

EFFECT OF HEAT TREATMENT ON NATURAL INDIAN PYRITES

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ABSTRACT

An experimental study of the oxidation of Indian natural pyrites is presented here. Three pyrite samples, two obtained directly as mineral fractions from the ores of Amjhore and Deri and third as a constituent of coal from Talchir, have been studied by Mössbauer spectroscopy after heating at different temperatures in air. Mineralogical, chemical and infrared absorption analyses have also been carried out. In all three cases, the first product of oxidation observed is sulphate instead of α -Fe₂O₃. The oxidation is seen to proceed in the sequence $\text{FeS}_2 \rightarrow \text{FeSO}_4 \cdot 7 \text{H}_2\text{O} \rightarrow \alpha\text{-Fe}_2\text{O}_3$ and/or $\text{Fe}_2(\text{SO}_4)_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$. The start of the thermal decomposition in these samples has been found to be governed by the degree of crystallinity, whereas complete conversion to α -Fe₂O₃ is observed to depend upon the particle size and the carbonaceous matter and sulfur contents.

INTRODUCTION

Pyrite is the most abundant of all the minerals of the Fe—S system and Mössbauer studies on its various structural and magnetic properties have been reported in literature [1—6]. Attempts have also been made to study the thermal effects on pyrite [7—10]. The studies, however, have not been systematic and the techniques employed, e.g. DTA, TGA, magneto-kinetic etc., give only an average picture of the iron-containing minerals present in a sample and do not give results corresponding to separate phases in the mineral. X-Ray diffraction, also is not very useful because of the low crystallinity of ashes and clays and the amorphous nature of minerals formed after the heat treatment of pyrite [11,12].

Keeping this in view, Mössbauer spectroscopic studies were done on three Indian pyrites, two obtained as mineral fractions from the ores of Amjhore (Bihar) and Deri (Rajasthan) and the third as a constituent of coal obtained from Talchir (Orissa), before and after their heat treatment. This technique

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gives separate spectra for different iron sites in the minerals and is equally well suited for amorphous materials. Chemical and IR absorption analyses were also employed to corroborate the findings. The studies were carried to understand the process of thermal decomposition and oxidation in case of pyrites from different localities and possessing different orders of crystallinity, since this process is expected to depend largely upon the genetic history of the minerals. The work finds application in exploring the possibility of magnetic separation of pyrite from coal.

MATERIALS

Amjhore pyrite

This is a stratiform type of deposit having an average sulfur content of 40% [13]. Pyrite crystals vary in size from 0.01 to 0.08 mm and the associated minerals are calcite, crypto-crystalline silica, and siderite. Some amount of carbonaceous matter is also associated with it.

Deri pyrite

This is also a stratiform type of deposit. The mineralisation is a massive sulfide type. Studies [14] show this deposit to have experienced an initial regional metamorphism and later low-pressure thermal metamorphism. The pyrite grains are polycrystalline with size varying from 0.1 mm to 0.7 mm.

Coal from Talchir

It has been reported [15] to have formed in a flood plain under fresh water conditions. Its formation took place at low temperatures ($<350^{\circ}\text{C}$) and its particle size is <0.04 mm.

The detailed characterization of these natural deposits have been given in the references cited.

EXPERIMENTAL DETAILS

Pyrite mineral used in the present study was carefully hand separated under the microscope from rock samples of Amjhore and Deri after crushing the rock in an agate mortar. However, the coal sample was directly used for studying the third pyrite as the amount of pyrite was very little in coal and too widely dispersed in fine particle form and hence was unseparable. The chemical analysis of the samples thus obtained was performed using standard procedures [16] and the results are given in Table 1.

