Oxidation states and site symmetries of iron in ilvaite using Mössbauer spectrometry.

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The Mössbauer spectrum of ilvaite has been measured at room temperature, and indicates the presence of both high-spin ferrous and ferric iron. Two distinguishable ferrous sites are detected, with the proportion of Fe^{2+} ions differing by about 20 %. The ferric site is highly distorted.

Ilvaite (or lievrite) is a silicate mineral containing iron in both the ferrous and ferric oxidation states. The chemical composition is represented by the formula $CaFe_2^{2+}Fe^{3+}(SiO_4)_2OH$. Independent investigations of the crystal structure by X-ray diffraction methods have led to diverse results (Belov & Mokeeva, 1951; Ito, 1950).

One structure, proposed by Ito (1950), resembles the structure of the olivine group and is based on a hexagonal close-packed oxygen framework. This structure contains independent SiO_4 groups held together by Ca and Fe^{2+} ions and $Fe^{3+}OH$ groups. In this structure, the ferrous ions are octahedrally coordinated to oxygen, while the ferric ions are reported to have an unusual fivefold coordination to four oxygen atoms and one OH group.

An alternative structure proposed by Belov & Mokeeva (1951) does not contain the independent SiO_4 groups of an orthosilicate, but instead contains Si_2O_7 groups. These authors reject the fivefold coordination of the ferric ions in favor of octahedral coordination. This results in both the Fe^{2+} and Fe^{3+} ions being octahedrally coordinated to oxygen atoms. The similarity of the infrared spectrum of ilvaite to that of a sorosilicate rather than that of a neso-silicate (Krause, 1960) tends to support this latter proposed structure.

Mössbauer spectrometry permits the selective study of iron atoms in a crystal. It usually provides some separation between the ferrous and ferric contributions and often provides a separation of the contributions of atoms of the same oxidation state at different lattice sites. This makes it an appropriate method with which to extend the investigation of this mineral.

The ilvaite specimens were obtained from Southwest Scientific Company, Hamilton, Montana, and originated at Rio Marina, Island of Elba. Samples of the mineral were ground to powders of 200 mesh or finer. Absorbers were prepared either by forming hot molded lucite discs from uniformly mixed powders of lucite and the mineral or by compacting the mineral powder in a holder between thin
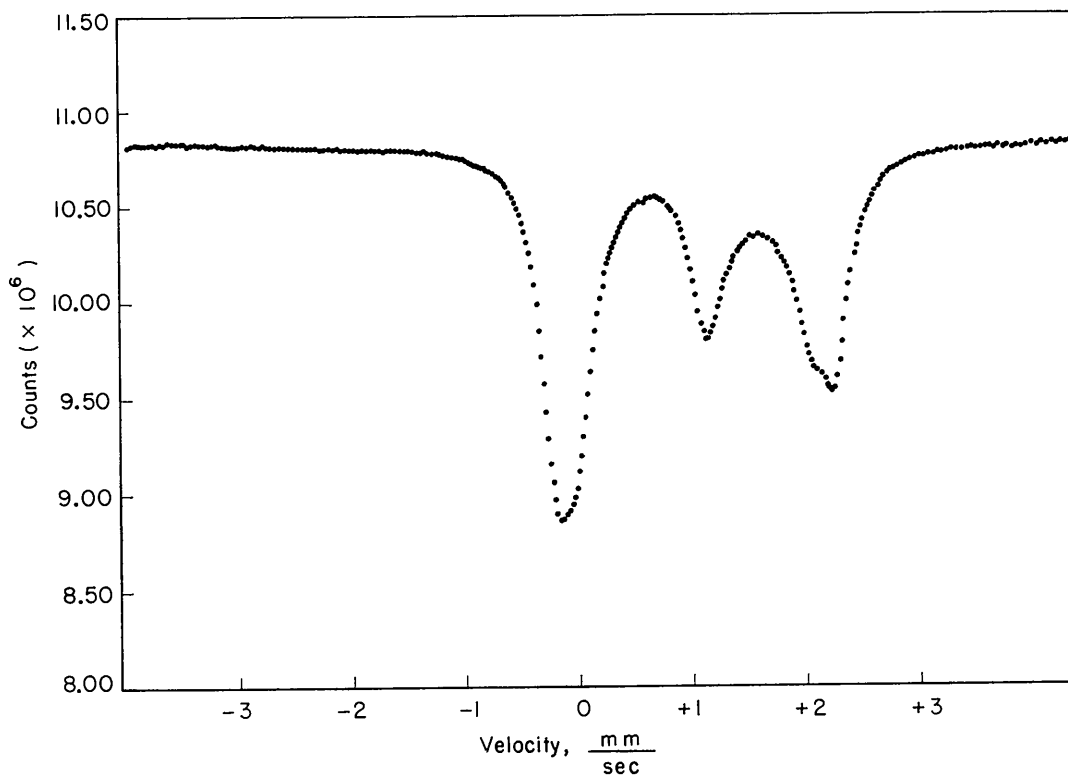

