & Floss (2012) *LPSC*, XL III, # 1107. [2] Leitner *et al*. (2012) *MAPS*, **47**, A394. [3] Metzler *et al*.(1992) *GCA*, **56**, 2873. [4] Brearley (1993), *GCA*, **57**, 1521. [5] Stojic & Brenker (2010) *EJM*, **22**, 17-21. [6] Davidson *et al*. (2012) *AMM*, **47**, A115.

High-precision LA-ICP-MS analysis of microanalytical reference materials for environmental research

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The high spatial resolution available with LA-ICP-MS microanalysis of speleothems, biogenic calcium carbonates, bones and teeth holds the promise to improve the understanding of past climate conditions and environmental change. However, there are analytical problems with this method, such as interferences, elemental fractionation and matrix-dependent mass load effects using non-matrix-matched microanalytical reference materials (MRM) [1]. We therefore have investigated new carbonate MACS-1, MACS-3 and phosphate MAPS-4, MAPS-5, STDP5, Durango apatite MRM by a sector-field ICP-MS coupled either with 213 nm or 193 nm Nd:YAG nanosecond (ns) lasers, or a 200 nm Ti-sapphire based femtosecond (fs) laser.

Our studies show that many masses are affected by interferences, such as $^{24}Mg^{++}$ by $^{48}Ca^{++}$ in the carbonate and $^{47}Ti^{+}$ by $^{31}P^{16}O^{+}$ in the phosphate matrix. Elemental fractionation and mass-load-dependent matrix effects have been detected for the ns laser systems. They are small for refractory lithophile elements, such as Ba and Sr (< 5 – 10%). For chalcophile/siderophile trace elements with low boiling points (e.g., Pb, Zn) these effects are high (up to 20 - 40%) and different for the NIST silicate glasses, commonly used for calibration and the carbonate and phosphate MRM. Experiments with the femtosecond laser demonstrate that these matrix-related effects are negligibly small with this system [2]. This means that NIST glasses are suitable as calibration material [3] for carbonate and phosphate LA-ICP-MS microanalyses when using fs-UV lasers. They are also appropriate for the determination of lithophile element concentrations in environmental samples when using UV-ns lasers. However, when using ns lasers, matrix-matched calibration is still preferred for an accurate analysis of chalcophile/siderophile and volatile elements.

To further characterize the few available carbonate and phosphate MRM, we have analyzed them using the different laser ablation systems. Overall analytical uncertainties at the 95 % confidence level are about 5 – 10% for most elements. Our fs-UV laser results agree well with available reference values.

[1] Jochum *et al*. (2012) *Chem. Geol*. **318-319**, 31-44. [2] Weis *et al*. (2013) this conference. [3] Jochum *et al*. (2011) *GGR* **35**, 397-429.

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