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Mössbauer, XRD and positron annihilation studies on natural magnetite and hematite ore from Ari Dongri, Central India

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Abstract. Natural magnetite and hematite samples taken from iron ore deposits associated with Precambrian banded iron-formation (BIF) at Ari Dongri (20°23′N:81°3′E), Bastar district in Central India have been studied by Mössbauer, XRD and positron annihilation techniques. Three magnetite samples show a genetic association with α-Fe_2O_3 with a wide range of variations in Fe_3O_4:α-Fe_2O_3 ratio. The fourth sample, a typical specular hematite, shows α-Fe_2O_3 content of the order of 90%, the rest being magnetite. The magnetite present in the samples was found to be stoichiometric. None of the samples contains maghemite (γ-Fe_2O_3). Some geological implications of the observed variation in the oxidation states of the samples are considered.

Keywords. Mössbauer; X-ray diffraction; positron; magnetite; hematite ore.

1. Introduction

Iron oxide minerals are sensitive indicators of physicochemical conditions (e.g. temperature, pressure and Eh–pH states of the environment) prevailing during their formation and subsequent events. Mössbauer spectroscopy enables us to identify their phase assemblages and determine their precise oxidation states (Bancroft 1973). Earlier we reported the results of Mössbauer studies on a chlorite-siderite-magnetite assemblage developed under low temperature-pressure conditions in 'green shale' of Precambrian sedimentary banded iron formation (BIF) of South Singbhum, Eastern India (Das *et al* 1986). In this paper we present the result of Mössbauer studies of oxide facies viz. some magnetite and hematite samples collected from the iron deposits of a Precambrian metamorphosed BIF at Ari Dongri (20°23′N:81°3′E), Bastar district, Madhya Pradesh, India. X-ray diffraction and positron annihilation measurements in the same samples supplement and confirm the findings of the Mössbauer method.

The iron formation hosting the hematite and magnetite deposits belongs to a sequence of metasedimentary and metavolcanic rocks occurring within a granite-gneissic terrain and suffered deformation and progressive regional metamorphism. These were also affected by late phase basic and acidic igneous intrusions (Mukharya 1975). BIF has an oxide-facies mineral association (hematite and magnetite) with only minor content of silicates and sulphides. The ore deposits comprising hard microplaty (specular) hematite ore and hard granular magnetite ore are genetically related to banded hematite quartz rock and ferruginous argillite (metamorphosed clayey rock). The hematite ore shows clear evidence of having undergone deformation (e.g. development of schistosity, puckering, lineation etc.) along with the host BIF, thus being pre-tectonic. The magnetite ore, in contrast, is free of any such deformational imprint and apparently post-dates the peak of deformation. Magnetites, however, are associated with high temperature minerals like sillimanite (Al_2SiO_5) and cordierite (Mg–Fe^{2+}–Al-silicate) and at places, even with muscovite and pyrite (FeS_2).

Our interest centres on the ratio of α-Fe_2O_3 to Fe_3O_4 and the ratio of Fe^{2+} to Fe^{3+} in the bulk ore sample and on evaluating their variations in terms of possible natural processes. A related information required would be the presence, if at all, of maghemite or γ-Fe_2O_3. All these would throw more light on the precise oxidation state of the constituent minerals in the ore and their paragenetic relationship.

2. Experimental procedure

2.1 *Description of the samples*

Four field samples S_1, S_2, S_3 (all nominally magnetite) and S_4 (nominally hematite) are the materials for the present study. S_1 is associated with pyrite, S_2 is apparently wholly magnetite, whereas S_3 has muscovite in association. Magnetic strength appears to diminish in the samples from S_1 to S_3. S_4 is a typical microplaty specular hematite (with sparsely scattered coarse magnetite euhedra) but the bulk sample is found to be weakly magnetic.

Examination of the samples under microscope in the reflected light reveals the following mineralogical and textural characters.

Sample S_1 contains magnetite as the predominant phase in association with a younger hematite phase, occasionally engulfing almost the entire magnetite parent. Replacement is broadly controlled along (111) parting planes, but nowhere in fine detail, and thus the intricate 'cloth-texture' type replacement (a common weathering feature) is totally absent. Pyrite present as an additional phase in S_1 shows replacement relationship with magnetite. Samples S_2 and S_3 show the presence of magnetite with different degrees of martitization in intricately fine detail along (111) planes (cloth-texture type). Minor amount of goethite/limonite is present in these two samples. The hematite sample S_4 mainly contains microplaty hematite along with minute irregular relics of magnetite at the core of many hematite grains which point to their derivation from older magnetite. S_4 is, however, not cogenetic with S_1, S_2 and S_3 and belongs to a different ore body. In addition, there occur a few isolated large magnetite euhedra which texturally bear evidence of a thermal history (Ramdohr 1980), crosscut the plane structure of hematite and indicate reversal of oxidation; however, these have not been included in the present study.

