Strontium isotope fractionation in soils and pedogenic processes

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Strontium isotope fractionation in soils and pedogenic processes

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Abstract

The stable isotope composition of strontium (the ratio ⁸⁸Sr/⁸⁶Sr expressed as $\delta^{88/86}$ Sr) showed significant fractionation in mountain soils of the Judea Highland. In order to understand this phenomenon we studied the elemental composition and the stable and radiogenic Sr isotopic composition in soil transects conducted from semi-arid (desert fringe) to wetter (Mediterranean) climate zones. These transect were selected because the degree of soil leaching depends on the amount of precipitation and the permeability of the underlying bedrock. These soils are the pedogenic products of leaching of the accumulated desert dust and the underlying carbonate bedrocks resulting, among others, enrichment of the residual soils in Al-clays. A clear negative correlation was found between the $\delta^{88/86}$ Sr and Al₂O₃ (Al-clays content) values of the soils, the high $\delta^{88/86}$ Sr-low Al₂O₃ being the dust end-member. The preliminary study demonstrates the feasibility of using stable ⁸⁸Sr-⁸⁶Sr isotopes as tracers of terrestrial weathering processes.

1. Introduction

While the variations in ⁸⁷Sr/⁸⁶Sr ratios are widely used in geosciences studies, where the radiogenic isotope ⁸⁷Sr (daughter of ⁸⁷Rb) is normalized to ⁸⁶Sr, the natural variations in the ratio of the non-radiogenic Sr isotopes ⁸⁶Sr and ⁸⁸Sr were considered until recently to be undetectable and insignificant [1]. However, advanced MC-ICP-MS and TIMS instruments and development in analytical methods, enabled identifying natural variability in the ⁸⁸Sr/⁸⁶Sr ratio in sedimentary marine and terrestrial environments [1–4]. These findings opened a broad field of new applications, e.g., paleothermometry, biomineralization, pedogenesis and the oceanic Sr budget [1], [3–4].

Currently, little is known about the natural processes responsible for strontium isotope fractionation. Based on preliminary measurements of igneous rocks, the $\delta^{88/86}$ Sr value of bulk silicate earth is estimated to be ~0.27 (‰ SRM987) [5]. The $\delta^{88/86}$ Sr of inorganic and biogenic marine carbonates is "lighter" than the $\delta^{88/86}$ Sr of the water from which they were precipitated [1], [2], [6-7]. This Sr isotope fractionation is apparently controlled by temperature [1] and by the precipitation rate, with increasing fractionation occurring at higher rates [7]. The most negative $\delta^{88/86}$ Sr value measured to date, -0.42 ‰, was from the bottom of the cap carbonate in the Doushantuo Formation in Yangtze Gorges area, South China. This light value was interpreted as enhanced isotopic fractionation during precipitation from an originally "light" seawater [8]. So far, modern seawater has the highest measured $\delta^{88/86}$ Sr value of $0.387\pm0.002\%$ [9 and references therein], probably due to precipitation of "light" carbonates that leave seawater enriched in the heavy Sr isotopes [4]. This enrichment depends also on the oceanic residence time of Sr.

Fractionated $\delta^{88/86}$ Sr values were also found in secondary materials (products of chemical weathering) from the terrestrial environment of the Judea Mountain such as terra rossa soil and speleothem calcite (that derive its Sr from the above-lying soil). These weathering products yielded $\delta^{88/86}$ Sr value of $-0.17\pm0.06\%$ (2SD, N=3), significantly lower than the $\delta^{88/86}$ Sr of the carbonate rocks in the same area (0.30±0.1‰, 2SD, N=5) [3]. On the other hand, incipient chemical weathering, in a small-glaciated watershed in the central Swiss Alps, had no resolvable effect on the $\delta^{88/86}$ Sr values of bulk soils, which remained indistinguishable from their parent bedrock [10]. Analyses of plant tissue in the same system revealed $\delta^{88/86}$ Sr values that were significantly lower than those of the soils in which they grow. Preferential assimilation of the lighter isotopes by plants may possibly produce higher soil

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 $\delta^{88/86}$ Sr values, as opposed to the low $\delta^{88/86}$ Sr values of chemical weathering products from the Judea Mountain.

