CHONDRULE-MATRIX ISOTOPIC COMPLEMENTARITY, AND ISOTOPE ANOMALIES IN W AND MO IN FINE-GRAINED CAIS: DO THEY RESULT FROM METAMORPHISM IN ALLENDE?

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Introduction: Two unresolved issues surround the interpretation of isotope patterns in the chondrules, matrix and Ca-Al-rich inclusions (CAIs) of the Allende (CV3) chondrite: (a) the origin of the complementary isotopic anomalies between the chondrules and matrix [1,2] and (b) the source of the anomalies in ^{182}W and ^{183}W, and also anomalies in Mo isotopes, in fine-grained (f-g) CAIs [3,4]. All these anomalies have been attributed by [1-4] to processes in the nebula before accretion. Here we question the likelihood of the proposed nebular mechanisms, and suggest, instead, that the anomalies are better explained through parent body metamorphism.

Chondrule-matrix isotopic complementarity: Budde et al. [1,2] found an excess of s-process nuclides of W and Mo in Allende's matrix, and a corresponding deficit of these nuclides in its chondrules, relative to the bulk meteorite, which is isotopically normal. They regarded this ‘isotopic complementarity’ as a facet of chemical complementarity [5] and believed that chondrules and matrix were made together from a single reservoir of nebular dust with solar chemical and isotopic composition. They proposed that only some of the presolar carriers of Mo and W in the nebular dust (those with an s-process deficit) ended up losing their Mo and W to chondrule melt droplets, leaving a balance of s-process-enriched Mo and W in the residual dust that became the matrix. They argued that isotopic complementarity ruled out the formation of chondrules from molten protoplanets, since the latter would have been isotopically normal.

We contend that droplets of molten nebular dust would also have been isotopically normal, and fail to see, as did [6], how any nebular ‘flash melting’ process could affect specific isotopically distinct presolar grains from the dust, and leave other isotopically different grains unmelted. Another problem is that isotopes of many other elements, such as Ba [2], would also be expected to show isotopic complementarity between s-enriched and s-depleted nuclides, but do not.

A metamorphic origin: We propose here, in line with the ideas of Yokoyama et al. [7] who studied Os isotopic anomalies in acid-resistant residues from chondrites, that Allende's isotopic complementarity was produced during parent body metamorphism. Allende had a protracted history of metamorphism [8], and W and Mo in Allende are known from petrographic evidence [9,10] to have been mobilized. We suggest that the first warm flush of aqueous fluid, released during the initial breakdown of hydrous minerals and organic matter, attacked the most easily dissolved presolar grains, which were those with a deficit of s-process Mo and W. We suggest that the fluid only travelled a short distance before combining with anhydrous phases, e.g. olivine or glass in chondrules, where it deposited its isotopically anomalous Mo and W in secondary carrier phases. Thus the bulk meteorite remained isotopically solar, but chondrules became s-process depleted, and matrix was left correspondingly s-process enriched.

Our thinking was stimulated by the results of leaching experiments on CI and CM chondrites [11,12] in which the most easily dissolved presolar carriers have a large deficit of s-process Mo and W, and the most resistant carriers (insoluble residues) have a correspondingly large excess. We see the acids used in the laboratory as a proxy for metamorphic fluids in nature, and believe that Allende's matrix, at the outset, was similar to that of CI or CM chondrites. Our interpretation is consistent with the fact that the leachates define a clear correlation line on a ε^{94}Mo v ε^{95}Mo plot, and also on a ε^{182}W v ε^{183}W plot, and that the chondrules and the matrix plot precisely on each of these correlation lines, as shown by [1,2].

If our interpretation is correct, then isotopic complementarity has no bearing on chondrule formation, and the possibility that chondrules were formed by the splashing of molten planetesimals remains open.

