

# ISOTOPIC COMPOSITIONS OF W AND Mo IN ALLENDE'S CAIS, CHONDRULES AND MATRIX: POSSIBLE LEGACY OF AQUEOUS REDISTRIBUTION OF W AND Mo FROM PRESOLAR GRAINS?

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**Puzzling isotopic signatures in fine-grained CAIs:** The most recent Hf-W isochron for calcium-aluminium-rich inclusions (CAIs) [1] is based almost entirely on 8 coarse-grained (c-g) CAIs and 6 fine-grained (f-g) CAIs from the Allende (CV3) chondrite. The isochron is tightly constrained but to get the f-g CAIs to plot on the line their measured  $\epsilon^{182}\text{W}$  first had to be corrected to remove *variable* nucleosynthetic  $\epsilon^{182}\text{W}$  that correlates with  $\epsilon^{183}\text{W}$ . The origin of this nucleosynthetic  $\epsilon^{182}\text{W}$ , which is almost negligible in the c-g CAIs, is puzzling. It was attributed by [1] to 'initial heterogeneities in the primitive solar nebula ... at the scale of individual CAI'. We find this explanation unattractive because it seems to suggest a separate (local?) reservoir of hot nebular gas for each f-g CAI. Aware that Allende was extensively altered hydrothermally, [1] also considered, but dismissed, parent body alteration as a cause of the W isotope variation in f-g CAIs, claiming that mobilization of W would have disturbed the Hf-W isochron.

Brennecka et al. [2,3] measured Mo isotopes in the same CAIs that were analysed by [1] for W isotopes. They found that the f-g CAIs plot on the 'carbonaceous' (CC) 'outer solar system' line on the  $\epsilon^{94}\text{Mo}$  v  $\epsilon^{95}\text{Mo}$  diagram of [4], with  $\epsilon^{94}\text{Mo}$  varying enormously, from -20  $\epsilon$  units (enriched in s-process Mo) to +15  $\epsilon$  units (depleted in s-process Mo); the c-g CAIs all plot together above the CC line due to enrichment of r-process Mo. To account for these observations they, like [1], invoked nebular heterogeneity. Since we find this hard to envisage, we ask why else the Mo and W isotopic compositions of the f-g CAIs might differ from those of the c-g CAIs, and why the f-g CAIs plot far apart along the CC line on the  $\epsilon^{94}\text{Mo}$  v  $\epsilon^{95}\text{Mo}$  diagram. We appeal here to hydrothermal alteration.

**A possible solution:** Brennecka et al. [2,3] noted that Mo isotopes in leachates from Murchison (CM2), obtained by [5] using increasingly aggressive acids, also spread widely (from -40 to +25 in  $\epsilon^{94}\text{Mo}$ ) along the CC line. We suggest that if acid leaching of a CM chondrite in the laboratory can yield Mo extracts that spread far along the CC line, then similar leaching might have happened naturally in the Allende parent body where, instead of acids, there would have been a succession of aqueous metamorphic fluids, released as the temperature rose. We imagine that Mo in the first warm flush of fluid came from the more-easily dissolved presolar grains, depleted in s-process Mo, and that later on, hotter fluid scavenged Mo from less-soluble s-process-enriched presolar carriers like SiC. Successive flushes of fluid would have transferred their Mo solute to separate f-g CAIs to account for the diverse  $\epsilon^{94}\text{Mo}$  values of the latter. We do not know how the process might have worked, but suspect it was linked to disequilibrium metamorphic changes in Allende, involving dehydration and rehydration. We suggest that the c-g CAIs kept their original Mo, perhaps in refractory metal nuggets (RMNs) [2], and escaped significant alteration because of their grain size. We suggest that the f-g CAIs were isotopically identical to the c-g CAIs to begin with but, having few, if any, RMNs [2], they had little initial Mo, so their Mo isotopes became dominated by Mo that arrived later in solution.

We suggest that W was transferred like Mo from presolar carriers into the f-g CAIs. The Hf-W isochron was undisturbed, we think, because the empirical correction made by [1] for nucleosynthetic  $\epsilon^{182}\text{W}$  effectively removed the  $\epsilon^{182}\text{W}$  that travelled with correlated  $\epsilon^{183}\text{W}$  from the presolar carriers (like W in the Murchison leachates of [5]), while radiogenic  $^{182}\text{W}$  was safely sealed within unaltered silicate grains where its lithophile parent,  $^{182}\text{Hf}$ , decayed.

Our suggestions appear to be consistent with the facts (1) that Mo is a mobile element, as is seen, for example, in its behaviour in CM chondrites [6], and (2) that most elements whose isotopes have been measured in CAIs (for example Ti, Sr and Ba [2]) are isotopically similar in both c-g and f-g CAIs, whereas W and Mo stand out as being isotopically different in the two [2]. Also, (3) some c-g CAIs (including one of those analysed by [1]) are perhaps thermally modified f-g CAIs because they have the distinctive Group II REE pattern which is typical of f-g CAIs.

**Chondrules and matrix:** Budde et al. [4,7] found that chondrules in Allende are depleted, and matrix is enriched, in s-process W and Mo relative to the bulk meteorite. They presented this 'nucleosynthetic isotopic complementarity' as a key constraint for chondrule formation. However, the constraint is puzzling because it seems hard to reconcile it with any chondrule-forming model [see 8], though we tried to accommodate it with our splashing model [9]. We propose here that the complementary isotopic relationship of Allende's chondrules and matrix has no bearing on chondrule formation because it arose later, during hydrothermal alteration, when s-process-depleted W and Mo were leached from presolar grains in the matrix and transferred into the chondrules.

**References:** [1] Kruijer T. S. et al. (2014) *EPSL* 403:317-327. [2] Brennecka G. A. et al. (2017) *LPSC* abstract #1619. [3] Brennecka G. A. et al. (2018) *LPSC* abstract #2429. [4] Budde G. et al. (2016) *EPSL* 454:293-303. [5] Burkhardt C. et al. (2012) *EPSL* 357/8:298-307. [6] Friedrich J. M. et al. (2018) *GCA* 237:1-17. [7] Budde G. et al. (2016) *PNAS* 113:2886-2891. [8] Zanda B. et al. (2018) 81<sup>st</sup> Meteoritical Society Meeting abstract #6171. [9] Sanders I. S. and Scott E. R. D. (2018) Chapter 14 in *Chondrules*, Cambridge University Press.