

Identification of iron compounds in Kuwaiti surface sand deposits using Mössbauer spectroscopy

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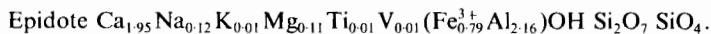
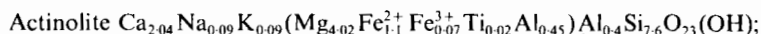
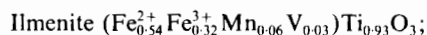
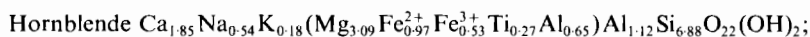
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ABSTRACT

Room-temperature Mössbauer spectra were recorded for sand samples from two locations in Kuwait which were prepared from bulk samples by separation according to colour or grain size. Peaks of Lorentzian shape were fitted to the measured absorption envelopes by a least square method. Five absorption doublets were observed in the spectra of the green colour sample; on the basis of extracted values of isomer shifts and quadrupole splittings two major iron compounds, namely, actinolite and epidote were identified. Seven absorption doublets were observed in the spectra of the bulk samples; the extracted values of isomer shifts and quadrupole splittings led to the identification of three major iron-bearing phases, namely, hornblende, ilmenite and magnetite. Analysis of spectra for various grain size samples confirmed previous findings that iron-bearing phases are only abundant in fine grain sizes of less than 88 μm and that this abundance increases with decreasing grain size. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of hornblende and ilmenite was found to be 1.86 and 1.7, respectively. The same values were obtained, within experimental error, from the spectra of the various grain size samples.

Combining the present Mössbauer results with new electron probe microanalysis performed on similar samples in the same laboratory, the following formulas were obtained for the iron-bearing compounds in the samples studied:



1. INTRODUCTION

The occurrence of iron in Kuwaiti sand limits its utilization in glass industry as it results in several problems in glass melting and annealing and also affects the quality and colour of glass. Studies by Abu Eid *et al.* (1983) using a combination of techniques including X-ray diffraction, optical microscopy and electron probe micro analysis (EPM) resulted in the identification of several iron-bearing phases in Kuwaiti sand.

It was further shown (Abu-Eid & Mansour 1985) that the majority of iron occurs as independent iron-bearing phases in the fine fraction of quartz sand grains while a small proportion of iron occurs in thin rims of clay minerals of 1–10 μm thickness which coat the coarse grain fractions.

The objective of the present study is to identify iron-bearing compounds in various grain sizes using the Mössbauer technique and to identify the iron oxidation state in such compounds. Green and black coloured samples were used for this purpose. Analysis of the spectra of samples of various grain sizes was used to verify the presence of the same iron-bearing phases in these samples and to correlate the abundance of these phases with grain size. These results were checked for consistency with/and complemented by parallel measurements using an (ICP-OE) spectrometer and EPM analysis on similar samples.

The experimental methods used in the preparation of samples and the recording of the Mössbauer spectra are outlined in Section 2 of this paper. In Section 3 the results of spectral analysis and the extraction of Mössbauer parameters are presented; these are used to identify five major iron-bearing phases and to calculate their corresponding $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios. By combining these results of Mössbauer measurements with those of chemical analysis on identical samples the chemical formulas for the five compounds were determined.

2. EXPERIMENTAL METHODS

Table 1 lists the samples used in this experiment. These are sand samples which were collected from Umm-Negga and Huwaimliyah areas in Kuwait and were subjected to successive stages of separation. Bromoform liquid with 2.89 g l^{-1} density was used to separate out the silica thereby enriching the sample in iron compounds. The product of this separation contained grains of various colours indicating different mineral concentrations. In a second stage of separation the grains of darker colour (black and green) were hand-picked using a pair of tweezers under a microscope. This resulted in the separation of about 100 mg of black grains and 120 mg of green grains. In addition, by sieving some of the original sand, eight samples ranging in grain size between 350 μm and 45 μm diameter or less were prepared. Each of the samples thus obtained was mixed with about three times its equivalent in mass of sugar. The mixture was ground very finely using a quartz mortar and then pressed onto a 2.5 cm

Table 1. List of samples used.

Sample	Type
A black	Mostly black grains of various sizes and shapes.
A green	Mostly green grains of various sizes and shapes.
B 45	Grain size 350 μm of various colour and shapes.
B 60	Grain size 250 μm of various colours and shapes.
B 80	Grain size 177 μm of various colours and shapes.
B 120	Grain size 125 μm of various colours and shapes.
B 170	Grain size 88 μm of various colours and shapes.
B 230	Grain size 63 μm of various colours and shapes.
B 325	Grain size 45 μm of various colours and shapes.
B Pan	Grain size < 45 μm of various colours and shapes.

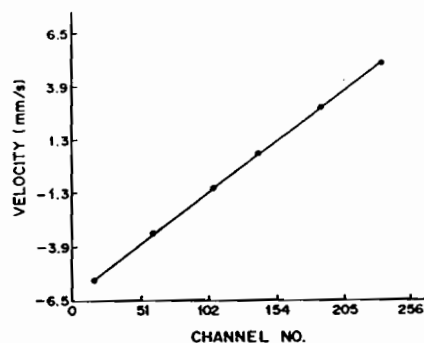


Fig. 1. A plot of the measured velocities for an Fe foil ($25\ \mu\text{m}$ thickness) *v.* channel number together with fitted linear curve.

diameter circular opening in a plexiglass holder to which it was cellotaped on both sides.

