Variable ^{13}C fractionation during $CaCO_3$ precipitation induced by ureolytic bacteria

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Precipitation of $CaCO_3$ induced by bacterial hydrolysis of urea has been recently proposed as a model to study the role of microorganisms in geological storage of CO_2 [1]. Theoretically, this process has the potential to capture CO_2 through pH rise and fix it as solid $CaCO_3$. To fully explore this potentiality, it is essential to quantify the amount of carbon transferred from CO_2 to $CaCO_3$ during bacterial ureolysis, a task that can be accomplished by carbon mass and isotope balance. For this purpose, the knowledge of the carbon isotope fractionation expressed during bacterial ureolysis is an essential prerequisite. In a series of batch experiments, we measured the $\delta^{13}C$ values of Dissolved Inorganic Carbon (DIC) and $CaCO_3$ formed during ureolysis induced by *Bacillus pasteurii*. The results are striking: (i) Initial DIC is 10 per mil heavier than urea, in contrast with the typical kinetic fractionation expected during bacterially–mediated reactions. (ii) DIC becomes increasingly lighter than urea, ^{13}C fractionation decreasing from 10 to -15 per mil during ureolysis. (iii) $CaCO_3$ becomes increasingly lighter than DIC, ^{13}C fractionation decreasing from 0 to -3 per mil during ureolysis. The causes for such variability of carbon isotope fractionation are not fully understood. We propose the hypothesis that fractionation is controlled by two factors: the metabolism of *B. pasteurii* and the ureolytic activity of the enzyme urease. This enzyme is progressively released in the medium during cytolysis and promotes kinetic fractionation between urea, DIC and $CaCO_3$, which results in ^{12}C to concentrate preferentially in $CaCO_3$.

[1] Ménez *et al*. (2007) *Geotechnologien Science Report* **9**, 150-163.

Multi-isotopic (H, O, C, S, Li, B, Si, Sr, Nd) approach for geothermal fluid characterization in Iceland

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A major objective of the HITI project (HIgh Temperature Instruments for supercritical geothermal reservoir characterization and exploitation), partially funded by the European Union, is to develop methods to characterize the reservoir and fluids of deep high temperature geothermal systems. In the framework of this project, we sampled about 25 geothermal waters from Reykjanes, Svartsengi, Nesjavellir, Hveragerdi, Namafjall and Krafla geothermal systems in Iceland. The main objective of this work is to characterize geothermal waters by using a multi-isotopic approach in order to 1) determine the origin of the geothermal water and 2) constrain the processes of water/rock interaction at high temperature with or without the presence of seawater.

Here we report δD, $\delta^{18}O$, $\delta^{34}S$, $\delta^{13}C$, $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $\delta^{7}Li$, $\delta^{11}B$ and $\delta^{29}Si$ isotope data for these geothermal waters. Each of these isotope systems on their own reveals important information about particular aspects of either water source or water/rock interaction processes, but considered together provide a more integrated understanding of the geothermal systems. Some of the more intriguing conclusions gained from this multi-tracer approach include:

1) the geothermal waters have $\delta^{29}Si$ <0‰ (relative to NBS28), unlike Icelandic surface waters that have $\delta^{29}Si$ >0‰.

2) Li concentration and isotope composition ($\delta^{7}Li$ ranging from +4.4 to +8.8‰) are controlled by the intensity of water/rock interaction and by dissolution and precipitation of secondary minerals at various temperatures.

3) H-O-B-C-S-Sr-Nd isotope compositions depend mainly on water source (i.e., freshwater vs. seawater), and thus are particularly useful for understanding groundwater flowpaths in near coastal geothermal systems.

These particular conclusions provide important constraints for our model of geothermal system development in Iceland.