

Formation of hydrozincite, Zn layered double hydroxide and Zn phyllosilicates in contaminated calcareous soils

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The incorporation of Zn into layered mineral structures such as layered double hydroxides (LDH) or phyllosilicates may reduce its mobility and bioavailability in soils. The quantity and structure of Zn bearing layered phases forming in soils depend on soil physicochemical properties and contamination level. To date, most spectroscopic studies on the speciation of Zn considered neutral to acidic non-calcareous soils. In this study, we investigate the reactivity and speciation of Zn in contaminated soils developed from calcareous and dolomitic parent material.

Five soils developed from limestone and one developed from dolomite were sampled below power line towers made from galvanized steel that had been constructed 30 to 50 years ago. All soils have been contaminated by input of runoff water containing dissolved Zn from corrosion. The soils cover a wide range in clay content (90-450 g/kg), inorganic carbon content (10-89 g/kg), and Zn concentration (1'300 - 30'000 mg/kg). They have pH values between 6.1 and 7.5. The molecular scale speciation of Zn in the soil matrix was investigated by Zn K-edge EXAFS spectroscopy on powdered soil samples. Thin sections from two calcareous soils (1'300 and 30'000 mg kg⁻¹ Zn) and the dolomitic soil (1'400 mg kg⁻¹ Zn) were further studied by μ -X-ray fluorescence (μ -XRF) and μ -EXAFS spectroscopy. Principal component analysis and target testing indicated that octahedrally coordinated Zn in layered minerals and tetrahedrally or octahedrally coordinated sorbed Zn are likely candidate species. In the dolomitic soil, pure Zn-phyllosilicate was identified in Zn-rich spots. In the calcareous soil containing 30'000 mg kg⁻¹ Zn, the Zn was diffusely distributed in the soil matrix with a spectrum similar to Zn-LDH. Crusts on calcite particles from the same soil were identified as hydrozincite using powder X-ray diffraction and EXAFS spectroscopy. Linear combination fits to the bulk EXAFS spectra indicate that LDH- and phyllosilicate-type precipitates account for a considerable fraction (17-53%) of the total Zn in all soils. To quantify the reactivity of Zn, the soils as well as synthetic references were fractionated using a 7-step sequential extraction procedure (SEP). Between 32-65% of the total Zn in the soils was extracted in the first two fractions (1M NH₄NO₃ and 1M NH₄-acetate at pH 6.0, respectively), suggesting that most Zn occurred in labile species. Zn-LDH, Zn-phyllosilicates and hydrozincite showed similar chemical reactivity with 46 to 84% of the total Zn mobilized in the first two fractions.

Solving the mystery of SNC meteorites

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Rb-Sr, Sm-Nd and U-Th-Pb isotopes have been intensively studied on SNC meteorites. There is a general consensus that these meteorites are magmatic rocks. While in terrestrial magmatic rocks the Rb-Sr system usually shows a greater melt-residue fractionation than the Sm-Nd system, it is just the reverse in the case of the SNC meteorites. While the whole rock SNC meteorites scatter along a 4.5Ga Rb-Sr reference isochron showing only a slight disturbance, the Sm-Nd isotopes for the same whole-rocks are strongly fractionated, with a considerable depletion of Nd for the shergottites and an enrichment of Nd for the nakhlites. One would expect that a magmatic fractionation would cause a strong enrichment in Rb in the melt, but only a moderate enrichment in Nd. The shergottites, however, which clearly originally crystallized from melts, show no significant enrichment in Rb but, by contrast, a strong depletion in Nd. The nakhlites, which are mafic cumulates with a residual major element chemistry, experienced a significant Nd enrichment. Model-calculations that are able to explain the Sm/Nd evolution cannot be extended to the other REE and completely fail to explain the observed Sm/Yb and La/Nd ratios. A mixing model reveals the need for three components to explain the composition of shergottites and nakhlites, but does not contribute to an understanding of a realistic magmatic process.

Recently we developed a magmatic model that consistently explains the observed petrographic and isotopic data for SNC meteorites. It is based on the premise that the basaltic shergottites, Shergotty, Zagami, and Los Angeles, have typical crustal compositions and were differentiated very early at 4.4 Ga, while nakhlites and olivine-bearing shergottites, Que, SAU, Y89, and others, derive from a nearly homogeneous mantle source [1].

Minor heterogeneities in the Sr and Pb isotopes are insufficient to argue against a common mantle source, and reported W isotopic differences might be caused by terrestrial contamination (the intrinsic W contents of the olivine shergottites, as estimated from the W/La in these meteorites, may be unmeasurable). To explain their unusual fractionation pattern, we postulate the presence of two phosphates in the Martian mantle: xenotime and monazite. At the time of fractionation, xenotime partitions into the olivine bearing shergottites while monazite partitions into the nakhlites. This phosphate chemistry has little effect on the Rb-Sr systematic, strongly fractionates between the light and heavy REE. Because in such an environment the trace-elements do not follow Henry's law, commonly employed melting models cannot be applied.