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Dissolved aluminium in interstitial water of recent marine sediments

NOTE

Dissolved aluminium in interstitial waters of recent marine sediments

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Abstract—Measurements of the concentration and vertical distribution of dissolved aluminium and silica, and of pH, in interstitial waters of recent marine sediments from the North Sea and the Mediterranean Sea were performed to evaluate the behaviour of aluminium during early diagenesis. The results suggest that thermodynamic equilibria alone do not control the concentrations of dissolved species in the system Al–Si–O₂–H₂O during early diagenesis. Rather, these concentrations are governed by dynamic factors involving mineral dissolution-precipitation reactions and diffusion.

INTRODUCTION

Knowledge of the concentration and distribution of dissolved aluminium (Al_{diss}) in natural waters has improved substantially since the development of Al fluorimetric method.

In the case of seawater, the vertical distribution of Al_{diss} in the water column strongly suggests the importance of the planktonic activity on the removal of Al from the oceanic system (MACKENZIE *et al.*, 1978; CASCHETTO and WOLLAST, to be published). The behaviour of Al_{diss} in estuarine environments is still a matter of controversy (HOSOKAWA *et al.*, 1970; HYDES and LISS, 1977).

To our knowledge, there are no data available on the distribution of Al_{diss} in the interstitial waters of marine sediments. However, to understand the geochemical cycle of Al and processes involved in the early diagenesis of clay minerals, it is necessary to know the concentration, distribution, and mineral sinks and sources of Al_{diss} in marine sediments.

This brief contribution provides some preliminary results from coastal marine sediments concerning these factors.

METHODOLOGY

General

Five cores were collected, two from the Mediterranean Sea and three from the North Sea. The Mediterranean cores 57-2 and 94 were obtained using a gravity corer about 2.7 km offshore of Calvi (Corsica) at depths of 57 and 94 m. The core sediments consist principally of medium-grained, quartzo-feldspathic sand containing accessory biotite, calcareous tests, siliceous sponge spicules and numerous remains of marine phanerogams. Cores 19 and 32 were taken in the Fladden Ground of the North Sea (58°25'5"N, 00°02'0"E and 58°30'3"N, 00°41'4"E) at depths of 135 and 140 m by means of a box-corer during cruise 54-6 of the *Kuorr* ("FLEX" program). These sediments are medium-grained sands. Glacial pebbles are recognizable in core 32. The third North Sea core was collected by Belgian Navy divers about 1.8 km offshore of the Belgian Coast at a depth of 10 m (Station M1149). It is characterized by a very fine, dark muddy sand. No laminations are present in the five cores.

Core 57-2 was sliced immediately after collection on board ship, and then stored in sealed polyethylene bags for 3 hr at 10°C. The interstitial waters were extracted from the sediments using a PVC 'squeezer' by pressure filtration through a 0.45 μm Millipore[®] filter under 3 bar of nitrogen. Cores 19, 32, 94, and M1149 were frozen immediately after collection. The interstitial waters of cores 19, 32 and 94 were later extracted following the above procedure. Waters from core M1149 however, were removed from the sediments by centrifugation and subsequent filtration. In all cases, the pore waters were extracted at the *in situ* temperatures of collection. Frozen cores were thawed overnight at the *in situ* temperature before treatment.

Analytical procedures

Interstitial waters were analyzed for dissolved silica by absorption spectrophotometry (Technicon Auto-Analyzer, Methodology 186-72W) and for dissolved aluminium by fluorescence spectrophotometry of the Al-lumogallion complex (NISHIKAWA *et al.*, 1967; SHIGEMATSU *et al.*, 1970; HYDES and LISS, 1976), using the method of Al increments. In all the pore waters we analyzed, this Al incremental calibration was able to prevent the problems involving interferences owing to F, SO₄²⁻, Fe and dissolved organic matter as previously shown by HYDES and LISS (1976). However, if sediments contain much organic matter, it must be photo-oxidized (1000W u.v. Hanovia lamp) prior to the Al_{diss} analysis, as was done in the case of core M1149.

