



## Ammonium in crustal and subduction zone fluids

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Ammonium,  $\text{NH}_4^+$ , can be an important constituent in many crustal and subduction zone fluids, but is usually overlooked because of analytical difficulties. Large amounts of  $\text{NH}_4^+$  are generated by the decomposition of organic material during diagenesis. Ammonium is readily mobilized in hydrothermal processes. Geothermal brines can contain more than 1000 ppm  $\text{NH}_4^+$ . Hydrothermal deposits often display substantial ammonium halos with up to 25000 ppm  $\text{NH}_4^+$  in the host rocks (Ridgway et al., 1990). In minerals, ammonium is mainly incorporated into potassium silicates, some of which can transport  $\text{NH}_4^+$  to eclogite facies conditions (Busigny et al., 2003), or even into the mantle (Watenphul et al., 2009). Usually, a large fraction of the incorporated ammonium is released upon progressive metamorphism (Mingram and Bräuer, 2001) because  $\text{NH}_4^+$  strongly fractionates into the fluid relative to mica and feldspar (Pöter et al., 2004).

The behaviour of ammonium in aqueous fluids was experimentally studied to 600 °C and about 1.3 GPa in a hydrothermal diamond-anvil cell. The observed Raman spectroscopic detection limit for  $\text{NH}_4^+$  in aqueous solutions is about 0.2 molal, which explains the disregarding in fluid inclusions. However, the Raman spectra also reveal that the addition of ammonium chloride causes a strong reduction of the dynamic three-dimensional network of water. This points to a substantial decrease in the water activity even if only quite small amounts of  $\text{NH}_4\text{Cl}$  (< 1 molal) are present. Experiments on the assemblages  $\text{NH}_4\text{Cl}$  solutions plus quartz or quartz + kyanite + K-feldspar  $\pm$  muscovite show that the silica solubility is significantly lower than that in equimolar NaCl solutions. This indicates that ammonium causes an even stronger decrease in the activity of water in chloridic solutions than sodium.

At temperatures above 300 °C, a significant fraction of  $\text{NH}_4^+$  is converted to ammonia,  $\text{NH}_3$ , indicating a large shift towards acidic conditions. The  $\text{NH}_3/\text{NH}_4^+$  ratio increases with temperature and decreases with pressure. This implies that more ammonium should be retained in K-bearing minerals coexisting with chloridic fluids upon high-pressure low-temperature metamorphism.

Experiments on the kinetics of the reaction K-feldspar + kyanite + water = muscovite + quartz show a much faster proceeding in experiments with  $\text{NH}_4\text{Cl}$  solutions than in comparable experiments with water. This is attributed to the enhancement of the rate-limiting alumina solubility. The nucleation and growth of mica on the expense of K-feldspar and  $\text{NH}_4^+/\text{K}$  exchange between fluid and K-feldspar occurs simultaneously. However, there are strong indications from Raman and IR spectroscopy that the incorporation of  $\text{NH}_4^+$  into K-feldspar is even faster than the consumption of the K-feldspar during the reaction, which is already a very rapid reaction.

Ammonium has strong effects on fluid properties, element solubilities, and reaction kinetics. It is not only determinant for the recycling of nitrogen, but also very important for the composition of crustal and subduction zone fluids and the reactions occurring during the subduction process.

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