CONSTRAINTS ON VOLATILE DEPLETION FROM CHONDRITE MATRIX.

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Introduction: The mechanism by which the inner Solar System became depleted in volatile elements continues to be a matter of debate. Although many models [eg. 1-7] have been proposed, no one process has received universal acceptance. A major complicating factor has been the difficulty of obtaining reliable compositional data, for large numbers of elements, from specific chondritic components.

Carbonaceous chondrites have something of a conglomeratic make-up, with each component (eg. chondrules, matrix etc.) differing in its relative volatile element abundance. Attempts have been made to analyse separated components [eg. 8], but trace and minor element data for chondrules and matrix have (until recently) been sparse. This arises from the difficulty in separating a sufficient quantity of sample from the bulk chondrite without contamination from adjacent components for instrumental multi-element analysis. Recent work using laser ablation ICP-MS [7] provided trace and minor element data for matrix from a large number of chondrites, but only as element ratios rather than absolute abundances. Our current work seeks to overcome the above limitations.

Method: Our approach involves solution Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analyses of microsampled separates. This technique allows for a ∼100µg sized homogeneous sample of a representative component to be removed from a chondrite in a highly controlled manner, which is then analysed via solution ICP-MS, resulting in absolute element abundances for the target area.

Separate extraction. A New Wave Micromill was used to drill pre-characterised areas (each ~100µg in mass) of Allende (CV3) matrix. The sample was milled through a droplet of MQ H_2O which not only cooled the mill bit, but also trapped the separate in suspension [9]. Upon completion of milling, the droplet was pipetted off the sample surface and placed on a pre-weighed 99.99% pure gold weighing boat resting on a hotplate. Here the water evaporated leaving the separate encrusted onto the surface of the gold boat. The boat plus separate was then re-weighed to determine the mass of the drilled separate (to an accuracy of ~0.8µg).

Digestion. The weighing boat complete with sample was then transferred to a cleaned savilex vial. A holmium spike was added to the separate prior to beginning a standard $HF:HNO_3$ digestion. At the completion of the initial HF stage the gold boat was removed and rinsed with MQ H_2O ensure transfer of as much sample as possible.

Solution ICP-MS. Upon complete digestion, the sample was dried down and then taken up in 2 ml 2% HNO_3 giving a final solution corresponding to a 20,000 fold dilution. The solution was then analysed using an Agilent 7500s ICP-MS fitted with a PFA micro-flow nebuliser operating at ~200µl min^{-1}, allowing 10minutes of signal for analysis. Detection limits for most elements are below 5 ppt and often below 1 ppt, equivalent to 0.02 ppm in the solid sample.

Re-characterisation. Once milling had been completed, the sample was re-polished a further 50µm and investigated via Back Scattered Electron (BSE) and element montages in a LEO-Scanning Electron Microscope (SEM). This allowed for the construction of a 3D view of the sample to confirm that no components other than matrix had been milled (see Fig. 1)
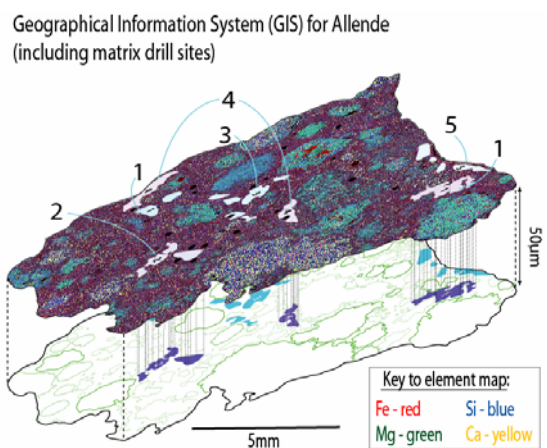

Fig. 1. Schematic to show how a thick section is analysed by SEM EDS, milled, and then re-polished and re-analysed, to ensure that no contamination of separated material has occurred.