The powdered samples were heated at different temperatures, ranging from 100 to 800°C , in air for 3 h and furnace cooled to room temperature. The grain size, heating and cooling rates were kept constant in all cases to avoid the dependence of thermal effects on these factors [17]. The Möss-

TABLE 1
Chemical analyses of pyrites and coal

Element (wt.%)	Sample		
	Amjhore pyrite	Deri pyrite	Talchir coal
Fe	35.64	42.89	4.47
S	48.35	49.25	7.42
Si	5.89	0.43	1.8
Mn	2.35	1.25	0.23
Zn	0.6	0.56	0.112
Cd	0.76	0.46	0.05
Ni	0.15	0.05	0.02
Al	Traces	Traces	0.17
Carbonaceous matter	2.49		84.00

bauer spectra were recorded on a spectrometer using a multichannel analyser and Kankeleit-type [18] constant acceleration drive. Details of the spectrometer used in the present investigations have been given elsewhere [19]. The γ -ray source used was 20 mCi ^{57}Co (Pd). The spectra of all the samples heat treated at various temperatures were recorded at room temperature in transmission geometry. The absorbers were prepared by forming pellets of 200 mg powdered samples of coal and of 20 mg samples in the remaining two cases. Mössbauer spectra of various samples are shown in Figs. 1–3 while the analysed Mössbauer parameters are given in Tables 2 and 3. Here, only those annealing temperature spectra in which some notable changes were observed are given and discussed.

IR absorption spectra were obtained on a Beckmann Spectrometer Model IR-20. Since this technique has been employed to supplement the Mössbauer results, IR spectra have not been shown and results have been quoted only where necessary.

RESULTS AND DISCUSSION

Amjhore pyrite

Its Mössbauer spectrum shows two doublets [Fig. 1(a)]. The stronger one (designated as A) corresponds to Fe^{2+} in FeS_2 [4] while the much weaker one (designated as B) appears to be due to Fe^{2+} in siderite [20] whose association with pyrite has been predicted in mineralogical studies. The dips appearing at 1110, 1125, 1150 and 1190 cm^{-1} (characteristic of iron sulfide [21]) and at 1400 and 700 cm^{-1} (due to siderite [21]) in its IR absorption spectrum further support the Mössbauer results. The heat treatment of this sample at temperatures below 365°C shows no change. However, the Mössbauer spectrum of the sample heated at 365°C shows a third doublet [designated as C in Table 2 and Fig. 1(b)] with parameters corresponding to

