Crystal Structures of the Sour Corrosion Products Mackinawite and Troilite/Pyrrhotite

To assist our understanding of the diverse structural characteristics of sour corrosion products, the interactive crystal structure visualization software package CrystalMaker 1.4.4 was recently purchased. Lattices are generated from inputted structural data, usually as "Crystal Information Files" (CIFs) from online databases. CIFs are a standard method of reporting crystallographic data for individual structures, *i.e.*, unit cell information, atomic coordinates and space group. The benefit of using CrystalMaker is that generated crystal structures can be manipulated, coordination environments displayed and basic measurements performed (bond lengths/angles, density). The software is user friendly and enables generation of crystal structure images for use in reports, papers, presentations, proposals, etc. Most importantly, CrystalMaker gives the researcher a "feel" for the structures with which they are working; this has proved useful for visualizing, and helping develop an understanding of, corrosion products such as siderite ($FeCO_3$), mackinawite (FeS), troilite (FeS), pyrrhotite ($Fe_{1-x}S$), smythite ($Fe_{3+x}S_4$), greigite (Fe_3S_4) and pyrite (FeS_2). Mackinawite and troilite/pyrrhotites are routinely observed in sour corrosion systems, as well as in our on-going research at the ICMT. Stoichiometric versions of each phase would have the formula FeS, with a pyrrhotite that is not deficient in iron possessing the troilite lattice. Structurally, the lattices of mackinawite and troilite are completely different. Each phase tends to form under particular conditions.

Mackinawite is a layered iron sulfide, often written with the formula $Fe_{1+x}S$ as it is usually found with a non-stoichiometric composition. It is readily formed at temperatures of less than 100°C at relatively short times in sour corrosion systems. Mackinawite has a tetragonal unit cell: a = b = 3.6735 Å, c = 5.0328 Å; $\alpha = \beta = \gamma = 90°$. Consequently, it is frequently referred to as "tetragonal iron sulfide". A single unit cell is shown in Figure 1 (brown = iron, yellow = sulfur). The iron atoms are at the apices and at the center of the square faces on opposite sides of the unit cell. The sulfurs are positioned on the elongated sides of the unit cell. The long axis of the cell corresponds to the direction in which the iron sulfide layers within the mackinawite structure stack, multiple unit cells are shown in Figure 2; its 2-dimensional structure is now obvious. A close-up of the crystal structure reveals that the iron atoms are essentially embedded within each layer, tetrahedrally coordinated to sulfurs. The sulfurs are similarly 4-coordinate, but in more of a pyramidal geometry, Figure 3. Mackinawite layers depicted with Shannon radii (Fe^{2+} radius set to 0.63 Å, S^{2-} to 1.84 Å), which more accurately reflect the actual/relative sizes of the atoms in the lattice, see Figure 4, reveal that the layers are sufficiently far apart for species to reside/diffuse "between the sheets". Wolthers *et al.* have hypothesized that water molecules intercalate into the mackinawite lattice during its hydrothermal formation.

Troilite and the pyrrhotites essentially possess the niccolite, or nickel arsenide, characteristic crystal structure; albeit with distortions and, in the case of pyrrhotites, iron deficiency. In corrosion systems, these phases typically occur at temperatures in excess of 100°C, although their formation over long periods of time at lower temperatures may also be possible. The hexagonal arrangement of iron and sulfur atoms in the troilite lattice, viewed perpendicular to the *xy*-plane, is shown in Figure 5. Troilite can be described as an expanded/distorted *hcp* anion array with cations in the octahedral holes, or *vice versa*. Its unit cell parameters are a = b = 5.9650 Å, c = 11.7570 Å; $\alpha = \beta = 90°$, $\gamma = 120°$. Unlike mackinawite, troilite possesses a 3-dimensional framework. It is worth noting that troilite is of significantly higher density than mackinawite, 4.835 g/cm^3 *versus* 4.298g/cm^3. Figure 6 depicts a view of its lattice after it has undergone rotation to illustrate the alternating nature of the iron and sulfur within the crystal structure. Inspection of the figure reveals the stoichiometric nature of troilite, with Fe:S = 1:1. The 6-coordinate, distorted octahedral character of the irons and sulfurs within the lattice is clear from Figure 7. Pyrrhotite has essentially the same framework architecture as troilite, except that irons are systematically absent from the lattice. Pyrrhotite formulae tend to be written as $Fe_{1-x}S$, where $x < 0.20$, or Fe_yS_z. The non-stoichiometry results from replacement of Fe^{2+} in the lattice with Fe^{3+}, fewer of which are required for charge balance of the S^{2-} anions.

