

Tracing the rise of atmospheric oxygen using Cr isotopes in carbonates as a paleoredox proxy

C. HOLMDEN¹ AND A.D. BEKKER²

¹Saskatchewan Isotope Laboratory, Department of Geological Sciences, University of Saskatchewan, SK, S7N 5E2 CANADA (*correspondence: chris.holmden@usask.ca)

²Department of Geological Sciences, University of Manitoba, MB, SK R3T 2N2 CANADA (bekker@cc.umanitoba.ca)

The Great Oxidation Event (GOE) is now well-constrained in age to ca. 2.4–2.3 Ga, but questions remain whether the pathway to oxidized surface environments was gradual, oscillatory with transient oxidation events, or stepwise. Various proxies, including fractionation of Cr isotopes in iron formations (Frei *et al.*, 2009), have been used to infer, at least locally, the development of oxidizing conditions as early as 2.7 Ga. Alternatively, Konhauser *et al.* (2011) argued that Cr concentrations were low in iron formations until 2.5–2.3 Ga when acidic groundwaters formed in response to the GOE and delivered reduced Cr to shallow-water environments.

Here, we tested whether $\delta^{53}\text{Cr}$ values in shallow-water carbonates spanning the GOE might also record steps in the rise of atmospheric oxygen. Cr isotopes are fractionated by redox reactions such as those occurring during Mn-mediated Cr oxidation on the continents or Cr reduction in anoxic marine environments. In the absence of molecular oxygen, the range of Cr isotope fractionation in exogenic materials would likely be confined to the range of igneous rocks ($\delta^{53}\text{Cr} = -0.1 \pm 0.1\%$). Carbonates from 15 formations were chosen with depositional ages ranging between 2.5 Ga and 1.9 Ga. Carbonate is more abundant than iron formation in the rock record, but there are pitfalls with carbonate-hosted seawater records that must be borne in mind. These include dolomitization, local cycling effects, depositional fractionation, and detrital sediment contamination.

$\delta^{53}\text{Cr}$ data collected, thus far, show no fractionation in samples older than 2.4 Ga, a very mild amount of fractionation at ca. 2.3 Ga of $\sim 0.1\%$, and permil level fractionation at 2.15 Ga in the peak interval of the Lomagundi carbon isotope excursion. Interestingly, the fractionations are both positive and negative relative to $\delta^{53}\text{Cr}$ in igneous rocks. Although fractionated Cr may be hosted in both carbonate and lithogenic components, Cr/Al ratios support the predominantly authigenic origin of the Cr in the carbonate fraction. These data are consistent with acidic weathering at the beginning of the GOE and Mn-mediated Cr oxidation during the Lomagundi carbon isotope excursion.

The Hf-W chronology of FUN CAIs

J. C. HOLST¹, M.B. OLSEN¹, C. PATON¹,
K. NAGASHIMA², M. SCHILLER¹, D. WIELANDT¹,
K.K. LARSEN¹, J. N. CONNELLY¹, J. K. JØRGENSEN¹,
A.N. KROT^{1,2}, Å. NORDLUND¹ AND M. BIZZARRO¹

¹Centre for Star and Planet Formation, University of Copenhagen, Copenhagen, Denmark.

²Institute of Geophysics and Planetology, University of Hawaii at Manoa, HI 96822, USA

Refractory inclusions (CAIs) represent the oldest solar system solids and provide information regarding the formation of the Sun and its protoplanetary disk. CAIs contain evidence of now extinct short-lived radioisotopes synthesized in one or multiple stars and added to the protosolar molecular cloud before or during its collapse. Understanding the origin of short-lived radioisotopes is necessary to assess their validity as chronometers and constrain the birthplace of the Sun. Whereas most CAIs formed with the canonical abundance of ^{26}Al corresponding to $^{26}\text{Al}/^{27}\text{Al}$ of $\sim 5 \times 10^{-5}$, rare CAIs with fractionation and unidentified nuclear isotope effects (FUN CAIs) [1] record nucleosynthetic isotopic heterogeneity and $^{26}\text{Al}/^{27}\text{Al}$ of $< 5 \times 10^{-6}$, possibly reflecting their formation before canonical CAIs [2]. Thus, FUN CAIs may provide a time-window into the earliest solar system, but their chronology is unknown.

Using the ^{182}Hf - ^{182}W chronometer, we show that a newly discovered FUN CAI, dubbed STP-1, formed coevally with canonical CAIs [3], but with $^{26}\text{Al}/^{27}\text{Al}$ of $\sim 3 \times 10^{-6}$. Moreover, the mineralogy and the group II rare earth element (REE) pattern coupled with a ^{16}O -rich composition, suggest that the precursor material of STP-1 formed by condensation from a gas of solar composition depleted in the most refractory REEs, similar to fine-grained CAIs. The level of $^{26}\text{Al}/^{27}\text{Al}$ in STP-1 is higher than the galactic background and suggests that our Sun formed as part of a cloud that was chemically enriched by earlier generations of massive stars. The observed decoupling between ^{182}Hf and ^{26}Al requires distinct stellar origins: steady-state galactic stellar nucleosynthesis for ^{182}Hf and late-stage contamination of the protosolar molecular cloud by a massive star(s) for ^{26}Al . Admixing of fresh stellar-derived ^{26}Al to the protoplanetary disk occurred during the epoch of CAI-formation and, therefore, the ^{26}Al - ^{26}Mg systematics of CAIs cannot be used to define their formation interval. In contrast, our results support ^{182}Hf homogeneity and the chronological significance of the ^{182}Hf - ^{182}W clock.

- [1] Wasserburg *et al.* (1977) *Geophys Res Lett* **4**, 299. [2] Sahijpal & Goswami (1998) *Astrophys. J.* **509**, L137-L140. [3] Burkhardt *et al.* (2012) *Astrophys. J.* **753**, L6.