

mechanics as described above have prompted the suggestion that overbank sedimentation is of only minor importance in the development of a floodplain (7). The data from the Faucett site allow us to detail a record of continuous overbank accretion for a long time period and also to demonstrate that, in the absence of lateral migration, overbank deposition is a very significant process, an observation which supports a similar conclusion made earlier by Schumm and Lichty (9). Since the floodplain level of most streams is equaled or exceeded once every 1 or 2 years (7), the Faucett site deposits are not technically part of the modern floodplain. However, even though the surface of the site is well above the floodplain stage, it is still periodically flooded (10) and the sediments continue to increase in elevation and thickness. Their designation as deposits capping a Pleistocene terrace does not alter the fact that they are part of a dynamic geomorphic feature which differs from a true floodplain only by definition, not process of origin.

We believe that the Faucett site sequence is devoid of point-bar sediment for several reasons. First, the variability in grain size and sorting commonly noted in point-bar deposits (7) is absent in this sequence. Size analyses of seven samples taken at regular depth intervals in the main excavation of 1970 show that the Faucett sediments are very consistent in size and sorting. Median grain sizes range from 0.09 to 0.14 mm, and sorting coefficients vary from 1.55 to 1.82. Second, the evidence of abundant scour and fill, normal in point-bar deposits, has not been observed at the Faucett site. Finally, the continuity of the 14 radiocarbon dates strongly supports the suggestion that deposition here has not been periodically interrupted by episodes of scouring.

If the characteristics described above portray a continuous accumulation of overbank sediments, it becomes clear that the Delaware River has maintained its present valley-bottom position for an extremely long time. Measured rates of lateral migration of rivers usually range from 0 to 2000 feet per year (0 to 600 m per year) (7). Even at a low rate of only 0.5 foot per year, the Delaware River should have been able to traverse its valley (3000 feet wide) during the 6000-year record of the Faucett site accumulation. Had it done so, the older sediments would have been disturbed and the earlier records of human oc-

cupation rendered unintelligible. Thus, the Faucett sequence demonstrates that a natural channel in unconsolidated material can be fixed for very long periods of time and that under those conditions overbank accretion becomes the dominant process involved in the development of the floodplain.

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Magnetic Transitions Observed in Sulfide Minerals at Elevated Pressures and Their Geophysical Significance

Abstract. *The magnetic behavior of iron in chalcopyrite (CuFeS_2) and pyrrhotite (Fe_7S_8) in the pressure range from 1 atmosphere to 20 kilobars has been studied by Mössbauer spectroscopy. Both chalcopyrite and pyrrhotite exhibit transitions from magnetically ordered to disordered states over the range from 5 to 16 kilobars. Both transitions, particularly the loss of ferrimagnetism in pyrrhotite, have geophysical consequences.*

Kasper and Drickamer (1) have demonstrated by Mössbauer spectroscopy that the antiferromagnetic ordering of FeS (troilite disappears before a pressure of 36 kb is attained. We have obtained Mössbauer spectra at high pressures on the related ferrimagnetic iron sulfide pyrrhotite (Fe_7S_8) and the antiferromagnetic sulfide chalcopyrite (CuFeS_2). The results, which are reported here, show that similar reversible magnetic transitions from ordered to disordered states occur in both chalcopyrite and pyrrhotite in the range from 1 atm to 20 kb. The results for troilite (FeS), chalcopyrite, and pyrrhotite have important implications for solid-state theory and the chemistry of the interiors of the earth and other planetary bodies. The pyrrhotite result, in particular, has geomagnetic and paleomagnetic consequences.

Data are reported here for CuFeS_2 and Fe_7S_8 synthesized from pure elements in sealed, evacuated silica-glass tubes according to the method of Kullerud (2). The iron used in the synthesis contained > 90 percent of the Mössbauer active isotope ^{57}Fe , and

all of the elements used were 99.99+ percent pure. Separate samples of both the iron and the copper were reduced in a stream of pure dry hydrogen at 700°C. After the mixtures had been sealed in the silica-glass tubes they were reacted at 700°C, and the products were reground and annealed at 250°C. The purity of the synthetic products was verified optically and by x-ray diffraction.

