

# Replacement mechanisms among iron sulphide minerals

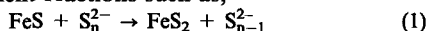
Y. Furukawa  
H.L. Barnes

Ore Deposits Research Section, The Pennsylvania State University, University Park, Pennsylvania 16802, USA.

## Introduction

Authigenic pyrite is common in both modern and ancient marine sediments. In natural aquatic systems, pyrite formation depends upon oxidation state, pH, and sulphate and iron concentrations, so pyrite is an indicator of geochemical environments. Berner (1970, 1984) described the genesis of sedimentary pyrite by three stages. In stage (a), bacterial reduction converts sulphate to aqueous sulphide species. Stage (b) reacts sulphide and dissolving detrital iron minerals to form amorphous  $\text{Fe}(\text{HS})_2$  (Rickard, 1989) which subsequently transforms to amorphous  $\text{FeS}$  and then to mackinawite ( $\text{Fe}_9\text{S}_8$ ). Stage (c) is a series of replacement reactions producing pyrite from mackinawite through progressively more sulphur-rich phases. Although these stages have been studied often, our understanding of stage (c) is far from complete.

Experimental studies have indicated that zero-valent sulphur species, such as polysulphides ( $\text{S}_n^{2-}$ ), are essential in forming pyrite through replacement reactions such as,



(e.g., Schoonen and Barnes, 1991). However, sufficient zero-valent sulphur species are not always observed in pyrite-forming environments. An alternative reaction may be by iron loss from the precursor iron sulphide to form pyrite, such as

$$2\text{FeS} + 2\text{H}^+ \rightarrow \text{FeS}_2 + \text{Fe}^{2+} + \text{H}_2 \quad (2)$$

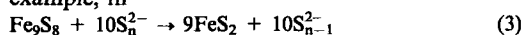
but there is no experimental evidence in support of this reaction (e.g., Schoonen and Barnes, 1991).

Sulphidation reactions, like (1), have positive changes in molar volumes ( $+\Delta\bar{V}_s$ ) of these solids.  $A + \bar{V}_s$  results in armoring of the original surface by the secondary phase, thereby impeding further direct interaction between the original core phase and aqueous solutions. Replacement reactions are favored by  $-\Delta\bar{V}_s$ , causing increased permeability for the efficient exchange of atoms among participating solid phases and aqueous solution. A  $-\Delta\bar{V}_s$  generates void spaces as a replacement reaction proceeds, and further promotes interaction among the solid surfaces and aqueous solutions. Replacement reactions among iron sulphide minerals must also follow these principles.

Therefore, the scarcity of zero-valent sulphur species in pyrite-forming environments plus the  $+\Delta\bar{V}_s$  makes such sulphidation reactions geochemically unrealistic.

## $\Delta\bar{V}_s$ among iron sulphides

Previous experimental studies of authigenic pyrite formation support sulphidation rather than iron loss as the principal mechanism of the replacement reactions that convert mackinawite to pyrite. Zero-valent sulphur species, such as polysulphides, are taken as the sulphur source, for example, in



Here, replacement is by sulphidation rather than iron loss with  $+\Delta_s$  of

$$\Delta\bar{V}_s (\%) = (9 \times \bar{V}_{\text{py}} - \bar{V}_{\text{mk}}) / \bar{V}_{\text{mk}} \times 100 = (9 \times 23.9 - 184.3) / 184.3 \times 100 = +17\% \quad (4)$$

Figure 1 summarizes  $\Delta\bar{V}_s$  for Fe-S minerals in replacement reactions. All but one reaction would lead to a  $+\Delta\bar{V}_s$  where the replacement reactions proceed by sulphidation. The greigite-to-pyrite step is the only sulphidation reaction that has a  $-\Delta\bar{V}_s$ .

An alternative reaction to sulphidation is

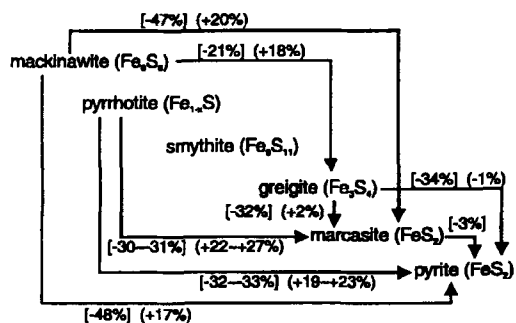


Fig. 1. Volume changes between the mineral reactants and products of FeS replacement reactions. Reactions which proceed by iron loss have decreases in volumes of solids shown by [%]. Reactions involving sulphidation of precursor minerals have increased solid volumes and their changes are represented by (%).

replacement accompanied by iron loss. In such reactions, sulphur is conserved in the solid structure whereas iron is leached and released into an aqueous solution. Such reactions result in  $-\Delta\bar{V}_s$ , as for pyrite replacing mackinawite below. A plausible process is the oxidation of mackinawite by generation and loss of hydrogen, as in  $\text{Fe}_9\text{S}_8 + 10\text{H}^+ \rightarrow 4\text{FeS}_2 + 5\text{Fe}^{2+} + 5\text{H}_2$  (5)

