

The halogen composition of hydrothermal fluids in the Taupo Volcanic Zone, New Zealand.

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9f. Innovative geochemical approaches to understanding geothermal systems

The halogen composition of seven geothermal fields and eight hot spring areas in the Taupo Volcanic Zone (TVZ), North Island New Zealand, were studied in order to constrain the origin of the geothermal fluids and to identify the effect of physico-chemical processes on the isotopic composition of these fluids. A set of 74 samples from well brines and hot springs were analyzed for Cl, Br, Li, $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$ and δD . In particular, this study offers a first approach to the application of the Cl/Br systematics in geothermal fluids to constrain the behaviour of stable chlorine isotopes.

The determination of the Cl/Br ratios in the set of samples analyzed, allowed the initial characterization of geothermal fields and hot spring areas in the TVZ. The highest Cl/Br ratios were found at Mokai (1,664), Orakeikorako (1,611), Rotokawa (1,478) and White Island (1,373). The chlorine isotopic composition of all the samples ranged from -0.97 to 0.67‰. With the exception of some samples from Orakeikorako and Rotokawa, most samples with high Cl/Br ratios had positive $\delta^{37}\text{Cl}$ values, the geothermal field Mokai was the most enriched in $\delta^{37}\text{Cl}$ (0.03 to 0.38‰). The sample from Broadlands Ohaaki had a negative $\delta^{37}\text{Cl}$ value (-0.57‰) and a Cl/Br ratio of 870. In the hot springs the Cl/Br ratios also correlate well with the $\delta^{37}\text{Cl}$ values. Waikite has the highest $\delta^{37}\text{Cl}$ values (0.47 to 0.67‰), followed by Taupo, White Island, Tokaanu and Waimangu.

The data suggest that in the central part of the TVZ, there is a deep fluid of magmatic origin with a Cl/Br ratio of at least 1,200, a positive $\delta^{37}\text{Cl}$ signature around 0.5‰, a Cl concentration above 3,200 ppm and a Li content of more than 29 ppm. Fluids with similar characteristics were found at Tokaanu, White Island, Mokai, Wairakei, Tauhara and Ngatamariki. A second fluid is characterized by negative $\delta^{37}\text{Cl}$ values (-0.02 to -0.97‰), Cl/Br ratios below 1,200 and Li concentrations around 10 ppm. The influence of this second fluid is more dominant towards the E and NE of the TVZ in hot spring areas and geothermal systems like Rotorua, Waiotapu, Rotokawa and Kawerau.

How citrate slows magnesite growth: a high temperature AFM study

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Preliminary work and experimental methods

Magnesite shows a high stability in natural environments and hence is of scientific interest due to its potential for long-term CO₂ sequestration. In a recent study we were investigating the inhibition of carboxylic ligands on magnesite growth and found out that among the investigated ligands citrate caused the highest degree of inhibition [1]. Besides the effect of complexation of Mg²⁺ in aqueous solution, a prominent surface effect of citrate was detected. This surface effect of citrate on magnesite growth at elevated temperatures, however, is still insufficiently understood.

In the present study, hydrothermal atomic force microscopy (HAFM) was used to investigate magnesite growth on the (104) surface as a function of citrate concentrations (0.1-10 mmol/kgw) and saturation state. Experiments were conducted at pressures up to 4 bars, temperatures of 100 °C and 120 °C and alkaline conditions (pH 7.5-8.5).

Results and outlook

HAFM experiments showed that spiral growth is the dominant growth mechanism over a wide range of saturation state in ligand-free solutions as well as in the presence of citrate. Accordingly, the determined growth rates follow an exponential dependency on supersaturation and are in close agreement with previous mixed-flow reactor experiments [1][2]. Furthermore, HAFM observations revealed that citrate interacts with steps on the (104) surface of magnesite producing growth islands elongated along the trajectory of the c-axis. This pronounced morphological change was taking place without an effect on obtuse step kinematics but with a reduced advancement rate of acute steps. These observations indicate specific blocking of acute kinks by citrate. For the rotation frequency of spirals and thus the growth rate, acute step advancement is essential. The rate of step generation via spiral growth in the presence of 1 mmol/kgw citrate was thereby decreased by a factor of more than 3.

Overall, this study confirms the control exerted by acute steps on magnesite growth rates. Therefore, numerical molecular simulations should preferentially focus on stereochemical effects between organic molecules and acute steps and kinks. This could help to better understand and predict the role of organic additives on magnesite growth.

[1] Gautier *et al.* (2012) in prep. [2] Saldi *et al.* (2009) *Geochim. Cosmochim. Acta* **73**, 5646-5657.