Strontium isotope ($\delta^{88/86}$Sr) fractionation in pedogenic processes and secondary carbonate precipitation

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Background: Sr stable isotopes

Until recently, natural variations in the ^{88}Sr/^{86}Sr ratio were considered to be undetectable and insignificant

Recent developments in instrumentation and in analytical methods, enabled identifying natural variability in the ^{88}Sr/^{86}Sr ratio (Fig. 1)

Negative $\delta^{88/86}$Sr values were measured in secondary materials (products of chemical weathering) from the terrestrial environment of the Judea Mountain including terra rossa soil and speleothem calcite, the latter deriving its Sr from the above-lying soil (Fig. 1; Halicz et al., 2008)

Yet, it is not clear whether the fractionation is related to pedogentic processes or to formation of secondary– chemical carbonates (e.g. within the soil environment)

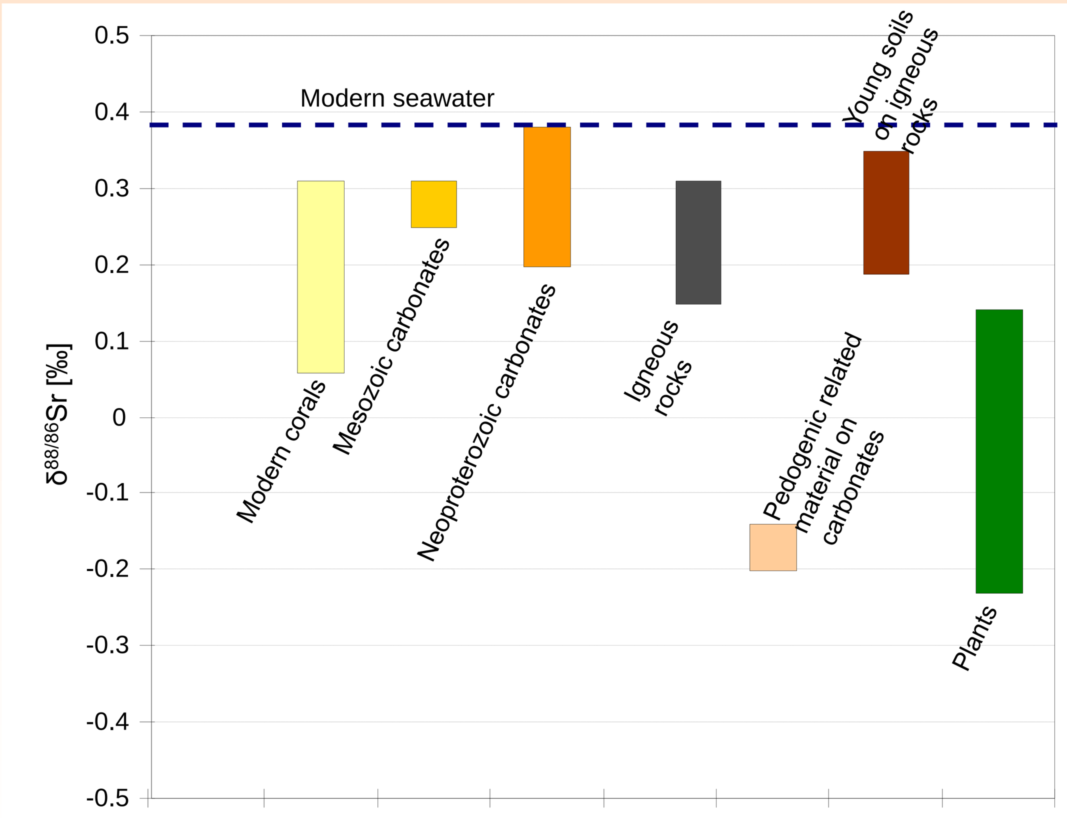

Fig. 1: Compilation of $\delta^{88/86}$Sr values (relative to SRM987) for various terrestrial reservoirs (data from Fietzke and Eisenhauer, 2006; Halicz et al., 2008; Ohno et al., 2008; Rüggeberg et al., 2008; Moynier et al., 2010; de Souza et al., 2010; Krabbenhöft et al., 2010)

Research objective

Determine the mechanisms and degree of Sr isotope fractionation during pedogenic processes and secondary carbonate precipitation