2.2 *Experimental details*

Each sample was crushed and the iron oxide minerals were separated from gangue and impurities other than iron oxides by a strong hand magnet. In the present case, the hematite sample S_4 posed no problem owing to its magnetic property and the textural character described earlier. The separated parts were then washed several times with distilled water, dried at room temperature and allowed to pass through a 30 sieve mesh. These powders were used for all experimental measurements.

Each Mössbauer measurement was carried out with 30 mg of the powder sandwiched between two thin cellophane papers. All measurements were made at room temperature in transmission geometry. A typical 512 channel multichannel analyser coupled to a precision velocity drive system (supplied by M/s Wissel, West Germany) was used to record the spectra. The source used was a 3 mCi ^{57}Co in Rh matrix. The calibration of the spectrometer was done by noting the peak positions of a pure natural iron foil. The Mössbauer spectra were analysed by a least squares fit program based on that of von Meerwaal (1975) on an IRIS-80 computer.

X-ray diffractograms of the powder samples were taken on a Philips (PW 1710) diffractometer using Cu–K_α radiation.

For positron lifetime measurements a weak ($\sim 2\,\mu$Ci) ^{22}Na positron source evaporated on a thin Ni foil and covered by an identical Ni foil was used. To minimize the contribution from air and absorbed gases, all the powders of the samples were degassed by heating at 100°C in vacuum for at least 2 h before starting any measurements. The positron source was placed centrally in a glass degassing chamber and the powder was poured around the source so as to have all the positrons annihilate in the powder specimen. The source-sample assembly was kept under vacuum throughout the duration of measurements which lasted about 16 h for every sample studied.

The positron lifetime measurements were performed using a conventional slow fast coincidence spectrometer. The prompt time resolution (fwhm) of the spectrometer was 260 ps for ^{60}Co gamma rays at the positron experimental window settings of the upper 50% of the Compton emission accepted in both the channels. The lifetime spectra were analysed by using the computer programs POSITRONFIT and RESOLUTION (Kirkegaard and Eldrup 1974, 1979). A source component of intensity 10% was removed from all the lifetime spectra.

3. Results and discussion

3.1 *Mössbauer studies*

Figure 1 shows the Mössbauer spectra recorded at room temperature of the powders studied. Three sextets were fitted to the experimental points to get a good χ^2 value for all samples. The six finger patterns with hyperfine field 492 ± 3 kOe and 459 ± 3 kOe with isomer shifts (IS) $0{\cdot}22 \pm 0{\cdot}04$ mm/s and $0{\cdot}66 \pm 0{\cdot}04$ mm/s, respectively, are identified as due to magnetite (Fe_3O_4); the former comes from the Fe^{3+} atoms at tetrahedral (A) site, the latter is due to both Fe^{2+} and Fe^{3+} at octahedral (B) site (Danniels and Rosencwaig 1969). The resonance areas under the A site and B site peaks, which are directly proportional to the number of iron atoms in corresponding sites, are evaluated and the ratio Fe(A):Fe(B) is found to be $\simeq 0{\cdot}5$. This and the general shape of the spectra indicate that all these samples are stoichiometric magnetite with no appreciable vacancy at octahedral sites. The third sextet with hyperfine field 515 ± 3 kOe and IS $= 0{\cdot}30 \pm 0{\cdot}04$ mm/s and quadruple splitting (QS) $= 0{\cdot}28 \pm 0{\cdot}04$ mm/s

