



# Abiotic oxidation of pyrite by Fe(III) in acidic media and its implications for sulfur isotope measurements of lattice-bound sulfate in sediments

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## ABSTRACT

We have evaluated the relative importance of Fe<sup>3+</sup> to dissolved oxygen in pyrite oxidation, and its implications for measuring an accurate sulfur isotope composition ( $\delta^{34}\text{S}$ ) in trace sulfates extracted from sedimentary rocks. Results from our pure pyrite oxidation experiments show that in a solution of acidic pH, the amount of sulfate formed is very similar under both oxygenated and oxygen-free experimental conditions which is suggestive of the dominant role of Fe<sup>3+</sup> in pyrite oxidation compared to dissolved oxygen. One implication of this study is the influence of artifact sulfate on determination of sulfur isotopic composition of lattice-bound sulfate in phosphorite and carbonate sediments.  $\delta^{34}\text{S}$  values of trace sulfates in some lesser Himalayan phosphorites studied in this work, show no significant influence of dissolved oxygen during sample dissolution. We have attempted to explore the possible pathways which can cause depleted sulfur isotopic composition of trace sulfate in some of our phosphorite samples accompanied by relatively enriched Fe<sup>3+</sup> concentrations. Although artifact sulfate generation by pyrite oxidation during sample dissolution seems to be a probable mechanism, however several diagenetic pathways can also result in  $^{34}\text{S}$  depleted lattice sulfate accompanied by Fe<sup>3+</sup> enrichment. The degree of influence of laboratory artifact sulfate generation on determination of  $\delta^{34}\text{S}$  of trace sulfates is governed by combination of several factors like the amount of pyrite, concentration of ferric iron, concentration of lattice-bound sulfate etc. We propose mass balance calculations to derive the  $\delta^{34}\text{S}$  value of the uncontaminated trace sulfate.

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## 1. Introduction

The sulfur and oxygen isotopic compositions of trace sulfate (lattice-bound  $\text{SO}_4^{2-}$ ) from carbonate or phosphorites have previously been measured with the objective to resolve possible secular variations in the isotopic compositions of marine dissolved sulfate (Burdett et al., 1989; Shields et al., 1999; Hurtgen et al., 2002; Kah et al., 2004; Kampschulte and Strauss, 2004; Newton et al., 2004; Shields et al., 2004; Strauss, 2004; Gellatly and Lyons, 2005; Goldberg et al., 2005). Lattice-bound sulfate may substitute for the carbonate ion in calcite and dolomite (Staudt and Schoonen, 1995; Lyons et al., 2004). Benmore et al. (1983), McArthur et al. (1986) and Piper and Kolodny (1987), on the other hand, demonstrated the potential for using the isotopic composition of trace sulfate in interpreting the early diagenetic conditions during phosphogenesis. Carbonate fluorapatite (francolite) represented by the general formula  $\text{Ca}_{10-a-b}\text{Na}_a\text{Mg}_b(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{CO}_3\text{F})_y(\text{SO}_4)_z\text{F}_2$  identifies the substitution of the sulfate ion at the  $\text{PO}_4^{3-}$  lattice site (McClellan and Van Kauwenbergh, 1991; Jarvis et al., 1994).

Pyrite ( $\text{FeS}_2$ ) is a common sulfide mineral in phosphorites and, to a lesser degree, in carbonates, provided they are enriched in organic matter and have enough iron to sustain pyritisation. Pyrite and organically bound sulfur were reported to be present in carbonate and phosphorite rocks of various ages (e.g. Joachimski et al., 2001; Gorjan et al., 2003; Newton et al., 2004; Goldberg et al., 2005; Fike et al., 2006; Marenco et al., 2008). Bacterially mediated early diagenetic pyritisation through sulfate reduction causes marked sulfur isotopic depletion in  $^{34}\text{S}$  (up to 46‰) in the iron sulfide precipitates relative to the coexisting sulfate pool (Canfield, 2001). Oxidation of respective iron sulfides would result in the formation of artifact sulfate with a (mostly  $^{34}\text{S}$  depleted) sulfur isotopic signature distinctly different from the lattice-bound sulfate in the host lithology. During sample dissolution, mixing of the two sulfate pools of different sulfur isotope ratios, i.e., trace sulfate and sulfate resulting from sulfide oxidation would govern the sulfur isotopic composition of the extracted sulfate and hence, affect the “apparent” sulfur isotopic composition of the lattice-bound sulfate (e.g. Staudt and Schoonen, 1995; Mallinson and Compton, 1998). Marenco et al. (2008) have demonstrated that addition of pyrite with a known  $\delta^{34}\text{S}$  to carbonate samples resulted in lower  $\delta^{34}\text{S}$  values of the extracted sulfate, which proves that pyrite is readily oxidised during sample dissolution. Thus, it is important to understand the pathways as

