

Transition of Metastable Pyrrhotites to a Stable Phase State

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Abstract—Equilibrium phase relations of synthetic minerals prepared by annealing metastable iron sulfides, followed by prolonged isothermal storage in the Earth atmosphere, have been studied by X-ray diffraction. The results demonstrate that prolonged storage of synthetic pyrrhotites annealed at different temperatures makes it possible to identify metastable and stable phases of Fe and S compounds.

Keywords: mineral, pyrite, troilite, impurity centers, magnetization

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INTRODUCTION

The FeS₂–FeS transition is a topical issue because it is of both theoretical and practical interest. It is known that, decomposing under the effect of an external influence, pyrite (FeS₂) converts into pyrrhotite and then to troilite, forming various combinations of phases. Note that the phase relations involved can vary with time [1–4] and that some phases and their relations still remain unexplored [5, 6]. Recent years have seen increasing interest in minerals of space origin. This is due in part to the fact that their formation is influenced by extreme conditions, such as high vacuum and extremely low or extremely high temperatures. One example is troilite (FeS) [7]. In pure form, it is only present in meteorites, so this mineral is of interest from the viewpoint of the formation of planets and mineral resources on them.

One mineral forming during underwater volcanic eruptions is pyrrhotite. It has a nonstoichiometric composition and its crystal structure contains cation vacancies [8, 9]. Processes underlying the transition of pyrrhotite minerals to a stable phase state have not yet been studied in sufficient detail. Typically, the transition takes a very long time, which makes it difficult to study experimentally, whereas theoretical predictions can turn out to be wrong in practice. Therefore, it is of interest to carry out prolonged experiments, in which one can observe transformations of minerals under isothermal conditions in the Earth atmosphere. The

formula unit of pyrrhotite has the form Fe_{1–x}S, where x is the number of vacancies, that is, the average number of vacancies per Fe atom (vacancy density).

The magnetic properties of nonstoichiometric ferromagnets are closely related to the cation vacancy distribution in their structure [10–12]. For example, the structure of pyrrhotite exhibits ferromagnetic spin order in the basal plane and antiferromagnetic order in neighboring planes. Pyrrhotite differs from troilite not only in that the crystal structure of pyrrhotite contains vacancies, in contrast to the structure of troilite, but also in spin direction: in troilite, the spin is directed along the C axis, whereas in pyrrhotite the spin is normal to this axis. Besides, the structure of troilite is distorted and can be identified as a $2C$ structure, whereas vacancies eliminate the distortion, so pyrrhotite has a $1C$ structure [2, 13–15].

The purpose of this work was to find equilibrium phase relations in synthetic minerals obtained from metastable iron sulfides at different annealing temperatures and during subsequent prolonged isothermal holding in the Earth atmosphere.

EXPERIMENTAL

Samples for this investigation were prepared in two steps: synthesis of pyrrhotites and prolonged storage under normal atmospheric conditions with the aim of identifying stable phases.

