

Speciation of Phosphate in Iron Rich Mineral Deposit in a High Mountain Lake Environment, a Study at the Micron Scale at the LUCIA Beamline

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Abstract. In a high mountain lake and catchment area, a natural process of phosphorus enrichment is observed, induced by the iron-cycle. Investigations focus on the speciation of P and Fe in iron and manganese rich oxidic mineral crusts formed at the surface of rock pebbles. Iron and phosphorus are spatially associated although they are not forming iron phosphate minerals. While Fe and P K edge XAS spectra suggest that phosphates are inner-sphere adsorbed by ferrihydrite-type minerals, slight variations in pre-edge and edge features and in EXAFS spectra suggest that the structure of the natural Fe-P mineral associations are more complex.

Keywords: phosphorus, iron, speciation, mineral coatings, x-ray micro-spectroscopy, environment

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INTRODUCTION

The Joeri lake plateau is located in the Silvretta mountain area, Switzerland between 2400 m and 2800 m at the foot of the Joeri glacier. Spectacular glacial retreat taking place since more than a century, gave rise to this remote environment. Some of the lakes, such as Lake XIII, have evolved from an originally oligotrophic state to mesotrophic within less than 80 years, despite a pristine rocky environment and the absence of direct anthropogenic or pastoral influence. Here eutrophication is due to a natural process of phosphorus enrichment [1]. Phosphorus is a growth limiting nutrient for micro-organisms and plants. It is normally relatively immobile in oxic environments as it adsorbs immediately onto various mineral surfaces, iron oxides in particular.

In the catchment area of Lake XIII, Fe and Mn oxidic mineral coatings are forming in the inflowing and outflowing streams and at the lake bottom, most certainly as a result of periodic oxidation-reduction cycles. These crusts are significantly enriched in phosphorus. In the present ongoing study, we are investigating the mineral crusts from the aerial (drainage basin) and the subaqueous (lake) environments to gain a precise understanding of the

phosphate speciation and of the mineral phases phosphate is associated with.

MATERIALS AND METHODS

Samples from the Joeri lake XIII inflow and outflow were collected in September 2004. Subaqueous samples were collected in July 2002. They consist of mineral crusts (50 to 500 μm thick), highly enriched in iron and manganese, covering gneiss pebbles. The coated pebbles were first embedded in resin (Araldite 2020 Huntsman). Then thin sections were cut out perpendicular to the surface using a diamond covered sawing disc. They were subsequently polished down to about 90 μm thickness with a diamond powder of decreasing grain sizes (3 to 0.25 μm).

Micro-XRF elemental maps and P and Fe K-edge μ -XAS spectra were collected at the LUCIA beamline [2], in fluorescence mode, using a monoelement Silicon drift diode detector and a Si (111) double crystal monochromator. The beam size at the sample surface was $\sim 5 \times 5 \mu\text{m}^2$. The Si maps are used to accurately overlay elemental maps collected at different energies.

ELEMENT DISTRIBUTION

Figure 1 shows the distribution maps of Fe, Mn and P in the crust of a subaqueous sample. The embedding resin comes through at the top of the image. It contains

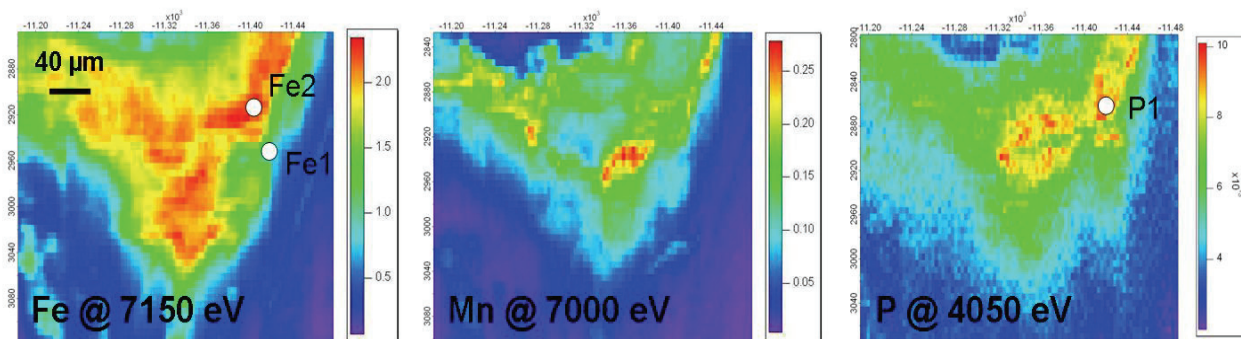


FIGURE 1. μ -XRF maps of elements in a $290 \times 270 \mu\text{m}^2$ area of a subaqueous sample. Step size $3 \times 6 \mu\text{m}^2$, dwell time 1s. The Fe, Mn and P maps were collected with incident energy fixed at 7150 eV, 7000 eV and 2480 eV, respectively.