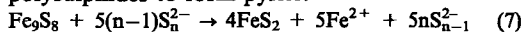
The molar volume change for the minerals of reaction (5) is

$$\Delta\bar{V}_s(\%) = (4 \times \bar{V}_{\text{py}} - \bar{V}_{\text{mk}}) / \bar{V}_{\text{mk}} \times 100 = (4 \times 23.9 - 184.3) / 184.3 \times 100 = -48\% \quad (6)$$

Figure 1 summarizes  $\Delta\bar{V}_s$  of replacement reactions with either iron loss or sulphidation. Contrary to sulphidation, all replacement reactions have  $-\Delta\bar{V}_s$  where reactions proceed by iron loss instead of sulphidation. However, note that there has been found no experimental or field evidence for such iron-loss reactions as (2) or (5) where hydrogen is produced (Schoonen and Barnes, 1991). Previous experiments required the presence of, and reaction with, zero-valent aqueous sulphur species to convert mackinawite to pyrite.

#### Reaction mechanisms

Replacement reactions in aqueous solutions are likely to proceed with  $-\Delta\bar{V}_s$  in the conversion of mackinawite to pyrite. In order for  $-\Delta\bar{V}_s$  to occur, all but one of the iron sulphide replacement reactions (greigite to pyrite) must proceed by iron loss. On the other hand, previous experimental studies support sulphidation, because zero-valent aqueous sulphur species were required. This apparent discrepancy is resolved if the intermediate sulphur species act as oxidizing reactants rather than just sources of sulphur. To illustrate, take the example of mackinawite reacting with polysulphides to form pyrite:



In this example, replacement occurs by removing iron from the solid. Here the polysulphides are not the sources of sulphur for sulphidation, but are effective oxidizing agents. Other products of the reaction,  $\text{Fe}^{2+}$  and  $\text{S}_{n-1}^{2-}$ , may then react, as found by Luther (1991), to precipitate amorphous iron sulphide, which gradually transforms to more pyrite by repeating reaction (7) which also produces more shorter chain polysulphides. Pyrite produced by this later reaction may become an overgrowth on the earlier pyrite. Although previous studies of pyritization suggest that the dominant process was by simple sulphidation reactions, the  $\Delta\bar{V}_s$  criteria show that there must have been an overall reaction involving both oxidation and apparent sulphidation. The elemen-

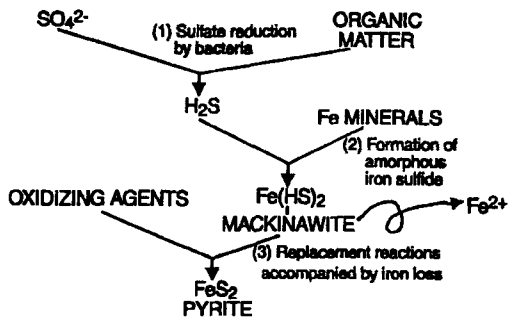
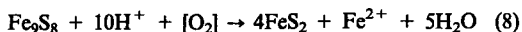


FIG. 2. Revised sedimentary pyrite formation mechanism (after Berner, 1970, 1984).

tary steps of the overall reaction are a series of iron-loss reactions, with associated reprecipitation of amorphous  $\text{Fe}(\text{HS})_2$ , and further reaction first to form mackinawite and then pyrite by iron loss.

Such iron-loss replacement means that the availability of zero-valent sulphur species is not a limiting factor in the conversion of mackinawite to pyrite. Instead, the availability of an appropriate oxidizing agent directly controls authigenic pyrite formation. In general, the conversion of mackinawite to pyrite can be written schematically using  $[\text{O}_2]$  also to indicate other oxidizing agents,



implying that authigenic pyrite formation is possible even in sulphur-poor, fresh water environments. Consequently, the diagrammatic path of pyrite formation by Berner (1970, 1984) can be modified as shown in Figure 2. The initial two stages remain unchanged, whereas Stage (3) now involves other general oxidizing agents in addition to zero-valent sulphur species. Zero-valent sulphur species are effective oxidizing agents because previous experimental studies have successfully converted mackinawite to pyrite in the presence of polysulphides or elemental sulphur. However, they are not the only reactants causing pyritization.

#### References

- Berner, R. A. (1970) *Amer. J. Sci.*, **268**, 1–23.  
 Berner, R. A. (1984) *Geochim. Cosmochim. Acta*, **48**, 605–15.  
 Luther, G. W. III (1991) *Geochim. Cosmochim. Acta*, **55**, 2839–49.  
 Rickard, D. (1989) *Chem. Geol.*, **78**, 315–24.  
 Schoonen, M. A. A. and Barnes, H. L. (1991) *Geochim. Cosmochim. Acta*, **55**, 1505–14.