Surface complexation on birnessite controls Pb distribution in highly contaminated soil and karst groundwater

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At the historic mineries of Priddy near Bristol, soils are heavily contaminated with up to 2000 mg/kg Pb. However, porewater concentrations of Pb are undersaturated with respect with natural common Pb minerals such as cerrusite. Scanning electron microscopy and EDX analysis revealed that the Pb in Priddy soil is associated with a poorly-crystalline Mn oxide phase. The Mn oxide phase contains up to 40 wt. % Pb. Using μ-EXAFS spectroscopy, and μ-XRD, we identified the Mn oxide as birnessite, similar to the poorly crystalline microbial δ-MnO_2 described by Villalobos *et al.* [1]. However, the origin of the birnessite in Priddy soil is unclear. Using μ-EXAFS, we find that Pb is complexed on both edge and vacancy sites, as proposed by [2].

The hydrology of the mining area drains into a complex network of caves, with the resurgence at Wookey Hole. Within the caves are extensive coatings of birnessite (as identified using XRD and Raman spectroscopy). We hypothesise that this birnessite is of microbial origin as found elsewhere [3]. The soil birnessite must be reduced to release dissolved Mn(II) which is then oxidized in the dark cave system by chemolithoautrophic bacteria. The secondary birnessite in the cave also contains up to 40 wt. % Pb. μ-EXAFS shows that Pb associated with this birnessite in both edge and vacancy surface complexes.

We hypothesise that the complexation of Pb by birnessite controls the dissolved Pb concentration in soil pore water and groundwater. To test this, we have performed a series of batch sorption edge experiments with synthetic birnessite and fit these to derive equilibrium expressions and constants for the possible surface complexation reactions. Using our surface complexation model, we are predicting the concentration of Pb in soil porewater and groundwater. However, a reactive transport model needs to account for the microbial birnessite recyling.

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U-Pb and Hf isotope characteristics of zircon from chromitites at Finero

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The Finero phlogopite-peridotite represents a metasomatized residual mantle harzburgite, exposed at the base of the lower-crust section in the Ivrea Zone, Western Alps [1]. Previous studies point to one or more Late Paleozoic mantle metasomatic events in the Finero peridotite, although there is little agreement regarding the relative timing of different events or the source of the metasomatizing agents.

Studied chromitite samples derived from the dump in the prospecting trenches of Alpe Polunia and Rio Creves. Dominant zircon population is pale pink and show different shapes (subhedral, subrounded or elongated). In cathodoluminescense (CL), the main set of population is represented by complex grains, which show development of core-rim relationship (most likely recrystallized rim on a preserved core). Subordinate zircon grains are colourless, with a smoky cathodoluminescense and almost no internal pattern. Three main U-Pb age clusters have been identified. The youngest cluster, typical for subordinate zircon population and rims in complex grains from dominant population, yielded two $^{206}Pb/^{238}U$ ages (e.g., 208.6 ± 4.0 Ma, MSWD=2.0, n=8 and 194.9 ± 3.4 Ma, MSWD=0.45, n=3, respectively). The other clusters represent cores and rims in the composite grains, with ages 288.3 ± 7.3 Ma (MSWD=3.3, n=6) and 248.6 ± 3.3 Ma (MSWD=0.13, n=8), respectively. In Lu-Hf systematics, zircons of all age populations show a relatively narrow spread in $^{176}Hf/^{177}Hf(t)$ values, with majority (~90 %) falling between 0.282652 and 0.282533. An increase in $^{176}Hf/^{177}Hf(t)$ ratio from old to young zircon populations defines a trend, which follow CHUR evolution curve.

Our data do not concur with the assumption [2] of a single metasomatic event during chromitite formation. In contrast, a prolonged formation and multistage evolution of zircon growth is considered a feature typical of a metasomatized subcontinental mantle at Finero.

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