Room-temperature Mössbauer spectra were obtained using a $103\ \text{mCi}\ ^{57}\text{Co}$ source in a palladium matrix. A constant-acceleration Austen Science Spectrometer was used with a Tracor Northern multichannel analyser in the multiscaling mode. Mirror image spectra of 256 channels each were obtained for each sample over exposure periods ranging between one and seven days. Velocity calibration of the channel numbers was achieved using an enriched (99%) ^{57}Fe absorber, as shown in Fig. 1. The linear fit to these calibration data corresponds to a slope $0.0488 \pm 1.2\%$ mm/s. A similar calibration was performed before each run and the calibration data were fed into the input file of the computer fitting calculation for that run. The slope of the calibration curve was always found to be equal to the value given above within the range of the experimental error.

3. RESULTS, ANALYSIS AND DISCUSSION

3.1. MEASURED SPECTRA AND THE EXTRACTION OF MÖSSBAUER PARAMETERS

Mössbauer spectra were taken at room temperature for the two coloured samples, A-Black and A-Green, and for eight grain size samples listed in Table 1 where each sample has been labelled by the letter B followed by the sieve mesh number. The absorption peaks in the obtained spectra were fitted with Lorentzian shapes using the ZXSSQ routine (from International Mathematical and Statistical Library Package) which allows a maximum of twelve peaks to be fitted simultaneously. In addition to the position, width, and area of each peak, the fitting parameters included a baseline value, a baseline drift and a sinusoidal correction to the baseline. This last term was found, however, to be negligible and the drift term was less than $0.5\ \text{ppm/channel}$. However, the actual number of free parameters was significantly reduced through the constraint that peaks occur in the form of doublets of identical intrinsic parameters. χ^2 values were considered acceptable if the fit was visually satisfactory and the value of χ^2 was within the range $(\nu + 2.2 \pm 3.3\nu)$ where ν is the number of degrees of freedom. This range corresponds to the portion of the χ^2 distribution which is contained between the 1% and 99% limits and thus corresponds to a 98% confidence level.

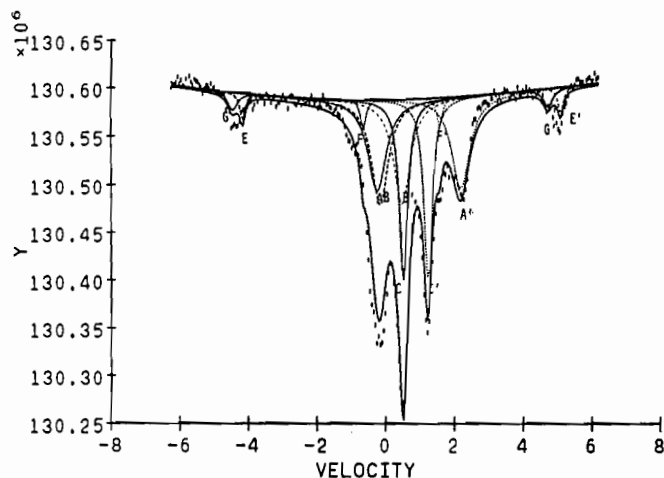


Fig. 2. Measured and fitted Mössbauer spectrum for the A-Black sample.

The fitted spectra are shown in Figs 2–9. Peak centroids were observed to be constant within ± 0.03 channel over 24 h runs and ± 0.18 channel over a seven day run; the latter shift corresponds to an uncertainty in line position of 0.01 mm/s. The main error incurred in the values of isomer shift and quadrupole splitting was therefore due to uncertainty in the calibration formula which is of the order of 1.2%.

The Mössbauer parameters for each doublet, namely, the isomer shift (δ) and the quadrupole splitting (Δ) were extracted from the fitting parameters and are listed in Table 2 for the coloured samples and Tables 3 and 4 for the grain size samples. A total of twelve doublets labelled A–A' to L–L' were identified. As shown in Table 2, seven doublets (A–A' to G–G') were identified in the A-Black samples and five doublets (H–H' to L–L') were identified in the A-Green samples. As for the grain size samples

Table 2. Extracted values of δ , Δ , Γ (mm/s) and χ^2 values for coloured samples.

Spectra	A-Black (a)			A-Black (b)			A-Green		
	δ	Δ	Γ	δ	Δ	Γ	δ	Δ	Γ
A–A'	1.14	2.46	0.63	1.15	2.43	0.63	—	—	—
B–B'	0.28	0.80	0.34	0.34	0.64	0.59	—	—	—
C–C'	1.09	0.63	0.29	1.06	0.71	0.29	—	—	—
D–D'	0.33	0.41	0.24	—	—	—	—	—	—
E–E'	0.60	0	0.24	0.65	0	0.20	—	—	—
F–F'	0.60	0	0.20	0.65	0	0.20	—	—	—
G–G'	—	—	—	0.32	0	0.34	—	—	—
H–H'	—	—	—	—	—	—	1.18	2.85	0.59
I–I'	—	—	—	—	—	—	1.18	2.41	0.34
J–J'	—	—	—	—	—	—	1.18	1.86	0.20
K–K'	—	—	—	—	—	—	0.24	0.99	0.20
L–L'	—	—	—	—	—	—	0.32	2.09	0.15
χ^2	277			277			277		

Table 3. Extracted values of δ , Δ , Γ (mm/s) and χ^2 values for doublets identified with hornblende and ilmenite in grain size samples.

