Infrared Spectroscopic Studies on Pyrite

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Infrared spectroscopic study on pyrite shows that it is no longer valid to assign IR bands in the region 1200-900 cm^{-1} to oxidation products: SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_5^{2-}$. It is shown that atmospheric CO_2 and H_2O are adsorbed on iron sites with the formation of carbonic acid, carbonate, basic carbonate and iron hydroxide. These compounds are responsible for the appearance of absorption bands in this region. Experimental evidence shows that, contrary to published data, xanthate can be adsorbed on both natural (unoxidized) and oxidized pyrite surface without replacement of oxidation products. Consequently, the appearance of absorption bands in the spectrum of pyrite, to which is attached xanthate, in the region 1200-900 cm^{-1} should not be attributed to xanthate alone as claimed by many investigators. It is an indication of the existence of oxidation products and/or corresponding metal xanthate and/or dixanthogenate and/or carbonate, basic carbonate and/or metal hydroxide.

THE oxidation of sulphide minerals with atmospheric oxygen is of great interest because it increases the adsorption of xanthate used in the flotation technique for the separation and purification of minerals. In this paper the oxidizability of pyrite (FeS_2) and the assignments of the IR bands of the oxidized products in the absence and presence of xanthate have been studied.

Materials and Methods

Well developed crystals of reasonably pure natural pyrite from the Eastern Desert of Egypt were used. Microscopic and infrared examination of these crystals showed that they were pure and free from locked particles or gangue. In order to study the decided tendency of pyrite to oxidation during grinding, the latter was achieved in atmosphere (sample 1a), under water (sample 1b), and under inert liquid (sample 1c) such as carbon tetrachloride in agate mortar. Grinding of pyrite crystals was carried out to micron size. The methods of preparation of the samples and recording the spectra are described elsewhere[1-4].

Results and Discussion

A strong absorption band at 1110 and a medium one at 680 cm^{-1} in the IR spectrum of pyrite ground in atmosphere (Fig. 1a) indicated the formation of oxidation product, namely sulphate[1-5]. Also, several strong absorption bands at 550, 680, 990 and at 1110 and a weak one at 1650 cm^{-1} were noticed, which confirm the existence of thiosulphate[4,5]. The IR spectrum (Fig. 1b) of pyrite sample ground under water shows, besides ν OH ~3400 cm^{-1}, bands at 1100, 1125 cm^{-1}, characteristic of iron hydroxide and carbonic acid[5]. Indeed, it has been reported that some metal hydroxides exhibit M-OH bending modes at 1200-600 cm^{-1} (ref. 5). The presence of such absorption bands has been reported in various metal hydroxides and in weak acids[5]. The frequency of this vibration
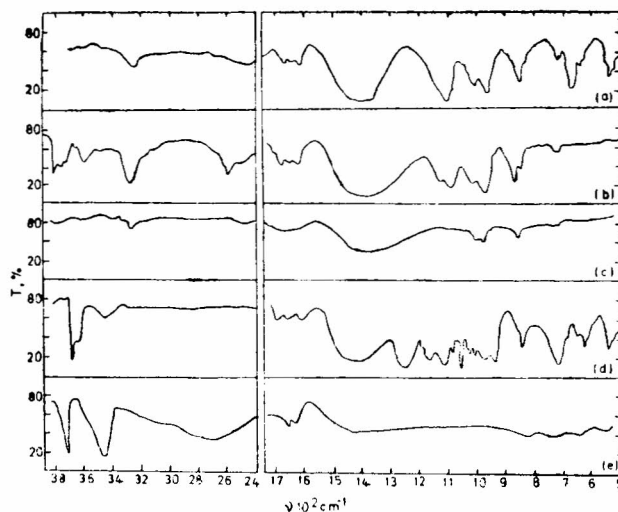

Fig. 1 — Infrared spectra of pyrite ground: (a) in atmosphere, (b) under water, (c) under carbon tetrachloride, (d) ground under carbon tetrachloride and/or under water and afterwards treated with H_2O_2, and (e) treated with H_2O_2 and afterwards washed with distilled water, or sulphidized with sodium sulphide

may depend on the strength of M-O bond as well as on hydrogen bond formation. This is supported by the great affinity of iron sites for hydroxyl ions over hydrogen ions. The spectrum of the sample 1b differs from 1a by the disappearance of bands belonging to oxidation products, which may be due to either the cooling effect of water and hence strong local heating at the moment of fracture of the grains under the pestle did not occur, or to the solubility of the resulting ferrous and ferric sulphate in water. The absence of bands due to Fe_2O_3 and FeO may indicate the absence of oxidation in pyrite. The bending mode at 1610 cm^{-1} may be due to adsorbed water molecules and not due to surface hydroxyl groups. This is supported

by the appearance of the characteristic absorption band of SH⁻ at 2530 cm⁻¹ (ref. 5).

