

Oxygen in pyrrhotite: 3. A mechanistic model

JAMES GRAHAM

Division of Minerals and Geochemistry, CSIRO, Wembley, Western Australia 6014, Australia

ABSTRACT

Evidence is summarized that oxygen is present at observable levels in many pyrrhotites. There is some circumstantial and some experimental evidence that the oxygen level may affect the hexagonal-monoclinic equilibrium and that monoclinic pyrrhotite may not be a phase in the system FeS.

INTRODUCTION

The work on natural pyrrhotites described in the two preceding papers in this issue (Graham et al., 1987; Graham and McKenzie, 1987) and in a series of papers going back to 1972 (Bennett et al., 1972a, 1972b; Bennett and Graham, 1980, 1981; Thorber, 1972; Ewers, 1972; Ewers et al., 1976; Graham, 1978) had its origin partly in a conflict apparent in the literature between many natural occurrences (particularly in black shales) and the accepted equilibrium phase diagram for the system Fe-S and partly in a need to document a particular sulfide orebody. The problem is the coexistence of pyrite and hexagonal pyrrhotite. The usual explanation for this assemblage, which is regarded as nonequilibrium, is the difficulty of nucleation and of reaction of pyrite; but it appears that an impurity such as oxygen might modify the phase diagram or the kinetics of reaction in such a way as to give a more satisfying explanation of the evidence. Impurity contents have been proposed to explain the stability of polymorphs such as wurtzite-sphalerite and marcasite-pyrite, but have not gained full acceptance by the mineralogical community. The first requirement in elucidating this question for pyrrhotite is to show that a common impurity often exists in significant quantities. In the process, other properties of pyrrhotites have been studied.

The need to understand the phenomenon was reinforced by discrepancies evident in experimental results on pyrrhotite from different laboratories. Literature on the Fe-S system abounds, and many of the relevant references are cited in our previous papers.

OXYGEN AS AN IMPURITY IN PYRRHOTITE

Largely on the basis of a phenomenon known as "magnetic reversal" in pyrrhotite (Bhimasankaram and Lewis, 1966), Bennett et al. (1972a) concluded that oxygen was a prime suspect for the impurity in pyrrhotite. We were able to show (Bennett et al., 1972b) that magnetite in monoclinic pyrrhotite ranges from the few relatively broad lamellae sometimes visible in the optical microscope, to multitudes of extremely fine lamellae that could only be directly observed by electron diffraction, or indirectly by magnetic techniques (Bennett and Graham, 1980). Sim-

ilarly, a difference between dry and hydrothermal annealing of pyrrhotites (Bennett and Graham, 1980) pointed to oxygen or hydrogen as a possible impurity and to the fact that phase stability is noticeably affected by the surrounding medium.

Meanwhile, in an experiment designed for other purposes, some chromites were dissolved in a pyrrhotite-rich sulfide melt and cooled through the solidus (Ewers et al., 1976). Re-examination of these samples (Bennett and Graham, 1980) showed that the large pyrrhotite grains contained magnetite lamellae throughout their bulk. The lamellae were much less frequent near grain boundaries (which contained spinel phases) and near chromite grains and precipitates. The arrangement of spinels and magnetite could be explained on the basis that appreciable amounts of oxygen are soluble in solid pyrrhotite, supporting an early observation of Naldrett (1969), and that exsolution occurs as the temperature is reduced. The depletion zones suggest that oxygen diffusion at high temperatures is very rapid. Thermal cycling in a magnetic balance had already hinted at a significant oxygen solubility (Bennett and Graham, 1980).

The magnetite lamellae are topotactically related to the pyrrhotite, and enjoy a low interfacial energy (Bennett et al., 1972b). This explains the small hysteresis involved in exsolving magnetite, although at low temperatures, nucleation becomes more difficult (Graham et al., 1987). It seems possible that the monoclinic structure may be stabilized by the presence of magnetite lamellae as nuclei, or merely by the distorting effect of the smaller oxygen ion in solid solution in the NiAs-type structure. We have now added observations of reversible exsolution of magnetite from monoclinic pyrrhotite at low temperatures, and the determination therefrom of an activation energy for oxygen diffusion in solid pyrrhotite, which indicates no appreciable barrier to such diffusion. We have derived an approximate solubility of oxygen as a function of temperature below 700°C, and have shown that the transformation of monoclinic to hexagonal pyrrhotite at temperatures below 300°C is accelerated in the presence of a specific oxygen getter.

Direct observation and measurement of oxygen in two

natural pyrrhotites using a deuterium probe showed a high and heterogeneous oxygen content in the monoclinic pyrrhotite and a uniformly low but measurable content in the hexagonal pyrrhotite. Bulk analysis proved to be ambiguous because of the possible presence of surface-adsorbed oxygen and of fine silicates. It will be necessary to study many more pyrrhotites from different locations to decide whether this observation is of general validity.

The Nairne pyrite deposit in South Australia consists largely of pyrite and hexagonal pyrrhotite, with monoclinic pyrrhotite present only as oxidized rims on hexagonal pyrrhotite grains. Graphite is often present within the hexagonal pyrrhotite, suggesting that the hexagonal pyrrhotite-pyrite association is the result of highly reducing conditions (Graham, 1978). A recently described example in which the C is largely amorphous is the "earthy pyrite" banding at Flin Flon (Laufer et al., 1985). In some stratified sulfides of the central Appalachians, native Bi instead of graphite indicates reducing conditions (Craig, 1980). I have not yet come across any contrary observations, and if highly reducing conditions are always encountered an inescapable conclusion is that monoclinic pyrrhotite is not a phase in the Fe-S system, but needs oxygen to stabilize it.

This suggestion is more satisfying as an explanation for a widespread phenomenon than the alternative popular idea of thermodynamic disequilibrium. As already stated, we do not believe that nucleation is a major problem, except perhaps where pyrite is a product. Magnetic experiments have shown (Bennett and Graham, 1981) that disequilibrium is not due to slow diffusion of metal ions in the S lattice [Fe vacancies move at an appreciable rate at 90°C; bulk diffusion of Ni into pyrrhotite at 240°C (Ewers, 1972) reinforces this view]. Related experiments at 50°C and at room temperature also confirm rapid ion movement in the NiAs-type structure and show the importance of pH and Eh, e.g., the uptake of S by troilite (Moh, 1963) and of Cu and Cd by NiS, (L'vovich and Vol'khin, 1968; Vol'khin and L'vovich, 1968). The rate-determining process in pyrrhotite synthesis may be a nucleation step if pyrite is formed, or it may be that migration of oxygen is required before equilibrium can be attained. If monoclinic pyrrhotite is indeed a phase in the system Fe-S, the inhibiting factor in forming monoclinic pyrrhotite-pyrite deposits from hexagonal pyrrhotite-pyrite cannot be nucleation of monoclinic pyrrhotite, since Fe can easily be removed from the pyrrhotite at low temperatures (Moh, 1963), but must be the removal of S from pyrite.

It became clear during the course of the work that, although surface oxygen reacts rapidly with pyrrhotite at 300°C or so, bulk diffusion of oxygen within the pyrrhotite lattice is restricted until about 450°C; by 600°C, diffusion is extremely rapid. Short-range movement of oxygen is observable at 300°C.

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