The practical detection limit of the Al-lumogallion method was found to be 0.003 μmole Al l⁻¹. From five independent analyses of a seawater containing 0.078 μmole Al l⁻¹, we obtained an estimated standard deviation of 0.003 μmole Al l⁻¹.

To determine the effect of storage on Al_{diss} determinations, a duplicate analysis of Al_{diss} was performed on the interstitial waters of core 57-2 after storage of the waters for 10 days at 7°C (Fig. 2). After storage most of the water samples exhibited a decrease in Al_{diss} but the general shape of the vertical concentration gradient of Al_{diss} was maintained.

HYDES and LISS (1976) investigated variations in the amount of Al_{diss} detected by this fluorimetric method in clay suspensions of various concentrations and in natural waters which were filtered through different pore size mem-

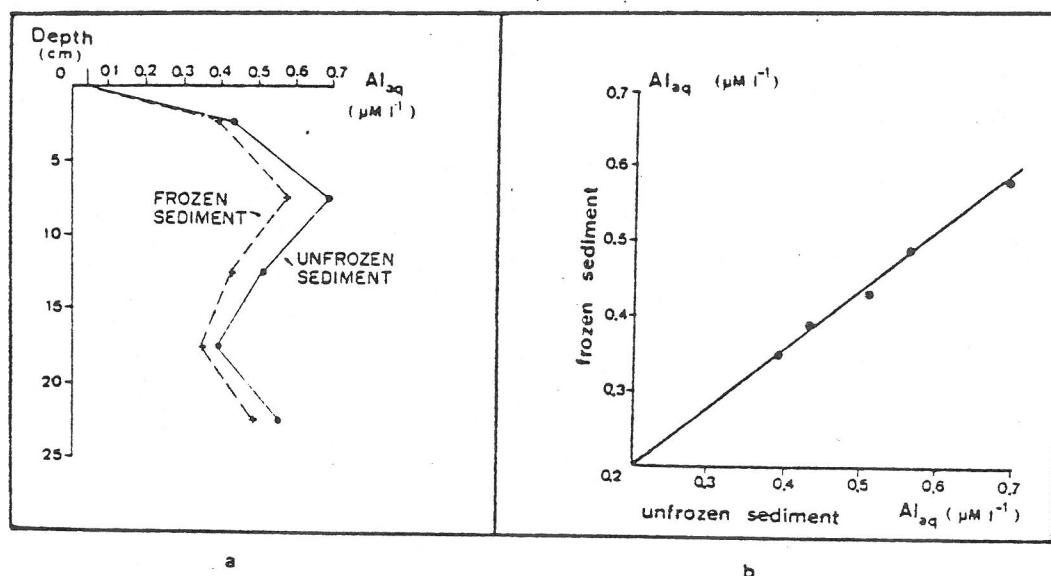


Fig. 1. Al_{aq} concentration in interstitial waters of sediments collected in an artificial lagoon on the Belgian Coast: (a) comparison between the vertical distribution in interstitial waters squeezed from the unfrozen sediment (\bullet) and the vertical distribution in interstitial waters squeezed from frozen sediment ($+$); (b) plot of the values from unfrozen sediment versus those from frozen sediment. The slope of the line through the points is 0.87.

branes. They were able to show that dissolution of clay material passing through the filters does not occur during the analytical treatment of samples and that only very small amounts of Al adsorbed on particles passing through the filters are detected by this technique. They concluded that this method is a very reliable measurement of the dissolved aluminium species. Therefore, the Al_{aq} concentrations presented in this paper represent total dissolved aluminium or at least the total sum of reactive Al species such as those involved in chemical reactions with aluminosilicates.