Examination of the spectra of pyrite ground under carbon tetrachloride (Fig. 1c) reveals the absence of bands that may be attributed to the oxidation products, namely SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_5^{2-}$, $S_2O_8^{c-}$, FeO and Fe_2O_3. Absorption bands of slight intensity occur at 1430, 1010, 990 and 880 cm⁻¹, characteristic carbonate and basic carbonate[1-5]. Prolonged exposure of specimen 1c to atmosphere did not lead to much change in its IR spectrum. The absorption bands characteristic of oxidation products, e.g., sulphate, thiosulphate, were still absent. Prolonged exposure merely led to the intensification of absoprtion bands due to carbonate and basic carbonate.

Almost all investigators claim that absorption bands in the spectrum of sulphide minerals in the range 1200-900 cm⁻¹ are due to the existence of oxidation products like sulphate and thiosulphate[4,6-9]. However, on the basis of the present results the conclusions of these investigators are untenable. Further the results of these investigators did not obtain additional evidence for these oxidation products from other regions, namely 900 to 555 cm⁻¹ and 1500 to 1200 cm⁻¹. Thus sulphate group exhibits band of medium intensity in the range 680-610 cm⁻¹ and a strong band at 1130-1080 cm⁻¹. Thiosulphate group shows strong bands at 550-520, 690-655, 1000-950, 1130-1100 cm⁻¹ and a weak one at 1670-1660 cm⁻¹. On the other hand, the co-appearance of a strong absorption band at 1450-1410 cm⁻¹ and one of medium intensity at 880-860 cm⁻¹ should indicate the presence of carbonate group. Similarly, medium absorption bands at 665-655 cm⁻¹ and strong ones at 1010-990 and 1500 1200 cm⁻¹ indicate the presence of bicarbonate[1,10] Thus the strong bands in the range 1200-900 cm⁻¹ in samples 1a, 1b and 1c are due to carbonate, basic carbonate, metal hydroxide arising from the adsorption of atmospheric water and carbon dioxide. Furthermore, basic carbonate and bicarbonate show characteristic bands in this range. Thus it can be concluded that the bands in the range 1200-900 cm⁻¹ in these samples are not an indication of oxidation of sulphides, as believed by almost all the investigators.

This was confirmed by recording the spectra of pyrite treated with H_2O_2 (Fig. 1). It is obvious from Fig. 1 that H_2O_2 caused clear and indisputable changes in the intensities and positions of absorption bands belonging to Fe_2O_3, FeO and SO_4^{2-}. Moreover, new bands are accompanied by change in the 1250-650 cm⁻¹ region, where there are bands corresponding to SO_3^{2-}, CO_3^{c-}, HCO_3^{2-} vibrations in the samples 1a and 1c. The intensities of the new absorption bands increase in conjunction with weakening of 660, 890 990, 1010 and 1435 cm⁻¹ bands. This seems to be due to the predominance of $S_2O_3^{2-}$, $S_2O_5^{c-}$ and $S_2O_8^{2-}$ groups as a result of the extensive oxidizing action of H_2O_1 on pyrite. Additional strong bands at 1290, 1080, 980, 720, 660 cm⁻¹ and bands of medium intensities at 1060 and 1100 cm⁻¹ appeared in the sample of pyrite treated with H_2O_2 (Fig. 1d). The co-appearance
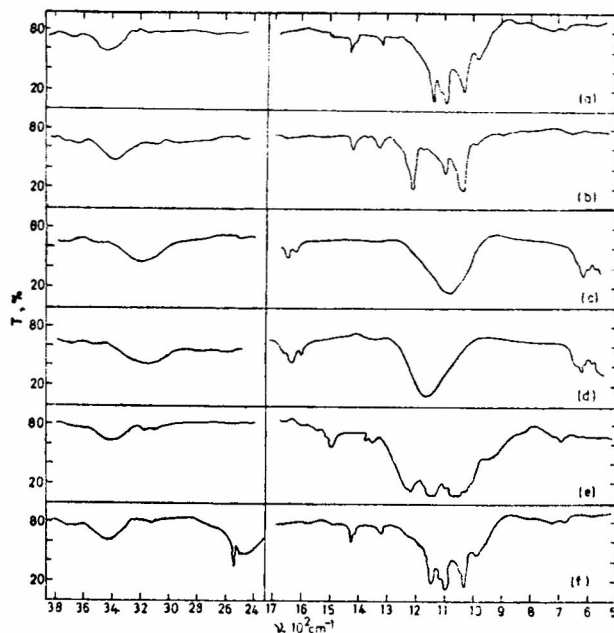

