MOLYBDENUM ISOTOPE SYSTEMATICS OF CALCIUM-ALUMINUM-RICH INCLUSIONS.
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Introduction: Ca-Al-rich inclusions (CAIs) are the oldest solids formed in the Solar System, and can thus provide unique insights into its earliest evolution. For instance, it has been proposed that CAIs formed from the earliest material infalling from the Solar System's parental molecular cloud and, therefore, recorded the isotopic composition of the initial disk [*e.g.*, 1]. In this context, nucleosynthetic Mo isotope anomalies are of particular interest, because they have great potential to provide critical information not only on the origin of CAIs, but also on their role in establishing the fundamental dichotomy between non-carbonaceous (NC) and carbonaceous (CC) meteorites [2]. However, the full extent as well as the origin of such anomalies in CAIs are still poorly understood, which is due to a general scarcity of data and the fact that virtually all current data were obtained for CAIs from CV chondrites (primarily Allende) for which effects of parent-body processing cannot be *a priori* ruled out. Here, we address this issue by investigating Mo isotope anomalies in various types of CAIs from multiple CV chondrites with variable degrees of aqueous alteration and thermal metamorphism.

Materials and Methods: To date, we have obtained new high-precision Mo isotope data for nine coarse-grained (cg) CAIs from oxidized (CV_{OX}: Allende, NWA 3118) as well as reduced (CV_{RED}: Efremovka, Leoville) CV chondrites. This sample set comprises compact Type A (CTA), Type B, and forsterite-bearing Type B (FoB) CAIs, some of which have been petrographically characterized in previous publications [*e.g.*, 3]. All samples were carefully cleaned and then digested in PFA vials on a hotplate using HF-HNO_3-$HClO_4$ and HNO_3-HCl mixtures. After dissolution, chemical compositions were determined on small aliquots using an *iCAP RQ* ICP-MS. Molybdenum was separated from the sample matrix by ion exchange chromatography following established procedures [2], and the Mo isotope compositions were measured using a *Neptune Plus* MC-ICP-MS equipped with an *Apex3* desolvator. The data are internally normalized using $^{98}Mo/^{96}Mo$ and reported as ε-unit deviations (parts per 10^4) relative to the bracketing solution standard (NIST SRM 3134).

Results: All investigated samples display flat (mostly Group I) REE patterns with strong enrichments (~10–20×) relative to CI chondrites. Similarly, Mo concentrations are highly elevated and vary between about 5 and 18 µg/g (~5–18× CI), consistent with previous data for cg-CAIs [4,5]. Overall, the samples show well-resolved $\varepsilon^{i}Mo$ anomalies and *w*-shaped Mo isotope patterns indicative of a nucleosynthetic origin. However, while most samples display a pronounced kink at $\varepsilon^{94}Mo$ that is typical for cg-CAIs [6], two Type B CAIs stand out by having distinct Mo isotope patterns (Fig. 1). For the following discussion we refer to the former as '*ordinary*' and to the latter as '*unusual*' cg-CAIs.

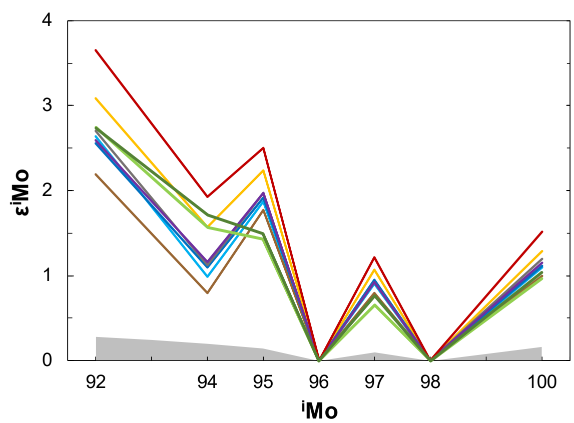

Fig. 1. *Mo isotope patterns for nine cg-CAIs analyzed here. External reproducibility shown as gray envelope.*

Mo Isotope Systematics of cg-CAIs: In Mo isotope space, the ordinary cg-CAIs analyzed here largely overlap with literature data, but also expand the range of observed Mo isotope anomalies by ~30% (Fig. 2). In combination with the high precision of the new data, this reveals that ordinary cg-CAIs (incl. CTA, Type B, FoB) follow a linear trend in the $\varepsilon^{95}Mo$–$\varepsilon^{94}Mo$ diagram. Including the anomalous Allende CAI 'A-ZH-5' ($\varepsilon^{94}Mo \approx 17$ [4]) yields a well-defined correlation line (denoted 'CAI-line'), whose slope (~0.6) is virtually identical to those of the NC/CC-lines [2]. As such, the observed variability does not simply reflect analytical scatter around a uniform Mo isotope composition, but represents genuine nucleosynthetic heterogeneity that is consistent with variable deficits in *s*-process Mo nuclides. In contrast, the general offset of ordinary cg-CAIs (relative to the NC/CC-lines) is most readily attributed to a substantial *r*-excess, where the fact that all samples plot on the CAI-line, within uncertainties, indicates that there is no resolvable *r*-process variability and that ordinary cg-CAIs can be characterized by a common Δ^{95}Mo value of ~131 (defined by CAI-line intercept; see [2]).