Effect of freezing

To determine the effect of freezing on the analysis of Al_{aq} in sediment pore waters, two 25 cm cores composed of homogeneous, grey, medium-grained, quartzose sand containing calcareous tests of molluscs (from 0 to 20 cm), and of compact, black mud (from 20 to 25 cm) were collected in an artificial lagoon on the Belgian Coast. The cores were taken within 50 cm of each other. From one of the cores, pore waters were extracted soon after collection by pressure filtration, and then stored at 5°C prior to analysis of Al_{aq} by the fluorimetric method. The second core was sliced into 5 cm sections which were stored frozen in sealed polyethylene bags for 4 days. After thawing overnight at the *in situ* temperature of collection, the pore waters were extracted from the sediments by pressure filtration and stored at 5°C prior to Al_{aq} analysis.

Figure 1a shows the Al_{aq} concentrations obtained for the pore waters extracted from these frozen and unfrozen sediments. The data show that in this case freezing of sediments prior to analysis of the pore waters for Al_{aq} results in about a 13% decrease in the original Al_{aq} concentrations. This conclusion is based on the assumption that the pore waters of the frozen and unfrozen sediments had the same original Al_{aq} concentrations at similar core depths under *in situ* conditions.

Furthermore, the shape of the vertical concentration gradient of Al_{aq} in pore waters from both the frozen and unfrozen sediments is very similar (Fig. 1a). Thus, it appears that although sediment freezing may affect Al_{aq} concentrations in interstitial waters, the shape of the concentration profile of Al_{aq} may not be significantly altered by freezing. Also, it appears that in these experimental cores,

the absolute decrease in Al_{aq} concentrations because of freezing is linearly related to original Al_{aq} concentrations (Fig. 1b).

Freezing of extracted interstitial waters however, does not seem to significantly affect Al_{aq} concentrations. Pore waters were obtained by pressure filtration from a 32 cm core collected in the Mediterranean Sea. The waters before and after freezing and thawing were analyzed for Al_{aq} . The results (Table 1) show that differences in Al_{aq} concentrations for waters at similar depths analyzed before and after freezing and thawing are in the range of analytical error.

In summary, although freezing of sediments before extraction of pore waters does significantly reduce Al_{aq} concentrations, the effect is not large enough to invalidate the conclusions drawn later in this paper.

RESULTS AND DISCUSSION

As has been reported for several other dissolved species, the concentration of Al_{aq} in the interstitial waters of sediments is considerably higher than in the overlying water (Figs. 2-6). The concentration of Al_{aq} in pore waters may attain values 3-30 times its concentration in bottom waters.

Furthermore, the shape of the Al_{aq} concentration gradients in interstitial waters near the sediment-water interface implies a flux of Al_{aq} from the sediments to the overlying water column. This flux may be responsible for the relatively high Al_{aq} values observed in deep seawater

Table 1. Al_{aq} concentration in interstitial waters extracted from the sediments of a core collected in the Mediterranean Sea (Corsica). Comparison between the values measured before and after freezing of the interstitial waters

Depth (cm)	Al_{aq} ($\mu mole l^{-1}$)		% relative change
	Before freezing	After freezing	
0-10	0.59	0.55	5
10-20	2.02	1.96	5
20-32	0.80	0.58	3