Fig. 2 — Infrared spectra of bulk: (a) potassium ethyl xanthate, (b) dixanthogenate, (c) ferrous sulphate, (d) ferric sulphate, (e) ferric xanthate, and (f) xanthic acid

of these bands is an indication of the existence of $S_2O_5^{2-}$ group. The co-appearance of strong, bands at 1280, 720 cm⁻¹ and a strong sharp band at 1080 cm⁻² indicate the presence of persulphate ($S_2O_8^{c-}$).
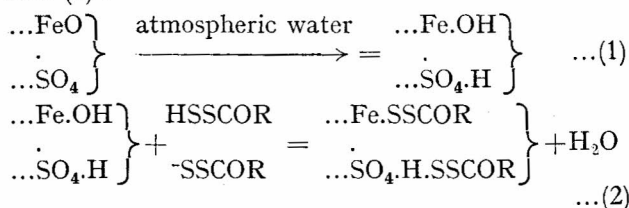
The difference in the spectrum of pyrite treated with H_2O_2 and that of the sample (1a) (Figs. 1a and 1d) is particularly pronounced around 1300, 1100 and 600 cm⁻¹, where bands related to $S_2O_3^{2-}$, $S_2O_5^{2-}$ and SO_3^{2-}, FeO and Fe_2O_3 occur. Thus, there is a marked difference in the shape and positions of the bands due to Fe-O. In the specimen (1a) ground in atmosphere the band due to Fe-O appears at 687 cm⁻¹, as against 667 cm⁻¹ in the sample treated with H_2O_2. This shift may be due to the change in Fe-O bond character on account of polarity and the difference in the ratio of divalent to trivalent iron resulting from oxidation. It was noted that pyrite treated with H_2O_2 has predominantly trivalent iron. The electronegativities and ionic radii indicate that the Fe^{III}-O bond should be stronger than the Fe^{II}-O bond, while the vibration frequencies should occur at correspondingly higher frequency, as is observed in the specimen treated with H_2O_2. No bands appeared at 2530 cm⁻¹ for the SH⁻ group, indicating complete oxidation of pyrite surface by H_2O_2.

It has been claimed[3,4,6,8-10] that immersion of a sulphide mineral in a solution of alkali xanthate results in the replacement of metal thiosulphate or sulphate film on the pyrite by a layer of metal xanthate, which also show bands in the IR region 1200-900 cm⁻¹ like the oxidation products of pyrite.

However, the shift in frequencies of absorption bands in the region 1200-900 cm⁻¹ after treatment of pyrite with xanthate is not an indication of the replacement of oxidation products, namely sulphate and thiosulphate by xanthate as claimed by many

investigators[4,6-10]. The results obtained in this study (Figs. 2 and 3) show that the shift in band positions in this region is due to the interference of absorption bands of xanthate with those of oxidation products. The IR spectra of unoxidized and oxidized pyrite samples treated with potassium ethyl xanthate revealed that insufficient emphasis has been placed on the interpretation of absorption bands of sulphide minerals in the region 1200-900 cm^{-1}. Fig. 3 shows that the bands in this region did not disappear after adsorption of xanthate. Consequently, xanthate could not have replaced the oxidation products with the formation of the corresponding metal xanthate as suggested by most investigators. Xanthate must have been physically adsorbed, since the spectrum in the adsorbed state closely resembled that of the bulk xanthate (Fig. 2). Thus, it may not have been possible for some investigators to characterize bands of different oxidation products (sulphate, thiosulphate, persulphate) from those of carbonate, bicarbonate, basic carbonate and from those of xanthates.

The IR spectrum of pyrite samples 1a, 1b and 1c treated with xanthate (Fig. 3a-c) and of these samples together treated with xanthate (Fig. 3d) exhibit bands at 1060, 1110, 1140, 1216 cm^{-1} due to stretching modes of the C=S and C-O-C groups of the xanthate species. In addition, bands characteristic of SO_3^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$ and $S_2O_3^{2-}$, the oxidation products were noticed as in the spectrum of the sample treated with H_2O_2. Absorption bands characteristic of sulphate group were noticed in the spectrum of the sample ground in atmosphere and then treated with potassium ethyl xanthate (Fig. 3a); a relatively intense and broad band at 2500-2530 cm^{-1} appeared in the spectrum of pyrite ground under carbon tetrachloride and subsequently treated with xanthate (Fig. 3c). Consequently, the mechanism of adsorption of xanthate on pyrite ground in atmosphere and/or treated with H_2O_2 seems to follow the mechanism shown in Eqs. (1) and (2):

