

Study on mineral surface reacted with water at high temperatures above 300°C

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Reactions at solid-water interface play an important role in a number of natural processes. Steady-state dissolution rates of pyroxene, actinolite, wollastonite, garnet and basaltic rock have been measured at temperatures (T) from 25 to 400°C and at 23-35MPa. All dissolution experiments were performed in mixed-flow reactor or packed bed reactor (with Zr metal liner). The mineral samples used in these experiments have been analyzed chemically. The compositions and structures of their surfaces are also analyzed through SEM and TEM before and after reactions. All experiments were performed at far-from-equilibrium conditions. The dissolution of silicate mineral in water, such as pyroxene, actinolite, may require the breaking of more than one metal-oxygen bond type. Different metal elements in silicate mineral behave different release rates, so that the dissolution product is often non-stoichiometric. Usually, Na, Mg, Fe, Ca dissolve faster than Si at $T < 300^\circ\text{C}$. In contrast, at $T \geq 300^\circ\text{C}$, Si release rate is higher than other metals. For actinolite and diopside, Ca/Si release ratio at near 200°C is stoichiometric. SEM and TEM analyses of surfaces found the non-stoichiometric surface leaching-layer occurred at surface when dissolution is non-stoichiometric. At $T < 300^\circ\text{C}$, surfaces of actinolite and pyroxene after reacted with water is a light Si-rich and little Fe (or / and Mg, Ca) deficient. In contrast, at $T \geq 300^\circ\text{C}$, the reacted surfaces are a light Fe-rich and little Si deficient. TEM study indicates that amorphous nanothin layer was found at the surface. Metal- H^+ exchange and hydration reaction at mineral surface will pass through this layer. As dissolution is non-stoichiometric, composition and structure of non-stoichiometric surface layers change with elapsed time. For instance, when basaltic rock reacted with aqueous solutions at 90°C , release rates of Ca (Mg) decrease with the elapsed time in 7 days, the rates of Si increase with the time. The surface area (m^2/g) and total pore volume (cc/g) increase with the time. Compositions of the surface vary with the time.

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Raman spectroscopic study of the system $\text{NaCl-Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$: Implications for the determination of Cl^- concentration in fluid inclusions

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Raman spectroscopy has been demonstrated to be an efficient method for the determination of salinities in aqueous solutions [1, 2]. This study demonstrates the sensitivity of the method and the effects of other common anions, SO_4^{2-} and CO_3^{2-} , on calculated salinities.

In this study, we synthesized aqueous fluid inclusions containing various salts in fused silica capillary capsules (FSCCs) [3], and collected Raman spectra of these fluids. The OH stretching vibration bands of water between 2700 and 3900 cm^{-1} wavenumbers were fitted with PeakFit v. 4.0 using two Gaussian sub-bands at ~ 3220 and $\sim 3440\text{ cm}^{-1}$, which are considered to result from strong (HBS) and weak hydrogen bonds (HBW), respectively [2]. Our results show that, in Cl^- solutions, the ratio (K) between the peak height (I) to width (H) ratios of the two Gaussian sub-bands ($K = (I/H)_{\text{HBW}} / (I/H)_{\text{HBS}}$) varies with salt concentration, and that the difference in the K values between salt solution and pure water ($\Delta K = K_{\text{salt solution}} - K_{\text{H}_2\text{O}}$) can be used to calculate Cl^- concentration.

Our results for NaCl solutions are in good agreement with those of Sun *et al.* [2], and demonstrate that a variation of 0.5 mass % of NaCl can be easily detected. We also observed that the ΔK values increase with increasing SO_4^{2-} and CO_3^{2-} concentrations at a constant NaCl concentration, and that the effect of SO_4^{2-} is much stronger than that of CO_3^{2-} . For example, the presence of 0.05 m of CO_3^{2-} and 0.05 m of SO_4^{2-} in 0.5 m of NaCl solutions will result in the increase of 0.03 and 0.12 m in the calculated Cl^- concentrations, respectively. Therefore, the relationship between ΔK and Cl^- concentration can only be applied to Cl^- dominated solutions; otherwise, the Raman spectrometer needs to be calibrated with standards such as those prepared in FSCCs.

[1] Dubessy *et al.* (2002) *Appl. Spectrosc.* **56**, 99-106. [2] Sun *et al.* (2010) *Chem. Geol.* **272**, 55-61. [3] Chou *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 5217-5231.