Reactive transport modeling of natural attenuation processes in sulfide-bearing mine tailings

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Natural attenuation processes in sulfide-bearing mine tailings may involve the formation of hardpans or cemented layers, which are characterized by increased concentrations of secondary phases. As these secondary phases often consist of amorphous or partially crystalline phases, a substantial temporary natural attenuation of toxic compounds as well as a reduction in porosity and permeability may occur. Hardpans / cemented layers have predominantly been found in regions of increased stratification [1].

The reactive transport model FLOTRAN [2] was applied to study the potential of sulfide-bearing mine tailings to form cemented layers in the presence and absence of biotite-rich silt/clay layers. Kinetically controlled reaction parameters were calibrated in column experiments and initial concentrations of primary phases were estimated from field data. In the case of a homogeneous distribution of primary phases, the simulated secondary phases were found to precipitate uniformly over the entire profile. However, in the presence of biotite-rich silt/clay layers, an accumulation of secondary phases was predicted in biotite-rich layers. The simulated major secondary phases (jarosite, Fe gel, Si gel, and gypsum) are in accordance with the phases identified in field samples. The simulated cemented layers act as local water tables which largely prevent the downward migration of oxygen.

The simulation results can be explained by a combination of the following processes: (a) generation of acid mine drainage due to the oxidation of sulfides, (b) downward transport of Fe^{2+}, SO_4^{2-}, and H^+, (c) buffering of the acid solution by dissolution of biotite, which causes the release of K^+ and results in the precipitation and accumulation of jarosite, Si-(Al) gels, and of Fe-hydroxides in biotite-rich layers, as well as (d) the dissolution of Ca-plagioclase from the sandy matrix, which causes the release of Ca^{2+} and contributes to the precipitation of gypsum and Si-(Al)-gels.

[1] Graupner *et al.* (2007) *Appl. Geochem.* **22**, 2486-2508. [2] Lichtner (2007) LANL Report LA-UR-01-2349.

Complete sample digestions for accurate isotope measurements? The Re-Os isotope system under scrutiny

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Though exiting discoveries of isotopic variations of radiogenic, radioacitive and non-traditional stable isotopes have been made, questions about the trueness of the results remain in systems where sample dissolution is a key problem. This applies to both new and established isotope systems. Analytical protocols that use MC-ICP-MS systems have the pre-requisite that solutions are required for high precision determinations and hence a dissolution step is a key pre-requisite. Dissolution of solid materials can be sequential, partial and complete which can be carried out intentionaly or unknowingly. The highest degree of control can be reached for the “whole rock” isotopic composition as partial dissolution steps are often not reproducible. Even if certified reference materials exist for whole rock studies, some doubts may remain as indenpent methods of determination usually do not exist.

Although it was demonstrated that higher yields of osmium at higher temperatures lead to lower whole rock Os isotopic compositions of peridotites (e.g. acid attack at 300°C using a high pressure asher system (HPA) vs. 230°C in Carius tubes), some doubts remain about the completeness of Re and Os liberation from basalts, even at higher temperatures. Debate has centred around whether a desilification step with HF is required prior to a regular acid attack at higher temperature is essential or not (see round robin of basalt EN026 10D-3 [1]).

In this work we systematically tried to resolve this issue, through the comparision of dissolutions with and without HF in microwave ovens and in a HPA system, using either TFM or glassy carbon vessels, respectively. PGE CANMET refence material TDB-1 was used throughout to assure comparability. First results indicate that HF is indeed essential for a more effective extraction of Re from basaltic sample powders. The effect on other highly siderophile elements remains inconclusive and will be further investigated.

[1] Kingsley *et al. AGU abstract* 2004AGUSM.V51B..02K