Sample	Fe ⁺² in hornblende			Fe ⁺³ in hornblende			Fe ⁺² in ilmenite			Fe ⁺³ in ilmenite			$\frac{\text{Fe}^{+2}}{\text{Fe}^{+3}}$	χ^2	
	Doublet A-A'			Doublet B-B'			Doublet C-C'			Doublet D-D'					
	δ	Δ	Γ	δ	Δ	Γ	δ	Δ	Γ	δ	Δ	Γ			
B-170	(a) 1.03	2.37	0.44	0.34	0.78	0.29	1.825	1.06	0.64	0.49	0.34	0.33	0.24	1.71	344
	(b) 1.09	2.33	0.44	0.33	0.70	0.59	—	1.04	0.84	0.39	—	—	—	—	343
B-230	(a) 1.05	2.30	0.49	0.34	0.74	0.49	1.825	1.02	0.89	0.49	0.31	0.36	0.24	1.70	346
	(b) 1.10	2.16	0.49	0.30	0.60	0.59	—	1.02	0.91	0.49	—	—	—	—	351
B-325	(a) 1.04	2.43	0.44	0.39	0.73	0.29	1.825	1.11	0.88	0.44	0.32	0.35	—	1.69	362
	(b) 1.08	2.26	0.44	0.34	0.59	0.59	—	1.08	0.96	0.44	—	—	—	—	400
B-Pan	(a) 1.07	2.38	0.44	0.37	0.85	0.29	1.800	1.08	0.86	0.44	0.32	0.40	0.24	1.70	370
	(b) 1.09	2.36	0.44	0.33	0.64	0.59	—	1.09	0.89	0.44	—	—	—	—	314

Table 4. Extracted values of δ , Δ , Γ (mm/s) and χ^2 values for doublets identified with actinolites, epidote and magnetite in grain size samples.

Sample	Fe ⁺² in actinolites			Fe ⁺³ in epidote			Fe ⁺² , Fe ⁺³ in magnetite			χ^2
	Doublet G-G'			Doublet J-J'			Doublet E-E'			
	δ	Δ	Γ	δ	Δ	Γ	δ	Δ	Γ	
B-170	(a) 1.12	2.91	0.49	0.35	2.16	0.44	—	—	—	344
	(b) 1.11	2.75	0.24	0.32	1.93	0.44	—	—	—	343
B-230	(a) 1.15	2.73	0.49	0.32	1.96	0.34	—	—	—	346
	(b) 1.16	2.72	0.49	0.31	1.93	0.34	0.62	—	0.24	351
B-325	(a) 1.17	2.74	0.44	0.35	1.86	0.34	—	—	—	362
	(b) 1.16	2.74	0.44	0.33	1.89	0.34	0.62	—	0.24	400
B-Pan	(a) 1.18	2.75	0.44	0.37	1.88	0.24	—	—	—	370
	(b) 1.19	2.75	0.44	0.37	1.89	0.24	0.65	—	0.24	314

only six of the twelve doublets were clearly identified and are listed in Table 3. This is due in part to the limitation by the program that only six doublets can be fitted simultaneously. The main reason, however, is that the grain size samples contain the various coloured phases and their spectra are therefore dominated by the strongest iron-bearing phases namely, the A-Black; the doublets of the A-Green component which has a much lower concentration of iron are submerged in the presence of the A-Black doublets. Further, iron concentration is quite sensitive to the grain diameter size and is very weak in large grain size samples, as will be shown later. Consequently, Tables 3 and 4 list Mössbauer parameters which were extracted from spectra of small grain size samples only, namely, B-170 to B-pan.

It should be noted that the best fits to the spectra are obtained when the extracted position and width parameters for the B-B' and the D-D' are identical, which is also consistent with known parameter values for these two doublets.

3.2. ANALYSIS OF RESULTS

3.2.1. Coloured phase samples (A-Black)

Seven doublets have been fitted for this sample as shown in Fig. 2 and in Table 2 where the corresponding Mössbauer parameters are also listed. The two doublets A-A' ($\delta = 1.15$ mm/s, $\Delta = 2.43$ mm/s) and B-B' ($\delta = 0.34$ mm/s, $\Delta = 0.6$ mm/s) were assigned to Fe²⁺ and Fe³⁺ in hornblende, respectively.

The chemical formula of hornblende (Deer *et al.* 1963) has the general form $\{x = \text{Ca, Na, K}\}_{2-3}(\text{Y} = \text{Mg, Fe}^{2+}, \text{Fe}^{3+}, \text{Mn, Al})_5[\text{Al, Si}]_8\text{O}_{22}(\text{OH})_2$. Its crystal structure consists (Bancroft *et al.* 1967b) of double chains of SiO₄ which are linked by the cations. There are three positions for cations of six-fold coordination (Y-cations) named M(1), M(2) and M(3), whereas the eight-fold coordination cations (X-cations) occupy M(4) position. Further, Fe²⁺ and Fe³⁺ ions occupy the three sites M(1), M(2) and M(3) with some preference of Fe³⁺ for M(2) site. The Mössbauer parameters obtained in this work for the doublets A-A' and B-B' fall well within the respective ranges of Fe²⁺ and Fe³⁺ in six-fold coordination sites in silicate minerals (Bancroft *et al.* 1967a). Further, these parameters agree well with those measured by Burns & Greaves (1971) for Hastingsite amphibolite, whose composition is known from chemical analysis to be similar to that of hornblende in Kuwaiti sand.

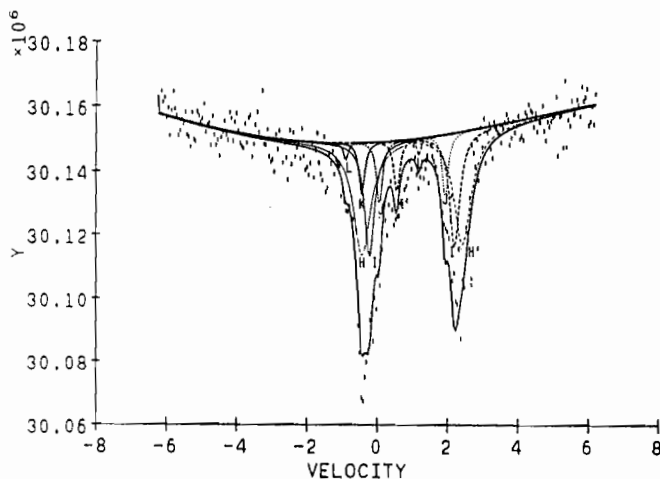


Fig. 3. Measured and fitted Mössbauer spectrum for the A-Green sample.