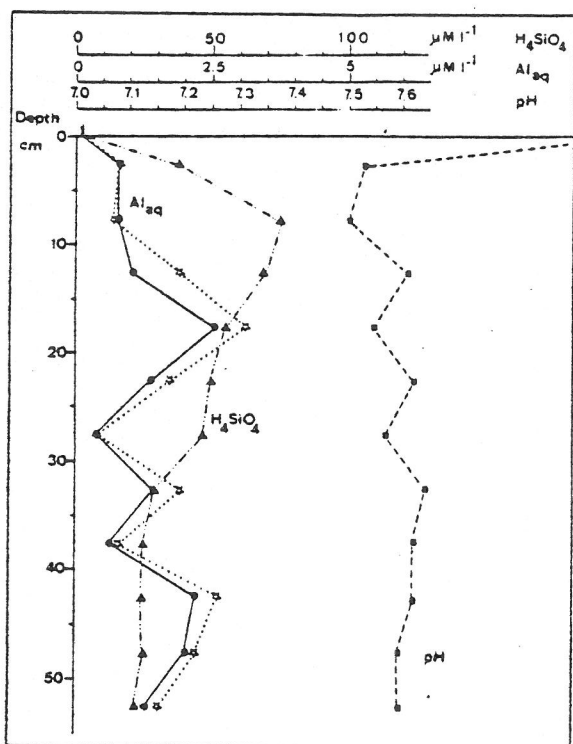


Fig. 2. Vertical distribution of dissolved silica (\blacktriangle), Al_{aq} (\bullet) concentrations, and pH (\blacksquare) in the interstitial waters of core 57-2 sediments (Mediterranean Sea, Corsica). Duplicate analyses of Al_{aq} (\bullet) were achieved on stored waters (see text).

(MACKENZIE *et al.*, 1978; CASCHETTO and WOLLAST, to be published).

The concentration of Al_{aq} in the interstitial waters of Mediterranean Sea sediments offshore of Corsica is greater than in waters extracted from North Sea sediment cores.

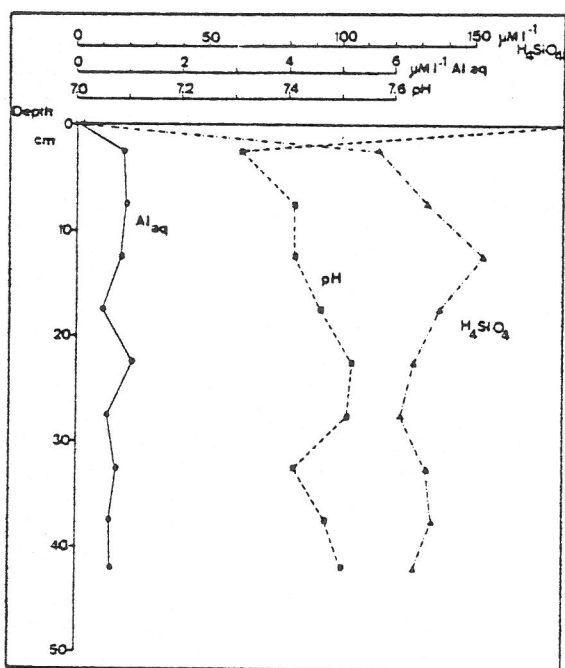


Fig. 3. Vertical distribution of dissolved silica (\blacktriangle), Al_{aq} (\bullet) concentrations, and pH (\blacksquare) in the interstitial waters of core 94 sediments (Mediterranean Sea, Corsica).

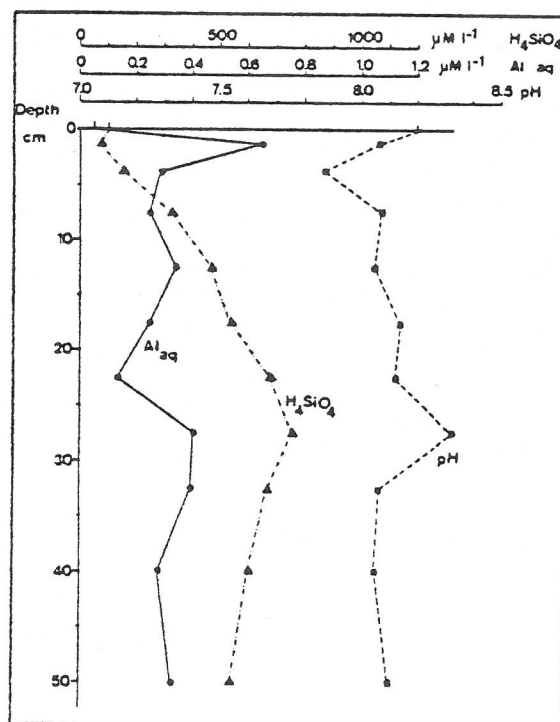


Fig. 4. Vertical distribution of dissolved silica (\blacktriangle), Al_{aq} (\bullet) concentrations, and pH (\blacksquare) in the interstitial waters of core M1149 sediments (North Sea, Belgian Coast).

