Fractionation of Sr isotopes in continental carbonate environments and its potential impact on oceanic $\delta^{88/86}Sr$

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Background: The Sr oceanic budget

- The major fluxes dictating the concentration and isotope composition of Sr in the oceans are continental crust weathering, hydrothermal flux and precipitation of marine carbonates (Fig. 1)
- These fluxes were traditionally evaluated by the radiogenic ratio of $^{87}Sr/^{86}Sr$, and recently by the stable isotope ratio of $^{88}Sr/^{86}Sr$ (Vollstaedt et al., 2014)
- This study focuses on the $\delta^{88/86}Sr$ value ($^{88}Sr/^{86}Sr$ ratio expressed in delta notation) of the continental weathering flux which is dictated by the relative contribution of Sr from the weathering of: (1) Silicate rocks and (2) Marine carbonate rocks of various ages
- Processes that fractionate terrestrial Sr isotopes can alter the $\delta^{88/86}Sr$ value of the continental flux
- While the $^{87}Sr/^{86}Sr$ ratio can be used to identify sources (provenance), $\delta^{88/86}Sr$ values are also indicative of processes causing isotopic fractionation

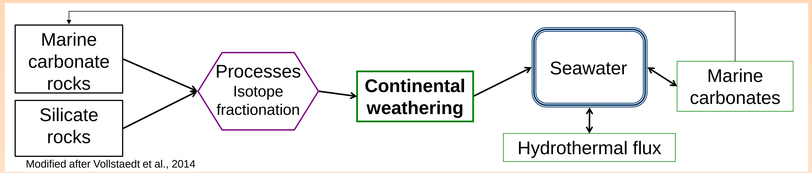


Fig. 1: A scheme of the Sr fluxes to the ocean focusing on sources and processes that dictate the Sr isotopic composition of the continental weathering flux

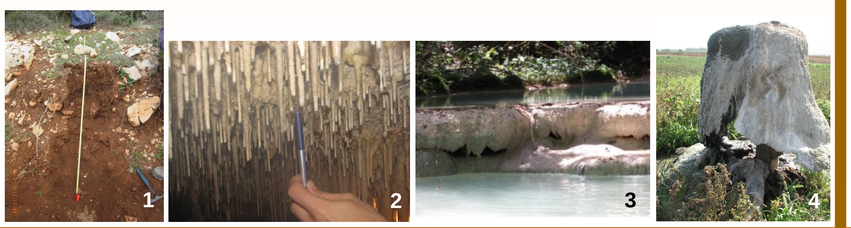
Research objectives

- Different continental environments were investigated in order to evaluate Sr fractionation processes that may impact $\delta^{88/86}Sr$ value of the continental flux
- The major research objectives are:
  1. Identify processes causing Sr isotopic fractionation (Δ)
  2. Determine the Sr isotopic composition of the system's products and reactants
  3. Evaluate the Sr fractionation factor of the process

Samples

Four continetal environments were studied:

1. Mountain soils
2. Cave karst-system
3. Tufa and its precipitating stream water
4. Tufa and its precipitating highly reduced groundwater (in swamp sediments)



Mountain Soils

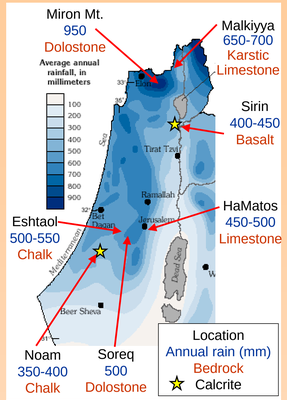


Fig. 2: Map of the soils sampling sites. The red arrows mark the locations with their names, annual rainfall and bedrock type indicated in black, blue and red letters, respectively. The sites of the pedogenic calcrite (secondary carbonate) samples are marked in yellow stars. The contour lines are the mean annual rainfall in mm·y^{-1}. Dust from central Israel was also sampled.

- Mountain soils on carbonate terrains (Upper Cretaceous to Neogene) were sampled in central and northern Israel. Settling dust, major parent material of these soils (Yaalon, 1997) and pedogenic calcrites (secondary carbonates) were also sampled (Fig. 2)
- Samples were selected to include soils subjected to various degrees of leaching as a function of annual precipitation and bedrock type (Fig. 2)

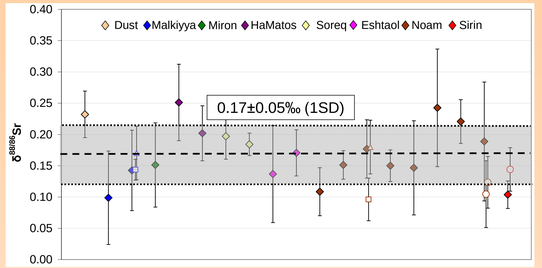


Fig. 3: $\delta^{88/86}Sr$ values of dust and soils (diamonds) and pedogenic calcrite (circles). The silicate (triangles) and carbonate (squares) fractions of the soil were analyzed separately in two soil samples. Error bars are 95% confidence limits. The dashed line is the average of all samples and the gray area is ±1SD.