In this study the $\delta^{88/86}$ Sr values were determined in mountain soil profiles, subjected to various degrees of leaching, in order to characterize the mechanisms and degree of strontium isotope fractionation during weathering processes of soils. The degree of leaching is determined by the amount of precipitation and by the permeability of the underlying bedrock.

2. Sampling sites and soils analyses



Fig. 1. Map of Israel with contour lines showing mean annual rainfall in $mm \cdot y^{-1}$. The red solid circles mark the sampling locations with their names indicated by the arrows.

The soil sampling sites were selected along a rain traverse across Israel (Fig. 1), ranging from ~350-400 mm·y-1 at Noam in the south to 950 mm·y-1 at Mt. Meron in the Upper Galilee in the north (Table 1 and Fig. 1). The soils were developed on loessial material overlying chalk (Noam) and on bedrocks of limestone and dolomite, forming the typical mountain soils of terra rossa. The pedogenic processes forming these soils were interpreted as leaching of settling desert dust and in situ weathering of the carbonate bedrocks [11].

The samples were grinded to fine powder and homogenized. Chemical compositions of majors and minors elements were measured by ICP-AES in solutions produced by lithium metaborate melt decomposition or by sintering of the soils. Isotopic analyses were conducted by "Nu Plasma" (Nu Instruments, Wrexham, UK fitted with Aridus sample introduction system) MC-ICP-MS, using double-spike method (for details see Shalev et al., submitted [9]).

Sampling	Surface Soil type	Bedrock type,	Annual precipitation	Sampling
Site #	(Israeli nomenclature)	Geological age	(mm)	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

Table 1. Soils sampling sites	(their location	ons are marked	in Fig.	1).
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Fig. 2. (A) CaO (%wt) and (B) $\delta^{88\%6}$ Sr values of dust and soils samples versus Al₂O₃ (%wt). Chemical data of dust is an average of 23 dust storms samples collected in central Israel [12]. Dust storms collect and homogenize fine material of various lithologies over vast areas with negligible volcanic contribution. One dust storm sample, collected in central Israel, was analyzed for $\delta^{88\%6}$ Sr value. Error bars in (A) are 5%. Error bars in $\delta^{88\%6}$ Sr (B) are 2SEM of the analyses and the rather large spread in the errors between individual samples depend on the conditions during mass-spectrometric measurement. The numbers to the left of each symbol in **B** refer to soils sampling sites (Table 1).

3. Soils chemical and isotopic compositions

Pedogenic processes include dissolution of carbonate material, and hence enriching the soils with residual Al-clays. These processes are demonstrated by the negative correlation between Al_2O_3 and CaO (Fig. 2a). The higher the annual rainfall and the permeability of country rocks, the higher the leaching and the higher the relative Al_2O_3 content. The soil overlaying karstic limestone, located at a high rainfall region and having the highest Al_2O_3 is therefore the most leached soil (Malkiyya), Figs. 1, 2). On the other hand, the least leached soils with the lowest Al_2O_3 are located at the low rainfall region (Noam).

The Sr stable isotopic composition, $\delta^{88/86}$ Sr, of the soils is plotted versus Al₂O₃ as a proxy for the degree of leaching (Fig. 2b). The plot shows a clear negative correlation between $\delta^{88/86}$ Sr and Al₂O₃, modern dust being an end-member with high $\delta^{88/86}$ Sr and low Al₂O₃. This correlation may represent either fractionation during pedogenesis or mixing of fractionated Sr reservoirs. It appears that the more leached material from Malkiyya has the lowest $\delta^{88/86}$ Sr value (Fig. 2a,b) while the highest $\delta^{88/86}$ Sr value in these soils was very close to the value of desert dust, which is a major component of the parent material of these soils [11]. In this case the "light" $\delta^{88/86}$ Sr values of leached soils was not caused by preferential assimilation by plants (as in the case of the central Swiss Alps soils [10]), since the fractionation by this mechanism produces a $\delta^{88/86}$ Sr "heavy" residual soil.

These results demonstrate that stable Sr isotopes do fractionate during pedogenesis (e.g. leaching and precipitating) and therefore $\delta^{88/86}$ Sr may serve as a tracer for terrestrial chemical weathering. The mechanisms producing this isotope fractionation during weathering and pedogenesis are still unknown and are currently under investigation.

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