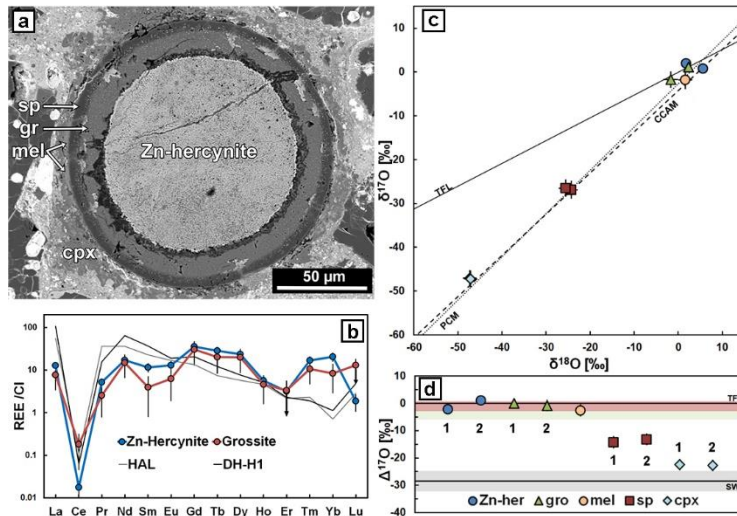


A WELL-ROUNDED Zn-RICH HAL-LIKE CAI: EVIDENCES FOR FORMATION UNDER VARIABLE REDOX CONDITIONS IN A NEBULAR GAS WITH VARIABLE O-ISOTOPIC COMPOSITION.

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Introduction: Ca,Al-rich inclusions (CAIs) are the oldest solids formed in our solar system ~4.567 Ga, most likely close to the proto Sun [1], providing a window for examining the earliest isotopic reservoir(s) in this region and how that reservoir(s) evolved through time. The vast majority of CAIs in unmetamorphosed carbonaceous chondrites (petrologic types 1–3.0) have uniform $\Delta^{17}\text{O}$ within individual CAIs, but show inter-CAI variations from –40‰ to –5‰, suggesting variable O-isotope composition of the nebular gas in the CAI-forming region [e.g., 2]. Here, we reevaluate previous data [3] with new investigations from a unique and well-rounded Zn-rich CAI from the CO3.1 carbonaceous chondrite Dar al Gani (DaG) 083 (Fig. 1a).



Results: The CAI core consists of fine-grained Zn-hercynite (7.4 wt% ZnO). The core is surrounded by a double-layered rim of grossite and spinel with tiny inclusions of perovskite. The rim is surrounded by a wrinkled layer of Ca-pyroxene with minor melilite. The CAI has a heterogeneous O-isotopic composition (Figs. 1c,d): Ca-pyroxene is the most ^{16}O -rich mineral ($\Delta^{17}\text{O} \sim -23\text{‰}$). Spinel is ^{16}O -depleted relative to the pyroxene ($\Delta^{17}\text{O} \sim -14\text{‰}$). Zn-hercynite, grossite, and melilite have similar ^{16}O -poor compositions within uncertainties ($\Delta^{17}\text{O} \sim -3 \pm 2\text{‰}$). The rare earth elements (REEs) have been measured in Zn-hercynite and grossite (Fig. 1b). Compared to CI, Gd is up to 35× enriched, whereas Ce is strongly depleted in both minerals. This kind

of pattern is known for HAL-type refractory inclusions [4]. However, the enrichment of light REEs with a smooth decrease in the heavy REEs that is characteristic to other HAL-type objects is not clear in the DaG 083 CAI. In addition, a depletion of Sm, Eu, Ho, and Er to their neighboring elements is observed.

Discussion and Conclusions: The DaG 083 CAI studied is not only a remarkable sample because of its texture and mineralogy but also by its O-isotopic composition and extraordinary REE-pattern. The REE patterns suggests the CAI formed under variable redox conditions. Under oxidizing conditions, Ce and Pr become volatile, which could be responsible for the large depletion of Ce. However, Eu, Sm, Ho, and Er are also depleted and these four elements become volatile under reducing conditions. Therefore, the CAI underwent either two heating events under different oxygen fugacity or a single heating with evolving $f\text{O}_2$ [5].

The CAI was still within the CAI formation region close to the proto Sun as indicated by the outermost Ca-pyroxene having solar-like ^{16}O -rich composition. Melilite, grossite, and the Zn-hercynite are depleted in ^{16}O . Their $\Delta^{17}\text{O}$ values are similar to that of an aqueous fluid on the CO parent asteroid ($\Delta^{17}\text{O} \sim -1\text{‰}$) inferred from O-isotope composition of aqueously formed magnetite and fayalite [6,7]. We infer that these minerals experienced post-crystallization O-isotope exchange with the fluid [8]. Zn-rich hercynite most likely formed by replacement of krotite and/or grossite during aqueous alteration [e.g. $\text{CaAl}_2\text{O}_4(\text{s}) + x\text{Zn}(\text{aq}) + (1-x)\text{Fe}(\text{aq}) = (\text{Fe,Zn})\text{Al}_2\text{O}_4(\text{s}) + \text{Ca}(\text{aq})$; the origin of Zn will be part of future investigations]. The Mg-rich composition of the spinel rim suggests that the alteration occurred at low temperature that prevented significant Fe-Mg interexchange in it. Spinel and Ca-pyroxene are resistant to O-isotope exchange by parent body alteration. Therefore, the intermediate O-isotopic composition of spinel is primary and provides a clear evidence for variations in O-isotopic composition of nebular gas in the CAI-formation region.

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