A long term goal of the CC-JIP is to study the formation and interconversion of iron sulfides under conditions where localized corrosion occurs.

References

(1) Lennie, A.R.; Redfern, S. A. T.; Schofield, P.F.; Vaughan, D.J. Synthesis and Rietveld Crystal Structure Refinement of Mackinawite, Tetragonal FeS. *Mineralogical Magazine* 1995, 59, 677-683.
(2) Wolthers, M.; Van der Gaast, S.J., Rickard, D. The Structure of Disordered Mackinawite, *American Mineralogist*, 2003, 88(11), 2007-2015.
(3) Skala, R.; Cisarova, I.; Drabek, M. Inversion Twinning in Troilite. *American Mineralogist*, 2006, 91, 917-921.

Figures

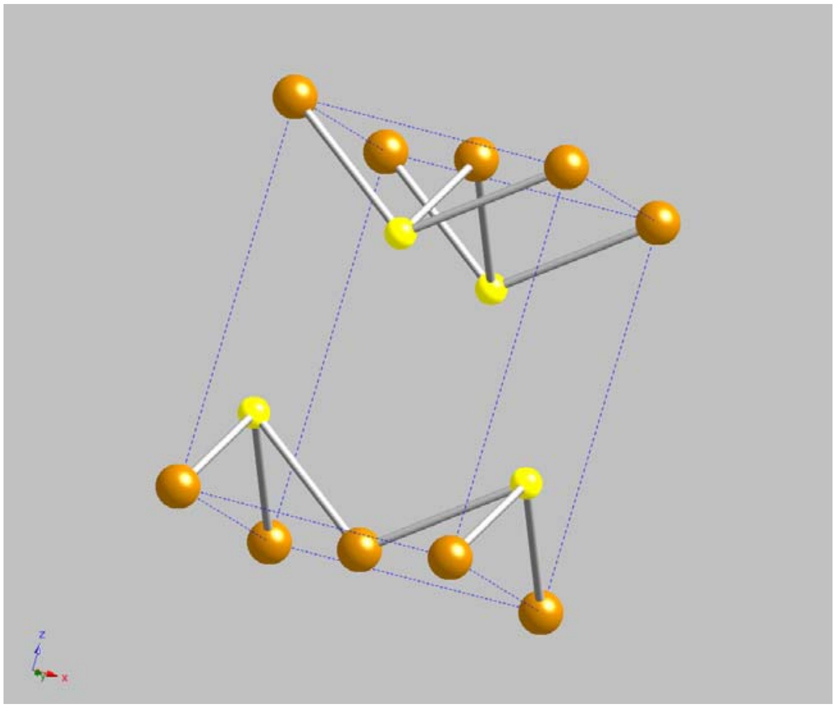

Figure 1 Tetragonal unit cell of mackinawite.

