The age of serpentinization by the SHRIMP dating of zircon from the metasomatic rocks in serpentinite

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Serpentinization does not generally produce minerals suitable for direct isotopic dating. Therefore the age of serpentinization is usually estimated on the basis of age of other rocks associated with serpentinites. In this study, we found zircon grains in the metasomatic rocks such as rodingite vein with blackwall and zoisitite (zoisite-rich rock) in serpentinites from the Nagasaki Metamorphic rocks, Japan.

On the basis of the field observation and petrology, we infer that the zoisitite, rodingite and antigorite-serpentinite formed at the same time. After antigorite-serpentinization, they partially underwent the latter period of serpentinization which produced chrysotile.

Two types of zircon were found in these rocks. Zircons from 10 μm to 250 μm in length are characterized by irregular margins, oscillatory zoning, spongy, high cathordluminescence, and microfractures filled by zircon. Another type of zircon grains (1-10 μm) is euhedral shape with homogeneously luminescence texture, but some grains show the sign of complex texture. Consequently, the zircon grains from the zoisitite, the rodingite, and the blackwall are interpreted as the following. Zircon which shows oscillatory zoning formed as crystals in gabbro. Early stages of antigorite-serpentinization involve rodingite and zoisitite formation and partial dissolution of existing magmatic zircon grains. Zircon was completely altered. Growth of new micro-zircon grains occurs along fractures together with overgrowths on the magmatic zircon, probably in the presence of fluid.

Zircon grains were dated by the U-Pb ion probe method with SHRIMP at National Institute of Polar Research. The weighted mean of U/Pb ages of zoisitite shows 109.2 ± 1.4 Ma and 84 ± 11 Ma which is corresponds with high cathordluminescence rim. The age of rodingite also shows 105.04 ± 0.79 Ma and 91.7 ± 1.3 Ma. The zircons from blackwall show 106.9 ± 1.1 Ma. Those older ages could indicate the age of antigorite-serpentinization. The younger age may show the age of chrysotile-serpentinization.

Effect of sulfate-availability on coupled Cu and Cd transformation during soil reduction

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Periodically submerged soils such as freshwater floodplain or paddy soils are subject to fluctuations in soil redox state. In industrialized regions anthropogenic emissions have led to the accumulation of heavy metals in these soils. Cyclic redox changes can profoundly impact metal speciation, mobility and bioavailability in such contaminated soils. Sulfate reduction during soil flooding may lead to the precipitation of toxic chalcophile metals like Cd and Cu as sulfide minerals. However, the amounts of chalcophile metals in contaminated soils may often exceed the amount of available sulfate, resulting in competitive metal sulfide formation controlled by the thermodynamic stabilities and formation kinetics of individual sulfide phases [1]. Consequently, we postulate that e.g. the presence or absence of Cu as well as the amount of available sulfate has a major influence on redox-driven changes in the speciation of Cd, which forms more soluble sulfides than Cu. Under sulfate-limiting conditions, the presence of Cu may therefore have a major influence on the bioavailability and toxicity of Cd in flooded soils.

To improve our mechanistic knowledge of these coupled processes, we study the effect of sulfate-availability on the coupled speciation and solubility dynamics of Cu and Cd during soil reduction in laboratory incubation experiments. As a substrate, we use an uncontaminated carbonate-free paddy soil from Bangladesh with a low reducible sulfate content. Batch experiments are carried out with single (Cu or Cd) or binary (Cu+Cd) metal spikes at different sulfate-levels that are sufficient for partial or complete precipitation of Cu, Cd or (Cu+Cd) as metal sulfides. After an initial oxic equilibration phase, lactate is added as a readily biodegradable C-source. Subsequently, soil is incubated under anoxic conditions in headspace vials over a period of 40 days. We present first data on trace metal and sulfate dynamics in solution and on solid phase speciation by sequential metal extraction, acid volatile/chromous reducible sulfur quantification, and X-ray absorption spectroscopy. In the future, we aim to extent these studies on coupled metal dynamics to full reduction-oxidation cycles.

[1] Voegelin *et al.* (2009) *GCA*, this volume.