Mössbauer spectra were first obtained from the powdered synthetic chalcopyrite and pyrrhotite, each mounted as a thin disk of material as is customary in experiments at room temperature and 1 atm. These spectra are illustrated in Figs. 1A and 2A and closely resemble spectra previously obtained, respectively, from both natural and synthetic chalcopyrite and pyrrhotite (3–5). The spectrum of powdered chalcopyrite at 1 atm (Fig. 1A) consists of a single six-peak hyperfine magnetic spectrum and has been interpreted as due to the presence of high-spin Fe^{3+} in the tetrahedral sites of the sphalerite-type structure of chalcopyrite. These ferric ions are antiferromagnetically ordered

below the Néel temperature (823°K). The pyrrhotite spectrum at 1 atm (Fig. 2A) consists of several superimposed six-peak hyperfine magnetic subspectra. In samples of natural pyrrhotites as many as four six-line sets have been reported (5), although in synthetic samples only three subspectra have been resolved (4).

The high-pressure Mössbauer measurements were made with an assembly designed by Drickamer and his co-workers (6). Sample pellets were prepared from a 1-mg mix containing the synthetic sulfide powder diluted with boron in a weight ratio of 1:8. This produced a pellet with a diameter of 0.53 mm and a thickness of 0.38 mm, which was enclosed in a boron-lithium hydride annulus. The complete pellet, including the annulus, had been compacted under a pressure of approximately 18 kb. The pressure was determined by means of an approxi-

mate calibration based on the shift of the x-ray diffraction peaks of aluminum powder in an identically prepared pellet (7).

The spectrum of the chalcopyrite pellet (Fig. 1B) consists of a six-peak magnetic spectrum with essentially the same parameters as those of the powdered material (isomer shift, 0.24 mm/sec; quadrupole splitting, 0.03 mm/sec; internal magnetic field, ~342 kilogauss). However, there is an apparently single nonmagnetic peak close to the center of the spectrum in addition to the magnetic spectrum. The area under this peak is 23 percent of the total area. The isomer shift of this peak is identical to that of the magnetic spectrum (0.24 mm/sec). Application of a pressure of 5 kb to this pellet produced no change, a result which suggests that the locked-in strain produced by the pelletizing process exceeded 5 kb. A pressure of 10 kb

produced a considerable intensification of the central, nonmagnetic peak and a reduction of the magnetic peaks (Fig. 1C). At a pressure of 10 kb the central peak can be resolved as a doublet with essentially the same isomer shift (0.23 mm/sec) and a fairly large quadrupole splitting (0.72 mm/sec). The peak areas show that 64 percent of the total iron is in this nonmagnetically ordered state at 10 kb. At an applied pressure of 16 kb (Fig. 1D) only a faint trace of the magnetic spectrum remains, and, although the doublet has been partly obscured by broadening, the parameters are the same.

The spectrum of a pyrrhotite pellet at 1 atm is identical to that of the powdered material (Fig. 2A). It may be interpreted as at least three overlapping six-peak magnetic subspectra. [A detailed interpretation of the high-pressure spectra of pyrrhotite and

