

Gallium solubility and aqueous speciation in hydrothermal solutions (60–250°C): Experimental study and comparison with aluminum

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Introduction. Gallium is of technologic and geochemical importance, especially as a tracer of weathering processes. A quantitative understanding of the aqueous geochemistry of gallium bearing minerals requires accurate values of thermodynamic constants for both gallium solids and aqueous gallium species.

Few thermodynamic data are available in the literature for aqueous gallium species. To accurately characterize the behaviour of gallium, the solubility of αGaOOH has been measured at temperatures from 60 to 250°C over the pH range 1.6 to 9. Regression of these data allows calculation of the dissociation and hydrolysis constants of gallium species.

Owing to its location on the periodic table, gallium should have chemical behaviour similar to aluminium, so a comparison between these two elements have been made.

Experimental procedure. Solubility experiments were performed at saturated vapor pressure between 60 and 250°C. Synthetic αGaOOH was obtained via a 3 weeks hydrothermal treatment of gallium hydroxide from AluSweden at 200°C in deionized water. X-ray diffraction analysis of the final product reveals only the characteristic diffraction pattern of αGaOOH , the shape of the peaks indicating a good cristallinity. Thermogravimetric analysis yields a loss of structural water equal to the theoretical value; the specific area of the powder is 0.4 m²/g. Solubility experiments at 60 and 90°C were conducted in polypropylene flasks immersed in water-thermostated baths. At higher temperatures, pure titanium autoclaves were used, which allowed the injection of the mineral and solution sampling at the temperature of the run. The gallium content was analysed by flame or flameless atomic absorption in a graphite furnace. For gallium content less than 10⁻⁸ mol/l, the analysis were made by ICP/MS.

To cover a wide range of pH (1.5 to 9), four types of solutions were used: HCl/NaCl, CH₃COOH/CH₃COONa, NH₄OH/ NH₄Cl and NaOH/NaCl at constant ionic strength of 0.025. The pH's at 60 and 90°C were measured *in situ* with glass electrodes. At higher temperatures it was computed by solving a system of non-linear equations including an iterative method for the activity coefficients.

Results and discussion. One example of the experimental results is illustrated in figure 1 where measured αGaOOH solubilities are depicted as symbols. The curve drawn through these symbols represents a least-squares fit of these data to a solubility model assuming the possible presence of the Ga³⁺, Ga(OH)²⁺, Ga(OH)₂⁺, Ga(OH)₃⁰ and Ga(OH)₄⁻ aqueous species. This fit yielded dissociation and hydrolysis constants of gallium aqueous species at each temperature.

In figure 2 the distribution of gallium species is illustrated as a function of pH at 200°C. In the temperature range investigated in this study, hydrolysis of Ga³⁺ is strongly dominated by the negatively charged species, Ga(OH)₄⁻ in natural waters. Moreover, the Ga(OH)₃⁰ species is significant only at higher temperatures.

Comparison between gallium and aluminium. The

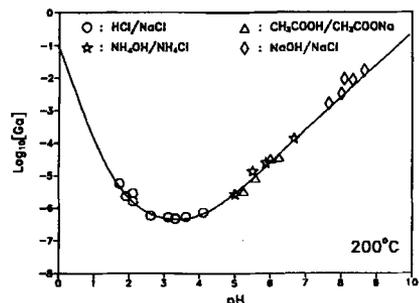


FIG.1. Solubility of αGaOOH at 200°C.

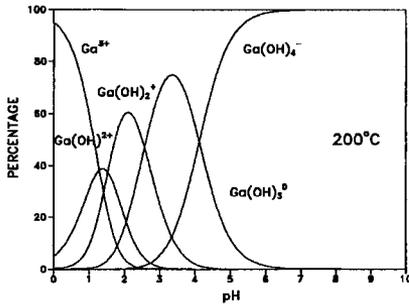


FIG. 2. Distribution of gallium aqueous species as a function of pH, at 200°C.

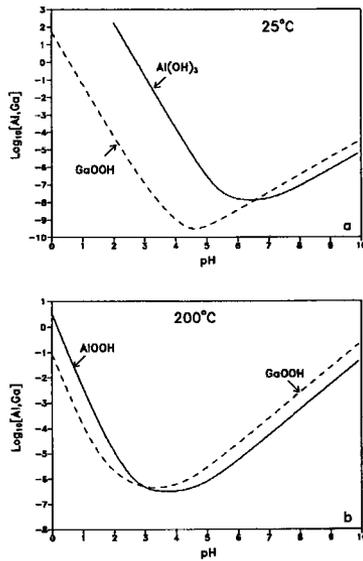


FIG. 3. Comparison of the solubility of α GaOOH and AlOOH or $\text{Al}(\text{OH})_3$ at 25°C (a) and 200°C (b).

thermodynamic data for aluminium aqueous species reported by Castet *et al.* (1993), Palmer and Wesolowski (1993) and Wesolowski and Palmer (1994), were used along with results generated in this study to better understand the behaviour of gallium in geochemical processes. Figures 3a and b compare the solubility of aluminium and α GaOOH at 25°C and 200°C, respectively. Figures 4a and b show the distribution of aqueous aluminium and gallium species at 25°C.

At 200°C, the solubility curve (fig. 3b) and thus the speciation of aluminium and gallium tend to converge. In particular, at pH's commonly encountered in natural fluids ($5 < \text{pH} < 8$), aluminium and gallium are simultaneously present as negatively

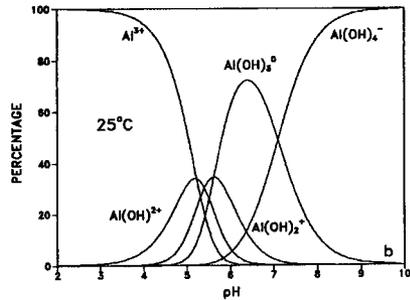
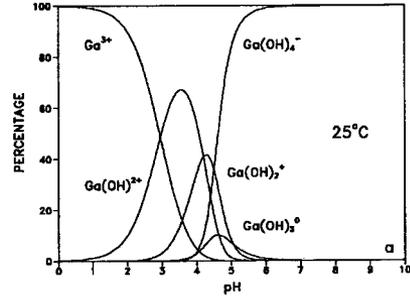


FIG. 4. Comparison of the distribution of aluminium and gallium aqueous species at 25°C.

charged species. This accounts for their similar behaviour in hydrothermal fluids. In contrast, at 25°C, the behaviour of Al and Ga differ significantly at the pH's range of natural solutions. At these conditions $\text{Ga}(\text{OH})_4^-$ is the dominant gallium species, whereas as the $\text{Al}(\text{OH})_3^0$ species dominates aluminium speciation. This could account for a selective removal of gallium in solution in contact with Fe, Al... oxides or oxyhydroxides whose surfaces are positively charged at pH's up to 8. In addition, the adsorption of gallium will be more difficult than that of Al or Fe, on negatively charged solid surfaces. In acidic range, gallium is less mobile than aluminium as it is less hydrolyzed (see Fig. 3b). Gallium is thus better suited to form complexes, particularly with organic ligands (Bénézech *et al.*, 1994).

References

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