

## Phosphate effects on copper and lead sorption to ferrihydrite

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### Introduction

Elevated concentrations of phosphate can retard transport of copper and lead in soil. More detailed knowledge about the mechanisms behind this is of interest for example in risk assessments of contaminated soils. It is well known that the mineral pyromorphite is formed at high concentrations of lead and phosphate in combination with high pH. This effect has been used to immobilize metals in remediation of contaminated soil. It has also been shown that the sorption of lead and copper to iron oxide surfaces [1, 2] may be enhanced in presence of phosphate but the details of how phosphate interacts with copper/lead and iron oxide has not yet been established, and there are seemingly contradictory results [1, 3]. This mechanism acts also at low concentrations of metal and phosphate when no precipitates are formed.

### Methods

Here, batch experiments, X-ray absorption spectroscopy (EXAFS) and surface complexation modeling with the three-plane CD-MUSIC model has been used to study the effect of phosphate on sorption of copper and lead to ferrihydrite. The aim is to investigate what surface complexes that are formed and to derive new and improved surface complexation constants.

### Results and conclusions

The results show that addition of phosphate increases the sorption of copper and lead to ferrihydrite in batch experiments as compared to the same system without addition of phosphate. The effect is stronger than predicted by the CD-MUSIC model when considering electrostatic interactions only and as will be shown, the results from EXAFS analysis support this observation. The EXAFS results show, in agreement with earlier studies [4, 5], that copper and lead form bidentate mononuclear complexes on ferrihydrite in systems without phosphate. However, in the presence of phosphate, other complexes are formed. The results are being used to suggest new surface complexation constants for reactions that consider ternary interactions.

[1] Xie and Giammar (2007) In *Adsorption of metals by geomedia II* (Eds. M.O. Barnett and D.B. Kent) **7**, 349-373

[2] Lin et al (2004) *Colloids and Surfaces A: Physicochem. Eng. Aspects* **234**, 71–75

[3] Weesner and Bleam (1998) *Journal of Colloid and Interface Science* **205**, 380-389

[4] Trivedi et al (2003), *Environ. Sci. Technol.* **37**, 908-914

[5] Scheinost et al (2001), *Environ. Sci. Technol.* **35**, 1090-1096

## Carbonatite metasomatism: evidence from geochemistry and isotope composition (U-Pb, Hf, O) on zircons from two Precambrian carbonatites of the Kola Alkaline Province

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Zircon grains from two Precambrian carbonatites of the Kola Alkaline Province (Siilinjärvi, Tikshezero) were studied by in situ geochemical and isotope investigations. Zircon domains which preserved the primary mantle signatures were identified by a combination of microscopic investigations of thin sections of the carbonatite rocks and separated zircon grains (optical microscopy, SE, CL, BSE images).

In case of the 2.6 Ga old Siilinjärvi carbonatite complex, the new carbonatite melt batch caused mainly solid state recrystallisation of former zircon grains. Zircon regions which preserved the primary signatures yielded high HREE/LREE ratios, undisturbed U-Pb ages,  $\epsilon_{\text{Hf}}$  values close to CHUR (chondritic uniform reservoir),  $\delta^{18}\text{O}$  values typical for the mantle, and Ti concentrations in accordance with known carbonatite melt temperatures. The solid state recrystallisation of zircon caused by carbonatite metasomatism led to (i) diffusion driven loss of HREE, Th, U, (ii) partial disturbance of the U-Pb system, (iii) a small shift of the  $\delta^{18}\text{O}$  toward lower values.

In difference, in the 2.0 Ga old Tikshezero complex the infiltration of a new carbonatitic melt led to dissolution-reprecipitation of former zircon grains. Dissolved-reprecipitated zircon grains often have a spongy texture with a lot of micro-inclusions of apatite, calcite and phlogopite. Apatite micro-inclusions seem to be most abundant according to elevated Th and U concentrations, lowered  $\delta^{18}\text{O}$  values and increased Hf isotope ratios in such domains. These tiny apatite inclusions seem to be responsible for the widely occurring disturbance of the U-Pb dating system and for the unusually high Th/U ratios (>1) in many carbonatitic zircons worldwide. Hf and O isotope values varied widely even within a single zircon grain.