

## The effect of pressure and temperature on aluminium hydrolysis: Implications to trace metal scavenging in natural waters

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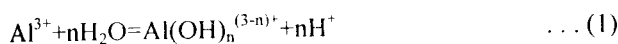
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Removal of aluminium through precipitation/scavenging in natural waters was evaluated based on its hydrolysis at different temperatures and pressures. In general,  $pH$  for the occurrence of cation hydrolysis was lowered with hike in temperature which further decreased with increase in pressure. Four kinds of natural water systems with varied  $pH$ , temperature and pressures were studied. Al removal seems to be more favoured in river and seawater at low pressures, that is not favoured in the deep oceans; that could have similar implications to the scavenging of other metal ions in natural waters.

The pressure and temperature are inherent properties of natural geochemical systems and can significantly influence the aqueous metal ion chemistry. Typical examples are the occurrence of high pressures in deep oceans, high temperatures in surficial geothermal waters and high pressures and temperatures near Mid-Oceanic Ridge Systems (MORS). The metal ion chemistry when influenced by these physical parameters can have a significant impact on the fate of the respective metal, in the systems in question. For instance, a metal ion that forms stable soluble species at standard temperature (25°C) and pressure (1 bar) might form more insoluble or scavengeable species at high temperature and/or pressures. In natural waters, the abundance of metal ions are maintained by processes, other than biological ones, such as precipitation and scavenging. The metals susceptible to oxyhydroxide precipitation are very few (Al, Fe, Th etc.) in natural waters<sup>1</sup>. Although scavenging process has been known, from the classical work of Krauskopf<sup>2</sup>, to be the controlling mechanism for many trace metal concentrations in seawater the influence of pressure and temperatures on this process is not well known. The intensity of scavenging is predicted, based on cation hydrolysis, to be high at elevated temperatures<sup>3</sup> that is experimentally found to be so<sup>4,5</sup>. Here, we attempt to understand the scavenging/precipitation behaviour of aluminium in natural waters, including hydrothermal systems at high pressures, through thermochemical considerations of Al-hydrolysis, with implications to the scavenging of other trace metals.

### Data and Computations

A general Al-hydrolytic reaction can be written as



for which the equilibrium constant ( $\beta$ ) is

$$\beta = \frac{[\text{Al}(\text{OH})_n^{(3-n)+}][\text{H}^+]^n}{[\text{Al}^{3+}]} \quad \dots (2)$$

During the stepwise hydrolysis one proton would be released and hence at equal concentrations of reactant and product species

$$\beta = [\text{H}^+] \quad \dots (3)$$

This relation could be utilised<sup>3,6</sup> for the evaluation of stability fields for hydrolytic species. Here, we calculated stability fields for  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$  and  $\text{Al}(\text{OH})_4^-$  for different temperatures at 1 bar using the thermodynamic equilibrium constants of Baes & Mesmer<sup>7</sup>.

### Results

The stability fields were shown as a function of  $pH$  in Fig. 1 with respect to Eq. (3). The lines in Fig. 1 represent  $pH$  and temperatures at which the two successive species are at equilibrium. Our results in Fig. 1 suggest a general decrease in  $pH$  for the occurrence of respective hydrolytic reactions with an increase in temperature, except for the negative species above 100°C. The  $\text{Al}(\text{OH})_4^-$  is unstable at temperatures below 150°C.

The stability diagram for Al-hydrolysis at 100 bar and various temperatures, Fig. 7 of Bourcier *et al.*<sup>8</sup>, was also considered in the present evaluation. The comparison between Fig. 1 and that of Bourcier *et al.*<sup>8</sup> revealed that increase in pressure further lowered the  $pH$  required for the respective hydrolytic reactions compared to those  $pH$  values in Fig. 1. For instance,  $\text{Al}(\text{OH})_4^-$  starts occurring above a  $pH$  7 at 1 bar (Fig. 1) but at  $pH < 6$  at 100 bar. While  $\text{Al}(\text{OH})_4^-$  is unstable at temperatures below 150°C at atmospheric pressure (Fig. 1) it appears to exist even at 25°C at a pressure of 100 bar. However, at temperatures above 150°C the stability field for  $\text{Al}(\text{OH})_4^-$  increased. Essentially, the present comparison suggests that the

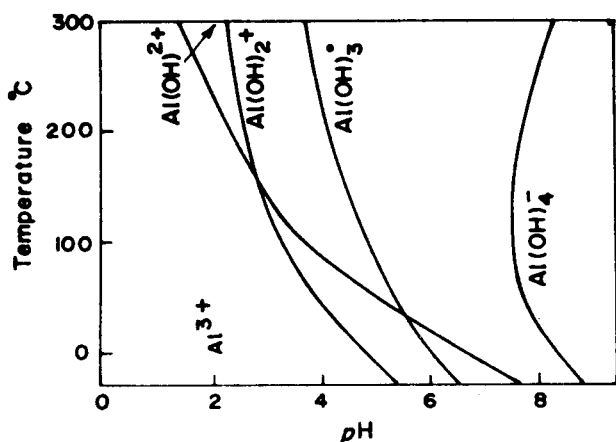


Fig. 1—Stability fields for aluminium hydrolytic species as functions of pH and temperature at 1 bar.

