Clumped isotopes and concretions: The Prairie Canyon member of the Mancos Shale, Colorado

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Carbonate concretions and septarian fracture fills have been key in developing our understanding of early burial processes in siliciclastic rocks [1]. Often, septarian fractures and concretion matrix cements have unusually light $\delta^{18}O$ values. A common explanation for near-shore marine concretions is that they precipitated at the sediment-water interface in aquifers of mixed meteoric-marine water [2][3]. Alternatively, the light $\delta^{18}O$ could be due to precipitation at higher temperatures during burial. It is often difficult to distinguish between the two hypotheses, which has hindered previous interpretations of the mechanisms of concretion formation and the timing of diagenetic processes.

Here, we apply the novel carbonate 'clumped' isotope palaeothermometer [4] to Fe-dolomite/ankerite concretions and calcite septarian fracture fills from the Upper Cretaceous Prairie Canyon Member. The derived temperature is independent of the bulk isotopic composition, so the parent fluid can be back-calculated. Our results show that the fracture fill precipitated between 107-117°C, corresponding to depths of up to ~3 km. The parent fluid has a $\delta^{18}O$ value of 0.5 ± 0.13 (VSMOW), consistent with slightly ^{18}O-enriched Cretaceous seawater. Interpretation of the concretion matrix is complicated by mixed phases of cements and by the non-linear mixing of clumped isotopes, which can lead to an uncertain temperature. However, even accounting for this, a temperature trend from cooler cores (34°C ± 8) to hotter edges (53°C ±1) is observed. Therefore, the light $\delta^{18}O$ values, at least in the Praire Canyon, are caused by higher temperatures during burial and not meteoric mixing.

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Rapid core formation and an early 'veneer' on Earth: Highly siderophile elements in pre-lunar mantle domains

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Highly siderophile elements (HSEs) are strongly sequestered into metallic planetary cores, leaving silicate mantles almost devoid of HSEs. Late accretion of primitive meteoritic material, after core formation had ceased, partially replenished HSEs in planetary mantles and occurred within a few million years of solar system formation on most parent bodies (1), but probably later on Earth, after a final episode of core formation associated with the giant Moon-forming impact (50-150 million years later (2)).

Ancient isolated domains in Earth's mantle, which formed prior to the giant impact, have recently been recognised by anomalies in the short-lived ^{182}Hf-^{182}W isotope system. These domains - such as the source of 3.8 billion-year-old Isua basalts (3) - might represent mantle that largely escaped late accretion. Here we show, however, that the Isua source mantle had HSE abundances at ~60% of the present-day mantle, inconsistent with a pre-late accretion model.

Such early-formed domains require preservation through the Moon-forming giant impact and isolation thereafter, precluding subsequent addition of HSE by mixing with material accreted later. Thus, their HSE contents were set by early 'pre-lunar' late accretion, while the Hf-W system was still extant. This early HSE replenishment requires that core formation was rapid and ceased early, and therefore, on the basis of W isotope evidence, implies a high degree of equilibration of metal with mantle silicate during accretionary impact events. The retention of such early HSE-enriched mantle also implies incomplete giant impact-related melting of Earth's mantle. Conversely, the HSE budget of the Moon was reset during its formation, thereby partially accounting for the disparity in HSE content and apparent late accretion rates between the Earth and Moon.

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