



## **An improved pyrite pretreatment protocol for kinetic and isotopic studies**

Natella Mirzoyan (1), Alexey Kamyshny (2), and Itay Halevy (1)

(1) Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, 76100, Israel, (2) Department of Geological & Environmental Sciences, Ben-Gurion University of the Negev, P.O. Box 653, Beer Sheva 84105, Israel

An improved pyrite pretreatment protocol for kinetic and isotopic studies

Natella Mirzoyan<sup>1</sup>, Alexey Kamyshny Jr.<sup>2</sup>, Itay Halevy<sup>1</sup>

<sup>1</sup>Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot 76100, Israel

<sup>2</sup>Geological and Environmental Sciences, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

Pyrite is one of the most abundant and widespread of the sulfide minerals with a central role in biogeochemical cycles of iron and sulfur. Due to its diverse roles in the natural and anthropogenic sulfur cycle, pyrite has been extensively studied in various experimental investigations of the kinetics of its dissolution and oxidation, the isotopic fractionations associated with these reactions, and the microbiological processes involved. Pretreatment of pyrite for removal of oxidation impurities to prevent experimental artifacts and inaccuracies is often practiced. While numerous pyrite-cleaning methods have been used in experiments, a common pyrite pretreatment method, often used to investigate pyrite chemistry by the isotopic fractionations associated with it, includes several rinses by HCl, acetone and deionized water.

Elemental sulfur (S<sub>0</sub>) is a common product of incomplete pyrite oxidation. Removal of S<sub>0</sub> is desirable to avoid elemental biases associated with its participation in pyrite transformations, but is more complicated than the removal of sulfate. Although rinsing with an organic solvent is in part aimed at removing S<sub>0</sub>, to the best of our knowledge, the extraction efficiency of S<sub>0</sub> in existing protocols has not been assessed.

We have developed and tested a new protocol for elemental sulfur removal from the surface of pyrite by ultrasonication with warm acetone.

Our data demonstrate the presence of large fractions of S<sub>0</sub> on untreated pyrite particle surfaces, of which only approximately 60% was removed by the commonly used pretreatment method. The new protocol described here was found to be more efficient at S<sub>0</sub> removal than the commonly used method, and was capable of removing virtually all S<sub>0</sub> from the pyrite grains. As pyrite oxidation and dissolution processes are surface-dependent, and even the slightest coating by Fe<sup>2+</sup> or sulfide oxidation products can sharply decrease pyrite reactivity, the improved removal of S<sub>0</sub> prevents such decreases and allows clearer insights into pyrite reaction mechanisms to be gained from experimental studies. In addition to S<sub>0</sub> removal, the suggested method was shown not to introduce any biases in the particle size distribution. The main difference observed between the two protocols is the removal of larger amounts of surface-attached fine particles in the proposed method along with S<sub>0</sub>. This also removes a potential bias, associated with the surface area of pyrite available for chemical reaction.

The suggested pyrite pretreatment protocol is more efficient in removal of S<sub>0</sub> contamination from pyrite grains and provides multiple advantages for both kinetic and isotopic investigations of pyrite transformations under various environmental conditions.