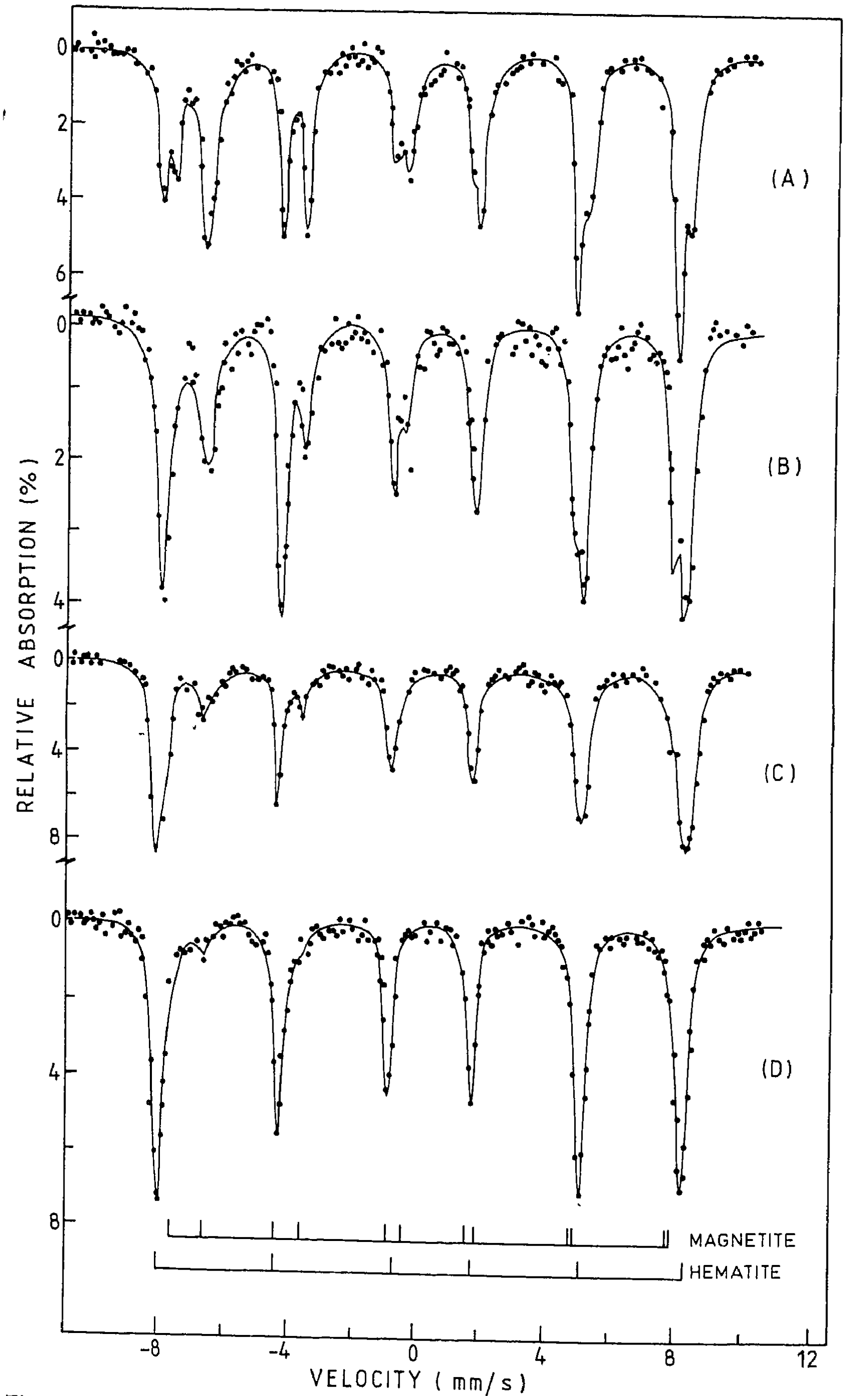

Figure 1. Mössbauer spectra of the powders: (A) sample S_1, (B) sample S_2, (C) sample S_3 and (D) sample S_4.

Table 1. Relative amounts of α-Fe_2O_3 and Fe_3O_4 phases calculated from Mössbauer resonance areas and Fe^{3+}:Fe^{2+} ratio.

Sample	% of Fe_3O_4	% of α-Fe_2O_3	Fe^{3+}/Fe^{2+} in the bulk sample
S_1	70	30	76:24
S_2	52	48	82:18
S_3	25	75	92:8
S_4	10	90	96:4

Error in area measurements = ± 3%.

is identified as due to hematite (α-Fe_3O_3). Assuming the same Lamb-Mössbauer factors for α-Fe_2O_3 and Fe_3O_4 the relative amounts of α-Fe_2O_3 and Fe_3O_4 in the powders were calculated from the resonance areas and the Fe^{3+}/Fe^{2+} ratios were obtained from them. The results are shown in table 1.