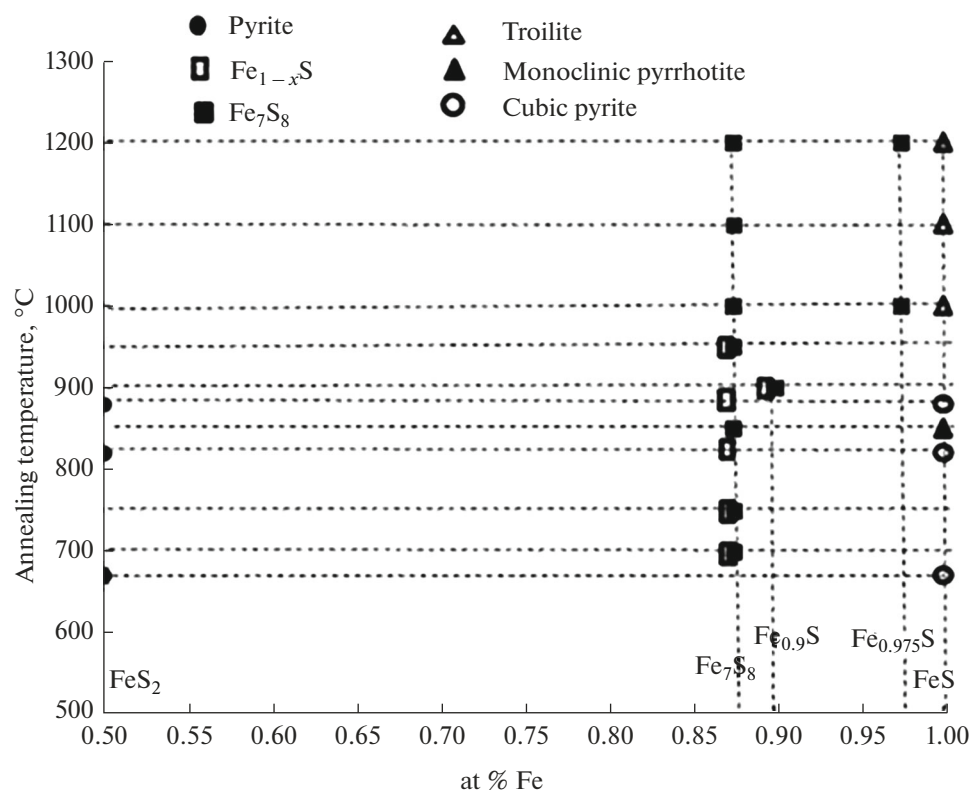


Fig. 1. Phase compositions of the samples obtained via annealing of pyrite at different temperatures and prolonged storage.

Pyrrhotites were prepared by annealing natural single-crystalline pyrite. To this end, pieces of the mineral were ground into powder, which was then annealed in a quartz tube under a dynamic vacuum of 10^{-2} Pa produced by pumping air and sulfur vapor. The tube was 1 m in length, and the sample was located at its closed end and heated by a Nichrome coil. The annealing time was 1 h and the temperature t_{ann} was varied from 400 to 1200°C. The cooling rate of the samples was 20°C/min. The opposite end of the tube was maintained at room temperature and connected to a vacuum system.

Chemical homogeneity of the samples was ensured by the fact that the particle size in the powder did not exceed 1 μm . This was confirmed by the fact that samples taken at random from a batch annealed at a preset temperature had identical X-ray diffraction patterns.

In the second stage of the experiment, the synthesized pyrrhotites were stored for a long time in air at room temperature under atmospheric conditions. The storage time was 38 years. The phase compositions of those samples determined by X-ray diffraction are presented in this paper. Prolonged holding of the samples under fixed external conditions allowed us to

identify stable pyrrhotite phases, which was the purpose of this study.

The crystal structure of the samples was studied by X-ray diffraction on a DRON-3 X-ray diffractometer using $\text{CuK}\alpha$ radiation (scan step of 0.02° , counting time per data point of 1 s). The crystalline phases present in the powder samples were identified using the JCPDS database. Intensity data were collected at a rate of $1^\circ/\text{min}$ in continuous mode and $0.001^\circ/\text{s}$ in step scan mode. In collecting X-ray diffraction patterns, we used Fe beta-filter. Compositions were checked by X-ray diffraction as described elsewhere [16, 17]: the position of the 102 reflection was determined as a function of sulfur content.

Magnetization data and magnetization reversal curves were obtained at room temperature using a Quantum Design MPMS-XL SQUID magnetometer.

RESULTS AND DISCUSSION

The characterization results obtained for our samples immediately after synthesis were reported previously [16].

The phase compositions of the samples after prolonged storage are presented in Fig. 1.

Figure 2 shows X-ray diffraction patterns of the samples annealed at 670, 850, and 1200°C.

The samples obtained at $t_{\text{ann}} = 670^\circ\text{C}$ consisted of pyrite (FeS_2) and an FeS phase, which was identified as cubic pyrrhite.

Raising t_{ann} to 850°C led to the formation of a hexagonal pyrrhotite phase ($\text{Fe}_{0.875}\text{S}$) and monoclinic pyrite (FeS). The samples obtained at the highest annealing temperature, 1200°C, consisted of $\text{Fe}_{0.875}\text{S}$, $\text{Fe}_{0.975}\text{S}$, and troilite (FeS).