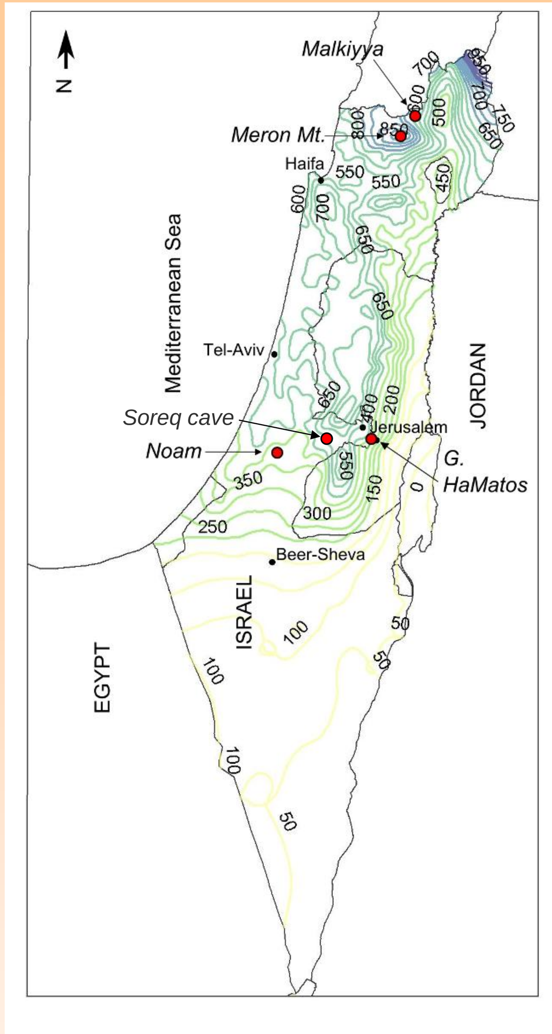

Fig. 2: Map of Israel with contour lines showing mean annual rainfall in mm•y-1. The red solid circles mark the sampling locations with their names indicated by the arrows.

Samples

The $\delta^{88/86}$Sr values were determined in two systems (locations shown in Fig. 2):

1) The soil system, includes: soils subjected to various degrees of leaching as a function of annual precipitation (table 1), dust from central Israel (major parent material of soils in the region) and pedogenic calcite (secondary carbonate) from Noam site

2) The Soreq cave karst-system, includes: soils, cap rock, dripping water and speleothems

Table 1. Soils sampling sites (their locations are marked in Fig. 2).

Sampling Site #	Surface Soil type (Israeli nomenclature)	Bedrock type, Geological age	Annual precipitation (mm)	Sampling Location
1	Terra Rossa	Karstic limestone, Eocene	650-700	Malkiyya
2	Terra Rossa	Dolomite, Cenomanian	950	Meron Mt.
3	Terra Rossa	Limestone, Turonian	450-500	G. HaMatos
4	light brown clayey loam	Chalk/loess, Eocene/Pleistocene	350-400	Noam
5	Terra Rossa	Dolomite/Limestone, Cenomanian/Turonian	500-550	Soreq

Verification of the measurements method

A novel method, based on double-spike (DS), to determine ^{88}Sr/^{86}Sr ratios in natural samples using MC-ICP-MS was developed (Shalev et al., 2013)

$\delta^{88/86}$Sr values obtained using this method are more precise compared to those obtained by the standard-sample-bracketing (SSB) method. The accuracy of the new method was verified by comparing with results obtained with DS-TIMS (Fig. 3)