3.2 *XRD analysis*

The X-ray diffractograms of the powders were recorded to check the Mössbauer findings. Figure 2 shows a typical diffraction pattern recorded for the sample S_1. Other samples show similar patterns. The d values calculated from the intense peaks observed are shown in table 2. Comparing the calculated d values and the relative intensities of the different peaks to those reported for pure Fe_3O_4 and α-Fe_2O_3, we conclude that all the samples contain both Fe_3O_4 and α-Fe_2O_3. Comparison of the peak intensities of the four recorded diffraction patterns indicates that the Fe_3O_4:α-Fe_2O_3 ratio gradually decreases in the samples, being highest in S_1 and lowest in S_4. All these support the Mössbauer spectroscopic observations.

3.3 *Positron lifetime study*

Natural magnetite sample may very often contain maghemite γ-Fe_2O_3 (Wasilewski 1979). Our Mössbauer and X-ray data indicate that maghemite is not present in any of the samples studied. The conclusion is supported by positron annihilation studies.

It is not always possible to detect γ-Fe_2O_3 in a sample by Mössbauer spectroscopy, particularly when associated with Fe_3O_4 and α-Fe_2O_3, because of the strong overlapping of the characteristic lines. XRD analysis also may lead to confusion while detecting γ-Fe_2O_3 in the presence of Fe_3O_4 because both have cubic structure and very close lattice constants (for Fe_3O_4 $a = 9{\cdot}397$ Å; for γ-Fe_2O_3 $a = 8{\cdot}33$ Å). Maghemite (γ-Fe_2O_3) actually is extremely non-stoichiometric Fe_3O_4 which can be represented as

$$[Fe^{3+}]_{tet}[Fe^{3+}_{1+2x}Fe^{2+}_{1-3x}\,\square_x]_{oct}O_4,$$

$x = 0{\cdot}33$ (Coey *et al* 1971). Here □ means vacancies present at the octahedral (B) site. Positron lifetime studies in other oxides have shown a larger lifetime component for a vacancy rich sample (Brauer *et al* 1984). Hence for γ-Fe_2O_3 which is nothing but vacancy-rich Fe_3O_4, one expects a lifetime larger in comparison to that in a defect-free

