Geophysical Research Abstracts
Vol. 20, EGU2018-17185, 2018
EGU General Assembly 2018

Effect of soil pH and carboxylates on the mobilization of Ge and REEs in soils

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The release of carboxylates and protons represents a widespread strategy of plants for the mobilization of sparingly soluble nutrients, particularly P, Fe and Mn in the rhizosphere. However, only little is known on the effects of different carboxylates and pH-values on the mobilization of strategic elements with special interest in phytomining research such as germanium (Ge) and rare earth elements (REEs). In the present study we conducted batch-equilibrium experiments with two different soils. The soils were mixed with solutions containing acetic, oxalic, tartaric and citric acid at three different concentrations (0.1, 1 and 10 mmol/l) and four different pH-values (4.5, 6, 7 and 7.7). After 24 h of extraction trace element concentrations were measured by means of ICP-MS. Compared to the non-acidified reference soil, decreasing the pH to 4.5 significantly increased the mobility of Ge, while there were no significant changes in the concentrations of REEs. However, there was a substantial mobilization of REEs in presence of carboxylates. Concentrations of REEs in solution increased in the order oxalic > tartaric > citric acid and were clearly dependent on the initial pH. In contrast, for Ge only at low pH (4.5) and highest concentrations of carboxylates (10 mmol/l a mobilization was observed. These results suggest that availability of REEs and Ge might be strongly influenced in the rhizosphere of plants that deploy a carboxylate based nutrition strategy.