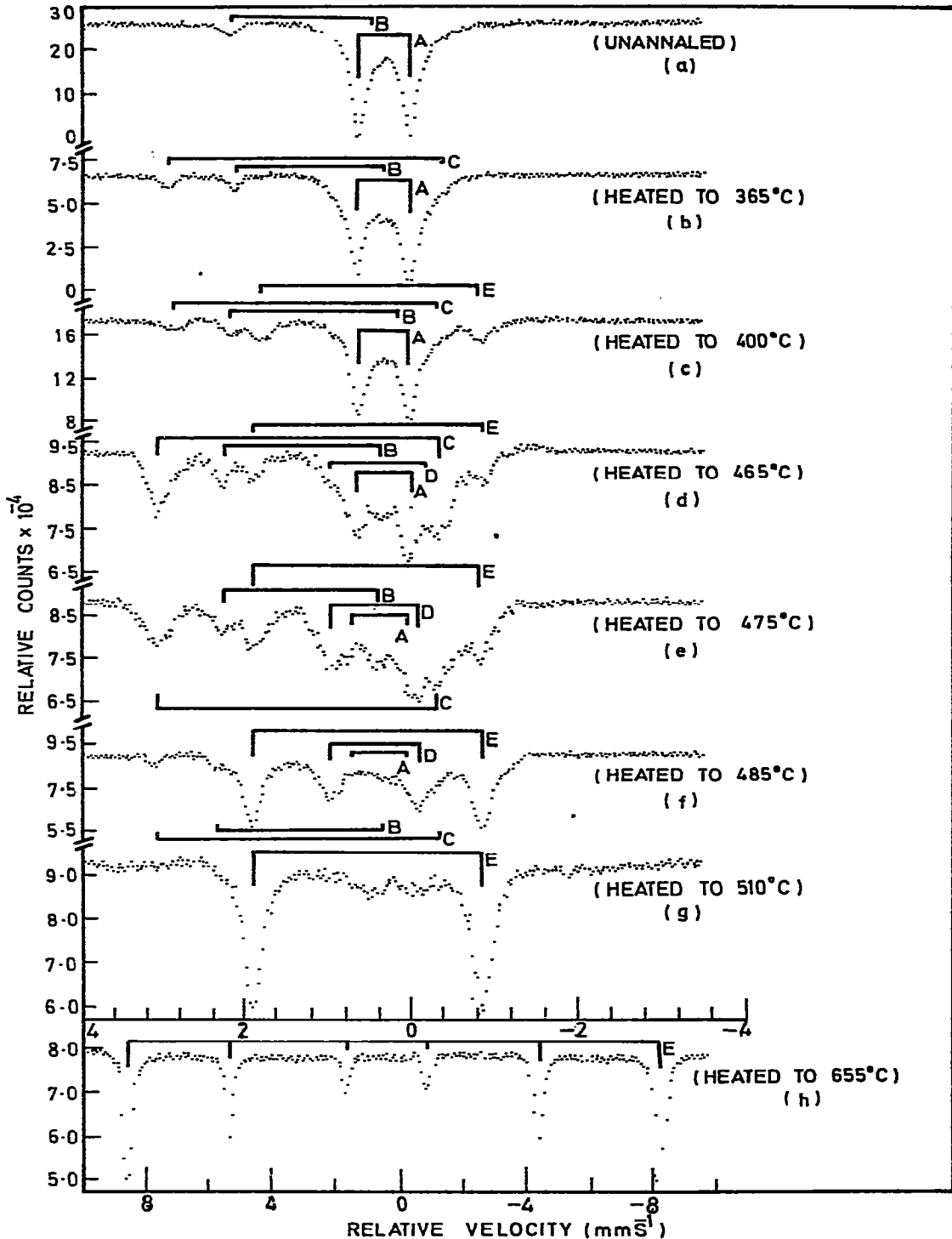


Fig. 1. Mössbauer spectra of Amjnore pyrite at room temperature.

$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ [22]. The presence of sulfate is corroborated by the IR spectrum of a sample heated at 365°C for 65 h (its Mössbauer spectrum shows doublets A, B and a stronger doublet C), which shows additional dips at

