A critical look at the titanium-in-quartz (TitaniQ) thermobarometer

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Synthetic quartz was grown in rutile-bearing $H_2O(\pm NaCl)$ fluids at 600-800 °C and 1-10 kbar by dissolution and reprecipitation of quartz in a small thermal gradient. Rapid attainment of rutile saturation is proved by the formation of rutile crystals at the contact between old quartz substrate and new quartz overgrowth. Titanium concentrations in new quartz correlate positively with the concentrations of Li and Al and depend strongly on quartz growth rate, increasing by up to a factor of 2.5 as the growth rate varied from ~4 μm/day to ~110 μm/day. Considering the composition of the most slowly grown quartz samples as most representative we obtain Ti concentrations that are about three times lower than those obtained during earlier calibrations of the TitaniQ thermobarometer [1, 2]. Our data can be fitted by the equation

$$\log \mathrm{Ti}\ (\mathrm{ppm}) = -\,0.27943 \cdot 10^4/T - 660.53 \cdot (P^{0.35}/T) + 5.6459$$

where T is given in Kelvin and P in kbar.

An independent test was made by analyzing igneous quartz from five intrusive and three volcanic magma systems that crystallized at known pressures (0.8–2.7 kbar) and temperatures (675–780 °C). The activity of TiO_2 was constrained from the composition of melt inclusions hosted in the analyzed quartz. Although the results depend on the model chosen to calculate $aTiO_2$, they agree much better with our calibration than with previous TitaniQ calibrations. Crystallization pressures calculated based on our calibration agree within 0.1-1.0 kbar with independent pressure estimates, whereas those calculated based on [1,2] are consistently higher by 3-9 kbar. Slight deviations between our calibration and the natural data are either due to uncertainties in the calculation of $aTiO_2$ of the natural melts or due to failure to synthesize structurally perfect quartz even at our slowest growth rates. Our findings imply that TitaniQ should not be applied to quartz grown from hydrothermal fluids, because growth rates in these environments can be very high. TitaniQ is more likely to work in igneous quartz, although the present models for TiO_2 solubility in quartz and silicate melts may still need to be refined.

[1] Wark & Watson (2006) *Contrib. Mineral. Petrol.* **152**, 743-754. [2] Thomas *et al.* (2010) *Contrib. Mineral. Petrol.* **160**, 743-759.

Hydrogen production from low temperature olivine alteration

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Hydrous alteration of olivine, the main component in ultramafic rocks, has received much attention because the reducing power in the form of H_2 generated in this process is proposed to have fueled the emergence of life [1] and the present deep biosphere [2]. While most previous research was done at high temperatures (over 200ºC) [3], the upper temperature for living organisms is recorded as 122ºC. This study is thus focused on the H_2 production from olivine hydration at 80ºC, the core temperature for thermophiles and hyperthermophiles. Reactions with fluids representing the variety of composition of natural waters is studied.

Reactions with ground Fo90 were carried out in serum bottles which was deoxygenated with N_2. Headspace gas and solutions were analysed. A correlation between pH, olivine dissolution and H_2 production was established experimentally. Our data show that saline water and seawater promote H_2 production from olivine hydration compared with pure water. This is partly due to higher alkalinity in the seawater that buffers the pH. The H_2 production is found to correlate to the end pH in these systems. Geochemical modelling will be coupled to further understand the mechanism.

Olivine dissolution in water showed no passivation over 80 days. This means H_2 produced in this environment is proportional to the surface area of olivine in contact with H_2O. Experimental data also suggest high rock:water ratio and low pH promote H_2 generation.

We then tested the effects of seawater level of sulfate, nitrate and bicarbonate on H_2 production. Enhanced values of H_2 concentration was observed for sulfate- and bicarbonate-added reactions, in which sulfate-containing solution produced most H_2. The effect of nitrate addition is not obvious. The H_2 production in this set of expriments is not related to pH. The reaction mechanism is under further investigation.

[1] Russell *et al.* (2010) *Geobiology* **8**, 355-371. [2] Hellevang (2008) *Int. J. Astrobiol.* **7**, 157-167. [3] Seyfried *et al.* (2007) *Geochim. Cosmochim. Acta* **71**, 3872-3886.