NUCLEOSYNTHETIC Mo AND W ISOTOPE ANOMALIES IN ALLENDE CAI. C. Burkhardt[1], T. Kleine[2] and R. Wieler[1]. [1]Institute of Geochemistry and Petrology, Clausiusstr. 25, ETH Zürich NW D84, CH-8092 Zürich. [2]Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm Str. 10, D-48149 Münster. (e-mail: burkhardt@erdw.ethz.ch).

Introduction: Ca,Al-rich inclusions (CAI) found in chondritic meteorites are thought to represent the first solids formed in the cooling solar nebula [1-3]. Consequently, they are commonly used to define the initial isotopic composition of the solar system. This composition then forms the basis for calculating ages obtained from short-lived chronometers. However, CAI also exhibit isotopic anomalies of nucleosynthetic origin (e.g. [4] and references therein). These anomalies are important for identifying stellar sources that contributed material to the solar system and for tracing solar nebula heterogeneities. However, nucleosynthetic isotope anomalies in CAI, if unaccounted, may also result in spurious age determinations.

Here we present Mo and W isotopic compositions of five Allende CAI. These data are used to evaluate the isotopic heterogeneity of the solar nebula at the time the first solids formed, and their potential implications for Hf-W dating are discussed.

Samples and methods: All CAI are from Allende and have been separated during our Hf–W study on CAI [5]. CAI A-ZH-1 to -4 are typical type B CAI. The petrographic type of A-ZH-5 is not yet known but this CAI is somewhat more fine-grained than the type B CAI and exhibits strong (pre-asteriodal?) alteration features including formation of secondary minerals and cavities (Fig.1). The W isotopic data of these CAI have been reported in an earlier Hf-W study [5]. Molybdenum cuts collected during the Hf–W chemistry were further purified using ion exchange chromatography. The Mo isotopic measurements were performed using the Nu1700 MC-ICP-MS at ETH Zürich. Instrumental mass bias was corrected by internal normalization to $^{98}Mo/^{96}Mo = 1.453171$ using the exponential law (details are given in [9]).

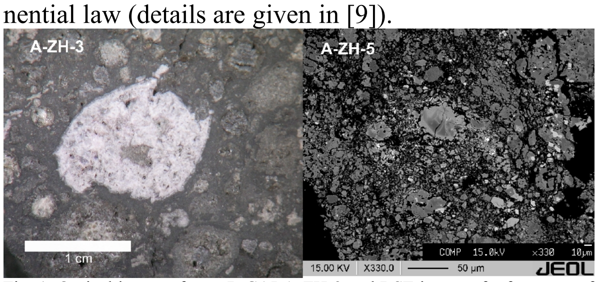

Fig. 1. Optical image of type B CAI A-ZH-3 and BSE image of a fragment of the altered CAI A-ZH-5.

Results: The Mo and W isotopic results for CAI are shown in Figs. 2 and 3 in ε-units (deviation in parts per 10,000 from the terrestrial standard value). Error bars either represent the external reproducibility (2SD) determined from repeated standard measurements or two sided student's *t* distributions ($\sigma t_{0.95,n-1}/\sqrt{n}$).

Molybdenum: All investigated CAI exhibit Mo isotopic compositions different from the terrestrial value. CAI A-ZH-5 shows anomalies of up to 22 ε-units and a w-shaped pattern characteristic for a deficit in s-process Mo isotopes relative to terrestrial Mo (Fig. 2a). All other CAI exhibit smaller anomalies and a pattern indicative of an excess in r-process isotopes relative to terrestrial Mo (w-pattern with an additional characteristic kink in $\varepsilon^{94}Mo$).