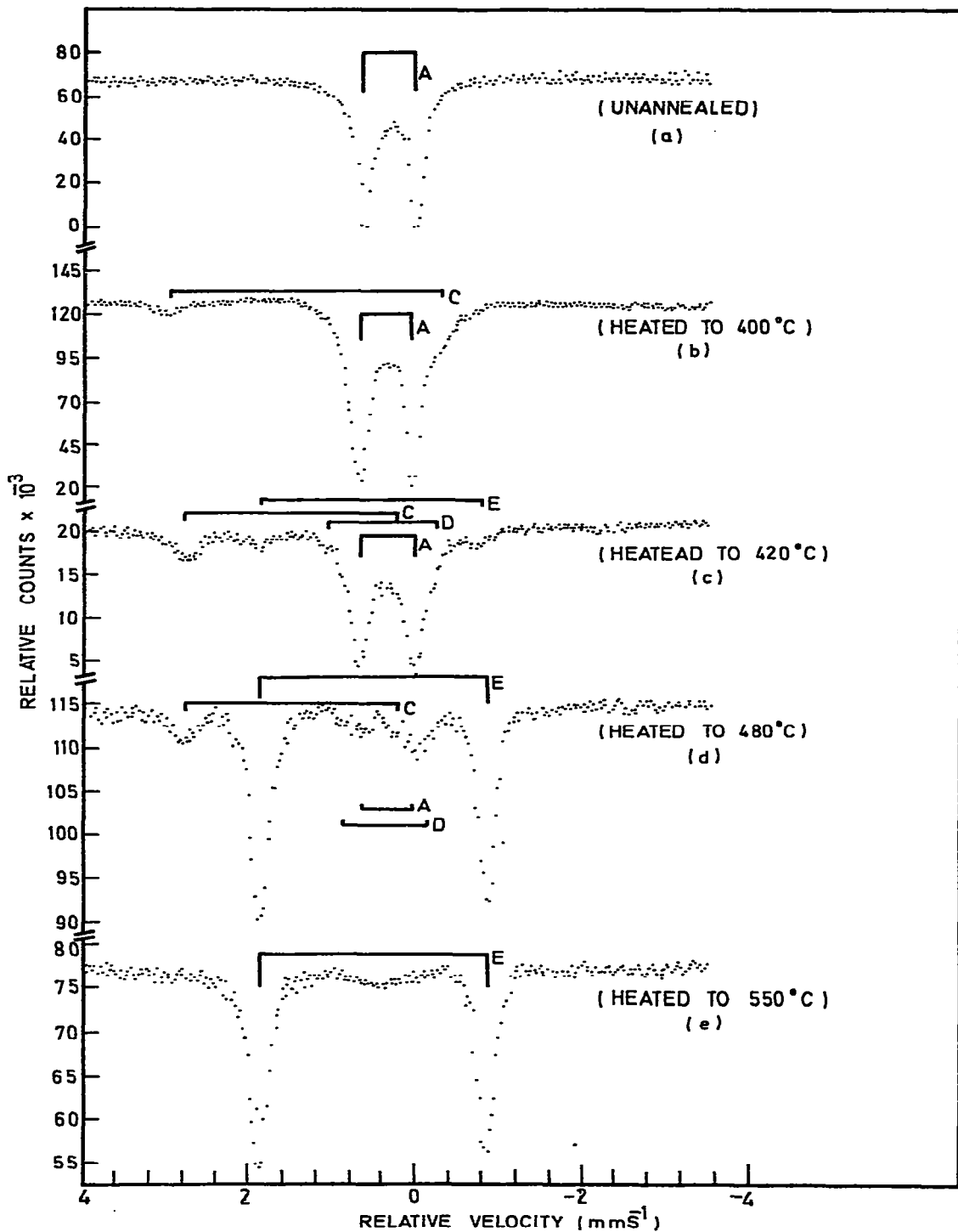


Fig. 2. Mössbauer spectra of Deri pyrite at room temperature.

3420, 3300, 1660, 1620, 1156, 990, 720, 610 cm^{-1} (characteristic of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ [21]). Comparison of the intensities suggests that C is formed at the cost of doublet A, implying the start of the decomposition of FeS_2 to