Two other doublets observed in the A-black spectrum, namely, C-C' ($\delta = 1.06$ mm/s, $\Delta = 0.71$ mm/s) and D-D' ($\delta = 0.34$ mm/s, $\Delta = 0.64$ mm/s) can be safely identified with Fe^{3+} and Fe^{2+} in ilmenite, respectively. The chemical formula of ilmenite may be expressed (Deer *et al.* 1963) as $(\text{Fe}, \text{Mg}, \text{Mn})\text{TiO}_3$, where the amounts of Mg and Mn are small compared to Fe; its crystal structure consists (Raymond & Wenk 1971) of successive layers of oxygen ions and layers of iron and titanium. The oxygen ions are arranged in a distorted hexagonal packing while successive cation layers contain equal number of iron and titanium ions all in six-fold coordination. Ti^{4+} occupies both M(1) and M(2) sites while Fe^{2+} and Fe^{3+} predominantly occupy the M(1) site. The two sites M(1) and M(2) have distorted octahedral symmetry. The M(1) site is equally occupied by Fe^{2+} and Fe^{3+} .

The measured values for these doublets are within ranges of values reported for ilmenite. More specifically, they are in agreement with the results of studies by Gibb *et al.* (1969) on twenty-two ilmenite samples from different locations throughout the world. They assigned for ilmenite Mössbauer parameters of $\delta = 1.09$ mm/s and $\Delta = 0.71$ mm/s for Fe^{2+} and $\delta = 0.36$ mm/s and $\Delta = 0.67$ mm/s for Fe^{3+} .

The remaining doublets which have been identified in the A-Black spectrum, namely E-E', F-F' and G-G', can all be assigned to Fe^{2+} and Fe^{3+} in magnetite. The crystal structure of magnetite at room temperature is an inverse spinel with each unit cell containing thirty-two oxygen ions in an fcc arrangement. There are sixty-four sites with tetrahedral symmetry which are denoted as A-sites and thirty-two with octahedral symmetry which are denoted as B-sites. The A-sites are occupied by Fe^{3+} ions while the B-sites are equivalently occupied by Fe^{2+} and Fe^{3+} ions. Since magnetite is cubic, the quadrupole splitting is zero and the spectrum consists of two superimposed six-line patterns due to Fe^{3+} (A) and to $\text{Fe}^{2+,3+}$ (B) due to the magnetic splitting of the nuclear levels caused by the internal magnetic field in magnetite.

In this work the E-E' and F-F' which have the common isomer shift value of 0.65 mm/s are identified with $\text{Fe}^{2+,3+}$ (B). These values are in excellent agreement with the isomer shift value of 0.65 ± 0.02 mm/s obtained by Evans & Hafner (1969) in their studies on magnetite at different temperatures.

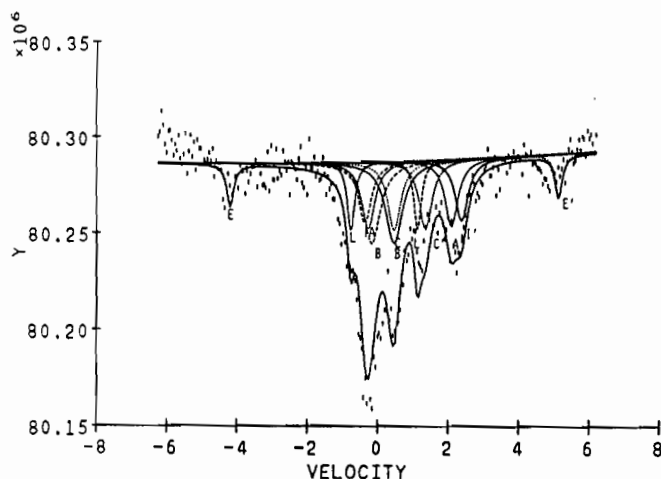


Fig. 4. Measured and fitted Mössbauer spectrum for the B-pan sample.

The remaining B-site doublet does not appear in the spectrum because the locations of its members, expected at 8.2 mm/s and -7.7 mm/s (Webner & Hafner 1971), lie outside the range of velocities covered in this experiment which is within ± 6.1 mm/s. As for the A-sites, only one doublet, namely G-G', is assigned to Fe^{3+} (A). The members of one of the other two doublets are expected (Webner & Hafner 1971) to occur at velocities outside the range covered in this experiment while the remaining third doublet is not resolved due to its low intensity. The measured isomer shift of G-G' is 0.32 mm/s which is in reasonable agreement with the value 0.25 ± 0.02 mm/s obtained by Evans & Hafner (1969) considering the relatively low intensity of this doublet. The small amount of magnetite detected in the A-Black sample is probably due to the attachment of magnetite grains to the tweezers during the handpicking separation of the A-Black grains.

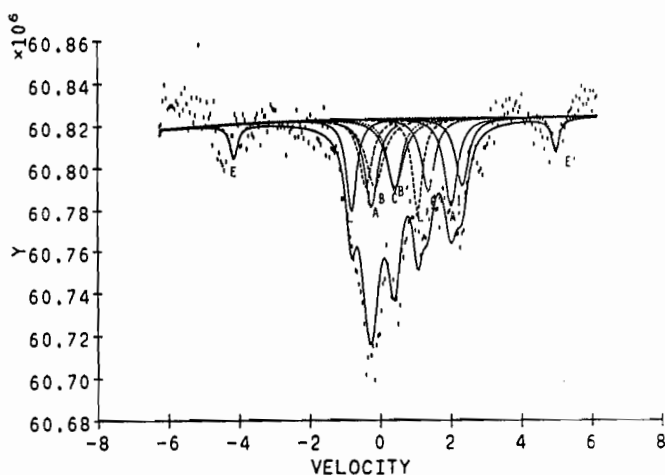
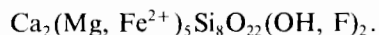


Fig. 5. Measured and fitted Mössbauer spectrum for the B-325 sample.