The concentration of Al_{aq} in pore waters of core 94 from the Mediterranean Sea (Fig. 3) shows a nearly constant value of about $1 \mu mole Al l^{-1}$ at depths greater than 2.5 cm, whereas core 57-2 (Fig. 2) from the same area exhibits distinct vertical variations in its Al_{aq} content. This vertical variation ranges from about 0.1 to $2.6 \mu mole Al l^{-1}$. In contrast, the concentration of Al_{aq} in pore waters from North Sea sediments ranges from <0.1 to about $0.7 \mu mole Al l^{-1}$ (Figs. 4-6).

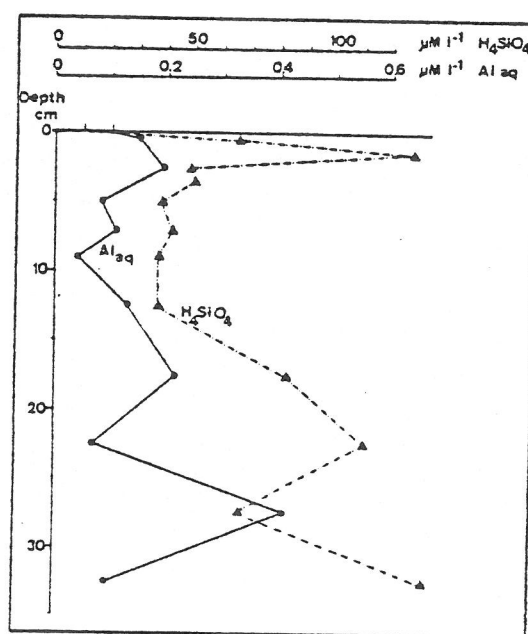


Fig. 5. Vertical distribution of dissolved silica (\blacktriangle) and Al_{aq} (\bullet) concentrations, in the interstitial waters of core 19 sediments (North Sea, Fladden Ground).

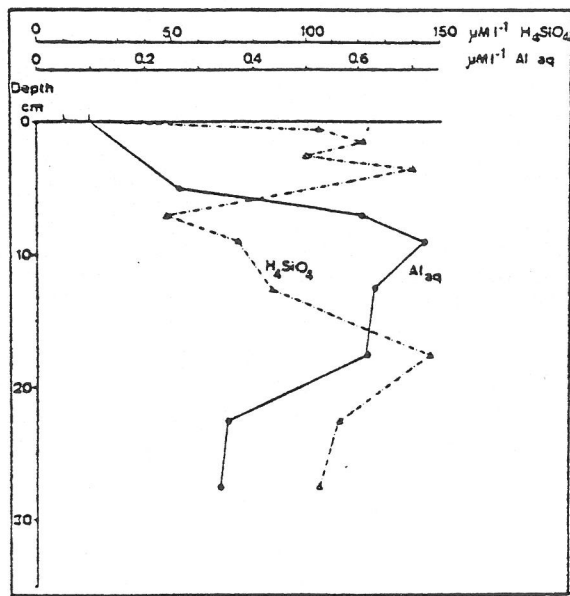


Fig. 6. Vertical distribution of dissolved silica (▲) and Al_{aq} (●) concentrations in the interstitial waters of core 32 sediments (North Sea, Fladden Ground).

