Pressure effects on sulfur mass-independent fractionation during SO_2 photolysis and its implication to the Archean atmospheric chemistry

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Large $\Delta^{33}S$ values are measured in pyrite sulfur in rocks deposited before 3.2 Ga and between 2.7 Ga and 2.4 Ga, whereas those between 3.2 and 2.7 Ga yield relatively small $\Delta^{33}S$ values [1,2]. This apparent structure in the Archean $\Delta^{33}S$ signal may reflect changes in the atmospheric chemistry such as an incipient, transient rise of oxygen before the great oxidation event (i.e., *whiff of oxygen*) [1,3], the formation of organic haze aerosols [4], or a change in the redox state of volcanic gases [5].

In order to test various hypotheses, we performed laboratory SO_2 photolysis experiments using a flow through photochemical reactor with a Xe arc lamp as the light source. We will report the results of experiments to test the effect of pSO_2 and pN_2 on the pattern of multiple sulfur isotope fractionation. A new experimental system allows us to experiment at lower pSO_2 (i.e., low SO_2 column density) than using static photochemical cells. The results show that the $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ signatures of the elemetnal sulfur product are a strong function of the SO_2 pressure under the tested range of pSO_2 (0.1 mbar and above), decreasing with decreasing pSO_2. The effect of bath gas pressure was also tested between 250 and 1000 mbar. The results of these experiments suggest that the change in the S-MIF pattern can be linked to the volcanic SO_2 loading in the atmosphere. The implications of this model will be discussed in the context of the early evolution of oxygenic photosynthesis and the resulting effect on the chemistry of the early atmosphere.

References

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Trace-element control on near IR transmittance of pyrite

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Pyrite, which commonly occurs intergrown with economic ore minerals in a variety of hydrothermal deposits, can be transparent to near-infrared (NIR) light and has been therefore studied by NIR microscopy to observe internal features, such as growth zoning or fluid inclusions. The main limitation of the NIR petrography and microthermometric studies on pyrite is the transmittance of the mineral, which depends on its trace element content, the thickness and the crystallographic orientation of the section used [1].

In this study, we investigate growth zoning in pyrites from two different localities: i) the Toromocho porphyry Cu-Mo deposit, Peru, and ii) the Butte district, USA, by NIR microscopy, electron microprobe (EMP) analysis and FTIR spectroscopy to quantify the effect of minor and trace element substitutions on the NIR light transmittance of the mineral.

Pyrite samples from Toromocho exhibit growth zoning pattern controlled by trace amounts of Co and As. Both elements were often below the detection limit of the EMP, 75 and 470 ppm, respectively. However, As reaches 0.49 wt.% in IR-opaque growth bands (no transmittance detected by FTIR spectroscopy from 0.7 to 5 μm), while the presence of Co was revealed by FTIR transmitted spectrum with its characteristic IR absorption peak at 2 μm [2]. In pyrite samples from the Leonard Mine at Butte, oscillatory growth and sector zoning, observed in NIR light, is controlled by a high Cu content, reaching up to 2500 ppm in some growth bands (Figure 1).

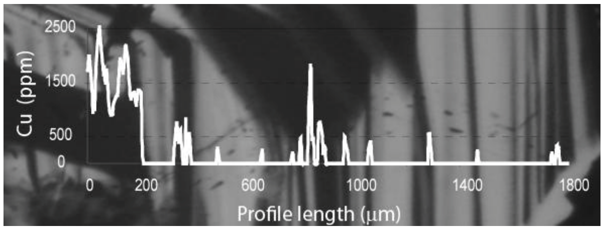

Figure 1 : IR transmitted-light photomicrograph of pyrite (Butte district) superposed to the electron microprobe line scan for Cu. The profile is 1800 μm long and is located along the X-axis.

Trace concentrations of As, Co and Cu decrease significantly the infrared transmittance in pyrite, which is the main limitation for a successful fluid inclusion study. Often trace element content is at the ppm level, thus requiring the use of more sensitive analytical technique, such as LA-ICP-MS, to correctly quantify trace amounts of these elements in the pyrite structure. Correlation between trace element content and quantitative FTIR transmittance spectroscopy allows preselection of samples potentially suitable for fluid inclusion studies.

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