3.2.2. Coloured samples (A-Green)

Of the five doublets identified in the A-Green spectrum as shown in Fig. 3, three doublets, namely H-H', I-I' and J-J' have, within experimental error, the same isomer shift value of 1.18 ± 0.01 mm/s and quadrupole splitting values of 2.85, 2.41 and 1.86 mm/s, respectively. These doublets are assigned to Fe^{2+} in actinolites. The doublet K-K' has a measured δ value of 0.24 mm/s and $\Delta = 0.99$ mm/s and is assigned to Fe^{3+} in actinolites.

Actinolite, whose crystal structure as described by Zussman (1955) is the same as that of amphibole, has the typical formula



It consists of double chains of SiO_4 groups linked by bands of cations which occupy four distinct positions of six-fold coordination usually designated M(1), M(2), M(3) and M(4). More detailed description of the amphibole crystal structure can be found elsewhere (Bancroft *et al.* 1967b). In this work the doublets H-H', I-I' and J-J' are assigned to Fe^{2+} in the sites M(1), M(2) and M(3), respectively. The doublet K-K' is assigned to Fe^{3+} ions which are concentrated in the M(2) site. These assignments are in agreement with previous work by Burns & Greaves (1971) who also resolved and identified the same four doublets as shown in Table 5. The present work is also consistent with that of Bancroft *et al.* (1967a) who resolved and identified two doublets only. The first which has measured values of $\delta = 1.22$ mm/s and $\Delta = 1.89$ mm/s clearly corresponds to H-H' in this work. The other doublet has measured values of $\delta = 1.24$ mm/s and $\Delta = 2.82$ mm/s and most likely corresponds to an unresolved combination of I-I' and J-J'.

The large value of the quadrupole splitting for the H-H' doublet ($\Delta = 2.85$ mm/s) is an indication of the large distortion in the M(2) site. The weakness of the J-J' doublet and the strong occurrence of the K-K' doublet give evidence of the weak concentration of Fe^{2+} in the M(2) site which, as mentioned earlier, is mainly occupied by Fe^{3+} cations. This difference between the concentrations of Fe^{3+} and Fe^{2+} ions in the M(2) site was explained by Burns & Greaves (1971) using chemical arguments.

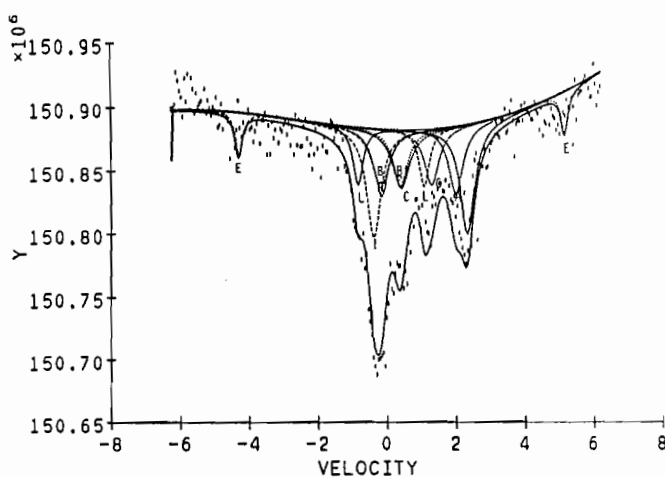


Fig. 6. Measured and fitted Mössbauer spectrum for the B-230 sample.

Table 5. Comparison of the Mössbauer parameters obtained in the present experiment with previous work.

Oxidation state	Compound	Present Work		Previous Work (1)		Previous Work (2)		Previous Work (3)	
		δ (mm/s)	Δ (mm/s)	δ (mm/s)	Δ (mm/s)	δ (mm/s)	Δ (mm/s)	δ (mm/s)	Δ (mm/s)
Fe^{3+}	Hornblende	0.34	0.64	0.38	0.65	—	—	—	—
	Ilmenite	0.34	0.64	0.36	0.67	—	—	—	—
	Actinolites	0.24	0.99	0.28	0.53	—	—	—	—
	Epidote	0.32	2.08	0.33	2.01	0.35	2.02	0.35	2.01
Fe^{+2}	Hornblende	1.14	2.46	1.11	2.71	—	—	—	—
	Ilmenite	1.09	0.63	1.09	0.71	1.07	0.70	—	—
	Actinolites	1.18	2.85	1.14	2.89	1.24	2.82	—	—
		1.18	2.41	1.12	2.57	—	—	—	—
Fe^{3+}, Fe^{+2}	Magnetite	0.65	1.86	1.14	1.91	1.22	1.89	—	—
		0.32	0	0.65	0	—	—	—	—
				0.25	0	—	—	—	—

The remaining doublet L-L' in the spectrum of the A-Green sample shown in Fig. 2, which has an isomer value of 0.32 mm/s and a quadrupole splitting of 2.08 mm/s, is assigned to Fe³⁺ in epidote whose typical chemical formula can be written as



The crystal structure of epidote consists (Bancroft *et al.* 1967b) of chains of AlO₆ and AlO₄(OH)₂ octahedra linked by independent SiO₄ and SiO₇ groups. These are bound in turn by (Al, Fe) in six-fold coordination and by Ca in two positions of six to tenfold coordination. The (Al, Fe)O₆ site has variable metal-oxygen distances and is compressed along one axis. The value of the quadrupole splitting of epidote is one of the largest observed for a high spin Fe³⁺ compound. This large value is consistent with Fe³⁺ being located in the most distorted (Al, Fe)O₆ site. Values of $\delta = 0.33$ mm/s and $\Delta = 2.01$ mm/s, obtained by Bancroft & Burns (1966) were assigned to an Fe³⁺ in distorted six-fold coordination (Al, Fe)O₆ site in epidote. As can be seen from Table 5 this is in excellent agreement with the values obtained in the present work. Further, both results are in agreement with those of earlier work done on epidote (Bancroft & Burns 1966; Bancroft *et al.* 1967a).