$$\left.\begin{array}{l}...FeO \\ . \\ ...SO_4\end{array}\right\} \xrightarrow{\text{atmospheric water}} = \left.\begin{array}{l}...Fe.OH \\ . \\ ...SO_4.H\end{array}\right\} \quad ...(1)$$

$$\left.\begin{array}{l}...Fe.OH \\ . \\ ...SO_4.H\end{array}\right\} + \begin{array}{l}HSSCOR \\ \\ ^-SSCOR\end{array} = \left.\begin{array}{l}...Fe.SSCOR \\ . \\ ...SO_4.H.SSCOR\end{array}\right\} +H_2O \quad ...(2)$$

In the case of pyrite with unoxidized surface (ground under carbon tetrachloride and/or sulphidized with sodium sulphide) the mechanism of adsorption of xanthate seems to be as shown in Eqs. (3)-(5).
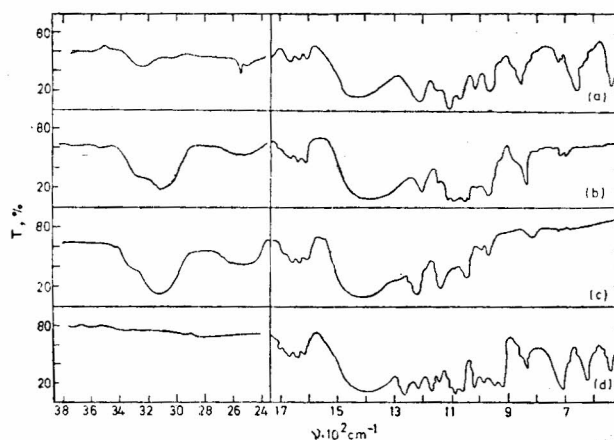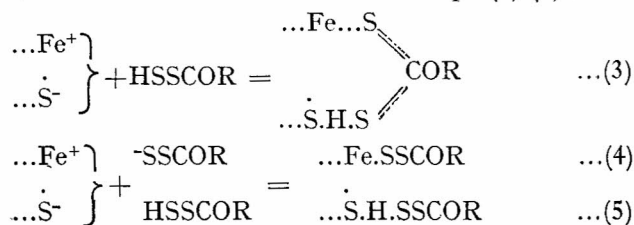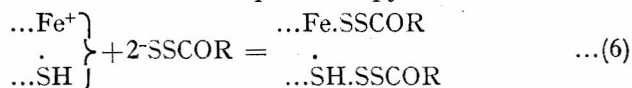
$$\left.\begin{array}{l}...Fe^+ \\ . \\ ...S^-\end{array}\right\} + HSSCOR = \begin{array}{c}...Fe...S \\ \diagdown COR \\ ...S.H.S \diagup\end{array} \quad ...(3)$$

$$\left.\begin{array}{l}...Fe^+ \\ . \\ ...S^-\end{array}\right\} + \begin{array}{l}^-SSCOR \\ \\ HSSCOR\end{array} = \begin{array}{l}...Fe.SSCOR \\ . \\ ...S.H.SSCOR\end{array} \quad ...(5)$$

Fig. 3 — Infrared spectra of pyrite samples: (a) ground in atmosphere and afterwards treated with potassium ethyl xanthate, (b) ground under water and afterwards treated with potassium ethyl xanthate, (c) ground under carbon tetrachloride and afterwards treated with potassium ethyl xanthate and (d) samples 1a, 1b and 1c together treated with potassium ethyl xanthate

In the case of sulphidized pyrite:

$$\left.\begin{array}{l}...Fe^+ \\ . \\ ...SH\end{array}\right\} + 2^-SSCOR = \begin{array}{l}...Fe.SSCOR \\ . \\ ...SH.SSCOR\end{array} \quad ...(6)$$

This mechanism is supported by the existence of a broad and intense absorption band near 2500-2530 cm^{-1} (Fig. 3). Indeed, it has been reported that the formation of X-H...Y bond (Eqs. 3, 5 and 6), where X represents xanthic acid molecule and Y sulphide site modifies the force field around the hydrogen atom thereby altering the X-H vibrational bands. The X-H stretching bands, which is usually sharp in the unbonded state (Figs. 2 and 3), usually becomes broader and more intense and is shifted to lower frequencies (Figs. 2 and 3) upon the formation of hydrogen bond[2-5].

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