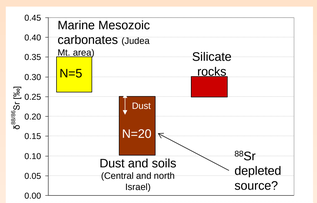


Fig. 4: Ranges of $\delta^{88/86}Sr$ mean values of the soils and dust and their potential sources: 1) marine carbonates from Judea Mt. area, data from: Halicz et al., 2008 and current research and 2) silicate rocks, data from: Moynier et al., 2010 (Basalts) and Ohno and Hirata, 2007 (Granites).

- ***Results***: The dust and soils have similar $\delta^{88/86}Sr$ values (Figs. 3, 4).
- The $\delta^{88/86}Sr$ range of the dust and soils is lower than those of their potential sources: the carbonate bedrocks and silicate rocks (Fig. 4)
- This suggests that the settling dust comprise of additional, yet unidentified, ^{88}Sr depleted source of Sr

Cave karst-system (The Soreq cave)

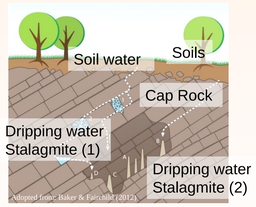
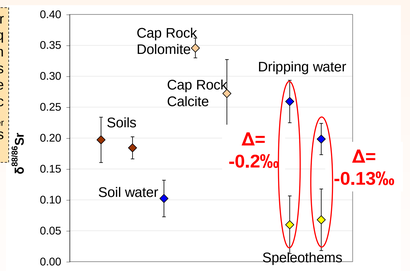


Fig. 5: Samples from the Soreq karst shown on a schematic figure of a karst-system

Fig. 6: $\delta^{88/86}Sr$ values of the Soreq cave karst system materials. Error bars are 95% confidence limits. The isotopic difference $\Delta_{carb\text{-}water}$ for the speleothems is also shown.



- Samples from the Soreq cave karst-system include: soils, soil water, cap rock (dolomite and secondary calcite) and two pairs of speleothems and their associated dripping water (Fig. 5)
- ***Results***: Sr fractionation between speleothem calcite and dripping water, $\Delta_{calcite\text{-}water}$, was found to be ~-0.17 ‰ (Fig. 6)

Tufas and their precipitating waters

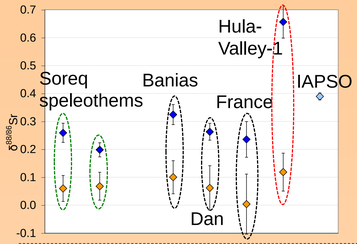
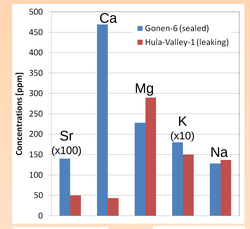


Fig. 7: $\delta^{88/86}Sr$ values of continental carbonates and their precipitating waters. Error bars are 95% confidence limits. The value for IAPSO seawater is shown for comparison.

- Tufas (Ca-carbonates) and their precipitating waters were sampled from the Banias and Dan rivers- Israel, Huveaune river- France and from a leaking artesian well in the swamp sediments of the Hula valley- Israel
- ***Results***: The tufas were isotopically depleted with respect to the precipitating waters (Fig. 7)
- $\Delta^{88/86}Sr_{carb\text{-}water}$=-0.20±0.08‰ (2SD, n=5)
- Hula-Valley-1 well water was exceptionally enriched with the "heavy" isotope, ^{88}Sr

- ***Hula Valley groundwater (Fig. 8)***: The water from the tufa covered Hula-Valley-1 well is heavily depleted in Sr and Ca compared to the water from the Gonen-6 sealed well, with no tufa cover, both wells were drilled into the same aquifer (with little difference in other major elements)
- The alkalinity of Gonen-6 water was extremely high ~100 meq·L^{-1}
- These results suggest that CO_2 outgassing at the surface in the leaking well (Hula-Vally-1) triggered substantial $CaCO_3$ precipitation and Sr depletion (by co-precipitation) and hence large Rayleigh type ^{88}Sr enrichment in the leaking water



Hula-Valley-1: leaking well covered by tufa

Gonen-6: sealed well, no tufa

Fig. 8: Comparison between the waters from Hula-Vally-1 well (a leaking well covered by tufa) and Gonen-6 well (a sealed well with no tufa), both drilled into the same swamp sediments aquifer.

Summary:
Continental Sr isotope fractionation and its potential effect on the oceanic $\delta^{88/86}Sr$

- On-site pedogenic processes cause little, if any, fractionation. The $\delta^{88/86}Sr$ of the soils, however, is lower than that of their potential source rocks
- Precipitation of Ca-carbonates in different continental environments is accompanied by significant isotopic fractionation ($\Delta^{88/86}Sr_{carb\text{-}water}$=-0.20±0.08‰), which is similar to the fractionation during precipitation of marine carbonates
- Continental carbonate precipitation is substantially smaller than the oceanic carbonate deposition and hence has limited impact on the $\delta^{88/86}Sr$ of the oceans
- The terrestrial Sr fractionation has large effect in environments (or periods) of enhanced $CaCO_3$ precipitation (e.g. from high alkalinity waters such as the Hula groundwater), or in small water bodies, such as semi-enclosed basins and lakes

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