3.2.3. Fine-sized grain samples (B-Pan, B-325, B-230, B-170)

The spectra for the fine-sized grain samples (B-Pan, B-325, B-230, B-170) are shown in Figs 4-7 where it is seen that only the doublets A-A', B-B', C-C', D-D', H-H' and L-L' are well resolved. No attempt was made to identify the weaker doublets as no additional information would be gained. It is worth noting that the measured values of the parameters δ , Δ and Fe²⁺/Fe³⁺ are constant within the range of experimental error. Fe²⁺/Fe³⁺ has an average value of 1.82 ± 0.01 for hornblende and 1.70 ± 0.01 for ilmenite, both being in very good agreement with values obtained from the analysis of the coloured phase samples. All average values of the Mössbauer parameters obtained for different grain size samples are compared in Table 6 with the corresponding values obtained for the colour phase samples. It will be noted that the two sets of results are in good agreement.

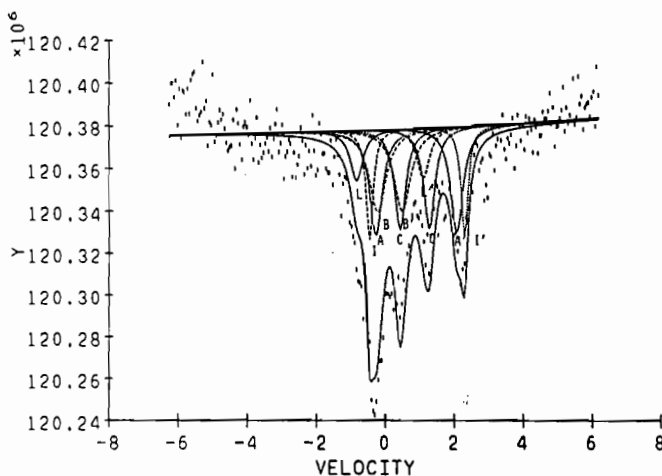


Fig. 7. Measured and fitted Mössbauer spectrum for the B-170 sample.

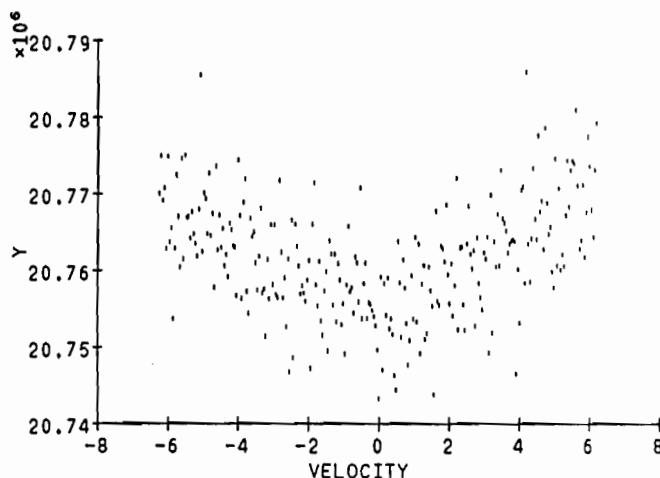


Fig. 8. Measured and fitted Mössbauer spectrum for the B-45 sample.

3.2.4. Large-sized grain samples (B-45, B-60, B-80)

Spectra for the samples B-45, B-60 and B-80 are shown in Fig. 8. No attempt was made to resolve the doublets as the absorption peaks are very weak. This is consistent with the suggestion by previous work (Abu-Eid & Mansoor 1985) that the content of iron in the large-sized grains is very small and is confined to thin rims which coat the quartz grains. Further quantitative evidence is provided by the results of chemical analysis of the same samples used in this work. As shown in Table 7, the total content of iron is less than 1% for each of the three large grain size samples. Fig. 8 gives, however, qualitative evidence for stronger absorption at velocities of about 0.1 and 0.5 mm/s which could correspond to a Mössbauer doublet of $\delta = 0.4$ mm/s and $\Delta = 0.65$ mm/s. This can be tentatively identified with Fe^{3+} in clay minerals such as

Table 6. Comparison of Mössbauer parameters obtained from measurements using grain size samples with those using colour phase samples.

Samples	Colour phase samples		Grain size samples	
	δ (mm/s)	Δ (mm/s)	$\langle\delta\rangle \pm \sigma_n$ (mm/s)	$\langle\Delta\rangle \pm \sigma_n$ (mm/s)
A-A'	1.14	2.46	1.07 ± 0.02	2.32 ± 0.08
B-B'	0.34	0.64	0.33 ± 0.02	0.64 ± 0.04
D-D'	1.09	0.63	1.05 ± 0.04	0.89 ± 0.09
E-E'	0.63	0	0.63 ± 0.01	0
H-H'	1.18	2.85	1.16 ± 0.03	2.76 ± 0.06
L-L'	0.32	2.08	0.34 ± 0.02	1.94 ± 0.09
$\text{Fe}^{2+}/\text{Fe}^{3+}$ (Hornblende)	1.855		1.819 ± 0.011	
$\text{Fe}^{2+}/\text{Fe}^{3+}$ (Ilmenite)	1.695		1.700 ± 0.010	

