

Magnesium-isotope fractionation in a monitored limestone cave

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The geochemistry of speleothem calcites and particularly that of stalagmites and flowstones is extensively exploited as archive of past environmental change in continental settings. This is because cave deposits, composed in many cases of stable low-Mg calcite, represent reliable climate archives as they combine a well established U-Th chronology with oxygen-isotope records. Despite intensive research including modelling and novel approaches, speleothems dominated by kinetic fractionation processes remain difficult to interpret. A possible approach is to apply a multi-proxy approach and particularly to involve non-conventional isotope systems [1]. For the first time we here present a complete analytical dataset of magnesium isotopes ($\delta^{26}\text{Mg}$) from a monitored cave in NW Germany (Bunker cave). The data set includes data on loess soil, carbonate hostrock, groundwater, dripwater, stalactite and stalagmite calcite, cave loam, runoff water and carbonate precipitates from pools and watch glasses placed under monitored drip points. Magnesium-isotope fractionation during weathering and interaction between soil cover, hostrock and groundwater are complex and depend on a number of variables. The fractionation between dripwater (mean = -1.21‰) and speleothem calcite (mean = -4.27‰) is considerable and requires attention. An aspect that deserves specific attention is the fact that Mg, similar to Ca^{2+} and other divalent cations, Mg^{2+} is not present as pure ionic form in aqueous environments but rather in its hydrated form as aquo coordination complex. Precipitation of Mg^{2+} from aquo complexes requires dehydration prior to CaCO_3 precipitation. In the opinion of the authors, the dehydration of mainly the large outer hydration shell is the main driving mechanisms of the ~ 3 ‰ fractionation between aqueous solution and speleothem CaCO_3 . This as lighter isotopes (here $\delta^{25}\text{Mg}$) are characterized by weaker bonds and are thus preferentially incorporated in the speleothem calcite. In summary, although complex, $\delta^{26}\text{Mg}$ isotope records of speleothem calcites represents a promising new proxy for climate-controlled weathering patterns, albeit one that requires careful calibration in monitoring experiments.

[1] Buhl *et al.* (2007) *Chemical Geology* **244**, 715-729.

Delayed continental crust formation on a hot Archaean Earth

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The formation of continental, as opposed to oceanic, crust is generally thought to be caused by melting of basaltic source material in the form of either garnet amphibolite or eclogite [1, 2]. The trace element characteristics of Archaean crust are best explained by the preservation of garnet in the source, and the finer points of these models consider details of Nb and Ta distribution.

However, there appears to be a mismatch between our current understanding of heat loss rates from the early Earth and the melting behaviour of mafic crust from experimental petrology. If geothermal gradients were appreciably higher in early to middle Archaean times, then higher degrees of melting would have caused a predominance of picritic over basaltic melts. Initial experiments indicated that picritic rocks do not proceed through amphibolite to eclogite with increasing metamorphic grade, but instead form amphibole-bearing pyroxenites due to the lack of plagioclase in high MgO compositions under high-grade metamorphic conditions [3]. Our understanding of the melting of Archaean mafic crust is biased by the predominance of modern MORB compositions in experimental studies.

Most models of continental crust formation consider the middle to late Archaean periods, but an important difference arises if we shift attention to presumably hotter early Archaean times. The logical predecessor to melting of garnet amphibolites would be melting of garnet-free amphibolites along hotter geotherms. In this case, large amounts of crust should have been produced in the early Archaean with appropriate trace element compositions, but are not known. In contrast, amphibole-pyroxenites would produce nephelinitic-basanitic melts which would not be registered as "continental crust" at all. The production of abundant continental crust would thus be stalled until internal differentiation of the mafic crust led to a predominance of basaltic, and not picritic, rocks, favouring gradual continental crust growth.

[1] Foley, Tiepolo & Vannucci (2002) *Nature* **417**, 837-840.

[2] Rapp, Shimizu & Norman (2003) *Nature* **425**, 605-609.

[3] Foley, Buhre & Jacob (2003) *Nature* **421**, 249-252.