

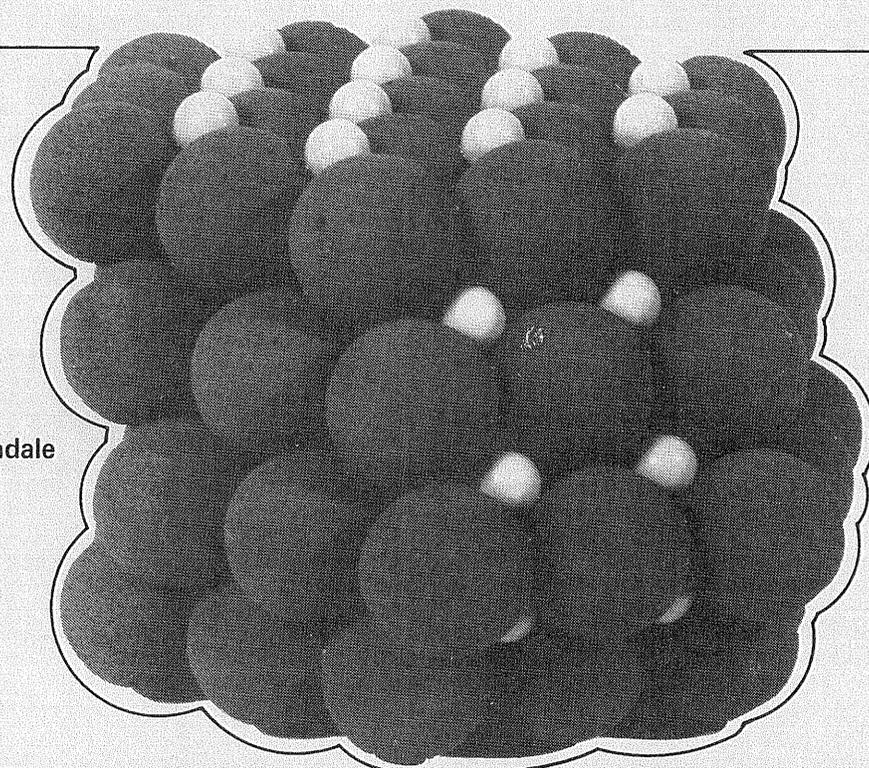
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# Effect of some metal chlorides on the transformation of pyrite to pyrrhotite

Cover: A model showing the position of the iron and sulfur atoms  
in the crystal structure of troilite (FeS).

*Cover design: Craig Ronto*

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# Effect of some metal chlorides on the transformation of pyrite to pyrrhotite

## ABSTRACT

Samples of the iron-sulfide mineral pyrrhotite were prepared using a procedure designed to closely model the pyrite-to-pyrrhotite conversion that occurs during coal-conversion processing. Pyrite mixed with graphite converts to mixtures of monoclinic and hexagonal pyrrhotite when heated at 500°C for 4.5 hours, and an iron-rich pyrrhotite ( $\text{Fe}_{10}\text{S}_{11}$ ) forms at 600° to 700°C.

In addition to temperature effects, the pyrrhotites formed from pyrite in graphite are also dependent on additives or impurities in the form of metal salts. The pyrrhotites used in this study were prepared in the presence of selected transition metal chlorides:  $\text{PdCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MoCl}_5$ , and  $\text{ZrCl}_4$ . When these metal salts were used, pyrrhotites with an increased number of iron vacancies were produced. For example, in the presence of  $\text{ZrCl}_4$  at temperatures as high as 700°C, a pyrrhotite was produced that exhibited Moessbauer magnetic-splitting values characteristic of pyrrhotite with a high number of iron vacancies (iron-poor).

These pyrrhotites were then converted to troilite at 400°C in the presence of  $\text{CO}$  and  $\text{H}_2$ ; and this troilite is an active catalyst for the Fischer-Tropsch synthesis, alkene hydrogenation, the Boudouard reaction, the water-gas shift reaction, and the hydrodesulfurization of organic sulfur compounds.

## ACKNOWLEDGMENTS

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## INTRODUCTION

Pyrrhotites that exhibit Moessbauer spectra similar to those found in coal-process residues have been synthesized (1). These materials differ from natural pyrrhotites in that they contain relatively large amounts of iron, and therefore, fewer iron vacancies. Troilite (FeS) appears to be a significant component of these residues.

Pyrrhotite is formed from pyrite in coal during heating at temperatures above 450°C (1,2,3). It has been reported that mineral matter exhibits a catalytic effect on coal-conversion processes (4,5), and Montano (6) showed that there is a correlation between coal conversion and the number of iron vacancies in the pyrrhotite formed from pyrite. The next step would be to determine the effects of temperature and metallic impurities upon the stoichiometric nature of the pyrrhotite obtained. Such information could be an important aid in developing a better internal catalyst. Because increasing the number of iron vacancies in the pyrrhotite matrix appears to have a beneficial effect upon its catalytic activity, our interest was directed toward the relative intensities of the hyperfine multiplets and the associated internal magnetic-field parameters of the pyrrhotite. These Moessbauer spectroscopic parameters are indices of the composition of the iron sulfides and give the iron-vacancy number.

Eight metal chlorides were used to demonstrate the effects of metallic impurities upon the stoichiometric nature of the pyrrhotite produced: ZnCl<sub>2</sub>, SnCl<sub>2</sub>, PdCl<sub>2</sub>, ZrCl<sub>4</sub>, PbCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, and MoCl<sub>5</sub>. The first two compounds, ZnCl<sub>2</sub> and SnCl<sub>2</sub>, are known to exhibit catalytic activity during coal liquefaction (7,8,9,10,11). A study of heat-treated natural pyrrhotite (Sudbury, Canada), to which no metal chlorides were added, was used as a comparative model.

## EXPERIMENTAL PROCEDURES

### Moessbauer Spectroscopy

Spectra were obtained at room temperature and analyzed as described in previous studies of coal (3,12,13), ash (14), oil shale (15), and gas shale (16).

### Samples Studied

Natural pyrrhotite, which was obtained from Sudbury, Canada, and contained some pentlandite as a contaminant, was heated in evacuated, sealed, quartz ampules at 450°, 600°, and 800°C for 4.5 hours. It was also heated at 450°, 600°, 800°, and 1000°C with Sp-2x Graphite (National) for the same period of time. At atmospheric pressure, the Sudbury pyrrhotite was heated at 800°C in a 14 wt% mixture with Herrin (No. 6) Coal from Perry County, Illinois; this procedure was repeated with its corresponding 650°C char. The coal contained pyrite, and the 650°C char contained both pyrite and pyrrhotite. Because these iron-

bearing minerals interfere with interpretation of the Sudbury pyrrhotite Moessbauer spectra, the pyrite and pyrrhotite were then removed from the coal and char by digestion with 3N nitric acid for approximately 48 hours.

