

Formation of secondary minerals A lysimeter approach

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Heavy metal contamination of large areas due to uranium mining operations poses a serious long-term environmental problem. In Ronneburg, in eastern Thuringia, Germany, leaching of low grade uranium bearing ores (uranium content < 300g/t) proceeded from 1972 to 1990 using acid mine drainage (AMD; pH 2.7-2.8) and diluted sulphuric acid (10g/l). Secondary mineral phases like birnessite, todorokite and goethite occur as natural attenuation process associated with enrichment of heavy metals, especially Cd, Ni, Co, Cu and Zn due to a residual contamination even after remediation efforts.

To reveal the processes of secondary mineral precipitation in the field a laboratory lysimeter approach was set up under similar conditions than in the field. Homogenated soil from the field site and quartz were used as substrates. Water supply was just from the bottom by a mariott's bottle using contaminated groundwater from the field. Evaporation processes were accepted to allow continuous flow of water. This leads to precipitation of epsomite and probably apowite on the top layer equal to field investigations. *In situ* measurements of redox potentials showed in general high oxidizing conditions (200-750 mV) due to different redox couples in the groundwater. After 4 weeks first secondary minerals became visible. Although Eh/pH data does not support formation of manganese minerals, SEM-EDX data show microorganisms in organic rich phases together with the occurrence of manganese, oxygen and nickel, indicating manganese oxides enriched in nickel. Infrared (IR) spectroscopy give hints for todorokite of being the secondary manganese mineral. Soil water samples were used for monitoring behavior of metals within the lysimeter. Hence saturation indices (SI) for different secondary minerals were calculated with PHREEQC. Clay minerals (e.g. kaolinite, illite) show SI values up to 5 indicating precipitation. This is coincided with a nearly completely depletion of aluminum in the soil water after entering the lysimeter and XRD measurements. The SI of goethite also shows oversaturation with respect to the soil solution. SEM-EDX analyses and IR spectroscopy confirm the formation of goethite. Data revealed that the formation of goethite is mainly dominated by Eh/pH processes in this system and that heavy metals like Zn and U could be enriched.

Are Large Igneous Provinces net-sinks for CO₂?

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Continental flood basalts are subaerially erupted Large Igneous Provinces (LIPs), often covering significant continental areas with millions of cubic kilometers of lava. Recent evidence from the Central Atlantic Magmatic Province (CAMP) record in the Eastern North American (ENA) Newark Rift Basin demonstrated that LIPs may result in a transient doubling of atmospheric pCO₂, followed by a ~300 ky falloff to near pre-eruptive concentrations (1). We use the pedogenic carbonate paleobarometer in the corollary Hartford Basin to confirm findings in the Newark, and to test the million-year scale effect of the CAMP eruptions.

We find that the Hartford basin pCO₂ record is consistent with observations from the Newark, where a ~4400 ppm pCO₂ peak is identified just after each volcanic episode. The significantly longer post-extrusive Portland formation of the Hartford Basin shows a fourth CO₂ pulse to ~4500 ppm, about 250 ky after the last lava recorded in the ENA section, which may correlate to a later basalt in the Central High Atlas Basin of Morocco. The Hartford record also shows a rapid post-eruptive decrease in pCO₂, reaching pre-eruptive background concentrations of ~2000 ppm in <~300 ky, consistent with observations from the Newark Basin. Furthermore, the Hartford post-extrusive section exhibits a long-term decrease in pCO₂ to levels below the pre-CAMP background over the subsequent 1.5 My following the final apparent episode of eruptions.

We use a simple geochemical carbon-cycle model to demonstrate that the rapidity of these decreases, and the fall to concentrations below background may be accounted for by a 1.5-times amplification of continental silicate weathering due to the presence of the CAMP basalts themselves. If basalt has 10-times the chemical reactivity of continental crust, such an amplification would require eruption of lavas over an aerial extent of ~8.3 x 10⁶ km², well within independent estimates of the CAMP at 1.1 x 10⁷ km². Together, these results indicate that continental flood basalts result in an extreme short-term perturbation of the carbon system, followed by a long-term decrease in pCO₂ to below pre-eruptive levels, implying they may have an overall net-cooling effect on global climates.

[1] M. F. Schaller, J. D. Wright, D. V. Kent (2011) *Science* **331**, 1404.