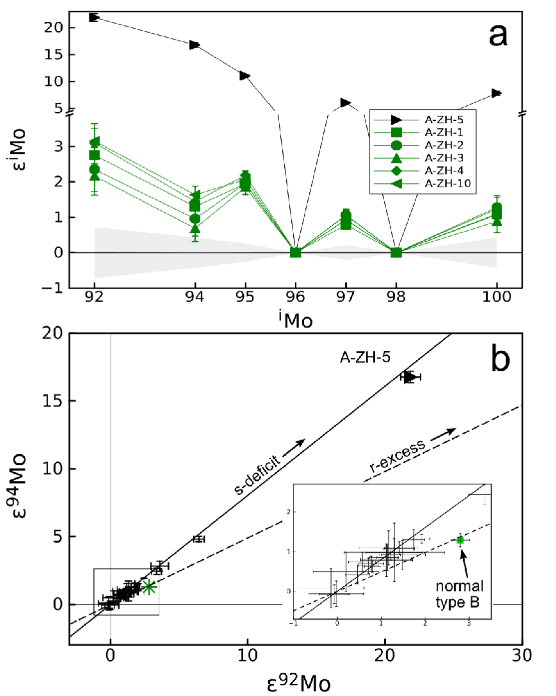

Fig. 2. (a) Mo isotope anomalies expressed in parts per 10,000 deviation from terrestrial Mo yield characteristic s-deficit (A-ZH-5) and r-excess (other CAI) patterns. (b) A-ZH-5 plots on s-deficit line defined by SiC, acid leachates from carbonaceous chondrites and bulk meteorites [9]; normal type B CAI plot on a r-excess line.

A plot of $\varepsilon^{94}Mo$ vs. $\varepsilon^{92}Mo$ (Fig. 2b) reveals that A-ZH-5 plots on a mixing line between terrestrial and s-process Mo [6,7]. Mo isotopic data for acid leachates from Murchison [8] also plot on this mixing line, as do isotopic anomalies measured in iron meteorites and bulk chondrites [9]. In contrast, type B CAI plot to the right of the s-process mixing line and are best explained by addition of an r-process component [6] to the terrestrial Mo isotopic composition.

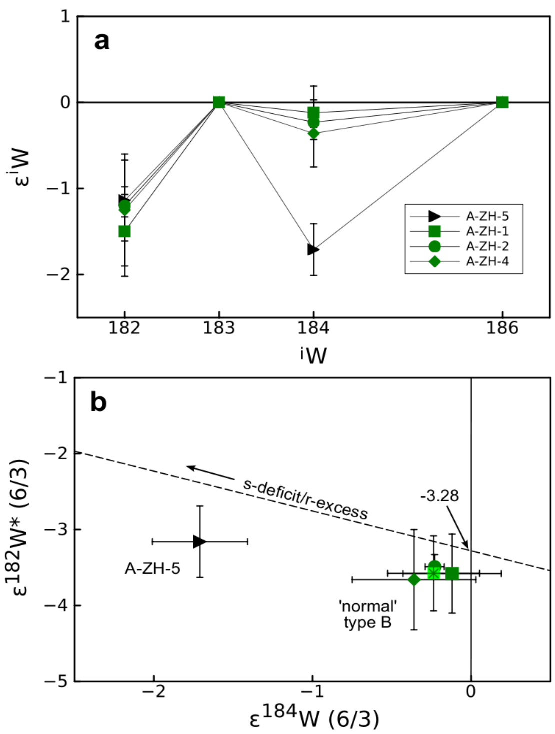

Fig. 3. (a) W isotopic composition of CAI for $^{186}W/^{183}W$ internal normalization. All samples have ^{182}W deficits, but only A-ZH-5 exhibit clearly resolved anomalies in non-radiogenic W isotopes. (b) decay-corrected $\varepsilon^{182}W^*$ and $\varepsilon^{184}W$ anomalies are negatively correlated, as expected from s-process calculations [6]; note, that the ^{182}W-^{184}W correlation suggests initial $\varepsilon^{182}W$ of CAI may be more negative than the currently accepted value of $\varepsilon^{182}W = -3.28$.

Tungsten: All the investigated CAI exhibit anomalies in radiogenic ^{182}W that result from the decay of now extinct ^{182}Hf. Clearly resolvable anomalies in the non-radiogenic isotopes of W (^{183}W, ^{184}W, ^{186}W) are only present in A-ZH-5 (Fig. 3a). The other CAI also seem to have small W nucleosynthetic anomalies but the error bar on their $\varepsilon^{184}W$ is slightly overlapping with the terrestrial value, so that these anomalies are not clearly resolved. However, corrections of the ^{182}W data for ^{182}Hf decay yields age corrected $\varepsilon^{182}W^*$ values of the CAI, which correlate with their $\varepsilon^{184}W$ values as expected from the stellar model of s-process nucleosynthesis [6] (Fig. 3b). This correlation highlights the potential presence of small nucleosynthetic W isotopic anomalies in all CAI investigated so far.