Synthetic pyrrhotites were prepared by heating a mixture of pure pyrite (Colorado Geological Industries) and graphite in a quartz combustion tube under a nitrogen purge for 6 hours, as described earlier (1). The experiments were conducted at 500°, 600°, 650°, and 700°C with ZnCl<sub>2</sub>, SnCl<sub>2</sub>, PdCl<sub>2</sub>, ZrCl<sub>4</sub>, PbCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, and MoCl<sub>5</sub>, each added in an amount that approximated the weight of the pyrite. Then the experiments were repeated without the addition of these metal chlorides. Following each treatment, magnetic forms of pyrrhotite were isolated using a Carpc Model M-127 and a Frantz isodynamic magnetic separator.

## RESULTS AND DISCUSSION

### Moessbauer Spectra of Reference Compounds

Moessbauer spectra of troilite (17), monoclinic pyrrhotite (18), and hexagonal pyrrhotite (19) are represented in figure 1 as schematic graphs of the intensities of the several 6-line hyperfine components versus the internal magnetic-field parameters for those components. It is characteristic of these spectra to show a regularity of the relative intensities of the components, with one of the magnetic-field parameters having a relatively low value of 225 to 235 kOe. However, this low-magnetic species does not occur in Fe<sub>9</sub>S<sub>10</sub> (20) or Fe<sub>10</sub>S<sub>11</sub> (19), which are iron-rich pyrrhotites.

### Changes in Structure of Natural Pyrrhotite Upon Heating

The spectrum of natural Sudbury pyrrhotite without any pretreatment showed the presence of four iron species with 6-line Moessbauer spectra characterized by magnetic hyperfine splitting, and one iron species exhibiting a doublet with a quadrupole constant and an isomer-shift characteristic of iron in pentlandite (21) (table 1). The first four species were assigned to iron in four different sites of monoclinic pyrrhotite in accordance with the Bertaut model (22); however, the relative intensities of the iron species in this pyrrhotite, 2.8:1.0:3.6:1.9 (fig. 2a), differed from those theoretically predicted for Fe<sub>7</sub>S<sub>8</sub>, 2:1:2:2 (22,23). We suggest that the pyrrhotite also contained a small amount of the hexagonal form. If we assume that this pyrrhotite contained 8% of the hexagonal form, and introduce fixed values for the magnetic splittings and relative intensities of 2:1:2:2 for the monoclinic form, then the computer fitting of the Moessbauer spectrum of this pyrrhotite would compare to the best fit made by the monoclinic itself, but with varying intensities.

When the relative intensities versus the magnetic-field parameters of monoclinic and hexagonal pyrrhotite were plotted together, the resulting graph was typical of natural

**Table 1.** Moessbauer parameters for iron species in Sudbury pyrrhotite heated alone and with graphite

Assignment	S* (mm/s)	E* (mm/s)	M* (kOe)	Fe* (%)
<b>Sudbury pyrrhotite before heating</b>				
Pyrrhotite	0.692(4)	0.040(4)	309(6)	26.8
Pyrrhotite	0.721(4)	0.132(6)	292(5)	9.4
Pyrrhotite	0.688(5)	0.116(4)	258(3)	34.6
Pyrrhotite	0.687(6)	0.168(4)	232(4)	17.8
Pentlandite	0.331(9)	0.40 (1)		11.4
<b>Sudbury pyrrhotite heated alone at 450° C</b>				
Pyrrhotite	0.709(6)	0.09 (2)	300(3)	36.6
Pyrrhotite	0.665(8)	0.08 (1)	260(4)	37.6
Pyrrhotite	0.668(9)	0.13 (1)	233(3)	25.8
<b>Sudbury pyrrhotite heated alone at 800° C</b>				
Pyrrhotite	0.705(4)	0.09 (1)	300(4)	38.2
Pyrrhotite	0.682(5)	0.05 (1)	263(3)	36.0
Pyrrhotite	0.687(7)	0.16 (1)	237(4)	25.8
<b>Sudbury pyrrhotite heated with graphite at 450° C</b>				
Pyrrhotite	0.678(3)	0.07 (1)	298(4)	30.9
Pyrrhotite	0.670(4)	0.12 (1)	248(3)	31.7
Pyrrhotite	0.660(3)	0.14 (1)	224(4)	21.7
Unassigned	0.35 (2)	0.62 (1)		15.7
<b>Sudbury pyrrhotite heated with graphite at 600° C</b>				
Pyrrhotite	0.73 (1)	0.06 (1)	299(3)	40.9
Pyrrhotite	0.75 (2)	0.07 (1)	287(3)	5.1
Pyrrhotite	0.73 (1)	0.12 (1)	275(2)	44.3
Unassigned	0.20 (2)	0.46 (2)		9.7
<b>Sudbury pyrrhotite heated with graphite at 800° C</b>				
Pyrrhotite + troilite	0.814(5)	-0.16 (1)	309(5)	11.4
Pyrrhotite	0.760(5)	0.06 (1)	300(4)	19.4
Pyrrhotite	0.729(6)	0.14 (1)	291(3)	11.1
Pyrrhotite	0.750(3)	0.12 (1)	278(3)	49.6
Unassigned	0.32 (1)	0.62 (2)		8.5
<b>Sudbury pyrrhotite heated with graphite at 1000° C</b>				
Pyrrhotite + troilite	0.79 (1)	-0.15 (1)	310(3)	7.6
Pyrrhotite	0.770(4)	0.11 (1)	301(2)	32.0
Pyrrhotite	0.763(1)	0.11 (1)	279(2)	47.8
Unassigned	0.33 (1)	0.56 (1)		12.6
<b>Sudbury pyrrhotite heated with coal at 800° C</b>				
Pyrrhotite	0.747(7)	0.05 (1)	303(4)	41.0
Pyrrhotite	0.77 (1)	0.08 (1)	290(3)	13.2
Pyrrhotite	0.740(7)	0.14 (1)	275(3)	28.2
Unassigned	0.26 (3)	0.51 (2)		17.6
<b>Sudbury pyrrhotite heated with char at 500° C</b>				
Pyrrhotite	0.733(6)	0.05 (1)	299(3)	40.9
Pyrrhotite	0.76 (1)	0.07 (2)	287(3)	5.1
Pyrrhotite	0.735(5)	0.13 (1)	275(2)	44.3
Unassigned	0.20 (2)	0.46 (2)		9.7

\* S = Isomer shifts reported versus NBS iron foil.

E = Quadrupole-coupling constant.

M = Internal magnetic field.

Fe(%): These percentages are relative to the iron species within each sample and are not relative from one sample to another on a quantitative basis.