The effect of prolonged storage on the phase relations of pyrrhotites clearly shows up in the magnetization of the samples (Fig. 3).

The rise in magnetization at annealing temperatures from 500 to 650°C is due to the fact that the samples were two-phase in this range and consisted of paramagnetic pyrite and ferrimagnetic pyrrhotite. With increasing t_{ann} , pyrite content decreases, whereas the content of pyrrhotite phases increases (in agreement with previously reported results [16, 18–20]). Raising the annealing temperature to 700–850°C leads to the highest magnetization of the samples. At higher t_{ann} , their magnetization decreases. This is due to the decrease in vacancy concentration and the weaker interaction between the vacancies because of the larger distance between them: it is these factors that determine the total magnetic moment.

The shape of the hysteresis loop of the sample obtained via annealing at $t_{\text{ann}} = 1000^\circ\text{C}$ and prolonged storage (Fig. 3b) indicates that it consists of a ferromagnetic and an antiferromagnetic phase. The samples prepared at 1100 and 1200°C had similar magnetic characteristics. The ferromagnetic properties of these samples were due to storage: the starting samples prepared at these temperatures were antiferromagnetic.

The present results lead us to assume that, during storage under isothermal conditions in air, metastable pyrrhotites reach stable phase states. Our samples consisted of various combinations of the $\text{Fe}_{0.975}\text{S}$, $\text{Fe}_{0.950}\text{S}$, $\text{Fe}_{0.909}\text{S}$, $\text{Fe}_{0.900}\text{S}$, $\text{Fe}_{0.875}\text{S}$, FeS, and FeS_2 compounds, depending on t_{ann} .

It also follows from analysis of X-ray diffraction patterns that metastable pyrrhotites can convert over time into various stable pyrrhotite phases and FeS, such as monoclinic or cubic pyrite or troilite, depending on annealing temperature.

The phases obtained here correlate with previously reported states of pyrrhotites observed in natural minerals [21–23]. Moreover, the presence of these phases is consistent with the phase diagram reported by Kullerud and Yoder [21]. As shown earlier [16], immediately after synthesis the sulfur ions in the structure of pyrrhotite undergo redistribution, resulting in the formation of metastable and stable phases. During storage, the metastable phases convert into stable phases, for