Discussion: From the Mo isotopic data it is evident that at least two groups of CAI that formed from different mixtures of nucleosynthetic components are present in Allende. One of these groups of CAI is characterized by an enrichment in r-process Mo, while the other has a deficit in s-process Mo isotopes. The presence of these anomalies suggests that either the CAI formed from too little material to sample the composition of the average solar nebula or that they formed in an area whose isotopic composition was modified by freshly injected material. The signature preserved in A-ZH-5 might be accounted for by the first of these scenarios. Unlike the other CAI, A-ZH-5 shows the same deficit in s-process Mo isotopes as characteristic for bulk planetary objects. Thus, A-ZH-5 may have formed from the same reservoir as the bulk meteorites and planets. In contrast, the r-process enriched composition of the other CAI is distinct from the composition of bulk meteorites and planets characterized by an s-process deficit. Thus, these other CAI probably formed from a different reservoir, which possibly was enriched in r-process material by injection of freshly synthesized material from a nearby supernova.

The Mo isotopic anomalies correlate with those in W as expected from nucleosynthetic theory; the W anomalies are about a factor of 13 smaller than the Mo anomalies (Fig. 4). This observation might be important for understanding why nucleosynthetic isotope anomalies in bulk meteorites are present in Mo [9], but not in W.

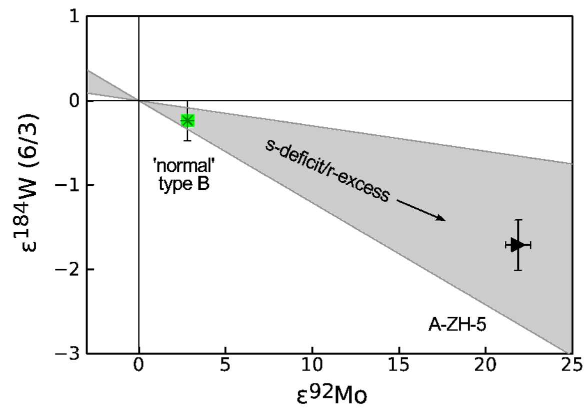

Fig. 4. Mo and W isotopic anomalies correlate with each other as expected from theoretical predictions for an s-process deficit/r-process excess relative to the terrestrial composition. Gray area represents the s-deficit/r-excess field obtained for varying the curvature parameter in the mixing equation according to the Mo/W ratios of CAI and carbonaceous chondrites.

Fig. 4 further reveals that nucleosynthetic W isotopic anomalies seem to be present in all CAI investigated so far. However, currently available Hf-W data are not precise enough to clearly resolve these anomalies. If all CAI have nucleosynthetic W isotope anomalies, then the initial $\varepsilon^{182}W$ at the time of CAI formation would be lower than the currently used value. A correction using the ^{182}W-^{184}W correlation shown in Fig. 3 suggests that the initial $\varepsilon^{182}W$ might be ~0.2 ε lower than the currently used value of -3.28±0.12. Note that the initial $^{182}Hf/^{180}Hf$ of the solar system as given by the CAI isochron is not affected by this correction.

References: [1] Grossman L. (1972) *GCA 36,* 597–619. [2] Amelin Y. et al. (2010) *EPSL 300,* 343-350. [3] Brennecka G. et al. (2010) *Science 327* 449-452. [4] Birck J. L. (2004) R*ev. in Min.&Geochem. 55,* 25-64. [5] Burkhardt C. et al. (2008) *GCA 72*, 6177-6197. [6] Arladini C. et al. (1999) *APJ 525*, 886-900. [7] Nicolussi, G.K. et al. (1998) *GCA 62*, 1093-1104. [8] Burkhardt C. et al. (2011) *LPSC 42,* #2592. [9] Burkhardt C. et al. (2011) *EPSL in review*.