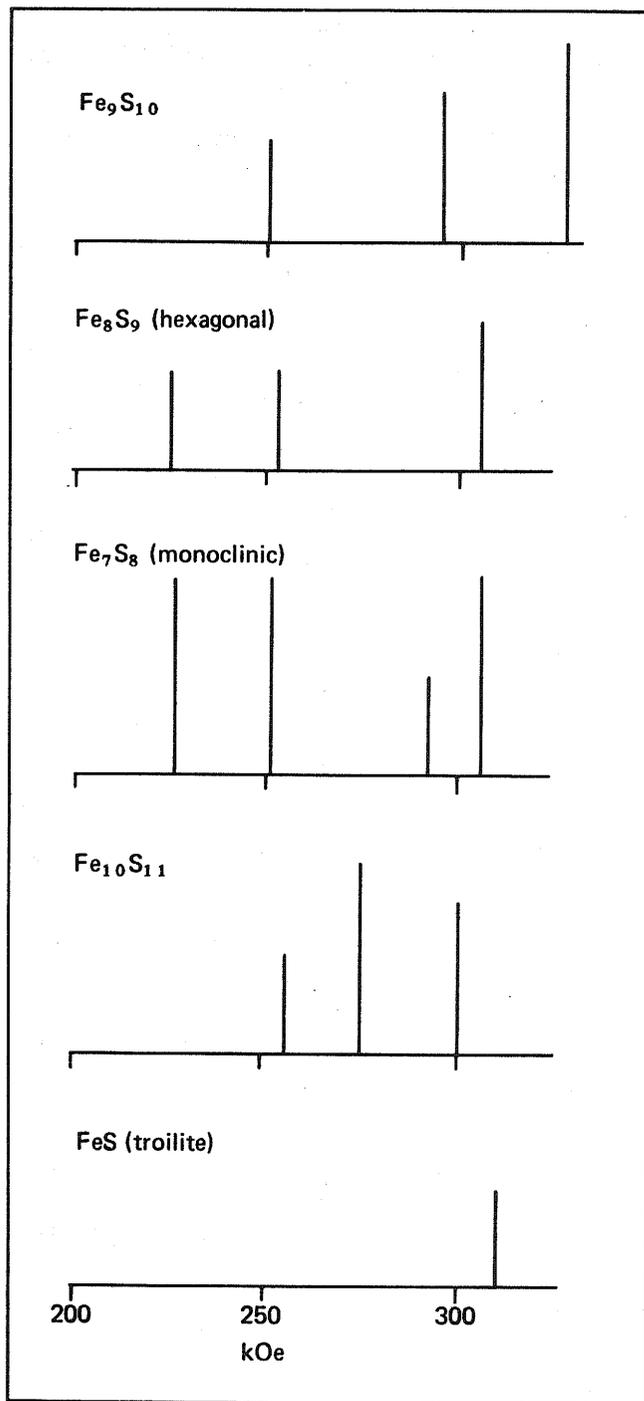


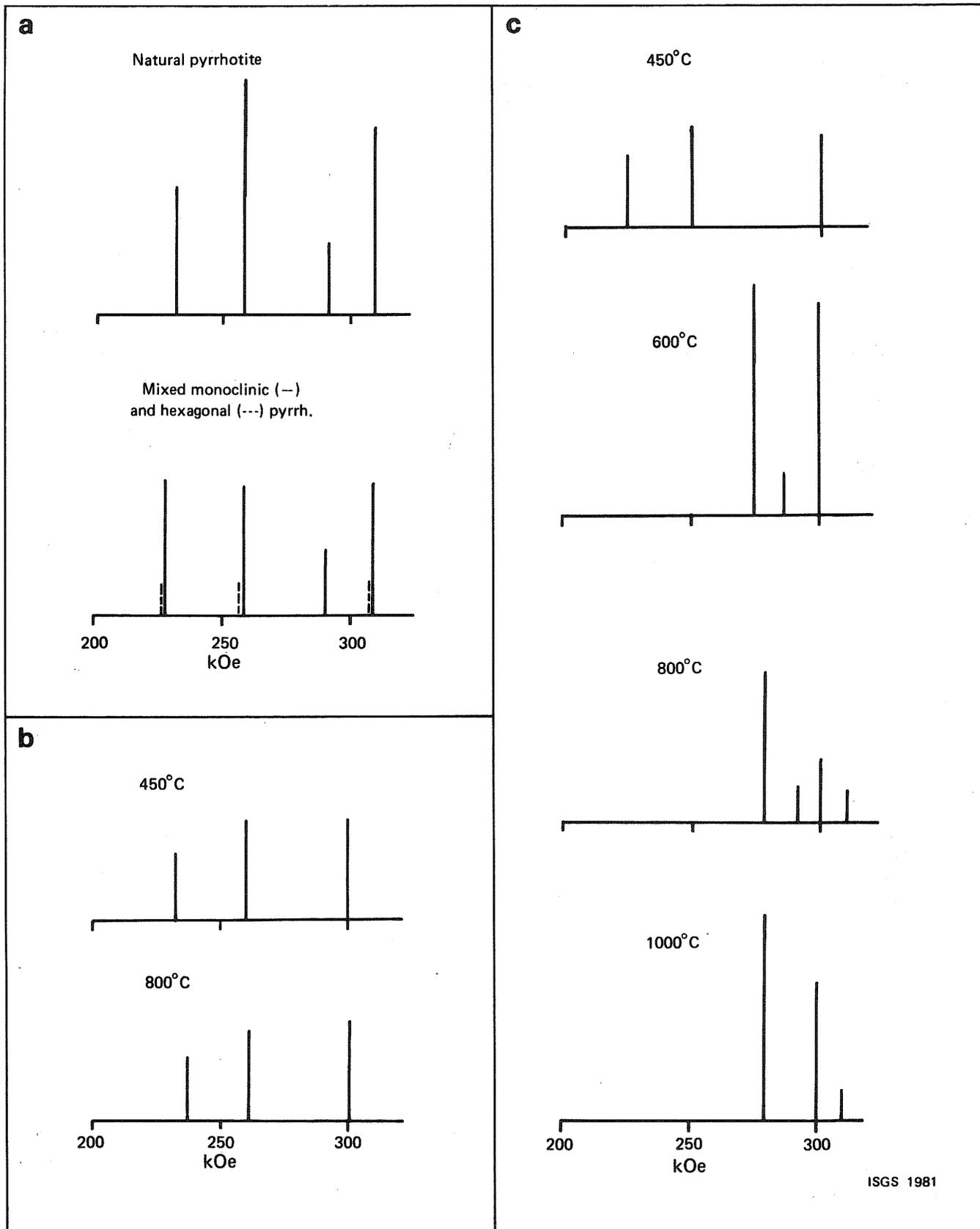
Figure 1. The relative intensities versus the magnetic-field parameters of the iron multiplets in the reference compounds.