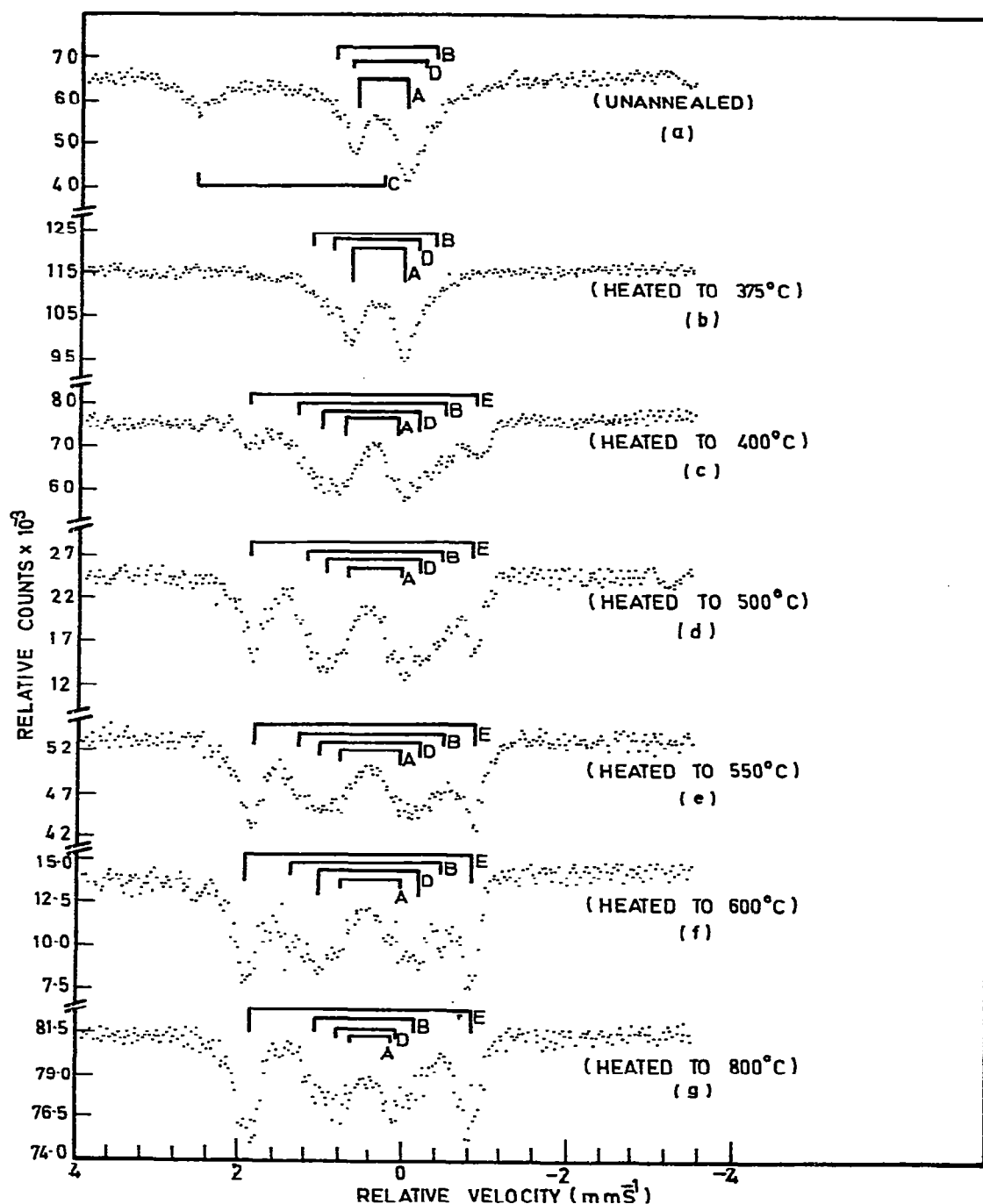


Fig. 3. Mössbauer spectra of Talchir coal at room temperature.

$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$. Heat treatment at 400°C results in the formation of $\alpha\text{-Fe}_2\text{O}_3$ whose innermost two lines appear in the Mössbauer spectrum [Fig. 1(c)]. The intensity variation suggests the following sequence of transformation at this temperature: $\text{FeS}_2 \rightarrow \text{FeSO}_4 \cdot 7 \text{H}_2\text{O} \rightarrow \alpha\text{-Fe}_2\text{O}_3$. The oxide lines also appear in the Mössbauer and IR spectra of the sample heated at 365°C for

TABLE 2
Mössbauer parameters of Amjhere and Deri pyrites at various annealing temperatures

Sample	Annealing temp. (°C)	Quadrupole doublet						Innermost lines of α -Fe ₂ O ₃ sextet (E) (mm s ⁻¹)				
		A		B		C			D			
		δ	2 ϵ	δ	2 ϵ	δ	2 ϵ			δ	2 ϵ	
Amjhere pyrite	Unannealed	+0.32	0.61	+1.3	1.68							
	365	+0.31	0.65	+1.2	1.77	+1.25	3.31				-0.81	+1.79
	400	+0.32	0.59	+1.29	1.71	+1.26	3.16	+0.37	1.07		-0.87	+1.88
	465	+0.30	0.60	+1.22	1.79	+1.28	2.43	+0.41	0.99		-0.84	+1.88
	475	+0.34	0.63	+1.24	1.76	+1.29	2.82	+0.40	1.02		-0.87	+1.88
	485	+0.33	0.60	+1.24	1.81	+1.28	3.22				-0.87	+1.88
	510										-0.86	+1.72
Deri pyrite	Unannealed	+0.32	0.61									
	365	+0.35	0.65									
	400	+0.36	0.61	+1.30	3.23			+0.39	1.30		-0.78	+1.87
	420	+0.33	0.67	+1.51	2.65			+0.35	1.01		-0.85	+1.85
	480	+0.33	0.67	+1.49	2.65						-0.84	+1.85

δ is measured with respect to atomic iron.
 δ and 2 ϵ have been measured in units of mm s⁻¹.

