

Mg Isotope Fractionation During Speleothems Formation

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Introduction

A preliminary survey of terrestrial Mg-isotope ratios showed very small isotopic variation (Catanzaro and Murphy, 1966). However, little progress was made on the processes of Mg isotope fractionation because of the lack of a precise measurement technique. High precision Mg-isotopic composition measurements can now be achieved by the application of a new mass-spectrometric technique: Multiple Collector Inductively Coupled Mass Spectrometry (MC-ICP-MS). Solutions are introduced through into the MC-ICP-MS (Nu Instruments) via a Cetac MCN-6000 nebulizer. Measurement of Mg involves simultaneous measurement of ²⁴Mg, ²⁵Mg and ²⁶Mg. Mg-isotopic compositions are expressed as a permil deviation from the isotopic composition of the international standard SRM 980. The external reproducibility of the MC-ICPMS obtained on pure Mg solutions is 0.06 per mil/amu (2σ, n=50).

Results

In this study we report preliminary results on Mg isotope fractionation during low Mg-calcite speleothems formation. Three cave sites from various climate locations in Israel were studied, among them the Soreq cave, which located within dolomite host-rock with an internal cave temperature of 18°C. The other two caves are Pekiin cave (PEK), located within calcite host-rock, with an average temperature of 16°C, and Mizpe Shlagim (MS) cave, located within dolomite, and the internal cave temperature is 7°C. Speleothems from each cave show characteristic $\delta^{26}\text{Mg}$ values (Fig. 1) (Soreq: -0.76 to -1.22; MS -0.12 to -0.35 and PEK 0.25 to 0.67 per mil). The corresponding variations in $\delta^{44}\text{Ca}$ are within the analytical error. The differences between PEK and the others caves can be attributed to the differences between the host-rock, while the difference between MS and Soreq are probably related to environmental variations (temperature, water/rock, etc).

We investigated in more detail the Soreq cave speleothems, which have been the subject of various present-day and palaeo-environmental studies using stable and radiogenic isotopes (Bar-Matthews et al., 1997, 1999, 2000; Ayalon et al., 1998, 1999). A time series (0 to 45Ky.) was studied for their $\delta^{26}\text{Mg}$, $\delta^{25}\text{Mg}$ values and compared with previous environmental proxies. The dolomite host-rock has a $\delta^{26}\text{Mg}$ value of +1.12 per mil, thus all the speleothems are enriched in the lighter isotope by between 1.9 to 2.4 per mil. These samples have Ca/Mg ratio (ppm/ppm) ranging from 50 to 96, which are interpreted as various efficiency degrees of speleothem precipitation, according to a Rayleigh distillation. The $\delta^{26}\text{Mg}$ values of all the speleothems, except one sample, are within the range of Rayleigh fractionation curves calculated for 12 to 20°C, which is the range of estimated deposition temperature for the speleothems (Bar-Matthews et al, 1997). The sample falling outside this range would have a temperature of precipitation >

30°C according to Rayleigh curve, which is not reasonable. Examination of the $\delta^{13}\text{C}$ secular variation during the last 45 Ky (Bar-Matthews et al., 1999) shows clearly that this sample is also one with the highest and most distinct $\delta^{13}\text{C}$ value, suggesting that climate related ¹³C-spike events have distinct $\delta^{26}\text{Mg}$ values.

Conclusion

This study clearly shows a 1.9 to 2.4 per mil fractionation of $\delta^{26}\text{Mg}$ values during low-temperature water-rock interaction. Therefore the Mg-isotopic composition is a promising tool for the study of weathering conditions and environmental records through time, especially when combined with more conventional methods such as $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$.

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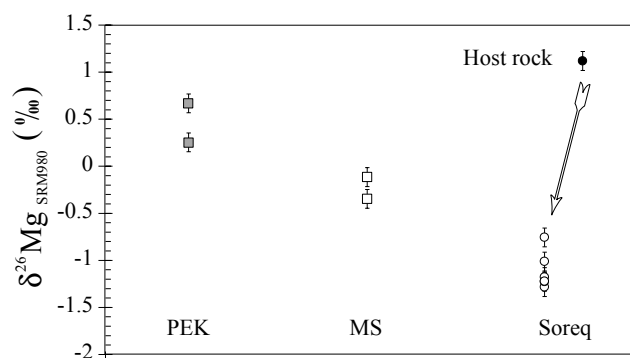


Figure 1: Mg isotopic composition of speleothems from 3 different locations in Israel

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