Sudbury pyrrhotite (fig. 2a). Ovanesyan et al. (19) showed that  $\text{Fe}_{0.900}\text{S}$ , which is a mixture of hexagonal and monoclinic pyrrhotite, had a Moessbauer spectrum that was not a simple superposition of the spectrum of the purely hexagonal and monoclinic phases. These results obtained for natural pyrrhotite agree with the findings of Vaughan et al. (24) who have investigated pyrrhotites taken from different sections of the Strathcona Mine in Sudbury, Canada. They have concluded that two pyrrhotite types occur: one composed of  $(\text{FeNi})_7\text{S}_8$  with 0.35 wt% of Ni, and the second composed of  $(\text{FeNi})_9\text{S}_{10}$  with 0.68 to 1.01 wt% of Ni. The relative amounts of these two types depend on the section of the deposit from which they originated (25).

Heating Sudbury pyrrhotite alone for 4.5 hours in a sealed ampule at  $450^\circ$  and  $800^\circ\text{C}$  (fig. 2b), then with graphite at  $450^\circ\text{C}$  (fig. 2c), caused the transformation of monoclinic pyrrhotite to the hexagonal form with iron atoms in three nonequivalent sites with relative populations of 1.5:1.5:1.0 (26). These ratios were close to those reported for  $\text{Fe}_9\text{S}_{10}$  (47.3 at. % of iron) by Schwarz and Vaughan (20). Pyrrhotites with ordered vacancies have structures composed of filled layers and layers containing iron vacancies. The  $\text{Fe}_9\text{S}_{10}$  compound has ordered vacancies; and a 9:10 ratio results from the vacancy-filled-vacancy-filled-filled layers. The small difference between relative populations found in pyrrhotite and those predicted theoretically for  $\text{Fe}_9\text{S}_{10}$  (4:3:2, fig. 1) could be explained by assuming that the order of the arrangement of the vacancies inside the cation layers have been violated completely or in part, but the alternation of the layers with and without vacancies remained undisturbed. Possibly the pyrrhotite was a mixture of  $\text{Fe}_9\text{S}_{10}$  with  $\text{Fe}_{10}\text{S}_{11}$  and  $\text{Fe}_{11}\text{S}_{12}$ , both of which have a different vacancy order.

Heating Sudbury pyrrhotite in the presence of graphite at  $600^\circ$ ,  $800^\circ$ , and  $1000^\circ\text{C}$  for 4.5 hours in a sealed ampule (fig. 2c) and with coal or char at  $800^\circ\text{C}$  produced a pyrrhotite with high magnetic-splitting parameter values and higher isomer shifts than those of the monoclinic or the hexagonal forms. Since an increase of the internal magnetic-field parameter accompanied an increase in the iron content (27, 28), the Moessbauer data suggested that this pyrrhotite was rich in iron with a formula of  $\text{Fe}_{1-x}\text{S}$ , where  $x = 0.03$  to 0.10.

The Moessbauer spectra of the heated samples resolved into three or four 6-line multiplets having approximately the same line widths and one doublet. The doublet remained unassigned, but it was probably a compound arising from pentlandite (table 1). All species with magnetic splitting have higher internal magnetic fields (310 to 275 kOe) and larger isomer-shift values than monoclinic or hexagonal pyrrhotite, and their relative intensities show no regularity. The species with the lowest magnetic splitting (230 kOe) was not present, although it was found in both the monoclinic and the hexagonal forms. The species around 310 kOe was assigned to troilite and the others to pyrrhotite.



**Figure 2.** The relative intensities versus magnetic-field parameters of iron multiplets in Sudbury pyrrhotite: (a) untreated samples; (b) pyrrhotite heated alone 4.5 hours in a sealed ampule; (c) pyrrhotite heated in the presence of graphite 4.5 hours in a sealed ampule.

Only two species of those assigned to pyrrhotite occurred in relatively large amounts—those having internal magnetic fields around 301 and 276 kOe. These results are in agreement with Goncharov et al. (27) who have investigated iron-rich pyrrhotites and found that samples of  $\text{FeS}_{1+x}$  with  $x = 0.05$  to  $0.10$  exhibited two 6-line patterns indicating the coexistence of two structures, NiAs and  $\text{FeS}_{1.00}$ . However, these two 6-line sets did not exhibit the features indicating the presence of two phases. Their appearance could be due to the influence of the vacancies upon the first neighbor iron atoms in the iron sublattice since the higher value of magnetic splitting corresponded to iron atoms having no vacancies nearby and the lower value to those that were close to a vacancy. The intensities of the 6-line patterns related to the number of vacancies in the  $\text{Fe}_{1-x}\text{S}$  structure.

The higher isomer-shift values of these pyrrhotites gave further indication that they contained relatively large amounts of iron. A decrease in isomer shift with an increase in excess sulfur has been observed in the composition range of  $\text{FeS}_{1+x}$  from  $x = 0$  to  $x = 0.15$  (27).

Moessbauer spectra from pyrrhotite heated alone at  $600^\circ\text{C}$  and higher temperatures were compared with spectra of pyrrhotite heated in the presence of graphite under the same conditions. In the presence of graphite, pyrrhotites with larger amounts of iron formed. The same phenomenon was noted when mixtures of pyrrhotite-coal and pyrrhotite-char were heated at  $800^\circ\text{C}$ .

These data indicate that graphite, coal, and related materials facilitate the removal of sulfur from pyrrhotite, and as a result, pyrrhotites with few iron vacancies form.

#### Effect of Selected Metal Chlorides on the Transformation of Pyrite to Pyrrhotite

The Moessbauer spectrum of pyrite heated for 6 hours at  $500^\circ\text{C}$  in the presence of graphite consisted of three 6-line multiplets and one doublet (table 2). Species with magnetic splitting were assigned to pyrrhotite and the doublet to unreacted pyrite. The values of the internal magnetic-field parameters of the pyrrhotite were the same as those of natural hexagonal pyrrhotite; the relative intensities were also similar. On the other hand, pyrite transformed to pyrrhotite with a high iron content when heated at  $600^\circ$  to  $700^\circ\text{C}$  in the presence of graphite. This spectrum is similar to that described for the Sudbury pyrrhotite-graphite mixture heated at a high temperature. The species with internal magnetic fields of 310 and 260 kOe were assigned to troilite and pyrrhotite, respectively; however, the 230 kOe species was not present. The degree of this conversion of pyrite to pyrrhotite depended upon the temperature of the reaction: 68.7% at  $500^\circ\text{C}$  and 100% at  $700^\circ\text{C}$ .