This is particularly noteworthy as there is no noticeable difference between ordinary cg-CAIs from CV_{RED} (this study) and those from CV_{OX} (this study, literature). None of the CV_{OX} samples resolvably deviate from the CAI-line towards the CC-line (as would be expected in case of contamination from the host chondrite), and some of the most extreme data along the CAI-line are cg-CAIs from the same CV_{RED}. Therefore, parent-body processing seems to have produced/affected neither the *s*-process variability nor the general *r*-excess, meaning that cg-CAIs even from meteorites that have experienced significant aqueous alteration (like Allende) can generally be assumed to have retained their original Mo isotope composition, which is likely due to their compact texture and high initial Mo concentration (~10× host chondrite).

Of note, the unusual cg-CAIs are characterized by large *s*-deficits and smaller *r*-excesses that are similar to NC/CC bulk meteorites (Fig. 2). Based on the above observations, however, it seems unlikely that their Mo isotope signatures result from parent-body processing, which is further supported by the fact that unusual cg-CAIs also show distinct nucleosynthetic titanium isotope anomalies [5,7] and include samples from CV_{OX} (two Allende FoBs [5,7]) as well as CV_{RED} (two Type Bs, this study).

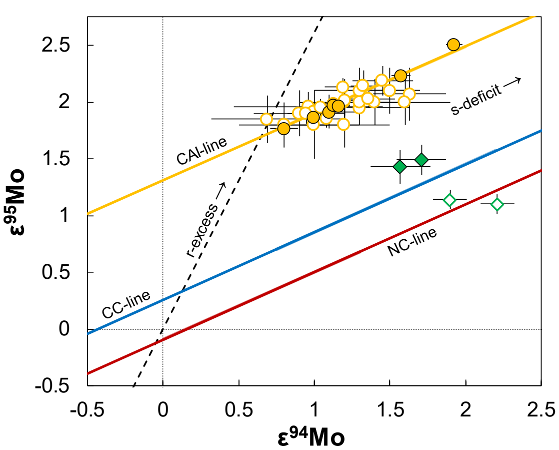

Fig. 2. *Mo isotope diagram, showing 'ordinary' (orange) and 'unusual' (green) cg-CAIs relative to the s-process lines for NC (red) and CC (blue) materials [2]. Literature data (open symbols) from [4–7].*

Implications for the Early Solar System: The Mo isotope trichotomy presented here is testament to the existence of three fundamentally different reservoirs in the early Solar System. While the NC and CC reservoirs likely represent the inner and outer protoplanetary disk, respectively, during the epoch of planetesimal formation [2], the CAI reservoir (as defined by ordinary CAIs) rather reflects only a transient phase in the nascent Solar System. As has been proposed previously [1], it likely represents the isotopic composition of the earliest infalling material that formed the initial disk, which was subsequently diluted by later infall, resulting in the NC and CC reservoirs. As such, its composition is only preserved in ordinary cg-CAIs and, indirectly, in the difference between the NC and CC reservoirs [1]. With the well-defined correlation lines for NC, CC, and CAI materials it is now possible to reliably constrain the excess of CAI-like material in the CC reservoir, regardless of the variations within these reservoirs. A mass balance using Δ^{95}Mo values of –9 for NC, +26 for CC [2], and +131 for CAI materials, yields a CAI-fraction of ~25%, meaning that the CC reservoir can be described as an NC-CAI mixture at a ratio of ~3:1. Because this constraint is independent of elemental fractionation and secondary (*s*-process) isotope variations, it can serve as an important anchor point for understanding the origin of the NC-CC dichotomy and the isotopic variations within these reservoirs.

With effects of parent-body alteration essentially being ruled out, the distinct Mo isotope signatures of the unusual cg-CAIs indicate that they represent a fundamentally different population of CAIs, which might have formed at a different time, location, and/or from different materials. For instance, they might have formed later than their ordinary counterparts, at a time when the initial disk had, in parts, already been overprinted by later (less *r*-enriched, NC-like) infall [5], which would be consistent with their anomalously low ε^{50}Ti [5,7]. As such, the unusual cg-CAIs might also be related to the refractory component identified in some NC chondrules [8]. At the conference, we will discuss the data presented here in the context of chronological constraints and isotopic data for other elements, in order to better constrain the origin of CAIs and the early evolution of the Solar System.

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