

Effects of microstructure and secondary phases on the dissolution of Fe-rich sphalerite

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Mining activities on sulfured ores transfer large amounts of rocks to waste heaps and thus into an oxidizing environment. Weathering of these deposited sulfides often result in acid mine drainage with the production of sulfuric acid and the release high concentration of metals into ground and surface waters. Accordingly, a large number of experimental dissolution studies on various sulfide minerals have been conducted in the past decades including both chemical and microbial leaching under a wide range of oxidizing conditions. Applying measured rates to another system requires knowledge about the mechanisms of dissolution and the *reactive* surface area. However, reactivity is considerably influenced by the microstructure (exsolution, twin planes, stacking sequences) and the defects (vacancies, dislocations, grain boundaries) present. Surprisingly, the influence of the microstructure on the dissolution is rarely addressed. Furthermore, hazardous element release is not only controlled by the reactivity of the primary sulfides but also by the formation of a secondary mineral assemblage. Many of the newly formed phases (oxides, hydroxides, elemental sulfur, sulfates) exhibit small grain sizes, which affects their stability as well as their adsorption capacity. The secondary phases can directly (as coating) or indirectly (adsorption, solubility) influence the dissolution kinetic of the primary sulfide.

Natural iron-rich sphalerites are well known for their wealth of microstructure including stacking faults, twin boundaries and oscillatory zoning, usually combined with elevated trace element concentrations. For this study, sphalerites of two localities (Hungary, Kosovo) with various iron contents have been characterized using TEM for the microstructure, EMPA and LA-ICP-MS for major and trace element compositions as well as SEM and AFM to document surface evolution. Batch dissolution experiments are performed using single crystals as well as powders under conditions that facilitate the precipitation of secondary phases. The influence of microstructure and secondary phases on the dissolution of sphalerite and the solution chemistry will be demonstrated and discussed.

Was the inventory of the marine fixed nitrogen twice as large at the LGM compared to the Holocene?

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Throughout the last deglaciation, the marine inventory of fixed nitrogen was altered by varying rates of water column denitrification, sediment denitrification and nitrogen fixation. Some studies have argued that this inventory decreased by about 30% between the last glacial maximum (LGM) and the Holocene primarily due to water column denitrification having nearly doubled across this period [1, 2]. Such variations of the fixed nitrogen inventory likely will have changed the magnitude and spatial pattern of oceanic productivity and may have contributed to the concomitant changes in atmospheric CO₂. Past variations of the fixed nitrogen inventory have been evaluated mostly through stable nitrogen isotope analyses of organic matter in sediment cores ($\delta^{15}\text{N}$). However, the interpretation of $\delta^{15}\text{N}$ variations is challenging because it is difficult to determine which part of the measured $\delta^{15}\text{N}$ signal is of local origin, e.g. due to change in the degree of fixed nitrate consumption, and which part is of basin-scale to global nature, e.g. reflecting a change of the mean oceanic $\delta^{15}\text{N}$ value due to global-scale changes in the fixed nitrogen inventory.

Here an oceanic geochemical multi-basin box model is used to investigate the inventory of the fixed nitrogen during the last deglaciation. We spatially extend the single-basin box model of Deutsch *et al.* [3] by adding boxes reflecting the Indo-Pacific, the Atlantic and the Southern Ocean.

Several deglaciation scenarios are simulated considering different water column and sediment denitrification forcings as well as various feedbacks between nitrate concentration and denitrification or nitrogen fixation. Simulation results that match the closest the $\delta^{15}\text{N}$ paleoceanographic records in each basin are selected and the LGM fixed nitrogen inventory is evaluated given the evolutions of the sink and source rates.

- [1] Ganeshram *et al.* (2000) *Paleoceanography* **15** (4) 361-376. [2] Altabet *et al.* (1995) *Nature* **373**, 506-509. [3] Deutsch *et al.* (2004) *Global Biogeochem. Cycles* **18** (4).