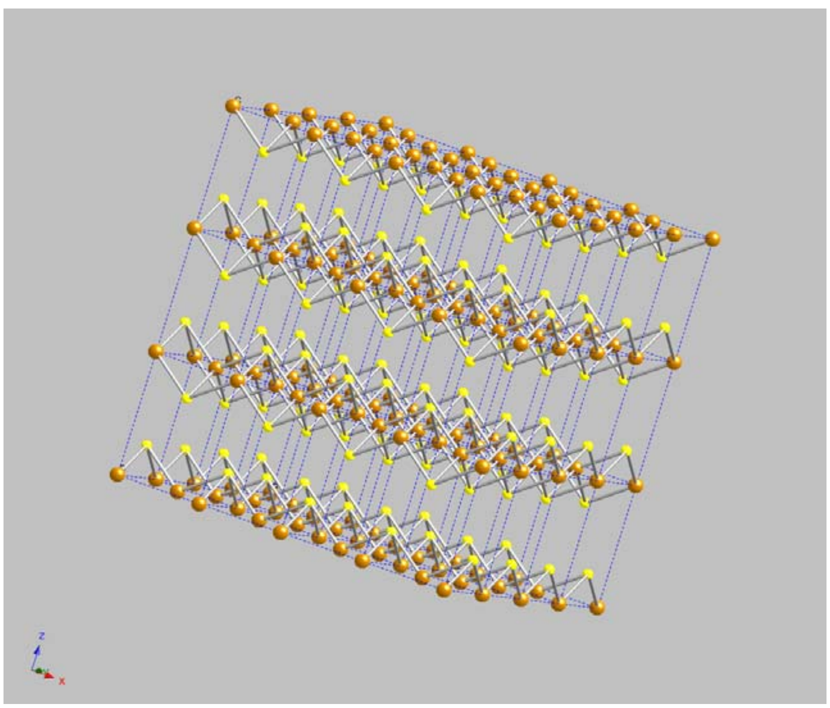

Figure 2 Multiple unit cells of mackinawite.

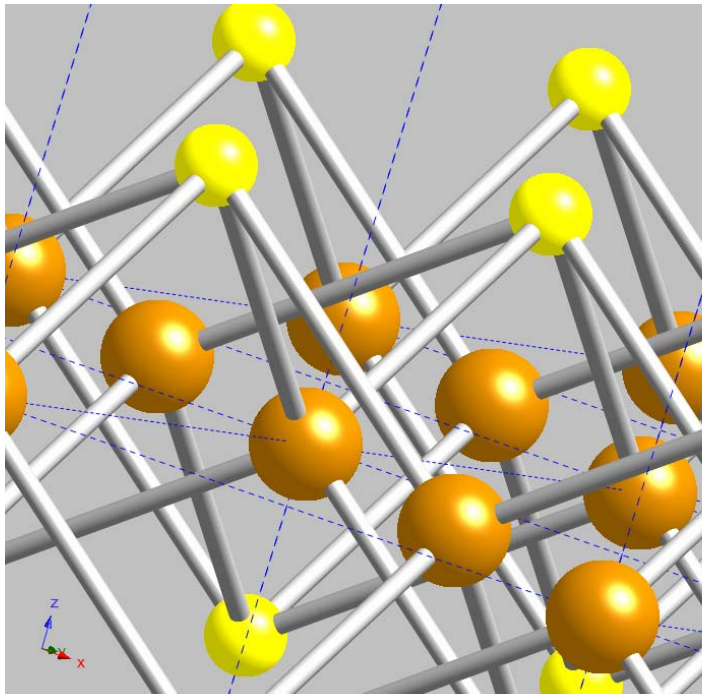

Figure 3 Coordination environments of iron (brown) and sulfur (yellow) in the mackinawite structure.

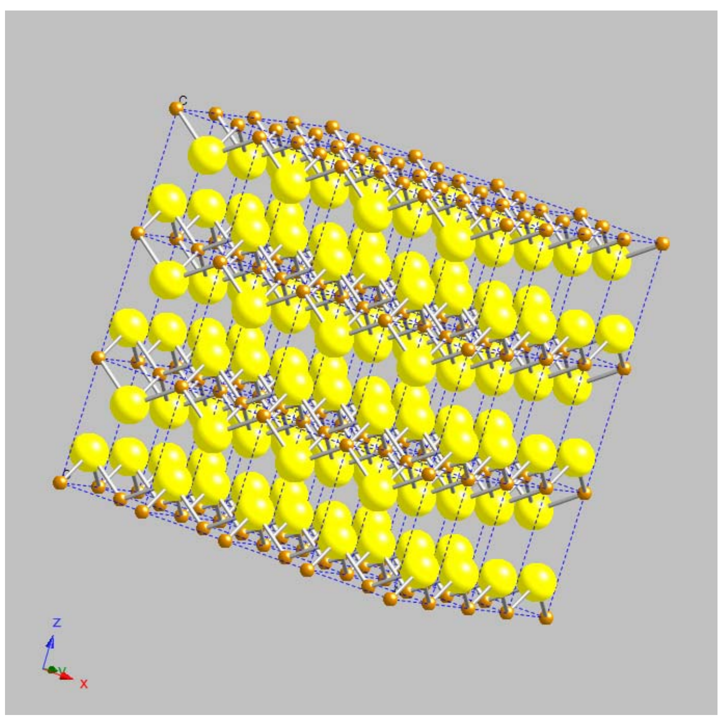

Figure 4 Mackinawite 2-D layer structure shown with Shannon radii.