In the presence of  $\text{PdCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{MoCl}_5$  at  $500^\circ\text{C}$ , pyrrhotite with magnetic-splitting parameters typical of monoclinic or hexagonal pyrrhotite formed from

pyrite. Four iron species typical of monoclinic pyrrhotite were present, but their relative intensities did not agree with those predicted theoretically (figs. 1 and 3). Again, this could be explained by the fact that the pyrrhotite, as a mixture of monoclinic and hexagonal forms, was similar to the Sudbury pyrrhotite. A relatively large amount of the monoclinic form existed in pyrrhotite obtained from pyrite with the addition of  $\text{NiCl}_2$ . In the presence of  $\text{PbCl}_2$  at  $500^\circ\text{C}$ , only three iron species were found, and their relative intensities were in good agreement with those of  $\text{Fe}_8\text{S}_9$  (19) (figs. 1 and 3). In all cases the low magnetic-field species was present.

Four iron species were also found in pyrrhotite formed from pyrite with the addition of  $\text{MoCl}_5$  heated at  $600^\circ\text{C}$  and the addition of  $\text{CoCl}_2$  heated at  $650^\circ\text{C}$ . This pyrrhotite was considered to be a mixture of the monoclinic and the hexagonal forms. Only three iron species occurred in the presence of  $\text{SnCl}_2$  and  $\text{ZnCl}_2$  at  $600^\circ\text{C}$ , and their relative intensities also corresponded to those of  $\text{Fe}_8\text{S}_9$  (figs. 1 and 3). The low magnetic-field species was still present. When  $\text{PbCl}_2$  was present in the reaction mixture at  $650^\circ\text{C}$ , however, a different pyrrhotite formed. The low magnetic-field species was no longer present in the product, and magnetic-field parameters determined for the three observed multiplets were characteristic of iron-rich pyrrhotites. Their relative intensities indicated that the pyrrhotite was a mixture of  $\text{Fe}_9\text{S}_{10}$  and  $\text{Fe}_{10}\text{S}_{11}$  (figs. 1 and 3).

Pyrrhotites produced at  $700^\circ\text{C}$  in the presence of  $\text{PdCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{ZnCl}_2$  had internal magnetic-field parameters similar to those of pyrrhotite formed with no chlorides present. The 230 kOe iron species was not present, and the relative intensities of the others suggested that this pyrrhotite had a formula close to  $\text{FeS}$  (figs. 1 and 3). Remarkably, a pyrrhotite with four nonequivalent iron sites and magnetic parameters typical of the monoclinic and the hexagonal forms (figs. 1 and 3) was still obtained when  $\text{ZrCl}_4$  was present at reaction temperatures as high as  $700^\circ\text{C}$ .

In summary, at  $500^\circ\text{C}$  conversion was more complete in the presence of  $\text{ZnCl}_2$  and  $\text{PdCl}_2$  than in the presence of  $\text{NiCl}_2$  and  $\text{MoCl}_5$ . At  $600^\circ\text{C}$  all of the pyrite transformed to pyrrhotite when  $\text{MoCl}_5$  was present. Also at this temperature, more pyrite was converted to pyrrhotite in the presence of  $\text{SnCl}_2$  than in the presence of  $\text{ZnCl}_2$ , probably owing to the mobility of tin, which was well distributed throughout the system (9). At  $700^\circ\text{C}$  the conversion of pyrite to a nonstoichiometric pyrrhotite was complete when  $\text{ZrCl}_4$  was present; but in the presence of  $\text{ZnCl}_2$  and  $\text{NiCl}_2$ , iron-rich pyrrhotites as well as mixed sulfides formed. Their isomer shifts and quadrupole-coupling constants are listed in table 2; their structures have yet to be elucidated. Mixed sulfides were also found in the nonmagnetic fractions from the conversion of pyrite to pyrrhotite in the presence of  $\text{PdCl}_2$  ( $500^\circ\text{C}$ ) and  $\text{SnCl}_2$  ( $600^\circ\text{C}$ ). Their Moessbauer parameters are also listed in table 2.

**Table 2.** Moessbauer parameters of iron species in the products from heating pyrite in the presence of graphite and some metal chlorides

Assignment	S* (mm/s)	E* (mm/s)	M* (kOe)	Fe* (%)
<b>Pyrite heated with graphite at 500° C (high magnetic)</b>				
Pyrrhotite	0.70 (1)	0.06 (1)	308(3)	24.5
Pyrrhotite	0.68 (1)	0.07 (1)	259(2)	19.3
Pyrrhotite	0.69 (1)	0.14 (1)	231(2)	24.9
Pyrite	0.324(5)	0.634(5)		31.3
<b>Pyrite heated with graphite and PdCl<sub>2</sub> at 500° C (high magnetic)</b>				
Pyrrhotite	0.70 (1)	0.07 (1)	307(3)	23.6
Pyrrhotite	0.70 (1)	0.05 (1)	284(3)	9.0
Pyrrhotite	0.70 (1)	0.07 (1)	263(2)	32.9
Pyrrhotite	0.69 (1)	0.17 (1)	234(2)	9.6
Pyrite	0.332(5)	0.640(6)		24.9
<b>Pyrite heated with graphite and PdCl<sub>2</sub> at 500° C (nonmagnetic)</b>				
Pyrite	0.317(5)	0.67 (1)		55.6
Unassigned	0.99 (2)	1.12 (4)		20.6
Unassigned	1.22 (1)	2.28 (2)		23.8
<b>Pyrite heated with graphite and ZnCl<sub>2</sub> at 500° C (high magnetic)</b>				
Pyrrhotite	0.71 (1)	0.09 (1)	307(3)	31.2
Pyrrhotite	0.72 (1)	0.08 (1)	286(3)	12.2
Pyrrhotite	0.71 (1)	0.09 (1)	267(2)	37.4
Pyrrhotite	0.68 (1)	0.16 (1)	239(2)	10.3
Pyrite	0.31 (1)	0.61 (1)		8.9
<b>Pyrite heated with graphite and NiCl<sub>2</sub> at 500° C (high magnetic)</b>				
Pyrrhotite	0.71 (1)	0.06 (1)	306(3)	15.8
Pyrrhotite	0.71 (1)	0.15 (1)	290(3)	5.1
Pyrrhotite	0.69 (1)	0.08 (1)	258(2)	13.5
Pyrrhotite	0.69 (1)	0.16 (1)	232(2)	15.4
Pyrite	0.333(5)	0.633(5)		50.2
<b>Pyrite heated with graphite and PbCl<sub>2</sub> at 500° C (high magnetic)</b>				
Pyrrhotite	0.70 (1)	0.08 (1)	306(4)	13.6
Pyrrhotite	0.71 (2)	0.13 (1)	255(3)	10.3
Pyrrhotite	0.70 (2)	0.17 (2)	228(3)	6.7
Pyrite	0.332(5)	0.633(7)		69.4
<b>Pyrite heated with graphite and MoCl<sub>5</sub> 250/500° C (high magnetic)</b>				
Pyrrhotite	0.70 (1)	0.09 (1)	304(4)	16.0
Pyrrhotite	0.71 (1)	0.12 (1)	289(3)	6.2
Pyrrhotite	0.69 (1)	0.11 (1)	260(3)	16.9
Pyrrhotite	0.68 (1)	0.18 (1)	233(3)	8.9
Pyrite	0.34 (1)	0.64 (1)		33.3
Ferrous sulfate	1.26 (1)	2.98 (1)		18.7
<b>Pyrite heated with graphite and MoCl<sub>5</sub> at 600° C (high magnetic)</b>				
Pyrrhotite	0.71 (1)	0.09 (1)	305(3)	25.3
Pyrrhotite	0.73 (1)	0.10 (1)	290(3)	13.5
Pyrrhotite	0.71 (1)	0.08 (1)	267(3)	46.4
Pyrrhotite	0.69 (1)	0.14 (1)	237(2)	14.8
<b>Pyrite heated with graphite and SnCl<sub>2</sub> at 600° C (high magnetic)</b>				
Pyrrhotite	0.69 (1)	0.07 (1)	303(4)	30.2
Pyrrhotite	0.67 (1)	0.08 (1)	254(3)	23.1
Pyrrhotite	0.66 (1)	0.15 (1)	229(2)	23.0
Pyrite	0.317(6)	0.634(7)		23.7

