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The effects and importance of trace element heterogeneities during pyrite oxidation

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Accurate pyrite oxidation rates are required for a wide range of applications spanning from environmental impact assessments (e.g., impact of acid mine drainage) to paleo-redox reconstructions studies to ore processing (heap leach). However, current rates of pyrite oxidation are developed using relatively pure pyrite with few chemical impurities, often via experimental approach using synthetized pyrite and lower amounts of trace metal than naturel levels. This choice results in the lowest possible value of pyrite oxidation rates given that incorporated trace metals lead to less stable pyrite under oxidizing conditions. Changes in trace element content in the pyrite structure typically destabilize the lattice, resulting in higher oxidation rates. Similarly, the presence of micro-inclusions of other minerals may result in the formation of a galvanic cell effect that may speed up pyrite oxidation, especially if copper-rich minerals are present.

To explore the relationship between associated trace metals and pyrite stability under oxidizing conditions, we conducted batch oxidation rate experiments across several orders of magnitude of oxygen concentration using natural pyrite with high trace element contents from the Leicester pyrite Member, a pyrite lag deposit from Geneseo, New York. We then investigated the micro- to nano-scale heterogeneity of the trace element enrichment and redox state of the trace elements in the pyrite using diverse micro and nano focused analytical techniques including XRD, Mössbauer spectrometry, LA-ICPMS spot and map analyses, nanoSIMS, atom probe tomography, transmission electron microscopy, and µ-XANES analysis. We determined that the oxidation rate of trace element-rich pyrite is approximately an order of magnitude higher than low trace element pyrite used in traditional studies. Further, we identified high levels of heterogeneity in trace element content and redox state of As through the Leicester pyrite member, which impacted our determined oxidation rates. These results suggest that a range of different rates should be used in models that include pyrite oxidation, such as those addressing evolution of atmospheric and marine oxygen contents and delivery of bio-essential trace elements to the oceans or those minimizing the impact of mining critical metals from pyrite ores.