NUCLEOSYNTHETIC TUNGSTEN ISOTOPE ANOMALIES IN ACID LEACHATES OF THE ORGUEIL, MURCHISON AND ALLENDE CARBONACEOUS CHONDRITES.

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Introduction: The sequential dissolution of primitive chondritic meteorites is a useful approach to probe the nature, origin, distribution and fate of the carriers of nucleosynthetic anomalies present in the solar nebula [*e.g.* 1-4]. Here we present W isotope data for acid leachates of the Orgueil, Murchison and Allende chondrites. The data provide insight into the parent body processing of presolar materials, W nucleosynthesis and the required correction of nucleosynthetic W isotope anomalies for the ^{182}Hf-^{182}W decay system.

Samples and methods: The W isotope measurements were performed on W cuts obtained in a Zr and Te leachate study, where powdered whole rock samples of Orgueil (CI, 1.0 g), Murchison (CM2, 1.5 g) and Allende (CV3, 2.0 g) were sequentially digested using the following sequence (see [3,5]):

1:	50% HAc	1 day, 20°C
2:	4 M HNO_3	5 days, 20°C
3:	6 M HCl	1 day, 80°C
4:	13.5 M HF+3 M HCl	4 days, 100°C
5:	conc. $HF+HNO_3$	3 days, 170 °C, bomb

The W cuts were purified by standard anion exchange chromatography. The W isotope compositions of the leachate samples were measured using the *Thermo Neptune Plus* MC-ICP-MS at the University of Münster. Instrumental mass bias was corrected using the exponential law and $^{186}W/^{184}W=0.92767$. Tungsten isotope data are reported as deviations from the terrestrial bracketing standard: $\varepsilon^{i}W=[(^{i}W/^{184}W)_{sample}/(^{i}W/^{184}W)_{std}-1]\times10^{4}$. Uncertainties correspond to 95% confidence intervals. Blank corrections were significant for some samples with low W concentrations and an uncertainty of 50% was assumed and propagated for the correction.

Results: The amount of W released in the different leaching steps is broadly similar for all chondrites examined and agrees well with a previous W leachate study of the Murchison chondrite [6] (Fig. 1). Small fractions of W are released in the first and the last digestion steps, higher amounts in steps 2 and 3 and the largest fraction is associated with the HF-HCl step, which dissolves silicate minerals.

The largest $\varepsilon^{183}W$ anomalies are observed for Orgueil (Fig. 2), ranging from ~+6.5 (step 1 and 4) to ~-40 (step 5). The anomalies in Murchison are ~half the magnitude of those of Orgueil (+3 for step 1 and -19 for step 5), in good agreement with the Murchison leachate data of [6]. For Allende the maximum value

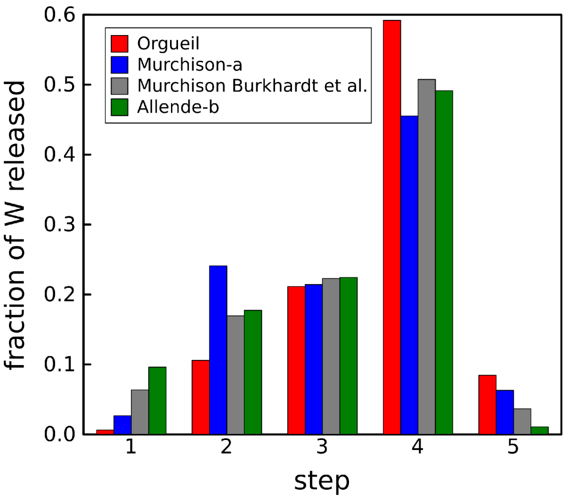

Fig. 1: Fraction of W released in different leaching steps. W concentrations in the samples were obtained after ion-exchange chromatography and a relative uncertainty of ~25 % must be assumed. Also shown is the Murchison data of [6] (for comparison steps L4 and L5 of [6] were combined to step 4 such that L6 is now step 5).

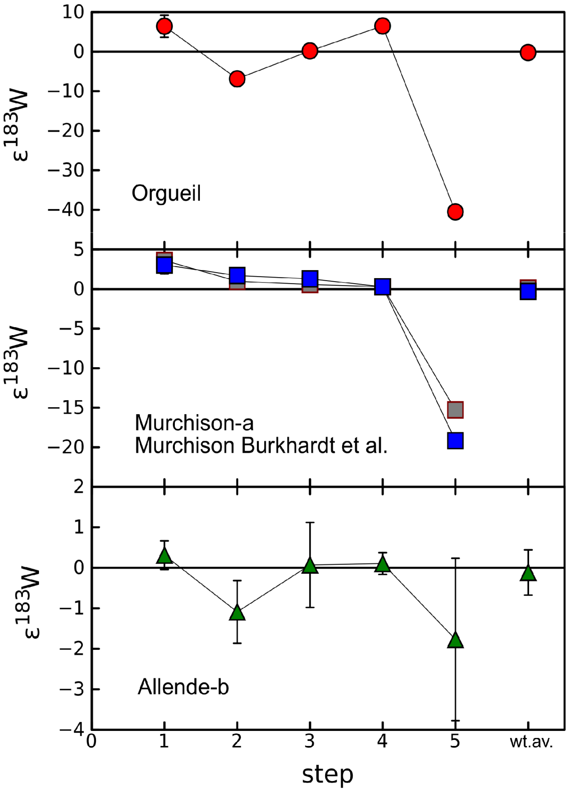

Fig. 2. $\varepsilon^{183}W$ vs. leachate step for the sequential dissolution of Orgueil, Murchison and Allende. Also shown are W data from [6] (grey symbol). Please note the different scales. The weighted average (wt. av.) of the leachates is isotopically normal for each sample.

is -1.7 (step 5), however, only the anomaly of step 2 (-1.1) is clearly resolved from the terrestrial standard. The weighted average of the W isotope compositions is isotopically normal for all samples, consistent with bulk rock measurements [*e.g.* 7] and thus indicates that all important nucleosynthetic W carriers were taped.