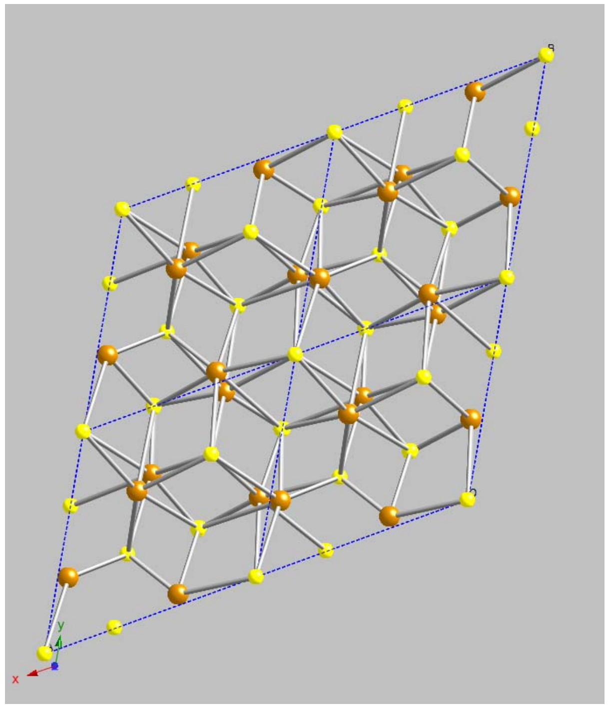

Figure 5 Structure of troilite**,** viewed perpendicular to the *xy*-plane.

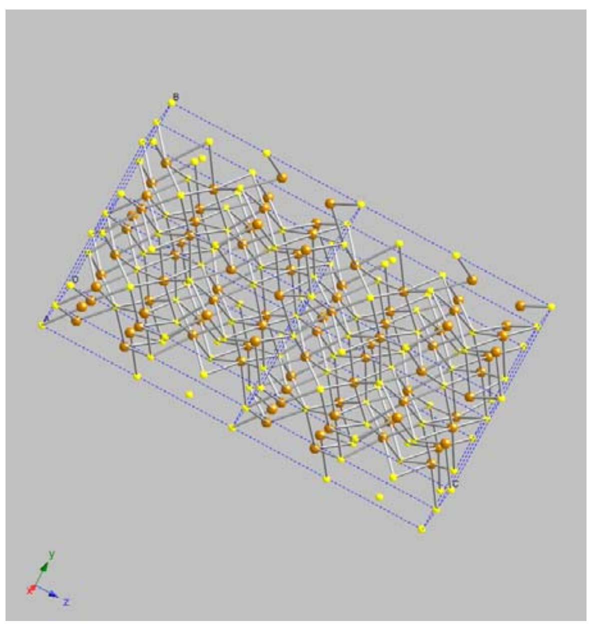

Figure 6 Structure of troilite and its 3-D framework architecture**,** viewed approximately perpendicular to the *yz*-plane.

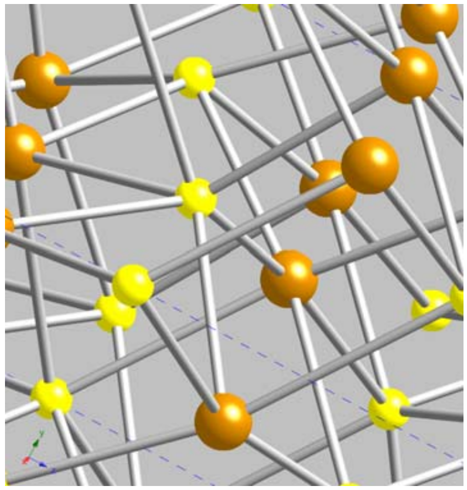

Figure 7 6-coordinate environments of iron (brown) and sulfur (yellow) inside the troilite structure.