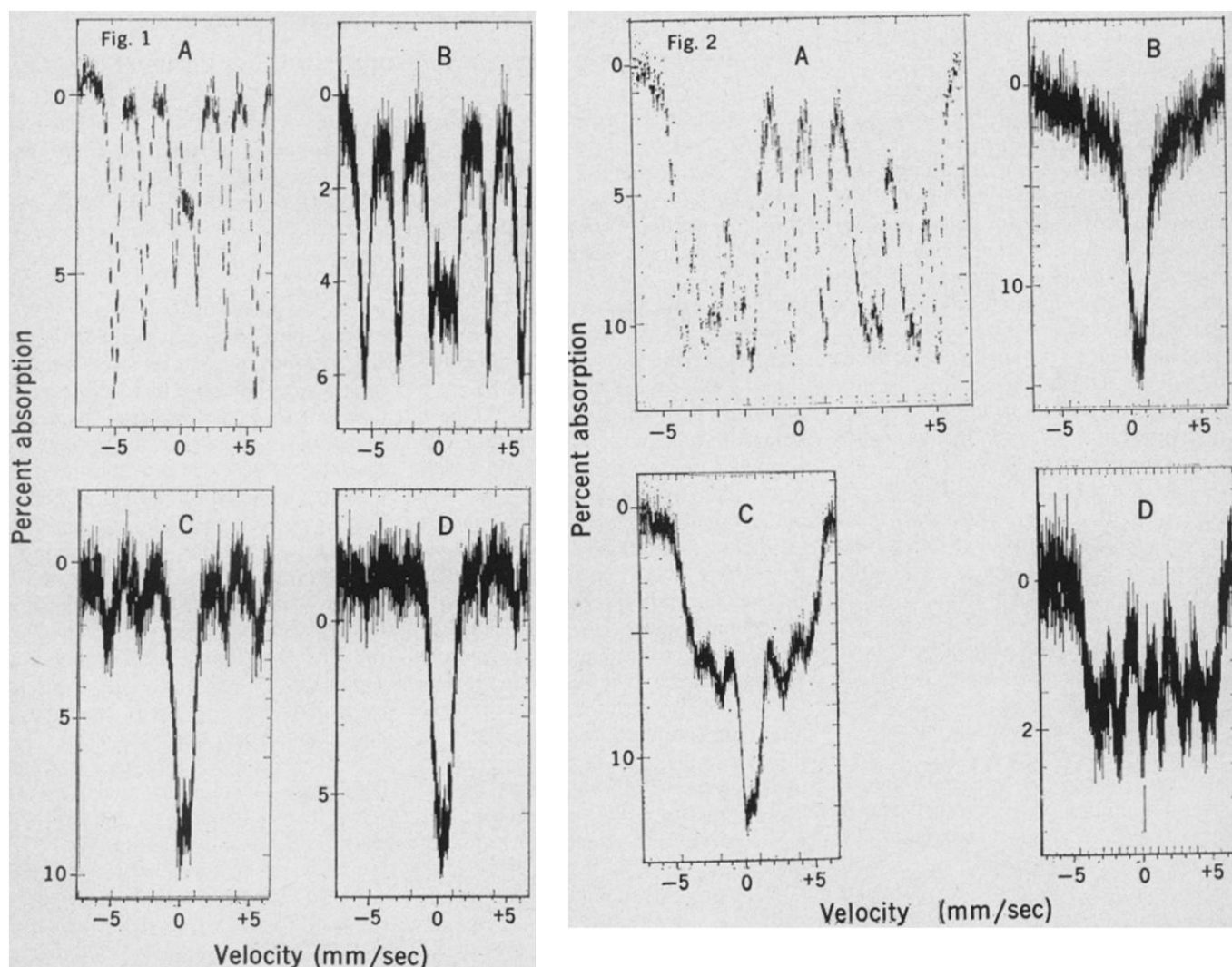


Fig. 1 (left). Mössbauer spectrum of: (A) powdered chalcopyrite at 1 atm; (B) chalcopyrite pellet at 1 atm; (C) chalcopyrite pellet at 10 kb; (D) chalcopyrite pellet at 16 kb. Fig. 2 (right). Mössbauer spectrum of: (A) powdered pyrrhotite at 1 atm; (B) pyrrhotite pellet at 16 kb; (C) pyrrhotite pellet at 5 kb (after release of the pressure); (D) chopped pyrrhotite pellet at 1 atm.

chalcopyrite will be presented elsewhere (8).] At a pressure of 16 kb the pyrrhotite spectrum, shown in Fig. 2B, is a single peak (or broadened quadrupole doublet) with an isomer shift of 0.36 mm/sec. A trace of the outermost magnetic peaks remain, in the same positions as at 1 atm. If the applied pressure is reduced to only 5 kb as in Fig. 2C, a partial reversal to the ordered state takes place; if the pelletized material is chopped up to remove any locked-in strain, a complete reversal to the magnetic spectrum occurs (Fig. 2D).