Crusts from the in- and outflow show a heterogeneous, patchy or stratified distribution of Fe- and Mn- enriched zones. In subaqueous samples, Mn and Fe rich crusts are spatially separated suggesting a stable redox gradient in the benthic boundary layer during crust formation. In aerial samples, similar overall concentration ranges are observed for Fe and Mn. No linear correlation is identified between these two elements. Beside Fe and Mn, Al and Si are detected in terrestrial samples but not in the subaqueous one. Phosphorus, although a minor component, consistently occurs in the aerial and subaqueous samples. Its distribution is correlated with iron. In samples from the aerial part of the catchment basin, a high P/Fe elemental ratio of 0.2 ± 0.05 is observed. Slope values are similar to the average atomic ratio P/Fe obtained from EDS quantitative calculations. In the subaqueous sample, the ratio is lower, equal to 0.003 ± 0.001 . This difference may reflect different chemical equilibria with the overflowing water in the first case and a surrounding waterbody in the other case.

These results suggest that Fe and Mn are forming separate phases while Fe and P species are associated.

ELEMENT SPECIATION

To characterise the Fe and P speciation, μ XAS experiments were performed at points of special interest at the Fe and P K-edges (Figs. 2, 3 and 4). Spot locations in the subaqueous sample are reported on Fig. 1.

The XANES spectra taken at the Fe K-edge at various spots in the samples strongly resemble one another. The edge position reveals that iron is mainly

none of the analysed elements but S and Si (images not shown) and appears in black (dark blue). The gneiss rock lies below the crust at the bottom of the images. It is low in Fe, Mn and P concentration, thus appears in black (dark blue) in the figure.

3+ oxidised. The XANES spectra compare very well with reference spectra of 2-line ferrihydrite, but not with references of iron phosphate minerals characterised by a double peak around 7140 eV. Also XRD results (data not shown) do not show any net reflections characteristic of iron minerals, suggesting that the main iron solid phase present throughout the crusts corresponds to a ferrihydrite type mineral.

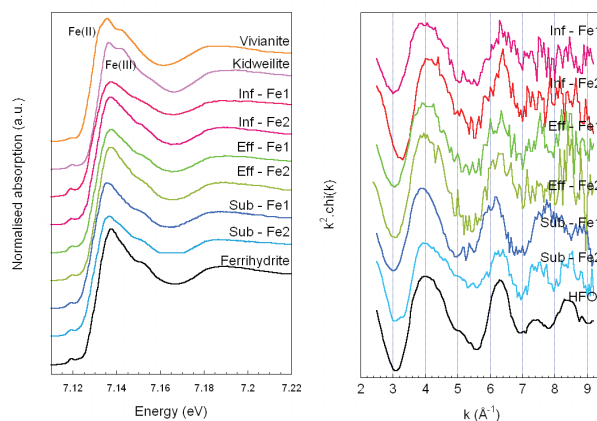


FIGURE 2. Fe K-edge XANES and EXAFS spectra of points of interest measured in influent (Inf), effluent (Eff) and subaqueous (Sub) samples. Reference spectra are also shown: vivianite, kidwellite and ferrihydrite.

However, features in the XANES spectra, such as the tiny energy shift of some edges and variations in the EXAFS spectra, suggest that the mineral phases are not homogeneous. The iron environment seems to vary: past the first shell of 6 oxygen at $\sim 2.04 \text{ \AA}$, different second neighbours and/or different distances occur in addition to Fe (III).

