

## Fluorescence Spectroscopic and Chromatographic Evidence for the Interaction of NOM and Metal Ions

F. H. FRIMMEL<sup>1</sup>, M. DELAY<sup>2</sup> AND K. VERCAMMEN<sup>3</sup>

<sup>1,2,3</sup> Engler-Bunte-Institut, Chair of Water Chemistry,  
Universitaet Karlsruhe, Engler-Bunte-Ring 1, 76131  
Karlsruhe, Germany

<sup>1</sup> (fritz.frimmel@ciw.uni-karlsruhe.de)

<sup>2</sup> (markus.delay@web.de)

<sup>3</sup> (karlien.vercammen@ciw.uni-karlsruhe.de)

### Introduction

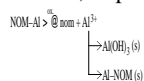
The presence of natural organic matter (NOM) in aquatic systems can strongly effect the transport of metal ions. Little is known about the influence of oxidation processes on the NOM complexing properties. As an example, the influence of photooxidation on the stability of NOM–Al complexes was investigated. The NOM sample originates from a brown water lake (Lake Hohloh, Northern Black Forest, Germany).

### Experimental

The interaction of NOM and metal ions can be characterized by fluorescence spectroscopy and size-exclusion chromatography (SEC) coupled with inductively-coupled plasma mass spectroscopy (ICP-MS). Fluorescence spectroscopic techniques allow a non-destructive investigation of the metal-NOM system. Coupling of SEC and ICP-MS gives information about molecular sizes, metal distributions, and the metal mobility.

### Results

At the beginning, fluorescence intensities of the NOM samples increased with increasing duration of irradiation due to cleavage of NOM molecules. Progressing irradiation and mineralization of NOM finally led to decreasing fluorescence intensities. The fluorescence signals in SEC chromatograms showed a shift towards higher elution volumes for the oxidized samples. The shift is probably attributed to the formation of smaller molecules (nom). A decrease of NOM–Al complex formation due to oxidation of NOM could be found. A shift of the Al signal towards higher molecular weight compounds indicates the formation of Al hydroxides and/or Al–NOM colloids, as pictured in the following reaction scheme:



Results of Pb and Zn will also be discussed.

### References

- Kumke, M.U., Tiseanu, C., Abbt-Braun, G. and Frimmel, F.H., (1998), *J. Fluorescence*, **8(4)**, 309-318.  
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## Dissolution experiments and natural weathering of carbonates.

S.FRISIA<sup>1</sup>, A.BORSATO<sup>1</sup>, F.T.MACKENZIE<sup>2</sup>, AND  
R. TOMASONI<sup>1</sup>

<sup>1</sup>Museo Tridentino di Scienze Naturali, via Calepina 14, 38100  
Trento, Italy (frisias@mtsn.tn.it)

<sup>2</sup>Dept. of Oceanography, University of Hawaii, Honolulu, HI  
96822 USA (fredm@iniki.soest.hawaii.edu)

The rate of dissolution of natural dolomite and calcite, which show similar rates of weathering in the outcrops, were investigated using free-drift experiments on samples for which physico-chemical properties had been determined by scanning (SEM) and transmission (TEM) electron microscopy, EDS and ICP-AES. The surface morphology and grain-size of ground particles prior to, and after the experiments were observed by SEM, and compared with karst spring suspended sediment and naturally weathered surfaces. The experimental conditions were pH = 5.16, and T = 25°C, particle size  $\phi = 90 \mu\text{m}$ . Samples were precleaned in a sonic bath, and slightly acidified. The Solution pH and chemistry were measured at fixed intervals. Reactions approached steady-state after 21 hours for the limestone, and 27 for the dolomite.

Pre-reaction dolomite grain size distribution ranged from < 10  $\mu\text{m}$  to 90  $\mu\text{m}$ , in the same range as those of suspended sediments. Grain surfaces had ledges, macrokinks and original etch-pits. Pre-reaction calcite grains-size distribution was 90  $\mu\text{m}$ , and grains had smooth surfaces. The dolomite reaction rate was more rapid than that of the calcite in the first 20 hours. After 1 hour, 0.203 mol. Ca and 0.200 mol. Mg were released to the solution by dolomite, and 0.046 moles Ca were released in the limestone reaction. Only after 22 hours, were the dissolution rates of calcite and dolomite similar. Post-reaction dolomite grain surfaces show the development of etch pits located along ledges and structural defects, and deepening and intersection of original etch pits. Post-reaction calcite grain surfaces show the development of ledges, etch-pits located along twins and cleavage planes, and preferred dissolution at subgrain boundaries, as observed in naturally weathered specimens.

The rates of dissolution seem to be affected by the original surface morphologies, and the distribution of defects. Pre-reaction dolomite grains had rugged surface morphology resulting from outcropping defects (ribbon microstructures, dislocations), and high surface/volume ratio in the smaller size-fraction. Pre-reaction calcite was almost defect-free, and had less reactive sites. Average grain surface/volume ratio was smaller than in the dolomite. Higher surface/volume ratio, and number of reactive sites are probably the cause of the initial, rapid dissolution rate for the dolomite. Dissolution rate of calcite reached that of dolomite (and then became faster) once a large number of ledges were exposed to the solution during the reaction. Experimental results are consistent with the physico-chemical properties of waters from aquifers that develop in the two carbonates of the present study.