Not only the magnitude of the isotopic anomalies, but also the overall pattern is different for each chondrite type: while the ε^{183}W values decrease from step 1 to step 5 for Murchison, Orgueil (and to a lesser extent Allende) show an increase from step 2 to step 4. This is unlikely the result of an analytical artifact, because ε^{183}W and ε^{182}W of the different leachates are well correlated (R^2=0.99) (Fig. 3).

Discussion: *Comparison to previous W leachate data.* The data presented here are in good agreement with the W isotope leachate study of [6] (Fig. 1-3). In the two studies different samples of Murchison were sequentially digested in slightly different protocols, W was separated using different ion-exchange procedures [3,6] and W measurements were performed on separate MC-ICPMS instruments (*Nu Plasma* and *Neptune Plus*, respectively). The good agreement thus highlights the robustness of the data and the absence of analytical artifacts in our measurements.

Nature and origin of W isotope anomalies. In an ε^{183}W vs. ε^{182}W diagram (Fig. 3) all the leachate data define a positive correlation with a slope of 1.42± 0.06 and an intercept of -2.2±0.1. Single-grain SiC data [8] also plot on this correlation line. A mixing line between the W isotope composition of bulk chondrites and the s-process abundances of the stellar model [9] yields an only slightly steeper slope of 1.69. The observed W isotope variations are therefore best explained by the presence of one or more carriers of s-process W that are mixed with s-process poor components. The Zr isotope work on the same leachate fractions indicate a strong s-process contribution released from SiC in the leachate residues (step 5) [3]. Presolar SiC grains are thus most likely also responsible for the negative ε^{i}W values of those steps. However, in contrast to the Zr data, leach step 2 of Orgueil and Allende are characterized by negative ε^{i}W values, indicating the presence of an additional carrier of s-process W in these chondrites, possibly a presolar sulfide.

Processing of presolar materials – nebular or parent body? The abundance of presolar grains in different chondrite classes decreases with increasing thermal alteration: CI-CM-CV. Also the magnitude of ε^{183}W in step 5 decreases in this order. This can be interpreted as the progressive thermal destruction of an initially homogeneous mixture of presolar grains by parent body processing or alternatively the initial sampling of different amounts of matrix, which contains a homogeneous mixture of presolar grains. However, the anomaly patterns of the three chondrites are different, in particular at step 2, which shows an s-process excess for Orgueil and Allende, but a deficit for Murchison. This may either be the result of alteration on the parent body (*i.e.* redistribution of anomalous W into a new phase) or the fingerprint of dust processing in the nebula (*i.e.* not all chondrites accreted the same blend of presolar materials). In the first case the redistribution would be more severe in CI and CV than in CM (or vice versa). Given that the thermal and aqueous alteration of the latter is between CI and CV chondrites, this seems unlikely. Evidence of thermal processing of presolar materials in the nebula on the other hand might be well possible and supports the scenario proposed to explain the presence of nucleosynthetic bulk scale Mo isotope anomalies, but their absence in W [10].

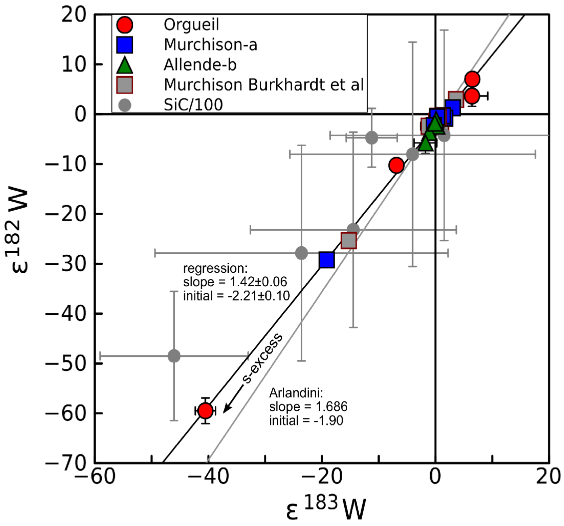

Fig. 3. ε^{182}W vs. ε^{183}W results of Orgueil, Murchison and Allende leachates are well-correlated. Also shown are SiC data of [8] and a theoretical s-process mixing line [9].

Implications for the ^{182}Hf-^{182}W dating system. An adequate correction for the presence of nucleosynthetic W isotope anomalies in planetary materials is required or the short-lived Hf-W decay system may yield incorrect age information. The data presented here fully support the correction scheme proposed by [6].

References: [1] Lewis R.S. et al. (1990) *Nature, 348,* 292–298. [2] Rotaru M. et al. (1992) *Nature, 358,* 465-470. [3] Schönbächler M. et al. (2005) *GCA, 69,* 5113–5122. [4] Qin L. et al. (2011) *GCA, 75,* 7806-7828. [5] Fehr et al. (2006) *GCA, 70,* 3436-3448. [6] Burkhardt C. et al. (2012) *ApJL, 753,* L6. [7] Kleine T. et al. (2004) *GCA, 68,* 2935-2946. [8] Avila, J.N. et al. (2012) *ApJ, 744,* 49. [9] Arlandini C. et al. (1999) *ApJ, 525,* 886-900. [10] Burkhardt C. et al. (2012) *EPSL, 357-378,* 298-307.