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well as the possible extent to which pyrite oxidation can affect the sulfur and oxygen isotopic compositions of sulfate.

Although pathways and kinetics of pyrite oxidation have previously been studied in great detail (e.g. Singer and Stumm, 1970; Williamson and Rimstidt, 1994; Guevremont et al., 1998; Rimstidt and Vaughan, 2003; Descostes et al., 2004; Gleisner et al., 2006), no systematic study has so far been carried out to elucidate the possible influence of laboratory induced sulfate generation as a consequence of pyrite oxidation in the process of extracting trace sulfate from rocks and sediments for S- and O-isotope measurements.

In this paper we document the effect of oxic vs anoxic dissolution procedures on sulfate yields as well as its sulfur and oxygen stable isotope ratios resulting from oxidation of pyrite in acidic media with Fe<sup>3+</sup> as electron acceptor. Combination of factors which can affect the sulfur isotopic compositions of lattice-bound sulfate in phosphorites/carbonates has also been discussed. Trace sulfate extracted from a set of early Cambrian phosphorites from lesser Himalaya have been used for comparison to pure pyrite oxidation experiments. We further discuss some alternative (diagenetic) pathways which can also lead to <sup>34</sup>S depleted sulfur isotope ratios of trace sulfate in phosphorites.

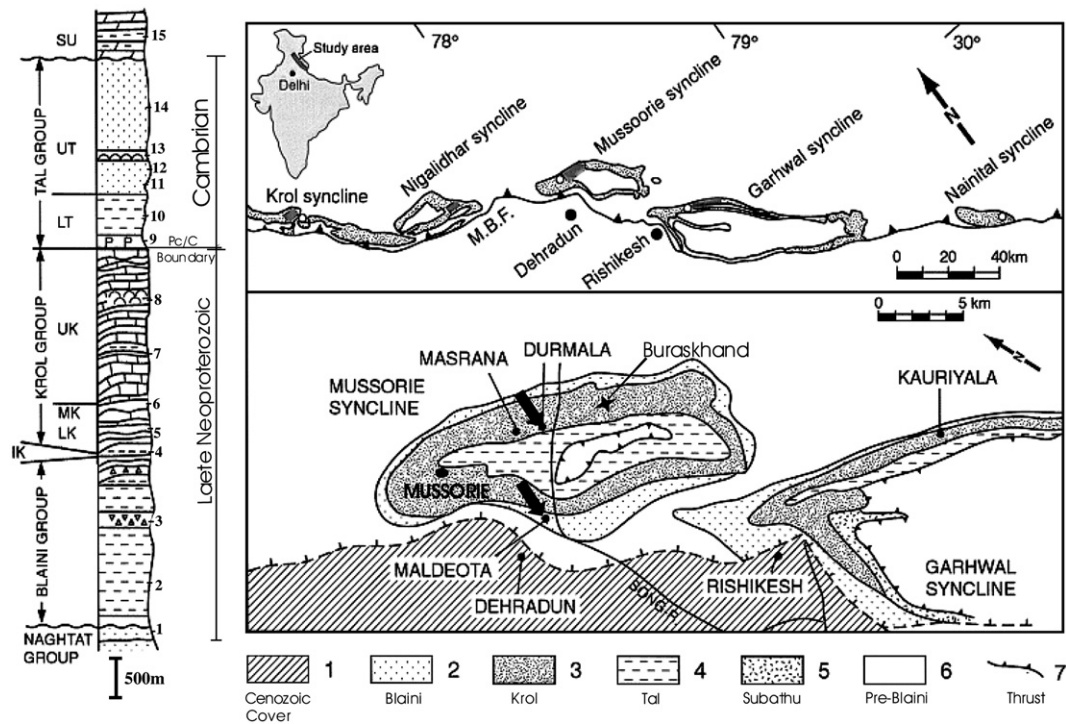
**2. Materials and methods**

**2.1. Extraction of trace sulfate**

For trace sulfate extraction 13 phosphorite samples of early Cambrian age were selected. These were collected from the Durmala and Maldeota phosphorite mines in the Lesser Himalaya, India (Fig. 1). Pyrite in these phosphorites is present as few micron size euhedral crystals or 5–20 μm size framboids or as anhedral/euhedral grains (Fig. 2A and B). Samples were ground in a tungsten carbide mill. 10 g

of sample powder were subjected to overnight leaching in 0.5 M NaCl solution under constant stirring. This process dissolves any easily soluble sulfate, including any secondary sulfates resulting from pyrite oxidation via weathering. BaCl<sub>2</sub> solution was added to the leachate in order to test the presence of dissolved sulfate. This step was repeated at least three times in order to ensure complete removal of secondary sulfates. The NaCl leached samples were filtered through 0.45 μm Millipore filter paper and immediately transferred to the reaction vessels without sub-aerial drying to avoid sub-aerial oxidation. The filtered residues were dissolved in 2 N HCl by constant stirring at room temperature (at 25 °C) for 4 h. Dissolution time was arbitrarily selected but was found