

## Genesis and the isotopic composition of nitrogen in the solar wind

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The isotopic composition of protosolar nitrogen is a long standing problem in planetary sciences. The goal of the Genesis mission (NASA Discovery class) was to determine the solar isotopic composition of some key elements in order to document the protosolar nebula and, by comparison, to investigate planetary formation processes that have led to the observed isotopic structures in planets and meteorites. Despite the hard landing of the sample return capsule, fragments of targets irradiated by the Sun during 27 months have been recovered and are currently analysed by several teams around the world. We have developed a new NB isotope analytical system in CRPG Nancy. The new line, partly automated, is made exclusively of stainless steel, Pyrex<sup>®</sup> and quartz, and is pumped by fluid-free pumps. Targets were ablated with a UV laser having a wavelength of 193 nm over surfaces up to 1 cm<sup>2</sup>. N<sub>2</sub> was concentrated on Pt at low temperature, then purified over CuO. Noble gases were purified classically in another section of the line. AuoS spare targets implanted with <sup>15</sup>N at energies mimicking those of SW N were ablated over surfaces of typically 1 mm<sup>2</sup> and we obtained a well reproducible recovery yield close to 100 %. The amount of implanted SW N ( $2 \cdot 10^{12}$  atoms N/cm<sup>2</sup>) is so low that contamination not only due to the crash but also resulting from target manufacturing is always dominant; Nevertheless, using the measured Ne amount and isotopic composition and the solar wind Ne/N ratio (from spacecraft measurement), we are able to put constraints on the N isotopic composition of the Sun. Results obtained so far suggest a terrestrial-like composition rather than a <sup>15</sup>N-depleted one, which, if confirmed, will lead to a significant change in our view of the distribution of nitrogen isotopes in the solar system.

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## Sulfur isotope geochemistry of sulfidic springwaters at Marche region, central Italy

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The genesis and development of caves are usually controlled by seepage of meteoric waters supplied from the surface. In contrast, some caves, known as hypogenic caves, are formed by fluids coming from the depth. Hydrogen sulfide is one of the most common gases in the springwaters related to cavern environments and has a great impact on the formation of hypogenic caves. The oxidation of H<sub>2</sub>S to H<sub>2</sub>SO<sub>4</sub> induces the corrosion of the host rock and the deposition of many secondary cave minerals, like gypsum. Gypsum is observed where the emission of H<sub>2</sub>S occurs in limestone caves and at least some portion of the gypsum deposits survives long after its emission ceases (e.g., Galdenzi and Maruoka, 2003). The gypsum deposits are often observed as a crust covered on limestone walls above the watertable. Such vadose gypsum crusts have  $\delta^{34}\text{S}$  values similar to those of H<sub>2</sub>S in the springwater (e.g., Galdenzi and Maruoka, 2003), implying the oxidation of H<sub>2</sub>S to H<sub>2</sub>SO<sub>4</sub> and the reaction between calcite and sulfuric acid occur above the watertable.

The  $\delta^{34}\text{S}$  values of H<sub>2</sub>S in the aquifer reflect the activity of sulfate-reducing bacteria. Therefore, those are not constant through the time. The  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  values in the past can be estimated from the  $\delta^{34}\text{S}$  values of the gypsum in the cave where the emission of H<sub>2</sub>S ceases. Therefore, the  $\delta^{34}\text{S}_{\text{gypsum}}$  values of the hypogenic caves can be used as a paleoindicator for environmental factors that influence the activity of the sulfate-reducing bacteria. However, so far it is uncertain what is the primary factor that controls  $\delta^{34}\text{S}$  values of H<sub>2</sub>S in the aquifer. To clarify this problem, we determined  $\delta^{34}\text{S}$  values of sulfide and sulfate collected from the springwaters related to hypogenic caves in Marche region, central Italy, and compared them with other parameters. In such parameters, sulfate concentration seems to be the most important factor that influences isotopic fractionation between sulfate and sulfide. Pure culture experiments demonstrated that the extent of isotope fractionation is not affected generally by sulfate concentration at concentrations above 1 mM; however sulfate concentrations in the springwaters studied here ranges from 1 to 18 mM. Therefore, the correlation between isotopic fractionation and sulfate concentration might reflect the difference of bacteria community compositions rather than the response of single bacteria community.

### Reference

Galdenzi, S., Maruoka, M. (2003), *J. Cave Karst Stud.* **65** 111-125.