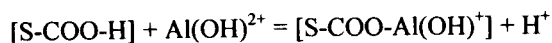
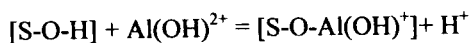
hydrolytic reactions are more progressive with enhanced temperature and pressures.

*Stability and abundance of  $Al(OH)_3^0$* —Albeit the occurrence of  $Al(OH)_3^0$  in aqueous solutions is debatable its existence is shown<sup>8</sup>. This species is significant as the neutral hydroxy metal complexes determine the minimum solubility limits of oxyhydroxide solid phases in aqueous solutions<sup>6</sup>. The stability field for the occurrence of neutral hydroxyl complex generally increases with rise in temperature (Fig. 1). At 200°C,  $Al(OH)_3^0$  is stable within a pH range of ~3.5 at 1 bar but over 2.7 at 100 bar. However, its stability at lower temperatures differed as the pressure changed. At 25°C the  $Al(OH)_3^0$  of >50% occurs in the pH range between 5.5 and 8 at 1 bar whereas it seems to be unstable at 100 bar. Consequently, Fig. 7 of Bourcier *et al.*<sup>8</sup> suggests that at temperatures <25°C at 100 bar pressure the neutral species does not seem to be a stable intermediate during the conversion of  $Al(OH)_2^+$  to  $Al(OH)_4^-$ . The behaviour of several other metal ions considered is similar to that of Al-hydroxyl complexes at 1 bar, i.e., the pH of respective hydrolytic reactions decreased and stability field for neutral hydroxyl complexes enhanced with elevated temperature<sup>3</sup>.

## Discussion

The most important solid phases in natural waters are oxyhydroxides<sup>9</sup> that form due to changes in pH and redox potentials. The oxyhydroxide, silica and organic (including those inorganic particles coated by dissolved organic ligands) surfaces are ubiquitous in natural waters and can

provide active surface sites for the adsorption of metal ions/complexes. The adsorption/scavenging is a complexation reaction between a ligand and a metal ion/complex, e.g.



where S is an active surface site on a particle. The stoichiometry might differ based on the number of ligands bound to a metal complex or ion. The  $Al(OH)^{2+}$  can react with two sites and form a bidentate complex.

Scavenging constants for the adsorption of trace metals on to inorganic and organic particles are found to be positively linearly correlated to the first hydrolysis constants<sup>10</sup>. Further, considering that the free energy of adsorption would be inversely proportional to hydrolytic constants, the latter are found to be negatively related to the residence times of metal ions in the oceans<sup>9</sup>. Brady<sup>4,5</sup> noted an increase in metal binding constants at silica and alumina surfaces with rise in temperature that are positively related to metal ion first hydrolytic constants at respective temperatures. This is in accordance with the prediction of the scavenging tendency of the cations based on the thermochemical considerations<sup>3</sup>. Hence, the hydrolytic species are useful in understanding the scavenging behaviour of trace metals in natural waters at various temperatures and pressures as well. We shall consider four kinds of natural water systems here: (1) normal river and pore waters with temperatures  $\leq 25^\circ\text{C}$  and  $\text{pH} \sim 5.8$ , (2) normal seawater with temperatures of  $\leq 25^\circ\text{C}$  and  $\text{pH} \sim 8$ , (3) surficial hydrothermal solutions with pH values of  $\sim 5.8$  and 8 at 1 bar and (4) sub-sea hydrothermal systems with pH values of  $\sim 5.8$  and 8 at 100 bar.

*Normal river and sediment pore waters*—River waters generally have a pH between  $\sim 5.5$  and 7 unless the catchment area is composed of basic rocks. On the other hand, the sediment pore waters have  $\text{pH} < 6$ , which will be lower than the pH of overlying waters, due to the intense oxidation of organic matter. Figure 1 suggests that the occurrence of equal abundance for  $Al(OH)_2^+$  and  $Al(OH)_3^0$  at  $0^\circ\text{C}$  shifts to higher abundance of the latter species at  $25^\circ\text{C}$ . Consequently, in river and pore (from shallow depths) waters Al is vulnerable for scavenging and precipitation. Increase in  $Al(OH)_3^0$  with rise in temperature to  $25^\circ\text{C}$  indicates that the tropical river waters could reach precipitation equilibrium faster than those in temperate and polar regions. On the contrary, at 100 bar pressure  $Al(OH)_2^+$  and  $Al(OH)_2^+$  prevail at  $0^\circ\text{C}$  whereas  $Al(OH)_3^0$  appears to occur at about  $25^\circ\text{C}$  (Fig. 2). Figure 2 was made from the information derived, from Fig. 7 of Bourcier *et al.*<sup>8</sup>