Table 2. *continued*

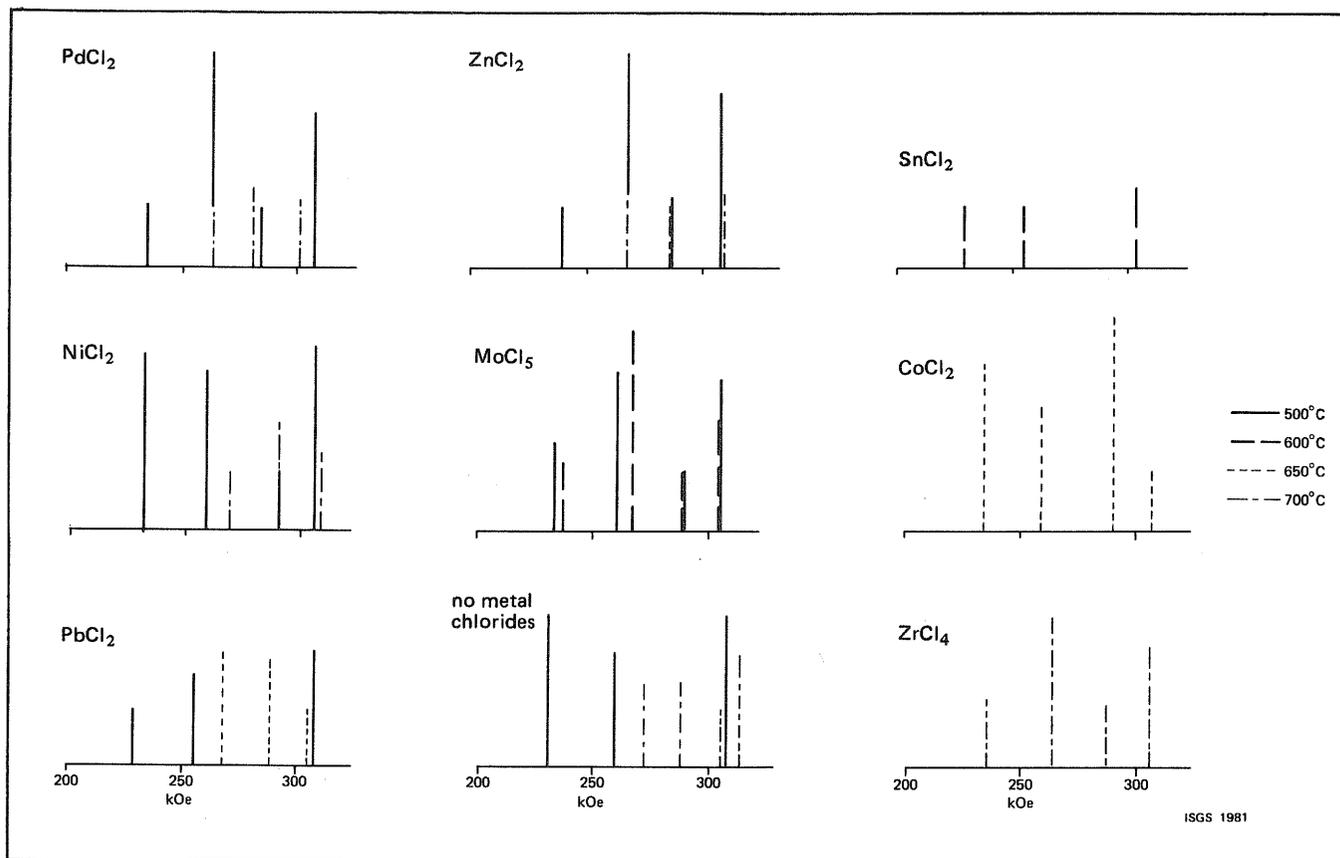
Assignment	S* (mm/s)	E* (mm/s)	M* (kOe)	Fe* (%)
<b>Pyrite heated with graphite and SnCl<sub>2</sub> at 600°C (nonmagnetic)</b>				
(FeSn)S	0.443(6)	1.22 (1)		100
<b>Pyrite heated with graphite and ZnCl<sub>2</sub> at 600°C (high magnetic)</b>				
Pyrrhotite	0.68 (1)	0.08 (1)	302(3)	13.9
Pyrrhotite	0.67 (1)	0.09 (1)	254(3)	11.1
Pyrrhotite	0.66 (1)	0.16 (1)	228(2)	10.3
Pyrite	0.323(3)	0.618(3)		64.7
<b>Pyrite heated with graphite and PbCl<sub>2</sub> at 650°C (medium magnetic)</b>				
Pyrrhotite	0.73 (1)	0.09 (1)	304(4)	18.8
Pyrrhotite	0.75 (1)	0.10 (1)	287(2)	33.1
Pyrrhotite	0.75 (1)	0.12 (1)	267(3)	35.9
Pyrite	0.32 (1)	0.64 (2)		12.2
<b>Pyrite heated with graphite and CoCl<sub>2</sub> at 650°C (high magnetic)</b>				
Pyrrhotite	0.71 (2)	0.09 (1)	306(4)	3.3
Pyrrhotite	0.71 (1)	0.07 (1)	289(3)	25.6
Pyrrhotite	0.69 (1)	0.06 (1)	258(3)	7.1
Pyrrhotite	0.67 (2)	0.07 (1)	234(2)	18.8
Pyrite	0.35 (1)	0.60 (1)		45.2
<b>Pyrite heated with graphite at 700°C (high magnetic)</b>				
Troilite	0.793(4)	-0.14 (1)	315(4)	32.9
Pyrrhotite	0.786(5)	0.09 (1)	307(3)	17.5
Pyrrhotite	0.767(4)	0.12 (1)	290(4)	24.8
Pyrrhotite	0.760(4)	0.15 (1)	274(4)	24.8
<b>Pyrite heated with graphite and ZnCl<sub>2</sub> at 700°C (high magnetic)</b>				
Pyrrhotite	0.75 (3)	0.106(6)	310(4)	30.3
Pyrrhotite	0.75 (4)	0.06 (1)	286(3)	24.4
Pyrrhotite	0.71 (3)	0.12 (1)	267(3)	29.2
(FeZn)S	0.58 (3)	0.84 (4)		16.1
<b>Pyrite heated with graphite and PdCl<sub>2</sub> at 700°C (high magnetic)</b>				
Pyrrhotite	0.74 (1)	0.09 (1)	300(4)	19.8
Pyrrhotite	0.74 (1)	0.10 (1)	280(3)	25.1
Pyrrhotite	0.74 (1)	0.14 (2)	263(3)	19.2
Pyrite	0.31 (1)	0.58 (4)		35.9
<b>Pyrite heated with graphite and NiCl<sub>2</sub> at 700°C (high magnetic)</b>				
Pyrrhotite	0.73 (1)	0.07 (1)	311(4)	27.6
Pyrrhotite	0.73 (1)	0.06 (2)	290(4)	38.7
Pyrrhotite	0.73 (1)	0.08 (2)	268(3)	21.4
(FeNi)S	0.3 (2)	0.44 (3)		12.3
<b>Pyrite heated with graphite and ZrCl<sub>4</sub> at 700°C (high magnetic)</b>				
Pyrrhotite	0.71 (1)	0.09 (1)	305(4)	30.4
Pyrrhotite	0.73 (1)	0.10 (1)	287(4)	15.6
Pyrrhotite	0.71 (1)	0.10 (1)	263(3)	37.9
Pyrrhotite	0.70 (1)	0.14 (1)	236(3)	16.1

