American Mineralogist, Volume 82, pages 302–309, 1997

Transformation of mackinawite to greigite: An in situ X-ray powder diffraction and transmission electron microscope study

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ABSTRACT

Synthetic mackinawite (tetragonal FeS) has been found to transform rapidly to greigite (Fe_3S_4) above ~373 K during heating experiments, as observed by in situ X-ray diffraction. Using monochromatic synchrotron radiation (λ = 0.60233 Å), we measured the unit-cell parameters of both synthetic mackinawite between 293 and 453 K and of greigite formed from this mackinawite between 293 and 593 K.

The coefficients of thermal expansion for mackinawite are $\alpha_1 = \alpha_2 = (1.36 \pm 0.11) \times 10^{-5}$, $\alpha_3 = (2.98 \pm 0.12) \times 10^{-5}$, and $\alpha_{vol} = (5.67 \pm 0.19) \times 10^{-5}$ between 293 and 453 K. The coefficients of thermal expansion for greigite are $\alpha_1 = \alpha_2 = \alpha_3 = (1.63 \pm 0.15) \times 10^{-5}$, and $\alpha_{vol} = (4.86 \pm 0.25) \times 10^{-5}$ between 293 and 593 K. On further heating in situ, we observed the reaction greigite $\rightarrow$ pyrrhotite + magnetite.

Partial transformation of mackinawite to greigite was also observed using transmission electron microscopy (TEM) following in situ heating. Electron diffraction patterns show that (001) of mackinawite is parallel to (001) of greigite, and [110] of mackinawite is parallel to [100] of greigite. This orientation relationship confirms that the cubic close-packed S array in mackinawite is retained in greigite and implies that oxidation of some Fe^{2+} in mackinawite drives rearrangement of Fe to form the new phase. Small regions of the crystallites show Moiré fringes resulting from the lattice mismatch between mackinawite and greigite. Electron diffraction patterns of mackinawite subjected to prolonged exposure to the atmosphere also show faint spots corresponding to greigite.

We propose that in these experiments surplus Fe is accommodated by reaction with either adsorbed O_2 or H_2O to form amorphous nanophase Fe-O(H). Because greigite is so easily formed by oxidation from mackinawite, greigite should be an important precursor for pyrite nucleation, although any orientation relationship between greigite and pyrite remains to be determined.