We compared the pore water results for Al_{aq} with the aluminium concentrations obtained by HYDES (1977) during laboratory dissolution experiments of kaolinite, fireclay and montmorillonite in seawater. After four months at final pHs and H_4SiO_4 concentrations of 7.35–8.1 and 43–207 $\mu\text{mole l}^{-1}$, respectively, Hydes found Al_{aq} concentration values ranging from 0.1 to 0.3 $\mu\text{mole Al l}^{-1}$. In one experiment with montmorillonite at pH of 7.35, the Al_{aq} concentration was only 0.05 $\mu\text{mole Al l}^{-1}$. This range of Al_{aq} concentrations is comparable to the range of concentrations observed in the North Sea sediment pore waters. Therefore, it is possible that Al_{aq} in these sediments is controlled by reactions involving clay minerals. However, the Al_{aq} concentrations in the pore waters of Mediterranean sediments are one order of magnitude higher than the experimental concentrations observed by Hydes.

Ion activity products (*IAP*) for aluminium hydroxides were calculated for the interstitial waters and compared with equilibrium constants (*K*) for mineral dissolution-precipitation reactions. No consistent relationship was found to exist between *IAPs* and equilibrium constants. Indeed, in the case of cores M1149 and 94, the concentration of Al_{aq} in the interstitial waters of these sediments is 5–50 times less than that required for equilibrium with aluminium hydroxides at the observed pH values. Also, there is no consistent *IAP* as one should expect if the concentration of the dissolved species are controlled by an equilibrium with clay minerals or other aluminosilicates.

The lack of any consistent relationship between *IAPs* and equilibrium constants for minerals may be due to the following reasons:

1. During early diagenesis dissolved silica in pore waters attains a steady-state concentration rather than a true

chemical equilibrium concentration. The stationary value results from the competition between the dissolution of biogeneous amorphous silica and uptake of dissolved silica by silicates (WOLLAST, 1974).

2. The mineral assemblage is extremely complex and several aluminosilicates may compete in the release and uptake of dissolved species.

3. As pointed out recently by LIPPMANN (1977), description of the aqueous equilibrium solubility of clay minerals such as illite, montmorillonite or interstratified intermediate, requires the use of up to five partial solubility products. Therefore, it is unlikely that these minerals form in nature under equilibrium conditions.

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REFERENCES

- CASCETTO S. and WOLLAST R. to be published Vertical distribution of dissolved aluminium in the Mediterranean Sea. *Mar. Chem.*
- HOSOKAWA I., OSHIMA F. and KONDO N. (1970) On the concentrations of the dissolved chemical elements in the estuary of the Chikugogawa River. *J. Oceanogr. Soc. Jap.* 26, 1–5.
- HYDES J. D. (1977) Dissolved aluminium concentration in sea water. *Nature* 268, 136–137.
- HYDES J. D. and LISS P. S. (1976) Fluorimetric method for the determination of low concentrations of dissolved aluminium in natural waters. *Analyst* 101, 922–931.
- HYDES J. D. and LISS P. S. (1977) The behaviour of dissolved aluminium in estuarine and coastal waters. *Est. Coastal Mar. Sci.* 5, 755–769.
- LIPPMANN F. (1977) The solubility products of complex minerals, mixed crystals, and three-layer clay minerals. *Neues Jahrb. Mineralog. Abh.* 130, 243–263.
- MACKENZIE F. T., STOFFYN M. and WOLLAST R. (1978) Aluminium in seawater: control by biological activity. *Science* 199, 680–682.
- NISHIKAWA Y., HIRAKI K., MORISHIGE K. and SHIGEMATSU T. (1967) Fluorophotometric determination of aluminium and gallium with lumogallion. *Japan Analyst* 16, 692–697.
- SHIGEMATSU T., NISHIKAWA Y., HIRAKI K. and NAGANO N. (1970) Fluorometric determination of trace amount of aluminium in natural water by lumogallion method: masking of ferric iron with *O*-phenanthroline. *Japan Analyst* 19, 551–555.
- WOLLAST R. (1974) The silica problem. In *The sea*, Vol. 5 (ed. E. D. Goldberg), pp. 359–392. Wiley.