Reduction of jarosite by *Shewanella oneidensis* MR-1 and its geochemical implication

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Jarosite is a common mineral in acidic, sulfate-rich environments formed by the oxidation of sulfide in mining area. Decomposition of jarosite by dissimilatory iron reducing bacteria (DIRB) under acidic conditions has been well proved previously [1], and this process influences the mobility of many heavy metals accommodated in jarosite. However, the effects of DIRB on the stability of jarosite under neutral pH conditions have been seldom studied. This study aims to evaluate these effects, and provide a more comprehensive understanding of the geochemical mechanism.

Jarosite was synthesized by microbial oxidation of ferrous ion at 30 °C. The used bacteria strain was Shewanella oneidensis MR-1. We designed a series of batch experiments to study the microbial reduction process of jarosite under anaerobic, aerobic, and no inoculation conditions for 20 days. Lactate was added to the solution as electron donor for MR-1. Temporal evolution of Fe(II) and total dissolved Fe in solution was monitored everyday by using o-phenanthroline method. The concentrations of sulfate, lactate and acetate were determined by ion chromatography (IC). The content of K+ was examined by inductively coupled plasma optical emission spectrometer (ICP-OES). The compositions of the secondary minerals were analyzed by X-ray diffraction and scanning electron microscopy coupled with energy dispersive spectrometer. Diffuse reflection spectroscopy was employed to investigate the component of Fe-bearing minerals. Transformations of jarosite in 40 days and 80 days were also investigated to confirm the reduction process.

Results and conclusions

Our results indicate that jarosite can be reduced by MR-1 under anaerobic condition, and secondary mineralization accompanies the reduction process. Increases in Fe(II), K+, sulfate and acetate concentrations, and a decrease in lactate were observed for the biotic experiment. The release rate of Fe(II) was constant in the beginning period. Microscopic results demonstrated bacterial attachment to the surface of jarosite, which can be regarded as evidence of bacterial absorption. The formation of new minerals as goethite and some green rust was identified. Compared to anaerobic treatment, the concentrations of Fe(II), K+, and sulfate in aerobic treatment and no inoculation treatment were undetectable at first, and tremendously lower than anaerobic treatment after 40 days of reaction. However, reduction of jarosite in aerobic treatment and no inoculation treatment was severely limited, and secondary minerals were either not produced or undetectable.

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[1] Bridge & Johnson (2000) *Geomicrobiol. J.* **17**, 193-206.

Dating zircons from volcanic ash beds in sedimentary successions: magmatic crystallization vs. ash deposition

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Detailed calibration of the Late-Middle Triassic time-scale requires precise and accurate age determinations from volcanic ash beds within biostratigraphically well dated marine sedimentary sections. High precision CA-ID-TIMS U-Pb zircon dates of volcanic ash beds have been used to quantify and calibrate the stratigraphic column across the Early-Middle Triassic boundary in South China. Despite an optimal control on the continuity of the stratigraphic record and on the accuracy of analytical procedures, some single ash-beds from the Monggan Wantuo section (Luolou Fm., NW Guangxi, S. China) yield ages that are too old and contradict the stratigraphic succession. How can we improve the confidence in the interpretation of zircon dates as proxies for the age of deposition of these ash beds?

We dated 15 samples of ash beds (four thereof with signs of sedimentary reworking) within the 15m Wantuo Mongan section, applying CA-ID-TIMS techniques on a number of single grains for each sample. In 13 out of 15 ash beds zircon dates are following the stratigraphic succession within analytical uncertainty (from the late Early Triassic Luolou Formation – 248.08 ± 0.12 Ma to the Middle Anisian Transition Beds – 246.43 ± 0.17 Ma). The zircons from two intermediate volcanic ash beds within the Transition Beds at the Early/Middle Anisian boundary yield well clustering $^{206}Pb/^{238}U$ dates at 247.10 ± 0.15 and 247.35 ± 0.11 Ma, clearly indicating that the zircons in this magma batch were crystallizing over a long period of time or remobilized from deeper levels within the same magmatic system. The problem of recurrent zircon dates in a sedimentary succession is common and can only be discovered by sufficiently dense sampling and a sufficient number of data for each ash bed.

We have to keep in mind that for the correct interpretation of dates in stratigraphic sections interlayered with fossil-bearing rocks we need: i) at least one single well preserved stratigraphic section with sufficient absolute or relative chronological control (biochronology, chemostratigraphy, astrochronology) to guarantee that the stratigraphic succession is accurately known; ii) volcanic ash beds that are as much undisturbed as possible (no volcaniclastic material, no sedimentary reworking); iii) sufficient sample and data density to be able to distinguish between magmatic and sedimentary signals coded in the crystallization ages of zircon.