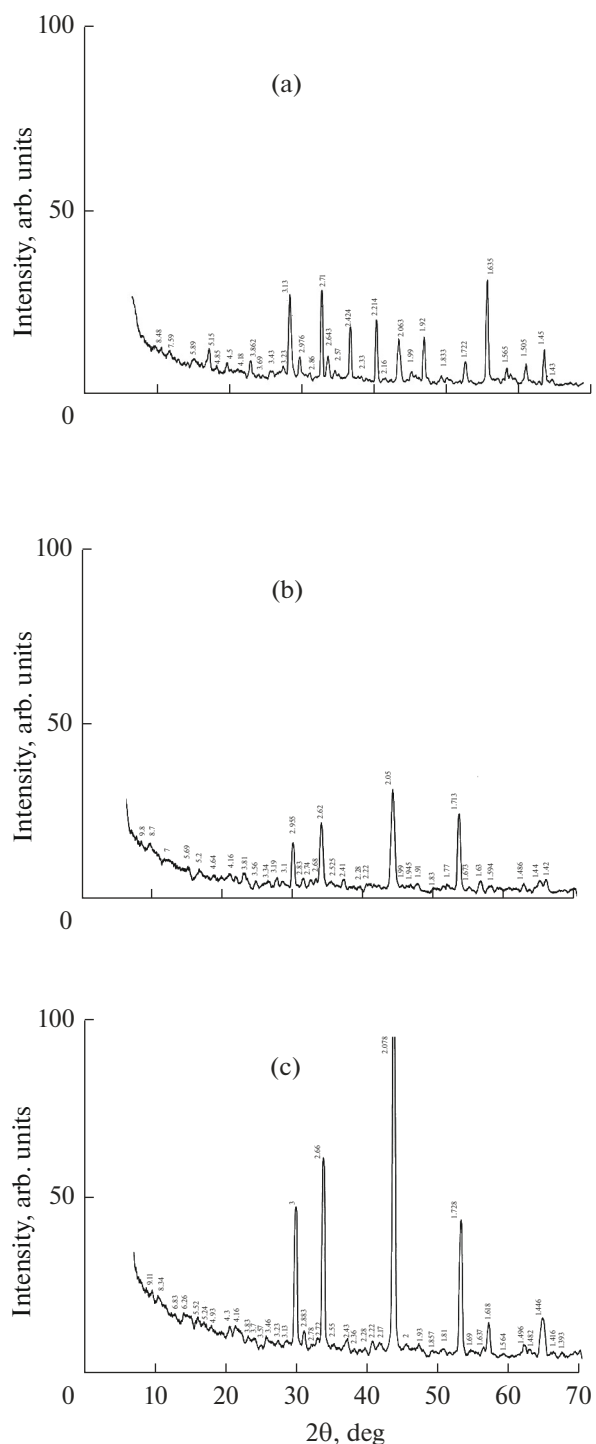


Fig. 2. X-ray diffraction patterns of the samples obtained by annealing at temperatures of (a) 670, (b) 850, and (c) 1200°C and prolonged storage.

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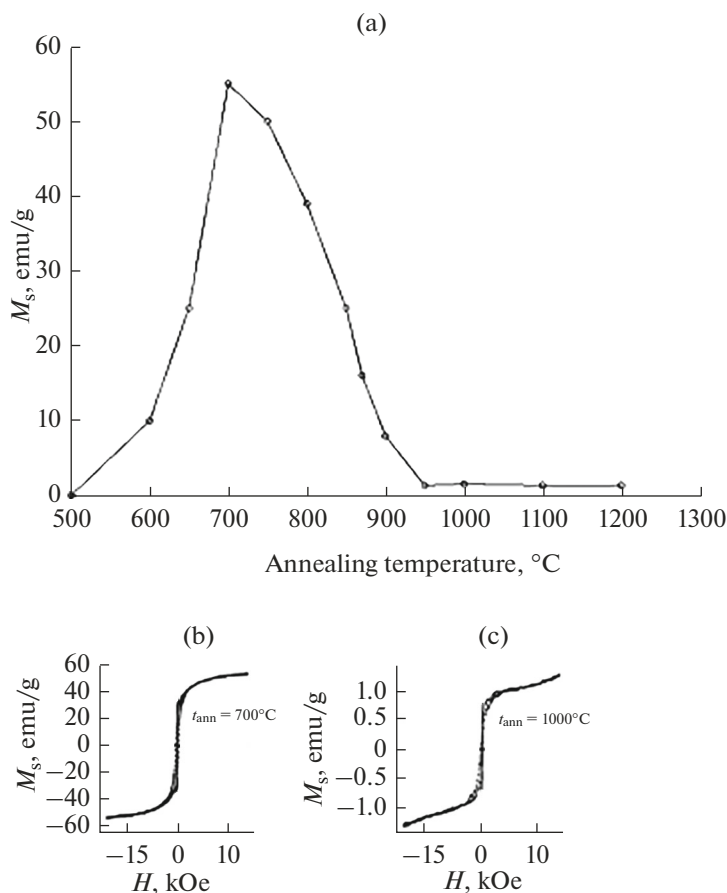


Fig. 3. Specific saturation magnetization as a function of annealing temperature for the samples after prolonged storage (a) and hysteresis loops of the samples prepared at 700 (b) and 1000°C (c).

example, $\text{Fe}_{10}\text{S}_{11}$, Fe_9S_{10} , Fe_7S_8 , which differ in the symmetry of the arrangement of cation vacancies [21–23].

Therefore, the metastable phase diagram transforms into the equilibrium phase diagram through, for example, decomposition of one metastable phase into two or three phases, even though no more than two phases were formed in the system immediately after synthesis.

CONCLUSIONS

The present findings lead us to conclude that, during prolonged storage under isothermal conditions in the presence of an atmosphere, metastable phases of pyrrhotites prepared by annealing pyrite at different temperatures convert into stable phases of Fe and S compounds. It also follows from analysis of the present results that metastable pyrrhotites can convert into stable phases of pyrrhotite and FeS under ordinary atmospheric conditions without external influences.

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