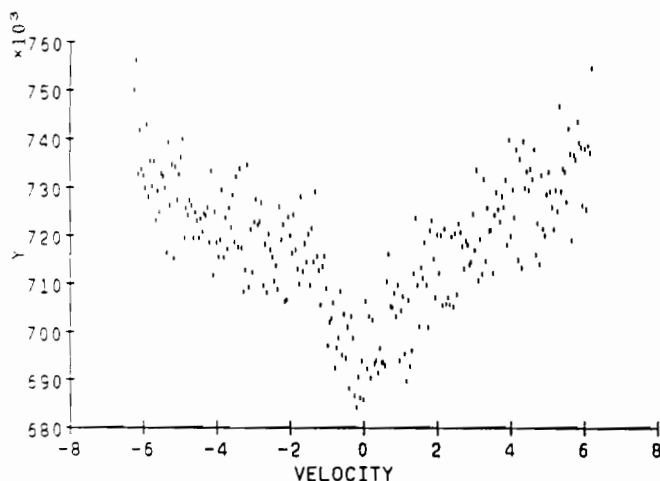


Fig. 9. Measured and fitted Mössbauer spectrum for the B-120 sample.

illite and kaolinites. There is also qualitative evidence for another doublet which can be tentatively identified with $\delta = 1.13$ and $\Delta = 2.68$ mm/s; this could correspond to Fe^{2+} in clay minerals as was reported by Rozenson *et al.* (1979). Detailed study of thin rim coatings of quartz grains conducted by Abu-Eid & Mansoor (1985) indicated that each quartz grain was surrounded by a thin rim of clay minerals of varying thickness in the range 1–10 μm .

3.2.5. Intermediate-sized grain samples (B-120)

The spectrum for the sample B-120 shown in Fig. 9 gives an example of an intermediate grain size sample where recognizable absorption doublets start to emerge. It suggests a combination of absorption peaks, albeit weak, from iron-bearing phases as well as rims of clay minerals. The total iron content of this sample is 1.13% (Table 7). This is consistent with the criterion suggested by Burns & Greaves (1971) that the iron concentration of a specimen should exceed 1% in order to be detected by the Mössbauer technique.

Table 7. Results of (ICP-OES) chemical analysis performed on the grain size samples.

Mesh No.	Grain size (μm)	Fe_2O_3 %
45	355	0.19
60	250	0.27
80	180	0.54
120	125	1.13
170	90	3.50
230	63	4.20
+ 325	45	6.40
- 325	< 45	7.50

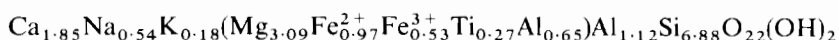
Table 8. Results of electron probe microanalysis of the colour phase samples.

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	V ₂ O ₅	MnO	FeO	Fe ₂ O ₃	H ₂ O	Total
Hornblende	1.58	14.17	9.91	47.00	0.44	11.67	2.28	0.16	0.20	8.13	4.52	—	100.06
Ilmenite	0.03	0.11	0.06	0.18	0.00	0.05	51.23	1.59	2.76	27.37	17.56	—	100.94
Actinolites	1.32	18.38	5.00	52.52	0.32	13.11	0.12	0.05	0.17	9.07	0.62	—	100.68
Epidote	0.78	0.92	22.94	35.89	0.13	22.70	0.08	0.05	0.33	—	13.03	2.00	98.85

SUMMARY AND CONCLUSION

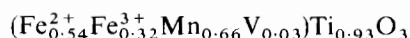
Using the Mössbauer technique it was possible to identify five major independent iron-bearing phases in Kuwaiti sand. These essentially occur in the fine grains of the sand while the coarse grains are coated with clay minerals and contain very little iron-bearing phases. The identified phases are hornblende, ilmenite, actinolite, epidote and magnetite. This is in general agreement with the results of chemical analysis carried out on the same samples. It is also in general agreement with the results obtained previously by Abu-Eid *et al.* (1983) using X-ray diffraction, optical microscopy and electron probe microanalysis.

The hornblende phase was found with an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 1.86 in the A-Black sample and a mean value of 1.82 ± 0.01 for all the various grain size samples. Using the information in Table 8 and an average value of 1.84 for the $\text{Fe}^{2+}/\text{Fe}^{3+}$, the following chemical formula for the hornblende is obtained



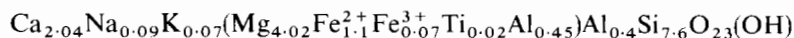
The total number of cations in this formula was normalized to 24 as given by the general formula for hornblende.

The ilmenite phase was found with an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 1.7 in the A-Black sample and an average ratio of 1.7 ± 0.01 as the mean value for the grain size samples. Repeating the same method used for hornblende the following formula was obtained for ilmenite:



where the total number of cations was normalized to three and an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 1.7 was adopted.

The third major phase found was actinolite which is characterized by the predominance of Fe^{2+} over Fe^{3+} ions as shown in Table 8. The obtained formula is



The last major phase found was epidote where all the iron is in the +3 oxidation state. The formula obtained is



where the number of cations was normalized to 13.

It will be noted that the relative numbers of the various cations obtained for each of the four phases are within the ranges given by the general formula for that phase.

It is worth mentioning that the chemical composition obtained for hornblende in Kuwaiti sand is similar to that obtained by Burns & Greaves (1971) for Hastingsite amphibolite. Further, the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ obtained for ilmenite in Kuwaiti sand is similar to that of Australian ilmenites.

REFERENCES

- Abu-Eid, R.M., Al-Sayed, M.I. & Salman, A.S. 1983. Chemical and geochemical studies of the sand and clay in Kuwait for industrial utilization. Kuwait Institute for Scientific Research, Report No. KISR, 972, Kuwait.
- Abu-Eid, R.M. & Mansoor, S.A. 1985. Characterization of thin irons on aeolian sand grains. Kuwait Institute for Scientific Research, Report No. KISR 2412, Kuwait.

