

Isotopic fractionation of copper during soil genesis

MORITZ BIGALKE^{1*}, STEFAN WEYER²
AND WOLFGANG WILCKE¹

¹University of Mainz, Geographic Institute, J.J. Becher-Weg
21, 55128 Mainz, Germany

(*correspondence: Bigalke@uni-mainz.de)

²University of Frankfurt, Institute of Geoscience,
Altenhöferallee 1, 60438 Frankfurt am Main, Germany,

Copper is an essential micronutrient for all organisms but may also be a pollutant. Therefore it is of interest to increase knowledge about the fate of copper in the soil system as link between geosphere and biosphere. Copper isotope ratios might be a new tool to improve knowledge about copper cycling in soil.

We investigated stable Cu isotope ratios in soils to test whether $\delta^{65}\text{Cu}$ values can be used as a tracer for soil genetic processes. Two replicates of each of four different soil types were studied representing different soil forming environments. The soils were affected by stagnic- and groundwater, by podzolization and by oxic weathering. We determined standard soil properties and Cu partitioning into seven fractions of a sequential extraction. Copper stable isotope ratios were measured with multicollector inductively-coupled plasma mass spectrometry in total soil digests of the soil horizons after purification.

Copper concentrations in the study soils were low at natural background levels. Copper isotope ratios ranged around 0‰ relative to NIST 976, with an isotope fractionation up to 1‰ in an individual soil. The organic layers tended to have lighter $\delta^{65}\text{Cu}$ than mineral soil, indicating isotopic fractionation of Cu during cycling in the soil plant system. The largest Cu isotope fractionation was observed in one Podzol, with light $\delta^{65}\text{Cu}$ values (-0.57‰) in the eluvial horizon compared to overlying horizons (0.44 and 0.18‰) and underlying illuvial horizon (-0.30‰). In Cambisols $\delta^{65}\text{Cu}$ became increasingly lighter with increasing depth, while in the water-affected soils Cu isotope ratios did not show clear trends in horizons directly influenced by water.

Copper isotope ratios in soil are measurably fractionated and might be used as a novel tool to trace the long-term biogeochemical fate of Cu in the soil system.

Flux of carbon dioxide across fluid and frozen interfaces: Constraining kinetic controls from high-pressure experiments

N.K. BIGALKE*, J.P. SAVY, G. ALOISI AND M. HAECKEL

IFM-GEOMAR, Wischhofstr. 1-3, 24148 Kiel, Germany

(*correspondence: nbigalke@ifm-geomar.de)

The controlling process during uptake of CO_2 by an aqueous solution is determined by the values of the kinetic rate constants of acid/base reactions and mass transfer coefficients. Although recent publications have considerably improved our knowledge of the kinetics in the carbonate water/seawater system at atmospheric pressures little work has yet been concerned with kinetics in pressurized aqueous solutions. Essentially unknown are the rate constants for carbonate equilibrium if kinetics are altered by the appearance of CO_2 -hydrate in the system. A quantitative description of the uptake of CO_2 into aqueous solutions within the hydrate stability field (HSF) thus requires the test if in addition to mass transfer acid/base reactions are of significant importance.

In the present study high-pressure experiments were carried out to quantify the uptake of CO_2 by de-ionized water and seawater across a two-phase interface. The nature of the interface was controlled by selecting P and T to conditions within and outside the HSF while considering both liquid and gaseous CO_2 . First results clearly demonstrate the negligible influence of acid/base reactions to CO_2 uptake kinetics within the HSF. Moreover, by providing hitherto unknown values of kinetic rate constants a detailed set of experimental data fundamental to the discussion of carbon storage in the marine environment is now available.