

## Gas geochemistry of spring waters along the Alpine Fault, NZ

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The Alpine Fault on the South Island of New Zealand is one of the longest, straightest, and fastest-moving transform faults, with oblique-slip at rates that accommodate over half of the Australia-Pacific plate motion and cause rapid uplift of the Southern Alps. No major earthquakes have occurred on the fault in historic time, but it last ruptured around 1717 AD and is thought to fail in large moment magnitude ( $M_w > 7$ ) to possibly great ( $M_w > 8$ ) earthquakes at ~330 yr recurrence intervals. Rocks southeast of the Alpine Fault are exhumed at rates faster than they can cool, resulting in a 63°C/km geothermal gradient, convective circulation and warm springs without related volcanic activity. Because the seismic cycle is fundamentally controlled by fluids, improved knowledge of fluid circulation in the shallow crust is paramount to understanding earthquake processes on the Alpine Fault.

In the context of the Deep Fault Drilling Project (DFDP), we have investigated gas compositions and noble gas isotopic abundances in spring waters from the vicinity of the fault. Free gas was sampled at four springs, while nine other springs provided water samples that were degassed in the lab. N<sub>2</sub> is commonly the most abundant gas, CO<sub>2</sub> concentrations vary widely from <0.1% to >96%, and CH<sub>4</sub> contributes up to 13%. He concentrations are up to ~500 ppm. <sup>3</sup>He/<sup>4</sup>He ratios are generally highest (up to 0.81 Ra) close to the fault and decrease to radiogenic values (<0.04 Ra) towards the southeast at distances of a few kilometers from the fault, with two exceptions: Copland Spring (0.42 Ra) is located ~12 km from the fault and exhibits the highest gas flow and the highest CO<sub>2</sub> content of all springs studied in this work. Kotuku Spring, the only location available for sampling on the Australian plate, yields a particularly high <sup>3</sup>He/<sup>4</sup>He ratio of ~3.1 Ra despite low gas flow and ~17 km distance from the fault. Obviously, mantle fluids can penetrate the thick crust beneath the Southern Alps directly at the fault and may be diverted away from it only where major passageways through the crust exist. It remains to be seen whether the high <sup>3</sup>He/<sup>4</sup>He ratio of Kotuku indicates a distinct fluid origin on the northwest side of the fault in general or is just a local feature.

## Calcium and Oxygen Isotope Fractionation during Precipitation of Calcium Carbonate Polymorphs

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Different isotopic systems are influenced in multiple ways and amounts by the crystal structure, surface properties, hydration and dehydration processes, deprotonation, adsorption, desorption, isotope exchange and diffusion processes. Herein we studied the structural and kinetic effects on fractionation of stable Ca- and O-isotopes during CaCO<sub>3</sub> precipitation in order to evaluate processes controlling their fractionation.

Calcite, aragonite and vaterite were precipitated using the CO<sub>2</sub> diffusion technique<sup>1</sup> at a constant pH of 8.3, but various temperatures (6, 10, 25 and 40°C) and precipitation rates (10<sup>1.5</sup> to 10<sup>5</sup> μmol h<sup>-1</sup> m<sup>-2</sup>).

The precipitation rate effect on fractionation of Ca-isotopes is mainly influenced by the precipitated polymorph. The calcium isotope fractionation between calcite/vaterite and aqueous Ca<sup>2+</sup> increases with increasing precipitation rate. In contrast the fractionation of Ca-isotopes between aragonite and aqueous Ca<sup>2+</sup> decreases with increasing precipitation rate. Hence, the influence of precipitation rate on the fractionation of calcium isotopes of aragonite is reverse compared to that of calcite and vaterite. The fractionation of <sup>18</sup>O/<sup>16</sup>O between CaCO<sub>3</sub> and H<sub>2</sub>O decreases with increasing precipitation rate. The latter behaviour is - in contrast to calcium isotope fractionation - similar for all three polymorphs.

Vaterite formation induces lower fractionation of calcium isotopes ( $\Delta^{44/40}\text{Ca}_{\text{CaCO}_3\text{-aq}} = -0.10$  to  $-0.55$  ‰) compared to calcite ( $-0.69$  to  $-2.04$  ‰) and aragonite ( $-0.91$  to  $-1.55$  ‰). In contrast the fractionation of oxygen isotopes is highest for vaterite, followed by aragonite and calcite at similar precipitation rates and temperatures. Although fractionation of oxygen isotopes is mainly dominated by temperature in our experiments with constant pH, whereas fractionation of calcium isotopes is dominated by polymorphism and kinetic processes.

<sup>1</sup>A. Niedermayr, S.J. Köhler and M. Dietzel (2013), *Chemical Geology*, 340, 105-120.