Allende's fine-grained CAIs and the Hf-W CAI isochron: The Hf-W isochron for CAIs [3] is important. It gives the initial ^{182}Hf/^{180}Hf ratio for the solar system and thus calibrates the Hf-W chronometer which has been widely used to date events during the first few million years. It also gives the initial value of ε^{182}W, and so calibrates the tungsten-deficit dating method for iron core formation. The CAI isochron is based on 8 coarse-grained (c-g) CAIs and 6 f-g CAIs from Allende, and just two CAIs from other CV meteorites. The isochron is well constrained but to get the f-g CAIs to plot on the line [3] first corrected the measured ε^{182}W using an empirical method to remove a variable amount of nucleosynthetic ε^{182}W which correlates with nucleosynthetic ε^{183}W.

The origin of this nucleosynthetic ε^{182}W, which is almost negligible in the c-g CAIs, is puzzling. Kruijer et al. [3] considered the possibility of metamorphic mobilization of W within the parent body, but they rejected this idea in part because they felt that such mobilization of W would have disturbed the isochron and rendered the Hf-W chronometer unusable, yet Hf-W ages have proven to be entirely consistent with ages based on other chronometers. Instead they opted for the formation of the isotopically-uniform c-g CAIs and the isotopically variable f-g CAIs in separate contemporaneous nebular reservoirs, with the f-g CAIs coming from an environment having 'initial heterogeneities in the primitive solar nebula ... at the scale of individual CAI'.

We find this explanation unappealing because the idea of a heterogeneous hot gas from which the f-g CAIs would have condensed seems improbable, and also because the Al-Mg isotopic systematics of CAIs suggest that all the CAIs in CV chondrites were made in a very brief interval of time (<20,000 years) presumably in a single reservoir [13].

We believe, instead, that the f-g CAIs were initially the same, isotopically, as the c-g CAIs. We suggest that the correlated ε^{182}W and ε^{183}W anomalies in the f-g CAIs were carried in during the metamorphic mobilization of W from carriers depleted in s-process nuclides, as we infer for the W isotopic anomalies in chondrules and matrix. We suggest that the c-g CAIs kept their original W, perhaps in refractory metal nuggets (RMNs) [14] and that the f-g CAIs, having few, if any, RMNs, had little initial W, so their W isotopes became dominated by the W that arrived in solution.

We suggest that, despite this movement of W, the Hf-W isochron remained intact because the empirical correction made by [3] for nucleosynthetic ε^{182}W stripped out only the ε^{182}W that travelled with correlated ε^{183}W from the presolar carriers. This W was presumably located in secondary phases, unlike the radiogenic ^{182}W that would have remained locked up undisturbed in its host silicate, presumably fassaite (an Al-rich pyroxene) [10] where its parent isotope, ^{182}Hf, would have been entirely located. This view is supported by the excellent correspondence between the correlation line for ε^{182}W-ε^{183}W in leachates from CI and CM chondrites [12] and the correlation line for ε^{182}W-ε^{183}W in the f-g CAIs [3].

Mo isotopes in CAIs: Burkhardt et al. [4] found that Mo, like W, is isotopically uniform in Allende's c-g CAIs, but is very different, with an enormous deficit in s-process Mo, in the only f-g CAI (sample A-ZH-5) that they measured. Subsequently, isotopic data for several more f-g CAIs have been presented in abstracts [15,16] and each was found to be different from the others, and different from the c-g CAIs, with all of them falling on, or close to, the ε^{94}Mo v ε^{95}Mo correlation line. Both excesses and depletions of s-process Mo were seen. Again, we believe that this pattern is best explained by metamorphic mobilization, in this case of both s-process enriched and s-process depleted Mo, presumably at different stages during the metamorphic evolution of the parent body.

The ε^{94}Mo v ε^{95}Mo correlation line for f-g CAIs, for chondrules and matrix, and for CI and CM leachates is, incidentally, exactly the same as the so-called CC line of [2] on which all bulk meteorites from the CC reservoir plot. We note that if parent body mobilization of Mo were to have operated in an open system, rather than the closed system considered above, then isotopically anomalous Mo would have been added to, or removed from, bulk rocks. Thus, open system behaviour may have been responsible for shifting bulk rocks along the CC line. In fact, such variation is observed in Allende, whose Mo isotopic composition varies along the line from one specimen to another, as reviewed in Fig. S2 of [2].

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