TABLE 3
Mössbauer parameters of coal from Talchir at various annealing temperatures

Annealing temp. ($^{\circ}\text{C}$)	Quadrupole doublet				Innermost lines of $\alpha\text{-Fe}_2\text{O}_3$ sextet (E)				
	A	B	C	D	δ	2ϵ	δ	2ϵ	
Unannealed	+0.28	+0.25	+1.42	+0.23	0.87	1.2	0.87	2.26	0.87
375	+0.35	+0.39		+0.38	1.04	1.48			1.04
400	+0.39	+0.40		+0.41	1.17	1.80			1.17
500	+0.36	+0.36		+0.36	1.13	1.65			1.13
550	+0.40	+0.40		+0.41	1.22	1.72			1.22
600	+0.39	+0.44		+0.41	1.20	1.81			1.20
700	+0.42	+0.46		+0.44	0.94	1.45			0.94
800	+0.39	+0.47		+0.45	0.72	1.17			0.72

δ is measured with respect to atomic iron.
 δ and 2ϵ have been measured in units of mm s^{-1} .

65 h. These observations suggest that the sulfation process takes place prior to oxidation, a result supported by some workers [23,24] but opposed by others [25,26].

The next significant change is observed when the sample is heat treated at 465°C. Its Mössbauer spectrum shows an additional doublet [designated as D Fig. 1(d) and Table 2] having parameters coinciding with those of $\text{Fe}_2(\text{SO}_4)_3$ [27]. A larger quadrupole splitting, 2ϵ , may be due to its disordered structure. From the intensity, the reaction $\text{FeS}_2 \rightarrow \text{FeSO}_4 \cdot 7 \text{H}_2\text{O} \rightarrow \alpha\text{-Fe}_2\text{O}_3$ and $\text{Fe}_2(\text{SO}_4)_3$ appears to have taken place at this temperature. It is interesting to note that the formation of $\text{Fe}_2(\text{SO}_4)_3$ is clearly indicated in both the Mössbauer and IR spectra of the samples heated at or above 465°C only, thus suggesting that a comparatively higher temperature is required for the formation of $\text{Fe}_2(\text{SO}_4)_3$ [28]. The Mössbauer spectrum of the sample heated at 485°C shows mainly $\text{Fe}_2(\text{SO}_4)_3$ and inner lines of $\alpha\text{-Fe}_2\text{O}_3$ with other doublets appearing quite weak [Fig. 1(f)], thus indicating that most of the decomposition has taken place around this temperature. Heating at still higher temperatures shows weakening of the $\text{Fe}_2(\text{SO}_4)_3$ as well as other doublets. Complete decomposition of the siderite doublet (B) is observed at 510°C with slight lowering in the middle portion of the Mössbauer spectrum [Fig. 1(g)], which is perhaps due to a small amount of undecomposed mineral. Finally, the Mössbauer spectrum of the sample heated at 655°C shows a neat six-line spectrum [Fig. 1(h)] with parameters corresponding to $\alpha\text{-Fe}_2\text{O}_3$.