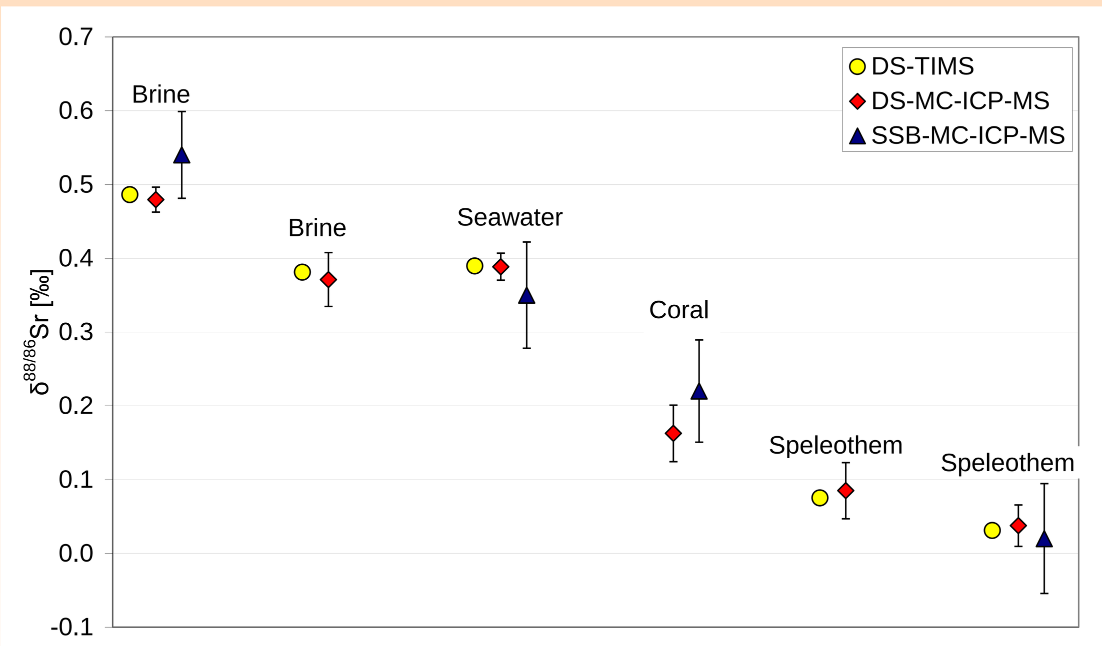

Fig. 3: Comparison of results obtained by the three methods tested in this study. Error bars are external 2SEM (for the TIMS measurements, error bars are smaller than the symbols).