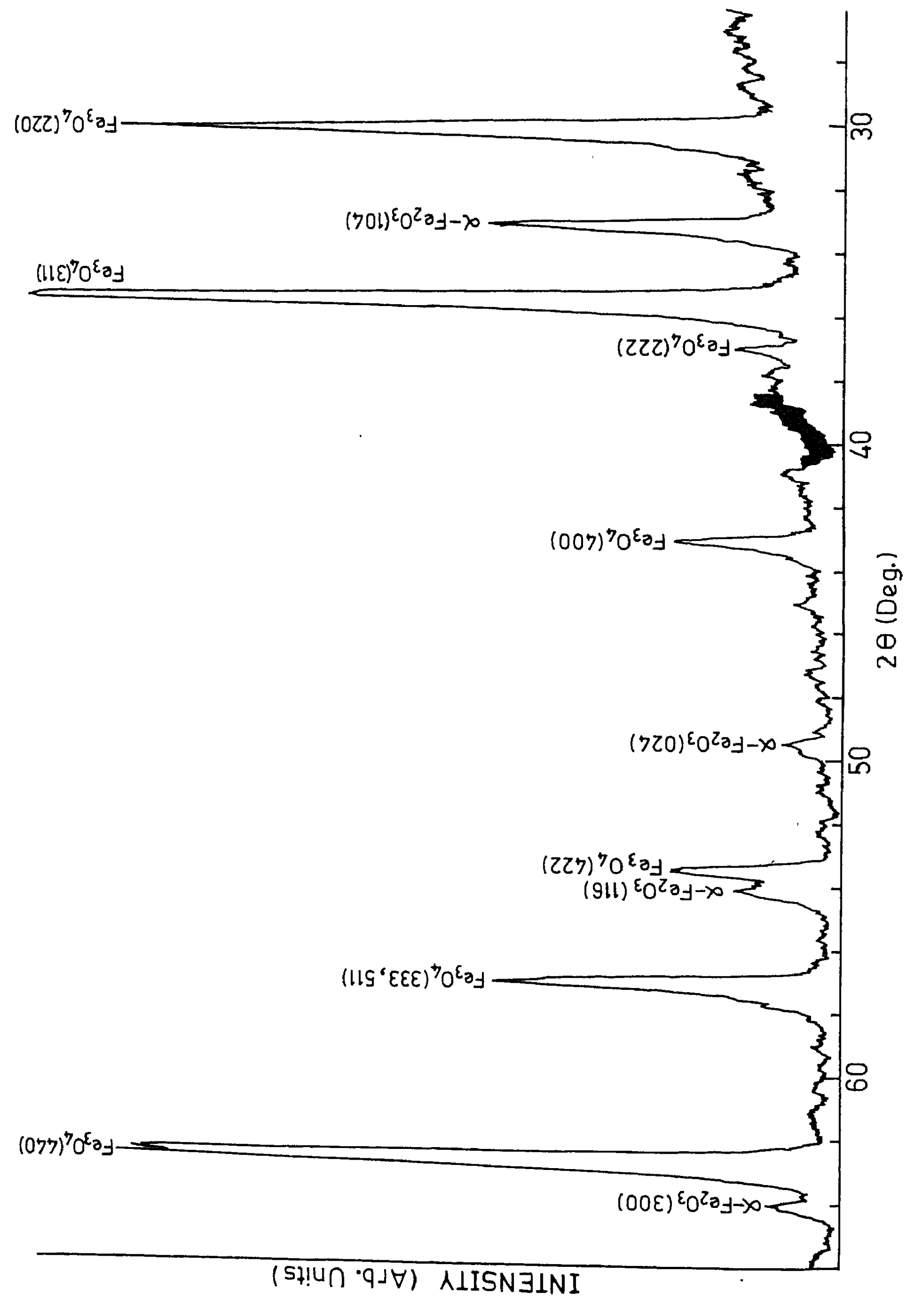

Figure 2. Characteristic X-ray lines for sample S_I.

Table 2. X-ray diffraction results.

Pure Fe_3O_4*	Pure Fe_2O_3*	S_1	S_2	S_3	S_4
2·966 (70)		2·98		2·96	2·97
	2·690 (100)	2·69	2·69	2·69	2·71
2·530 (100)		2·52	2·53	2·53	2·54
	2·510 (50)		2·51		2·53
	2·210 (30)			2·20	2·21
2·096 (70)		2·09	2·08		2·10
	1·838 (40)	1·84	1·83	1·84	1·84
1·712 (60)					
	1·690 (60)	1·69	1·68	1·69	1·69
1·614 (85)		1·61		1·61	
	1·484 (35)	1·48	1·48	1·48	1·48
1·483 (85)					
	1·452 (35)	1·44	1·44	1·45	
1·092 (60)					

The *d* values are in Angstroms. The observed lines at 1·69 and 1·48 are probably overlapping lines from Fe_3O_4 and α-Fe_2O_3.
*Data from Berry (1974).

sample. Keeping this in mind we have examined the present samples by positron annihilation technique. Figure 3 shows a typical positron lifetime distribution curve for sample S_1 along with the prompt time resolution. Since the samples are mixtures of different iron oxides, only the mean lifetime (τ_m) values are meaningful. Table 3 shows the lifetimes and corresponding intensities of the components. A two-component fit is made to the experimental data as it gave a better χ^2 value. To compare the lifetimes observed for the samples studied, one Fe_3O_4 and one α-Fe_2O_3 sample found to be pure by both Mössbauer and XRD analysis are used as reference. The observed mean lifetime of 199 ps for S_1 is very close to the reference Fe_3O_4 lifetime value suggesting that Fe_3O_4 is the major part in it. S_2 shows a mean lifetime 215 ps which is midway between the lifetimes of the reference samples indicating that the sample contained appreciable amounts of Fe_3O_4 and α-Fe_2O_3. For S_3 the lifetime observed is 221 ps. This being close to the reference α-Fe_2O_3 lifetime indicates that S_3 contains mainly hematite. For S_4 the lifetime observed is 191 ps. Though the Mössbauer and XRD results show the sample to be a mixture of α-Fe_2O_3 and Fe_3O_4, the remarkably low mean lifetime (even less than 197 ps observed in Fe_3O_4) implies larger particle size for this sample in comparison to the other samples studied. It is known that the