Deri pyrite

The Mössbauer spectrum of this sample shows only one doublet which corresponds to FeS_2 [Fig. 2(a)]. Unlike Amjhore pyrite, heat treatment of this sample at 365°C for 72 h does not show any change. This is different from what has been observed for Amjhore pyrite where decomposition of FeS_2 took place at this temperature, even for a heating time of 3 h. The higher degree of crystallinity of this sample may be a possible reason. The decomposition, however, starts at 400°C, as is apparent from the Mössbauer spectrum [Fig. 2(b)], which shows another doublet (C) at the cost of FeS_2 . The parameters indicate the new doublet to be due to $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ [22]. The spectrum of the sample heated at 420°C for 3 h shows four doublets [Fig. 2(c)]. One is due to FeS_2 and another to $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (doublet C) as appears from the parameters. It seems some of the structural water is removed from the sulfate which is unlike the observations in the previous case. As Deri pyrite is more crystalline, this temperature is effective enough to remove water molecules only. The third doublet (doublet D), is due to $\text{Fe}_2(\text{SO}_4)_3$ and fourth to inner peaks of $\alpha\text{-Fe}_2\text{O}_3$, indicating that some of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is converted to $\text{Fe}_2(\text{SO}_4)_3$ and $\alpha\text{-Fe}_2\text{O}_3$. The intensity trend of the peaks suggests the oxidation rate of ferrous to ferric sulfate to be slower than the conversion rate of ferric sulfate to oxide. The spectrum of the sample heated at 480°C for 3 h again shows these four doublets [Fig. 2(d)]. The intensities of FeS_2 and $\text{Fe}_2(\text{SO}_4)_3$ are very small, that of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is larger and that of $\alpha\text{-Fe}_2\text{O}_3$ is largest. This trend again supports the above view

regarding different transformation rates. For this reason, perhaps, the oxidation of pyrite to α -Fe₂O₃ is nearly complete at 550°C as indicated in the spectrum Fig. 2(e). This temperature is lower than that for Amjhore pyrite, although the latter is less crystalline. This is due to a smaller particle size and higher sulfur (relative to iron) and carbonaceous matter contents (see Table 1) in the case of Amjhore pyrite, which slow down the oxidation rate in comparison with that of Deri pyrite [26].

Coal from Talchir

The Mössbauer spectrum of the coal sample shows four doublets [Fig. 3(a)]. Doublet A of maximum intensity corresponds to Fe²⁺ in pyrite. Doublet B represents Fe³⁺ in the octahedral site of illite structure [29,30], C corresponds to the Fe²⁺ site and seems to be due to FeSO₄ · H₂O, and D indicates the presence of Fe³⁺ in Fe₂(SO₄)₃ · 9 H₂O as appears from the comparison of parameters with those of the respective compounds [27,31]. The IR spectrum of the coal shows broad dips because of the small particle size of the minerals present in the coal [9]. Further, only the stronger dips will be detectable since the above mentioned minerals form less than 20% of the coal. Thus, it shows peaks at 420 cm⁻¹ (corresponding to FeS₂), 1110, 1030, 910 cm⁻¹ (characteristic of illite), 2920, 1103, 1050 and 1014 cm⁻¹ (characteristic of Fe₂(SO₄)₃ · 9 H₂O [21]). Peaks of FeSO₄ · H₂O are not clear for the reasons mentioned above. The presence of these minerals has also been reported in the literature [9,10].

Here also, heat treatment of the coal at temperatures below 375°C does not show any change. However, heating at 375°C shows the disappearance of the FeSO₄ · H₂O [Fig. 3(b)] doublet, indicating its oxidation to Fe₂(SO₄)₃. This low-temperature change is different from that observed in the previous two cases and may be attributed to the small particle size of the minerals in the coal, which accelerates the oxidation rate of the first stage [26]. Heat treatment at this temperature, even for a longer time (65 h), does not show α -Fe₂O₃ peaks unlike Amjhore pyrite. This, however, appears in the Mössbauer spectrum of the sample heated at 400°C at the cost of FeS₂ and Fe₂(SO₄)₃. At higher temperature, the conversion sequence FeS₂ → Fe₂(SO₄)₃ → α -Fe₂O₃ seems to be taking place as shown by the increasing intensity of the α -Fe₂O₃ peaks and the decreasing intensity of the FeS₂ and Fe₂(SO₄)₃ as the sample is heated at different temperatures from 500 to 800°C (Fig. 3). The conversion to α -Fe₂O₃ is not complete even at a temperature of 800°C, unlike the cases of Amjhore and Deri pyrites. This may be attributed to the small particle size of the FeS₂ mineral and the larger amount of carbonaceous matter (Table 1) present in the coal, both of which slow down the oxidation rate considerably in the later stages [26]. Further the spectrum of the sample heated to 800°C also indicates the presence of pyrite [Fig. 3(g), Table 3] although pure pyrite is unstable above 700°C. This, however, may be due to a thick oxide layer around the pyrite. Which forms because of the fast oxidation rate in the initial stage and remains undisturbed at 800°C because of the slow oxidation rate in the later stage. This layer protects the pyrite from O₂ gas. Because of this, FeS₂ has been identified even after heating to 1000°C [26].