\* S = Isomer shifts reported versus NBS iron foil.

E = Quadrupole-coupling constant.

M = Internal magnetic field.

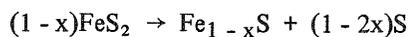
Fe(%): These percentages are relative to the iron species within each sample and are not relative from one sample to another on a quantitative basis.



**Figure 3.** The relative intensities versus the magnetic-field parameters of the iron multiplets in pyrrhotite formed from pyrite during a 6-hour heating period in the presence of graphite and metal chlorides.

To explain the effect of chlorides on the structure of pyrrhotite, one can assume that some Fe (II) in the pyrrhotite lattice was replaced by other metal cations. This substitution would cause a decrease in the internal magnetic field at the iron nucleus because guest cations are diamagnetic (29). It has been demonstrated that a number of metals could substitute for Fe (II) in the lattice of pyrrhotite (30,31), including all of the cations investigated as impurities in this study. Sulfides behaved as if they were bonded partly by ionic and partly by covalent linkages. In fact, metallic bonding should also be considered. Therefore, it was impossible to predict accurately the extent of impurity substitution in the sulfides on the basis of either the ionic or covalent radii. The concentrations of minor elements in the sulfide minerals depended on the amount of the element present and on the temperature during formation.

The effect of metal chlorides on the structure of pyrrhotite could involve the conversion of pyrite to pyrrhotite according to the chemical reaction:



According to this process, more sulfur in the -1 formal oxidation state would reduce to  $\text{S}^{2-}$  than oxidize to  $\text{S}^0$ .  $\text{Fe}_{1-x}\text{S}$  is a covalent material; however, formally it could

be considered  $(\text{Fe}^{3+}\text{Fe}^{2+})_{1-x}\text{S}$ . In this formula, the relative amount of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  would be determined by the value of  $x$  in such a way as to ensure overall electrical neutrality of the crystal. If  $x$  were increased, the number of iron vacancies would also increase; and in order to preserve electrical neutrality, the amount of  $\text{Fe}^{3+}$  must increase as well.

$\text{Fe}^{2+}$  could be oxidized to  $\text{Fe}^{3+}$  by sulfur as illustrated in the following reaction:



It is possible that the chlorides of some metals catalyze this reaction.

Both proposed mechanisms could occur together and their relative importance depend upon the specific reaction conditions as well as the reactants involved. On the basis of Moessbauer data, it is impossible to predict which mechanism occurred. Substitution of diamagnetic divalent cations for some  $\text{Fe}^{2+}$  and an increasing number of iron vacancies were both expected to have the same effect on the Moessbauer spectrum of pyrrhotite. Although chemical analysis of pyrrhotites obtained in the presence of metal chlorides indicated that some of the metals substituted in the pyrrhotite lattice, it did not explain how these cations were placed in the pyrrhotite structure.

### Formation of Mixed Sulfides

During the heating of pyrite in the presence of graphite and metal chlorides, other sulfides in addition to pyrrhotite were produced. Sulfides of the added metals, MS and MS<sub>2</sub>, and mixed sulfides, (M,Fe)S and (M,Fe)S<sub>2</sub>, could be formed under certain reaction conditions (32). These sulfides did not exhibit magnetic splitting; therefore, their Moessbauer spectra consisted of doublets.

Heating pyrite and graphite in the presence of ZnCl<sub>2</sub> at 700°C produced a mixed sulfide of zinc and iron, (FeZn)S, in addition to pyrrhotite; however, it was not found among the 500° and 600°C products. Its Moessbauer parameters, S = 0.6 and E = 0.8 mm/s, were in agreement with those found in the literature (33,34), but the lines were very broad.

Gerard et al. (33) studied synthetic sphalerite and wurtzite containing iron and observed a single peak as well as a superimposed quadrupole doublet for higher concentrations of iron (31%). They interpreted the single peak as an effect due to iron atoms having substituted metals as nearest neighbors, and the doublet as the effect of having one or more other iron atoms as nearest neighbors. Iron impurities strained the lattice because the ionic radius of Fe<sup>2+</sup> differs from that of Zn<sup>2+</sup>; this strain produced local distortions from cubic symmetry, and caused the appearance of quadrupole splitting. For low concentrations of Fe<sup>2+</sup>, the doublet represented mainly the contributions of ions associated in pairs. At higher concentrations, accumulations of three and more iron impurities became more frequent, causing a noticeable line broadening of the doublet. In the samples investigated in this study, the singlet was not found, possibly because of the small concentration of (FeZn)S and the complexity of the Moessbauer spectrum.

