The Formation and Preservation of Greigite.

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Greigite is an important, yet elusive intermediate phase on the transformation pathway of poorly ordered iron monosulphides (e.g. mackinawite) to pyrite. It has been shown to exist in anaerobic sediments and has been used extensively as a paleomagnetic marker. However, the chemical conditions that control the transformation of mackinawite to greigite and prevent its further conversion to pyrite are poorly understood.

We have investigated the chemical conditions under which greigite is preserved in an anoxic sediment by measuring redox-active species of sulfur in solution using a multi-detector ion chromatographic method and of iron using spectrophotometry. Iron and sulphur-species in the solid-state were determined as AVS and pyrite fractions. These results are compared and contrasted with results from a laboratory study in which the kinetics and mechanism of greigite formation under closely controlled low-temperature and hydrothermal conditions was investigated using synchrotron-based spectroscopy and electron microscopy.

The transformation of mackinawite to greigite under hydrothermal conditions and at low temperatures is driven by polysulphide as an oxidant. A kinetic study under hydrothermal conditions has shown that the reaction is kinetically limited by the rearrangement of atoms in the crystal following the electron transfer from the mackinawite conduction band to adsorbed polysulfide. The activation energy for this process has been estimated as E_a = 67.5 (± 10.6) kJ mol^{-1}.

Investigation of the chemical conditions in anoxic sediments and the results of the laboratory systems have confirmed that the availability of polysulfide acts as the chemical switch responsible for the preservation of greigite in the geologic record. Both at low temperatures and under hydrothermal conditions, greigite is transformed to pyrite with an excess of polysulfide present. Under polysulfide-limited conditions, however, the reaction results in mixtures of greigite and pyrite or mackinawite and greigite.