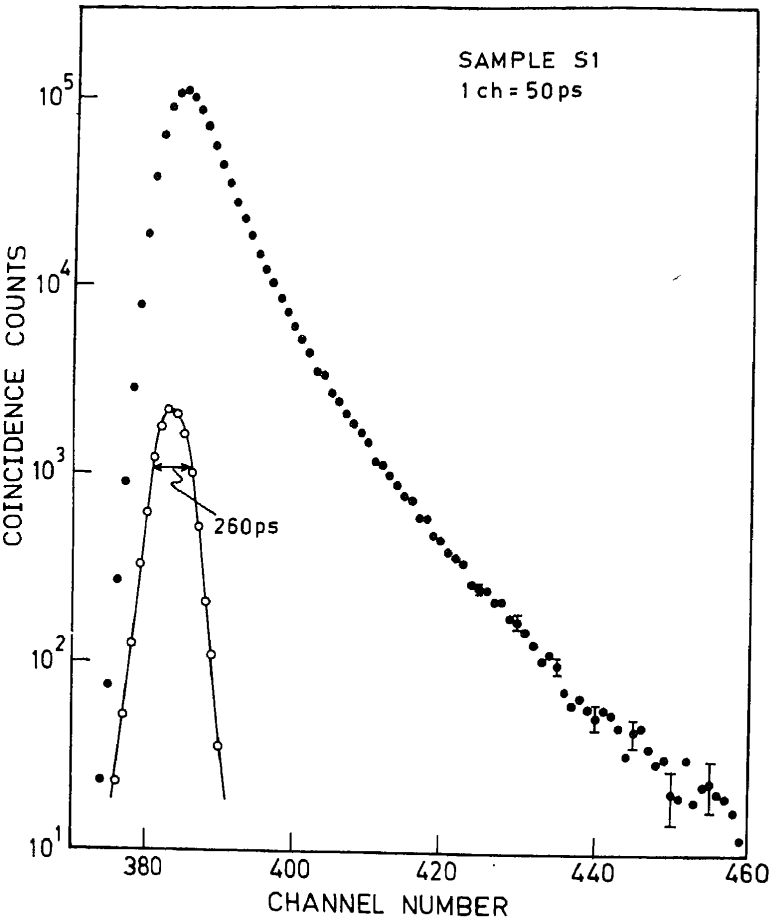

Figure 3. Positron lifetime spectrum in sample S_1.

Table 3. Results of positron lifetime studies. τ_1 and τ_2 are the two lifetimes, I_2 the intensity of the second lifetime component τ_2. τ_m is the mean lifetime.

Sample	τ_1(ps)	τ_2(ps)	I_2(%)	τ_m(ps)
Pure Fe_3O_4	140	289	38	197
Pure α-Fe_2O_3	173	352	28	224
S_1	131	273	43	199
S_2	154	337	33	215
S_3	164	367	28	221
S_4	140	305	31	191

Typical errors in $\tau_1 = \pm 3$ ps, $\tau_2 = \pm 5$ ps, $I_2 = \pm 3\%$ and $\tau_m = \pm 8$ ps.

finer the particle size the larger is the lifetime (Mitsuhashi *et al* 1972). The observed lifetimes for the samples also rule out the presence of γ-Fe_2O_3 in them as none of them show enhanced mean lifetime which would be expected if positrons were trapped at cation vacancies present in γ-Fe_2O_3. Thus the Mössbauer analysis of fitting only three sextets to the experimental points, one for α-Fe_2O_3 and two for Fe_3O_4 are justified.

4. Conclusions

The observed results reveal the presence of Fe_3O_4 and α-Fe_2O_3 in the samples and yield a quantitative relative estimation of the phases in these iron ores. The magnetite present in all the samples is found to be stoichiometric. The samples show large fluctuations in the oxidation states and the Fe^{2+}/Fe^{3+} ratios.

The presence of 30% hematite in S_1, which texturally bears no sign of weathering, indicates that the magnetite ore in the locality has suffered deep-seated oxidation (hypogene martitization) during the metamorphic cycle. This may have occurred in S_2 and S_3 also, but the evidence of the ore texture of these samples suggests that their additional hematite is partly due to weathering. Ready transfer to the highest oxidation state in them is probably due to the replacement of magnetite by secondary pseudomorphous hematite (supergene martitization) caused by oxygen-bearing surface water (meteoric water) percolating to different depths. The transformation takes place along the (111) planes as the (111) planes of the ccp structure of magnetite are equivalent to the (001) planes of the hcp structure of hematite. The hematite in S_4 arises from the conversion of magnetite under high temperature-pressure conditions in a hydrous environment (Kalliokoski 1965; Mel'nik 1982). The absence of maghemite indicates high temperature conditions during ore formation, as maghemite is known to be unstable above 500°C. More cannot be said from the present exploration with a few samples, but a more detailed study seems to be worthwhile.

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