A new compound was found in the products of the reaction of pyrite with SnCl<sub>2</sub> at 600°C in the presence of graphite. The Moessbauer spectrum of the nonmagnetic fraction showed a doublet that was assigned to (FeSn)S (table 2). Its Moessbauer parameters were not found in the literature; however, since all intermetallic compounds of tin and iron exhibited magnetic splitting (35), the doublet found in the spectrum was assigned to the mixed sulfide (FeSn)S of an undefined composition and structure.

The Moessbauer spectrum of (FeNi)S, which was produced in mixtures heated at 600°C, was strongly dependent upon the amount of nickel in the structure (36). The Moessbauer spectrum of reaction products of pyrite heated in the presence of NiCl<sub>2</sub> and graphite at 700°C showed a doublet with an isomer shift of 0.30 and a quadrupole-coupling constant of 0.44 mm/s (table 2). These parameters agree with those reported for (FeNi)S containing large amounts of nickel (36). This compound was not found among the 500°C reaction products.

The Moessbauer spectrum of the product from the heating of pyrite in the presence of CoCl<sub>2</sub> and graphite at 650°C contained components corresponding to pyrrhotite, a doublet with an isomer shift of S = 0.35, and a

quadrupole-coupling constant of E = 0.60 mm/s (table 2). The value of S is high for pyrite, and the value of E is a little low. Therefore, it is possible that Co (II) has substituted for Fe (II) in the pyrite structure. This type of substitution could cause an increase in the lattice constant of the sulfide leading to an increase in isomer shift and a decrease in the quadrupole-coupling constant (37,38).

When a mixture of pyrite, graphite, and MoCl<sub>5</sub> was heated slowly from 250° to 500°C, several materials were found in the products. The Moessbauer spectrum of these materials consisted of three 6-line multiplets assigned to pyrrhotite, a doublet corresponding to unreacted pyrite, and another doublet exhibiting parameters in conformity with those of iron sulfate (2) (table 2)—clear evidence for the oxidation of some pyrite to sulfate by Mo<sup>5+</sup>. At 600°C, all of the pyrite was converted to pyrrhotite.

The products formed in the presence of PdCl<sub>2</sub> and graphite at 500°C contained two new iron compounds in addition to pyrrhotite and unreacted pyrite (table 2). One had Moessbauer parameters (S = 1.22 and E = 2.28 mm/s) corresponding to Fe<sup>2+</sup> in a high-spin configuration, and the other had both parameters lower in magnitude (S = 0.99 and E = 1.12 mm/s) but too high for covalent sulfides. The structures of these compounds have not been elucidated.

### Catalytic Effect of Pyrrhotites

It was expected that defect-structured pyrrhotites would be the catalytic agents in coal-liquefaction processes. Preliminary experiments, however, indicated that pyrite and those pyrrhotites prepared in the presence of metal chlorides were converted to stoichiometric troilite (FeS) by CO and H<sub>2</sub>. This troilite is a catalyst for Fischer-Tropsch synthesis, alkene hydrogenation, the Boudouard reaction, the water-gas shift reaction, and the hydrodesulfurization of organic sulfur compounds—which leads us to believe that stoichiometric troilite is the active agent in coal-liquefaction processes. Troilite and pyrrhotite are normal products of coal liquefaction, but the troilite formed is not as active a catalyst as that formed from the defect-structured pyrrhotites prepared in the presence of the metal chlorides.

### SUMMARY AND RECOMMENDATIONS

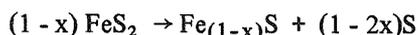
Pyrrhotite is the principle iron-containing mineral component in a number of coal-process residues, and in particular, coal-liquefaction residues. During direct liquefaction, pyrrhotite derived from the decomposition of pyrite apparently facilitates liquefaction as an in situ catalyst.

We prepared a number of pyrrhotite samples using a procedure designed to closely model the pyrite-to-pyrrhotite conversion that occurs during coal processing. When pyrrhotites were prepared in the presence of a variety of transition metal chlorides, which included PdCl<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub>, ZnCl<sub>2</sub>, MoCl<sub>5</sub>, PbCl<sub>2</sub>, and ZrCl<sub>4</sub>, pyrrhotites with a high

number of iron vacancies were produced. Pyrrhotites prepared in the presence of  $\text{CoCl}_2$  at  $650^\circ\text{C}$  and  $\text{MoCl}_5$  at  $600^\circ\text{C}$  exhibited a magnetic-splitting value in the range of 225 to 250 kOe, which indicates a high-vacancy (iron-poor) pyrrhotite. In the presence of  $\text{ZrCl}_4$  at temperatures as high as  $700^\circ\text{C}$  (the upper temperature limit was not reached), a high-vacancy pyrrhotite was also produced.

This high-vacancy pyrrhotite structure may be due to diamagnetic cations from the added metals substituting for some  $\text{Fe}^{2+}$  ions in the lattice of the pyrrhotite. Any diamagnetic ions introduced into the lattice will alter its magnetic properties. Furthermore, if the added metals are in the form of trivalent and tetravalent cations, they may affect the charge balance in the crystal and introduce additional vacancies.

Pyrite undergoes transformation to pyrrhotite according to the chemical reaction:



In this process, more sulfur in the -1 formal oxidation state is reduced to  $\text{S}^{2-}$  than is oxidized to  $\text{S}^0$ .  $\text{Fe}_{(1-x)}$  is a covalent material; however, formally it can be considered  $\text{Fe}^{2+}_{(1-3x)}\text{Fe}^{3+}_x\text{S}$ . When  $x$  is increased, the number of iron vacancies is increased; and in order to preserve electrical neutrality, the amount of  $\text{Fe}^{3+}$  must increase.  $\text{Fe}^{2+}$  can be oxidized to  $\text{Fe}^{3+}$  by sulfur as shown in the following reaction:



It is possible that the metal chlorides used in this study catalyze this reaction.

We have found that these pyrrhotites, as well as pyrite, are converted at  $400^\circ\text{C}$  to troilite ( $\text{FeS}$ ) in the presence of  $\text{Co}$  and  $\text{H}_2$ . The troilite so formed is an active catalyst for Fischer-Tropsch synthesis, alkene hydrogenation, the Boudouard reaction, and the hydrodesulfurization of organic sulfur compounds. The catalytic property of this troilite, which may account for the removal of organic sulfur from coal, should be further investigated.

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