Results: We chose a range of elements with properties spanning refractory to highly volatile, chalcophile, siderophile and lithophile. This array will be extended as the technique is developed. At this early

stage however, these data allow for a comparison between Allende bulk and matrix separates to be made with regards to volatile depletion (see Fig. 2). We ran a total of 5 matrix separates from Allende. External reproducibility for most elements was excellent (as indicated by error bars in Fig. 2) with only Ge, Pb, and Cd displaying a greater level of heterogeneity.

Our results show that for refractory elements (≥1300K) matrix is between 0.8 and 1.3 × CI compared with a bulk composition 1.5 – 2.0 × CI as suggested by previous studies [e.g. 7]. Moreover, whereas the depletion of volatile elements in the bulk composition affects all elements with 50% condensation temperatures of 1532 K or less (Co), our new matrix analyses indicate that elements with 50% condensation temperature as low as 1000 K (As and Sb) retain CI relative abundances. Finally, as previous LA-ICP_MS analysis [7] has indicated, the trace element pattern for CV matrix does not show the monotonic volatile depletion trend observed in bulk.
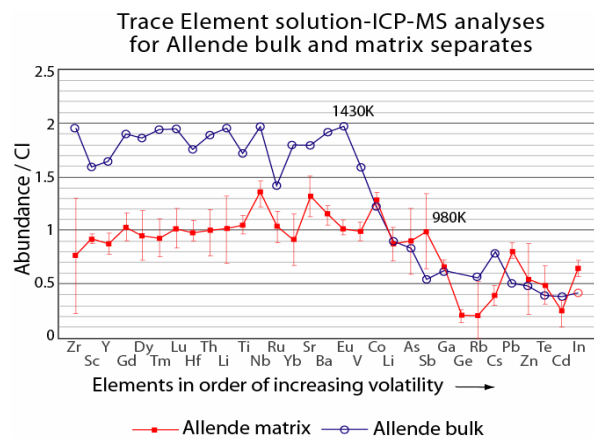

Trace Element solution-ICP-MS analyses for Allende bulk and matrix separates

Fig. 2

Discussion and Conclusions: It has been suggested that the failure to observe CI-like compositions in CC matrix is due to the addition of refractory-rich, volatile-depleted material e.g. chondrule fragments [11]. Estimating the abundance of chondrule fragments in matrix is problematic, but trace element data can provide a constraint. To modify C3 matrix compositions from a proposed CI-like starting point would require addition of several ten's of percent volatile-depleted chondrule (or chondrule-related) materials [11]. If this material was fragmented bulk chondrule [3,11] we would expect an excess in refractory elements. Previous LA-ICP-MS data suggested no such excess [7]. Our data confirm that result: refractories in Allende matrix show no excess over CI. Alternatively, if fragmented chondrule mesostasis is added instead of fragmented bulk chondrules [e.g. 11], additional prob-

lems are encountered. Chondrule glass is enriched in most refractory elements to ~×10 CI [12]. Sc and V, substituting in chondrule ferromagnesian silicates, are at ×5 CI and ×0.9 CI, respectively [12]. The refractory trace element signature of chondrule glass (substantial excess in most elements, more modest Sc excess, and no V excess), has not been detected in C3 chondrite matrix in this work, or in previous studies [7,13,14,15]. In summary, no available compositional data for carbonaceous chondrite matrix support addition of a substantial fragmental chondrule component.

Analysis of separated Allende chondrules is currently underway to assess the potential for chemical complementarity between chondrules and matrix. However, a number of relevant observations can already be made: 1) matrix is depleted relative to CI composition 2) the absence of a monotonic depletion in volatiles in CV matrix, and its presence in bulk, suggests the existence of some complementarity between chondrules and matrix 3) no enrichment of refractory elements in matrix is observed. The fact that matrix is depleted relative to CI, and that the depletion is not due to 'dilution' by fragmental chondrule material, are observations which contradict predictions of the popular two-component model [1].

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