sufficient for complete dissolution of francolite and the coexisting minor calcite/dolomite matrix. Another set of dissolution experiments was performed using the same set of sample powder but reaction proceeded under closed vessel condition with nitrogen purging to maintain anoxic condition. Except for the dissolution, all other steps like filtration and precipitation were performed under ambient atmosphere. The solutions were filtered through a 0.45 μm cellulose nitrate membrane filter (Millipore). 10 ml of 8.5% BaCl<sub>2</sub> solution was added to the filtrate to precipitate the dissolved sulfate as BaSO<sub>4</sub>. The suspensions containing barium sulfate were then kept overnight at around 70 °C for coarsening and purification of the BaSO<sub>4</sub> crystals. Subsequently, the BaSO<sub>4</sub> precipitates were filtered, dried, and weighed.

Quantification of chromium reducible sulfur (primarily pyrite sulfur) and the measurement of its sulfur isotopic composition were performed following standard wet chemical extraction methodology (Canfield et al., 1986). Approximately 1–2 g of phosphorite rock powder was reacted with 1 M CrCl<sub>2</sub> solution and 6 N HCl in an N<sub>2</sub> atmosphere. H<sub>2</sub>S produced by reduction of sulfide was trapped as ZnS



**Fig. 1.** Location and disposition of Mussoorie and Garhwal synclines with respect to other synclines in the Lesser Himalaya, geological map of Mussoorie and Garhwal synclines, sampling locations at Maldeota, Durmala, Masrana and Kauriyala and the corresponding generalised litholog depicting the Nagthat–Blaini–Krol–Tal succession. MBF = Main Boundary Fault. 1 = Cenozoic foreland deposits, 2 = Proterozoic Blaini and Infrakrol Formations, 3 = Neoproterozoic Krol Group, 4 = Lower Cambrian Tal Group, 5 = Subathu Formation, 6 = Proterozoic pre-Blaini and other rocks in tectonic windows, 7 = Thrust. *Litholog:* 1 = Quartz arenite of Nagthat Group, 2 and 3 = Shale, quartz arenite, diamictite and cap carbonate of Blaini Group, 4 = Bleached shale of Infrakrol (IK) Formation, 5 and 6 = Argillaceous limestone, dolomite, red shale and sandstone and shale of Lower (LK) and Middle (MK) Krol Formations, 7 = Algal dolomite/limestone/shale of Upper Krol (UK) Formation, 8 = Stromatolitic dolomite (UK), 9 = Chert, black shale and phosphorite of Lower Tal Formation (LT), 10 = Shale and siltstone of Lower Tal Formation, 11,12,13,14 = Feldspathic arenite, shale, microbial laminites and quartz arenite of Upper Tal (UT) Formation, 15 = Shale and limestone of Tertiary Subathu Formation (SU), FZ = Fossiliferous Proterozoic–Cambrian boundary zone, P = Chert–Phosphorite.

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