

Cosmogenic ^3He and ^{10}Be production rates at high elevation (> 3800 m)

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Recent cross-calibrations of cosmogenic ^3He in pyroxene and ^{10}Be in quartz [1] showed that, at low elevation (< 2000 m), the $^3\text{He}/^{10}\text{Be}$ production ratio was probably ~40% higher than the value of ~23 initially defined in the 90's. This recent update is consistent with the last independent determinations of the sea level high latitude production rates of ^{10}Be and ^3He , that are about 4 and 125 $\text{at}\cdot\text{g}^{-1}\cdot\text{yr}^{-1}$, respectively [e.g. 2, 3]. However, major questions remain about these production rates at high elevation, notably because the elevation dependence of the $^3\text{He}/^{10}\text{Be}$ production ratio is controversial [4]. It is thus crucial to produce new high precision cross-calibration data at high elevation.

Here we report new precise measurements of ^3He in pyroxenes and ^{10}Be in quartz, from dacitic moraines located at 4820 m in the Southern Altiplano (22°S, Tropical Andes). The obtained $^3\text{He}/^{10}\text{Be}$ production ratio is 33.3 ± 0.9 (1σ). This value is statistically undistinguishable from the production ratio measured at 1333 m [1], which reveals that the $^3\text{He}/^{10}\text{Be}$ production ratio in pyroxene and quartz is almost invariant with elevation. When combined with the absolute ^3He production rate locally calibrated in the Central Altiplano, at 3800 m, from a 15.3 ± 0.5 ka old surface, these new data permit to define the absolute production rate of cosmogenic ^{10}Be at high elevation. After scaling to sea level and high latitude, this calibration yields a sea level high latitude P_{10} ranging from 3.7 ± 0.2 to 4.1 ± 0.2 $\text{at}\cdot\text{g}^{-1}\cdot\text{yr}^{-1}$, depending on the used scaling scheme.

This new refinement of the cosmogenic dating tool will significantly improve both the accuracy and the precision of paleoglaciologists chronologies in the Tropical Andes.

[1] Amidon *et al.* (2009) *Earth Planet. Sci. Lett.* **280**, 194-204.

[2] Putnam *et al.* (2010) *Quat. Geochron.* **5**, 392-409.

[3] Blard *et al.* (2006) *Earth Planet. Sci. Lett.* **247**, 222-234.

[4] Gayer *et al.* (2004) *Earth Planet. Sci. Lett.* **229**, 91-104.

Calcium isotopes in evaporites constrain sulfate- vs calcite-rich seawater chemistry

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The calcium-isotope behavior of evaporite formations is proposed as a new method for constraining the composition of ancient seawater. Evaporite cycles that reach the halite facies are expected to record a different range of calcium-isotope values depending on the initial major-element chemistry of seawater. In the modern ocean, where sulfate is far in excess of calcium (28 mmol/kg SO_4^{2-} compared to 10 mmol/kg Ca^{2+}), approximately 90% of the initial calcium is removed as carbonate or sulfate minerals by the time halite saturation is attained. In contrast, an excess of calcium relative to sulfate, as suggested for intervals such as the Cretaceous and the Silurian [1], leads to significant depletion of sulfate, but a much smaller proportion of calcium removed at the point of halite saturation. Isotopic fractionations associated with the precipitation of carbonates, gypsum, and anhydrite lead to Rayleigh distillation of calcium within an evaporite basin, where precipitates from more concentrated brines become enriched in the heavy isotopes of calcium, dependent on the total amount of calcium removed. The range in calcium-isotope ratios obtained by sampling different stages of the carbonate-sulfate evaporite facies is therefore diagnostic of initial sulfate- or calcium-rich seawater.

In beaker evaporation experiments, the $\delta^{44/42}\text{Ca}$ value of modern sulfate-rich seawater becomes enriched by 1.2‰ from its initial composition to the beginning of halite precipitation, whereas the $\delta^{44/42}\text{Ca}$ of a calcium-rich and sulfate-poor solution evolves by <0.2‰. The $\delta^{44/42}\text{Ca}$ values of accompanying precipitates demonstrate the same characteristics, but are offset from the fluid by 0.5–0.7‰. Analyses of geological evaporites from various Phanerozoic periods show how this behavior translates to natural samples as well. This new method provides an independent test for variations in the major-element chemistry of paleoseawater.

[1] Lowenstein *et al.* (2001), *Science* **294**, 1086–1088.