In contrast to Amjhore and Deri pyrites, the parameters of the FeS_2 doublets are found to vary with the heating temperature and may be attributed to the change in the average distance between iron atoms in disordered or amorphous structures which FeS_2 acquires at different temperatures because of its fine particle size [10]. Quadrupole splitting 2ϵ of doublet B increases up to a heating temperature of 600°C and then decreases. This may be due to the precipitation of impurities from the illite structure at lower temperatures and then recrystallization of this structure at higher temperatures [32,33] (above 600°C in the present case). Parameters of doublet D differ slightly from those of $\text{Fe}_2(\text{SO}_4)_3$ due to the presence of water in the structure of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$. With heating, water molecules are removed from the structure and hence isomer shift δ approaches the value corresponding to $\text{Fe}_2(\text{SO}_4)_3$. Further, with its decomposition, the structure distorts and hence 2ϵ increases.

CONCLUSION

Amjhore pyrite shows, apart from pyrite (FeS_2), some siderite (FeCO_3). On heat treatment, pyrite decomposes to $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ at 365°C . Heating for a longer time (65 h) at this temperature also shows the formation of $\alpha\text{-Fe}_2\text{O}_3$, thus indicating that the process of sulphation occurs first followed by oxidation. Heating at 465°C shows the formation of $\text{Fe}_2(\text{SO}_4)_3$ along with $\alpha\text{-Fe}_2\text{O}_3$. Around 500°C , the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to $\alpha\text{-Fe}_2\text{O}_3$ is accelerated and is complete at about 650°C .

Deri pyrite, because of its higher crystallinity, does not show decomposition even after heating for 72 h at 365°C , unlike Amjhore pyrite. The transformation of FeS_2 to $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ starts at 400°C . Heating at 420°C shows removal of structural water from the sulphate. This then transforms to $\text{Fe}_2(\text{SO}_4)_3$ and $\alpha\text{-Fe}_2\text{O}_3$. The rate of the reaction $\text{FeSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{SO}_4)_3$ is slower than that of the reaction $\text{Fe}_2(\text{SO}_4)_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$. The decomposition to $\alpha\text{-Fe}_2\text{O}_3$ is complete around 550°C .

Coal from Talchir shows pyrite, illite, coquimbite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$] and szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) as to be present iron-containing minerals. These form less than 20% of the coal. Heating at 375°C shows the decomposition of FeS_2 and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ to $\text{Fe}_2(\text{SO}_4)_3$, which is different from Amjhore and Deri pyrites and may be due to the small particle size of the coal minerals in the case of which, oxidation rate is faster in the initial stage. The formation of $\alpha\text{-Fe}_2\text{O}_3$ starts at 400°C and is not complete even at a heating temperature of 800°C .

The observations thus indicate that decomposition of Amjhore and coal pyrite to $\alpha\text{-Fe}_2\text{O}_3$ is completed at a higher temperature than that of Deri pyrite, although the starting temperature of FeS_2 decomposition depends upon the degree of crystallinity. The coal pyrite does not completely oxidize to $\alpha\text{-Fe}_2\text{O}_3$ even at 800°C because of its smaller particle size and larger amount of carbonaceous matter, although oxidation starts initially with a higher rate which slows down at higher temperatures because of the Black-Coring phenomenon [26]. Since Deri pyrite has the largest particle

size and no detectable carbonaceous matter, oxidation rate is the fastest and hence it completely oxidises to $\alpha\text{-Fe}_2\text{O}_3$ at 550°C . Because of these factors, Amjhore pyrite has an oxidation rate lying between those of Deri and coal pyrites. It is thus observed that the thermal decomposition and oxidation of pyrites is highly dependent upon their particle size, degree of crystallinity and sulphur and carbonaceous matter contents in the deposits.

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