Results and discussion

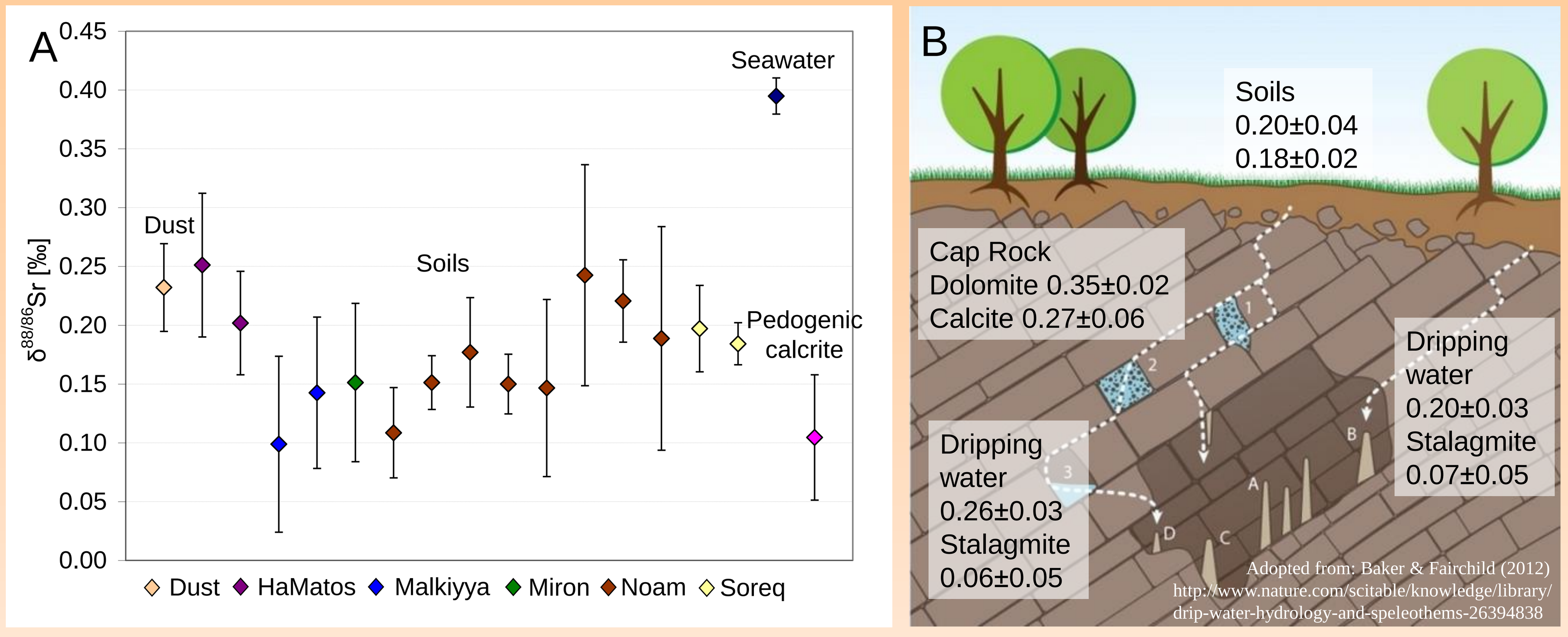

Fig. 4: A) $\delta^{88/86}$Sr values of the soil system. Seawater (IAPSO) value is also shown for comparison. B) $\delta^{88/86}$Sr values of the Soreq cave area are shown on a schematic figure of a karst-system. Errors are 95% confidence limits.

Soils (Fig. 4A): The range of $\delta^{88/86}$Sr values of soils subjected to various degrees of small to moderate leaching (including the dust, the soil's parent material) is small, within analytical uncertainty

The Soreq cave karst-system (Fig. 4B):

- $\delta^{88/86}$Sr values of Soreq soils is a typical dust-soils value
- Soreq cap-rock has higher $\delta^{88/86}$Sr values
- The $\delta^{88/86}$Sr values of the stalagmites are significantly lower than the dripping water from which they precipitate. This indicates that Sr fractionation occurs during the precipitation of calcite in speleothems
- Thus, it appears that calcium carbonate precipitation is the main mechanism controlling $^{88/86}$Sr fractionation

Summary (Fig. 5)

- The field data collected in this study corroborate the findings that Sr isotopes fractionate during the precipitation of $CaCO_3$, enriching the latter with the "light" ^{86}Sr as compared to the solution (as shown earlier by Fietzke and Eisenhauer, 2006 and Halicz et al., 2008)
- Sr fractionation due moderate leaching of soils is within analytical error. In order to evaluate the role of leaching in fractionation of stable Sr we plan to analyze highly leached soils (e.g. laterites)
- Secondary calcite precipitates show lower $\delta^{88/86}$Sr values than soil $\delta^{88/86}$Sr, which is the source for the Sr in the calcite. This probably reflects Rayleigh distillation which is expected to increase the $\delta^{88/86}$Sr of the freshwater from which the calcite precipitates to values above those of the soil. This issue will be checked by analyzing the Sr isotopic composition of waters and carbonates along the precipitation path of tufa and travertine deposits. The analyses will help in answering the open question of the temperature dependence of the fractionation of stable Sr isotopes.

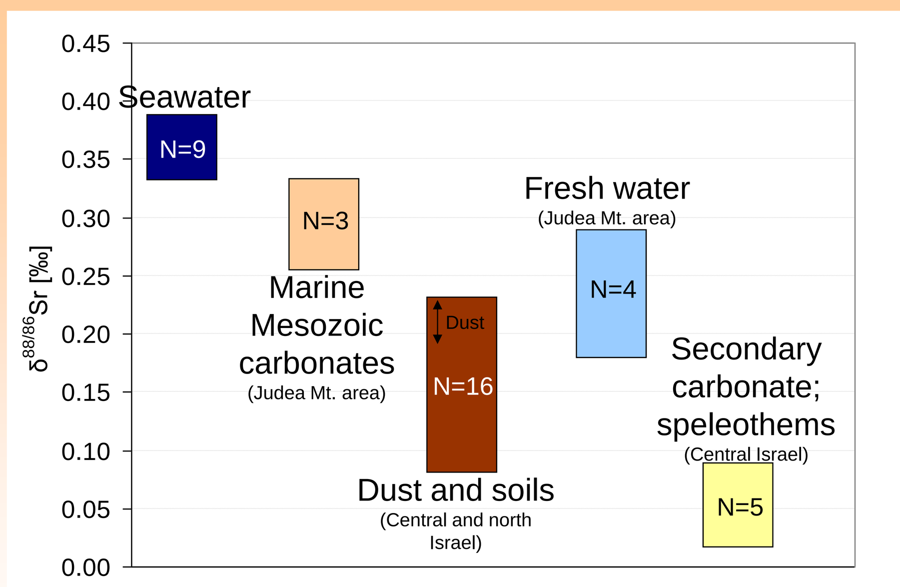

Fig. 5: Ranges of $\delta^{88/86}$Sr mean values of different groups of samples. The number of samples in each group is indicated by N. Data from: Halicz et al (2008), Shalev et al (2013) and references therein and current study.

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