The changes observed in the Mössbauer spectra of chalcopyrite and pyrrhotite as a function of pressure can be interpreted as evidence of a transition from the antiferromagnetic state to the paramagnetic state for chalcopyrite and a transition from the ferrimagnetic state to the paramagnetic state for pyrrhotite. These transitions are apparently totally reversible and take place over a range of pressures from 5 to 16+ kb. The proportion of the magnetically ordered material decreases with increasing pressure over this range, whereas the chemical nature of the ordered and disordered phases, as shown by their Mössbauer parameters, remains the same.

In both chalcopyrite and pyrrhotite, the magnetic transition could be accompanied by a change in crystal structure. A high-pressure polymorph of troilite has been reported by Taylor and Mao (9), but it does not exist below a pressure of 55 kb and a temperature of 25°C. The magnetic transition in troilite occurs below 36 kb (1) and therefore appears to be distinct from the structural change. It is probable that in pyrrhotite, which is closely related to troilite (10), the magnetic transition occurs before any structural change. However, there is a large change in isomer shift between the magnetic and nonmagnetic phases [from ~ 0.80 mm/sec (average value) to 0.36 mm/sec] which could be produced by a transition from a high-spin to a low-spin state associated with the magnetic change. In chalcopyrite, the isomer shift is already very small (0.24 mm/sec) at atmospheric pressure and shows no appreciable change at higher pressures, but the quadrupole splitting changes at the magnetic transition (from 0.03 to 0.72 mm/sec). Here again, a structural or spin-state change is possible, probably the latter.

Goodenough (11, 12) has discussed the behavior of electrons in solids in

terms of localized and collective electrons. At a critical value of the energy required to transfer an electron from one atom to another, the electrons are either localized and give rise to spontaneous magnetism (for example, antiferromagnetism or ferrimagnetism) or collective and exhibit Pauli paramagnetism (12). Such energies are strongly dependent on the interatomic distance. The transitions we observe in chalcopyrite and pyrrhotite may represent changes from localized to collective electron behavior resulting from a reduction in the distances between the metal and sulfur atoms. Conversely, the transition to paramagnetism at the Curie temperature results from increased interatomic separations and thermal displacements. In addition, our results for chalcopyrite and pyrrhotite suggest that similar changes in magnetic properties occur in other magnetically ordered sulfides at elevated pressures.

Troilite is an important phase in meteorites and in the lunar rocks. Moreover, several investigators have suggested that sulfur, as well as iron, may be a major component of the earth's core (13). It is probable, therefore, that iron sulfides exist at depth in planetary interiors. The metal-deficient pyrrhotite is one of the very few minerals which exhibit ferrimagnetism or ferromagnetism. As an accessory mineral in many rocks and as a major phase in many sulfide ore deposits, it contributes to geomagnetic anomalies and has been used in paleomagnetic investigations. This study shows that, at the pressures encountered in high-grade metamorphism or in subduction zones at continental margins, the magnetism of pyrrhotite would be

partially or completely eliminated and that deep-seated pyrrhotite ore bodies may produce no surface magnetic anomalies. Alternatively, if the temperature approaches the Curie point, the effects of increasing temperature and pressure may prove to be competing and ordering may be retained. Furthermore, the physical and chemical properties of the iron sulfides are very different at pressures only slightly above those of planetary surfaces.

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Red Sea Drillings

Abstract. Recent drilling in the Red Sea has shown that much of the basin is underlain by evaporites of a similar age to that of evaporites found in the Mediterranean Sea. These evaporites and their structural positions indicate that other brine areas are present—and, indeed, several others have been discovered.

Leg 23B of the Deep Sea Drilling Project (DSDP) aboard the R.V. *Glomar Challenger* was devoted to scientific drilling in the central and southern Red Sea. The major shipboard findings include the following. (i) The Red Sea appears to be underlain by Late Miocene evaporites, including rock salt, at relatively shallow depths throughout most of its extent. The

evaporites are absent only in the central rift valley. These data are not consistent with a model of continuous seafloor spreading since Miocene time. (ii) The Miocene age of the evaporites in the Red Sea is similar to that of an evaporite sequence found by drilling in the Mediterranean Sea. (iii) The interstitial waters of the cores continuously increase in salinity with depth, with