

Comparative XPS study between experimentally and naturally weathered pyrites

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The comparative study was carried out between the experimentally and naturally weathered pyrites. The naturally weathered pyrites were collected at the Tongling multi-metal deposit, China. The fresh pyrites with an euhedral shape were exposed in a humid environment supplied by an accelerated weathering tester. Both of them shared the similar chemical species of weathering products and weathering mechanism. The X-Ray Photoelectron Spectroscopy (XPS) was used to study the surficial chemical species of the weathered products, and the argon ion etching techniques was used to study the vertically structural profile.

The outmost weathering surficial products could be concluded into sulphur-bearing and iron-bearing groups. The sulphur-bearing group were comprised by sulphate, sulphite, thiosulphate, elemental sulphur (S₈), polysulphide, and mono-sulphide, etc. The iron bearing group was composed by goethite, hematite or magnetite, and iron sulphate. Though the chemical species were same, phases from naturally weathered pyrites differed from experimentally weathered ones in its crystalline degree. Excluded elemental sulphur, most of phases could be detected on the naturally weathered surface by GIXRD. This difference could be attributed to the weathering time scale and environment.

The weathering structural profile was also similar. The structural profile was constructed by surficial layer and transient layer. The surficial layer was made up of the sulphur-bearing and iron-bearing product, the transient layer was comprised by goethite and hematite or magnetite. The inward moving of weathering interface was stimulated by the diffusion of oxygen and moisture. The oxygen was considered to preferably squeeze the iron to form goethite, and ferric of goethite act as a bridge [1-3] of electron transferring between bulk S₂²⁻, Fe²⁺ of pyrite and oxygen. Hence, the weathering rate of pyrite was constrained by the diffusing rate of oxidized moisture, but the weathering degree was constrained by both diffusion rate and mainly the time scale of weathering.

[1] Nesbitt & Muir (1994) *GCA*. **58**, 4667-4679. [2] Knipe *et al.* (1995) *GCA* **59**, 1079-1090. [3] Rosso *et al.* (1999) *Am. Mineral.* **84**, 1535-1561.

Biom mineralization of the iroko tree (*Milicia excelsa*): How does this carbon sink work?

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Biom mineralization in the plant kingdom has been documented since a long time. A particularly interesting example is the iroko tree. CaCO₃ biom mineralization occurs in its plant tissue and unexpected CaCO₃ accumulations are observed in its surrounding soil. We present a conceptual model for iroko tree mineralization and soil CaCO₃ deposition based on a multiscale approach ranging from field observations and laboratory measurements to electron microscopy images and microprobe analyses.

Photosynthesis is the first step by which atmospheric CO₂ is sequestered as large amounts of calcium oxalate and accumulated in the iroko tissues. A flux of oxalate-rich dead Organic Matter (OM) from the tree to the soil (partly increased by termites) has been quantified. Various microorganisms decay soil OM and cause the release of calcium oxalate crystals inside the soil matrix. As demonstrated by Braissant *et al.* [1], soil oxalotrophic bacteria oxidize the release oxalate, increasing complexed Ca²⁺ and carbonate ions in the soil solution, and inducing a pH increase in the initially acidic soil. In the presence of calcium and favourable physicochemical conditions, carbonate ions can precipitate in the soil pores and lead to the formation of large CaCO₃ concretions. Alternatively, carbonate ions can be pumped through the roots and translocated by conductive vessels inside the tree. In the tree tissues, by some yet unknown processes, biom mineralization (e.g. calcitic pseudomorphosis of organic cells) can occur.

In conclusion, the iroko tree ecosystem, with its calcium oxalate-carbonate pathway, represents a carbon sink, which leads to a long term sequestration of large amounts of atmospheric CO₂ into a geologically stable form, CaCO₃.

[1] Braissant *et al.* (2004) *Geobiology* **2**, 59–66.