- Bancroft, G.M. & Burns, R.G. 1966.** Applications of the Mössbauer effect to mineralogy, in "Papers from the Proceedings of the General Meeting of the International Mineralogical Association, 5th" (Cambridge, 1966) (Mineralogical Society, London, 1968) pp. 36–42.
- Bancroft, G.M., Maddock, A.G. & Burns, R.G. 1967a.** Applications of the Mössbauer effect to silicate mineralogy, I. Iron silicates of known crystal structure. *Geochimica et Cosmochimica Acta* **31**: 2219–46.
- Bancroft, G.M., Maddock, A.G., Ong, W.K., Price, R.H. & Stone, A.J. 1967b.** Mössbauer spectra of iron (III) diketone complexes. *Journal of the Chemical Society A*: 1966–71.
- Burns, R.G. & Greaves, C. 1971.** Correlations of infrared and Mössbauer site population measurements of actinolites. *American Mineralogist* **56**: 2010–33.
- Deer, W.A., Howie, R.A. & Zussman, J. 1963.** An introduction to the rock forming minerals. John Wiley, New York.
- Evans, B.G. & Hafner, S.S. 1969.** FES7 Hyperfine fields in magnetite (FE304). *Journal of Applied Physics* **40**: 1411–13.
- Gibb, T.C., Greenwood, N.N. & Twist, W. 1969.** The Mössbauer spectra of natural illmenites. *Journal of Inorganic and Nuclear Chemistry* **39**: 947–54.
- Raymond, K.W. & Wenk, H.R. 1971.** Lurnar illmenite (Refinement of the crystal structure). *Contributions to Mineralogy and Petrology* **30**: 135–40.
- Rozenson, I., Bauninges, E.R. & Kallai, L. 1979.** Mössbauer spectra of iron in 1:1 phyllosilicates. *American Mineralogist* **64**: 893–901.
- Webner, H. & Hafner, S.S. 1971.** Vacancy distribution in non-stoichiometric magnetites. *Zeitschrift für Kristallographie* **133**: 327–40.
- Zussman, J. 1955.** The crystal structure of an actinolite. *Acta Crystallographica* **8**: 301–08.

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تعيين مركبات الحديد في ترسبات الرمل السطحية في الكويت باستعمال أطياف موسباور

راساء واصف و عصام النقيب قسم الفيزياء بجامعة الكويت ، ص . ب . ٥٩٦٩ ، الصفاة ١٣٠٦٠ ، الكويت	راتب ابوعيد معهد الكويت للابحاث العلمية ، ص . ب . ٢٤٨٨٥ ، الصفاة ١٣١٠٩ ، الكويت
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خلاصة

أخذت أطياف موسباور عند درجة حرارة الغرفة لعدة عينات من الرمل ، من موقعين في الكويت ، تم تحضيرها من العينات الخام عن طريق فرزها تبعا للون او تبعا لحجم الحبيبات الرملية . وقد تم مطابقة قمم أطياف الامتصاص بتابع ذي شكل لورنتزي باستعمال أسلوب المربعات الدنيا . وقد تبين وجود خمسة مزدوجات امتصاص في العينات ذات اللون الاخضر ، وبالإستناد الى القيم التي تم استخراجها للإنزياح الكيميائي والإنشقاق الرباعي القطبي فقد تم التعرف على مركبي حديد اساسيين هما الأكتينوليت والإبيدوت . وقد لوحظ وجود سبعة مزدوجات امتصاص في أطياف العينات ذات اللون الأسود ، وبالإستناد الى القيم التي تم استخراجها للإنزياح الكيميائي والإنشقاق الرباعي القطبي فقد تم التعرف على ثلاثة مركبات حديد أساسية هي الهورنبلند والإلمنيت والماجنتيت . وقد قاد تحليل أطياف العينات ذات الحجم الحبيبية المختلفة إلى تأكيد ما تم التوصل اليه سابقا من أن المركبات الحديدية تتواجد بوفرة في الحبيبات الناعمة التي يقل قطرها عن ٨٨ ميكرومتر ، وان تواجدها يزداد مع تناقص حجم الحبيبات . وقد وجد ان نسبة Fe^{2+}/Fe^{3+} في الهورنبلند والإلمنيت تبلغ ١,٨٦ و ١,٧ على التوالي . وقد تم الحصول على نفس هذه النسب ، ضمن هامش الخطأ التجريبي ، من أطياف العينات ذات الحجم الحبيبية المختلفة .

ومن خلال جمع نتائج قياسات موسباور مع قياسات جديدة أجريت على نفس العينات باستعمال التحليل الدقيق للكشف الإلكتروني فقد تم التوصل الى تحديد الصيغ الكيميائية التالية لمركبات الحديد في العينات المدروسة .

$Ca_{1.85}Na_{0.54}K_{0.18}(Mg_{3.09}Fe^{2+}_{0.97}Fe^{3+}_{0.53}Ti_{0.27}Al_{0.65})Al_{1.12}Si_{6.88}O_{22}(OH)_2$;	الهورنبلند
$(Fe^{2+}_{0.54}Fe^{3+}_{0.32}Mn_{0.06}V_{0.03})Ti_{0.93}O_3$;	الإلمنيت
$Ca_{2.04}Na_{0.09}K_{0.09}(Mg_{4.02}Fe^{2+}_{1.1}Fe^{3+}_{0.07}Ti_{0.02}Al_{0.45})Al_{0.4}Si_{7.6}O_{23}(OH)$;	الاكتينوليت
$Ca_{1.95}Na_{0.12}K_{0.01}Mg_{0.11}Ti_{0.01}V_{0.01}(Fe^{3+}_{0.79}Al_{2.16})OH Si_2O_7 SiO_4$	الإبيدوت