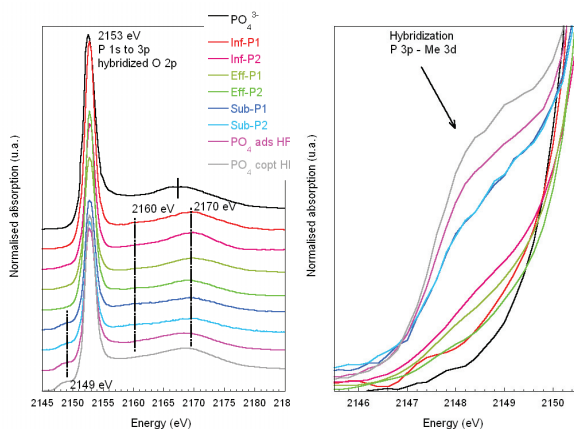


FIGURE 3. P K-edge XANES spectra and zoom on pre-peaks of points of interest collected in influent (Inf), effluent (Eff) and subaqueous (Sub) samples. Reference spectra are: aqueous PO_4^{3-} (PO_4^{3-}), PO_4^{3-} adsorbed and coprecipitated on ferrihydrite (resp PO_4^{3-} ads HFO and PO_4^{3-} copt HFO).

The P-K edge XANES spectra are very similar regardless of spot location. They strongly resemble the spectra of adsorbed or coprecipitated phosphate by ferrihydrite. The broad peaks in the continuum around 2170 eV and 2160 eV are assigned to multiple scattering with, respectively, the first O shell and the second neighbours beside oxygen. The pre-peak occurring at 2149 eV is assigned to hybridization of P 3p with the incomplete 3d electronic layer of Fe in a P-O-Fe bond [3]. In the case of adsorption, it is indicative of inner-sphere complexation. In iron phosphate minerals as well as in synthetic samples of ferrihydrite with adsorbed or coprecipitated phosphate, this pre-peak is clearly marked. In the natural samples, the pre-peak is much weaker, suggesting that while the P-O-Fe bonding exists, its signal is altered by the presence of some other elements. Among the natural samples, the subaqueous ones show the highest intensity of the pre-peak, which would indicate a higher number of iron neighbours, thus a purer iron oxy-hydroxide phase.

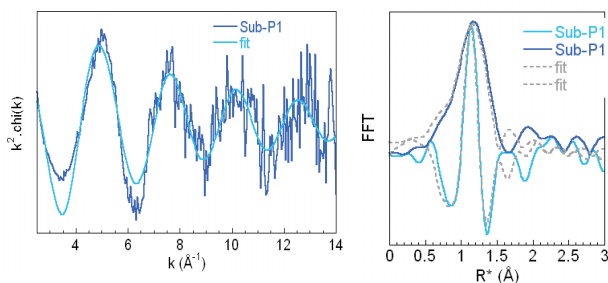


FIGURE 4. P K-edge EXAFS spectrum and radial distribution functions collected in subaqueous crust. The corresponding fits are given by the dotted line.

Fitting of the EXAFS data (Fig.4) gives P-O distances of 1.54 ± 0.02 , which is consistent with values for bounded phosphate.

CONCLUSION AND PERSPECTIVES

The initial investigations on Fe and P in oxidic mineral coatings conducted in this study suggest that P and Fe are strongly associated. This association is not characterized by formation of iron phosphate minerals, but rather by complexation of phosphate with a ferrihydrite type iron-oxide phase. Variations in XANES spectra such as energy shifts and features in pre-peak and in EXAFS spectra suggest that the mineral phases are quite complex, supposedly including element substitutions. The phosphorus speciation in the subaqueous samples differs from speciation in the aerial formation, suggesting different degrees of purity of the iron oxyhydroxide phase. Until now, the exact structure of these naturally formed Fe-P nano-particles is not clearly identified. The scientific literature on P enriched systems suggests that these ill-defined phases are widely distributed in the environmental compartments and may actually control the mobility and availability of phosphorus. Understanding what they are exactly and how stable they are could contribute to agricultural land and freshwater lake management.

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REFERENCES

1. G. Iqbal-Nava "Natural trophication and ecosystem evolution in oligotrophic high mountain lakes" Diploma Thesis, Zürich University, 2003.
2. A.-M. Flank, G. Cauchon, P. Lagarde, S. Bac, M. Janousch, R. Wetter, J.-M. Dubuisson, M. Idir, F. Langlois, T. Moreno and D. Vantelon, *Nucl. Instr. Meth. B* **246**, 269-274 (2006).
3. N. Okude, M. Nagoshi, H. Noro, Y. Baba, H. Yamamoto and T.A. Sasaki, *J. Elect. Spectr. Rel. Phenom.* **101-103**, 607-610 (1999).