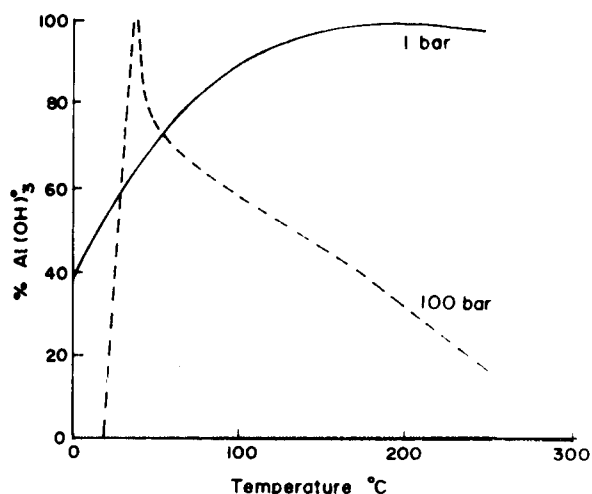


Fig. 2—Variations in %Al(OH)<sub>3</sub><sup>°</sup> with temperature at a pH of 5.8 and pressures of 1 and 100 bar.

and Fig. 1, shown above, on the relative abundance of Al(OH)<sub>3</sub><sup>°</sup> with rise in temperature. Thus scavenging is the plausible Al-removal mechanism in interstitial water at 1000m in the oceans where the precipitation is not likely.

**Normal seawater**—The Al(OH)<sub>3</sub><sup>°</sup> behaves in an opposite way in seawater (pH~8) compared to that in the river water considered above. As the temperature rises from 0 to 25°C its abundance decreases to 50%, with the related increase in Al(OH)<sub>4</sub><sup>-</sup> (Fig. 1). This suggests that the scavenging of Al would be more intense in river and pore waters than in seawater, because considerable amounts of anionic Al-species are present in the latter. At 100 bar the most abundant species<sup>8</sup> is Al(OH)<sub>4</sub><sup>-</sup> and hence the scavenging of Al will decrease with increasing depth in the oceans. Precipitation of Al-oxyhydroxides is also unlikely in deep seawater because the pH of 8 is basic enough to enable the prevalence of negative hydrolytic species. These observations reveal that the intensity of scavenging and/or precipitation removal of Al decreases from river water to seawater and further from surface to deep seawater, barring the pore waters in deep oceans.

**Surficial hydrothermal waters**—A pH of 5.8 was considered here since the laboratory experiments involving seawater and basalt glass showed an initial drop in pH that later stabilised<sup>11</sup> at slightly below 6. Besides, the consideration of linear mixing between hydrothermal solution and seawater with pH values of 3.5 (300°C) and of 8 (2°C), respectively, yielded a pH of 5.8 when the reaction mixture attained a temperature of 250°C, where the sulphate prevailed in solution<sup>3</sup>. In geothermal fresh waters (pH~5.8) at 1 bar, as the temperature increases from 25 to 250°C, the

abundance of Al(OH)<sub>3</sub><sup>°</sup> increased from ~50% to 100% (Figs 1 and 2), having Al(OH)<sub>2</sub><sup>+</sup> as the secondary complex.

On the other hand, during hydrothermal mixing, as the pH of 8 at 25°C changes to 5.8 at 250°C, Fig. 1 suggests a slight decrease in Al(OH)<sub>3</sub><sup>°</sup> abundance between 25 and 100°C that later increased with enhanced temperature. During this process, however, the secondary complex is Al(OH)<sub>4</sub><sup>-</sup>. Therefore, during hydrothermal mixing the abundance of neutral complex becomes greater at temperatures >100°C thus facilitating the precipitation of Al. However, between 25° and 100°C at 1 bar, Al is scavengable in waters of pH~5.8 since Al(OH)<sub>2</sub><sup>+</sup> is the second most abundant complex, but not in waters of pH~8 in which Al(OH)<sub>4</sub><sup>-</sup> is the secondary species.

**Sub-sea hydrothermal water**—In hydrothermal waters, under pressure (100 bar) with a pH of ~5.8, the Al species dominance changed from Al(OH)<sub>2</sub><sup>+</sup> to Al(OH)<sub>4</sub><sup>-</sup> when temperature increased from 25 to 250°C. In fact the abundance of Al(OH)<sub>3</sub><sup>°</sup> enhanced sharply above 20°C but below 40°C to ~100% (Fig. 2); thereafter increase in temperature resulted in the decrease of this neutral species and in increased stability for Al(OH)<sub>4</sub><sup>-</sup>. Hence, while Al could be removed through precipitation and/or scavenging at high temperatures at 1 bar, it is susceptible for removal at low temperatures, at 100 bar, during the geothermal mixing. This could be one of the reasons for the enhanced Al in the vicinity of hydrothermal sediments, in the Atlantic, where >6% has been found that decreased to 4-6% farther<sup>12</sup>.

It is concluded that Al removal through precipitation and inorganic scavenging is more favourable at surface than in the deep oceans. This is due to the prevalence of positive or neutral hydroxyl complexes in the former waters and anionic complex in the latter. As the behaviour of Al-hydrolytic species is similar to those of many other metal ions the latter ions might undergo scavenging processes in much the same way as those of Al in natural waters, i. e., relatively more susceptible for scavenging in river and surface seawater, particularly at elevated temperatures.

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