Fig. 1. Mössbauer hyperfine absorption spectrum of ilvaite.

lucite windows. Absorbers of thicknesses up to approximately 47 mg.cm^{-2} of ilvaite were prepared (corresponding to a nominal 19 mg.cm^{-2} thickness of natural iron). Both sources and absorbers were maintained at room temperature throughout the measurements. A number of separate measurements were taken using different instrumentation and radioactive sources. Fig. 1 shows a spectrum measured using an Austin Science Associates spectrometer and a 50 millicurie source of ^{57}Co in copper foil. This gave a minimum line width of 0·24 mm.sec^{-1} with a half-mil iron absorber. Parameters are reported with respect to the center of the iron spectrum.

All spectra measured for ilvaite exhibited the characteristic features of Fig. 1. They are qualitatively similar to spectra which we have measured for other paramagnetic minerals containing both ferric and ferrous iron. The spectrum is produced by the individual electric quadrupole doublet spectra characteristic of iron at the different lattice sites. The lower velocity members of the electric quadrupole doublets are superimposed upon one another near −0·1 mm.sec^{-1} and this produces the largest of the three absorption regions. The absorption region centered at +1·13 mm.sec^{-1} is produced by the upper member of a ferric doublet. The highest velocity absorption near +2·1 to +2·2 mm.sec^{-1} is produced by the upper members of ferrous doublets.

From the shape of the absorption region near +2·1 to +2·2 mm.sec^{-1}, it is obvious that there is more than one contribution present from the ferrous iron in ilvaite. This region appears to originate from the superposition of two partially resolved peaks located at approximately +2·07 mm.sec^{-1} and +2·25 mm.sec^{-1}, respectively. The most intense absorption region near zero velocity evidently is the result of a superimposition, as it shows excess peak broadening and a shape indicative of superposed peaks. Thus, Mössbauer spectrometry indicates that at least two physically distinct ferrous sites are present in the ilvaite crystal. It is not possible to establish which of the contributing peaks in the vicinity of zero velocity is associated with which of the upper peaks on the basis of these measurements alone. We have therefore extracted approximate ferrous parameters using the mean location of the lower members of the doublets.

The Mössbauer parameters obtained for the two ferrous absorption doublets are as follows: for the first isomer shift (with respect to iron), +0·98 ± 0·08 mm.sec^{-1}; electric quadrupole splitting (twice the nuclear level shift), 2·18 ± 0·14 mm.sec^{-1}; and for the second isomer shift, +1·07 ± 0·08 mm.sec^{-1}; electric quadrupole splitting, 2·36 ± 0·14 mm.sec^{-1}.

The Mössbauer parameters obtained in a similar fashion for the ferric absorption are as follows: isomer shift, +0·51 ± 0·08 mm.sec^{-1}; electric quadrupole splitting, 1·24 ± 0·14 mm.sec^{-1}. The large magnitude of the quoted errors reflects the problem of identifying the associated unresolved lower velocity peaks.

Some insight into the nature of the sites occupied by the iron may be obtained by comparing the observed Mössbauer parameters with previous measurements of iron silicates of known crystal structure (Bancroft, Maddock & Burns, 1967; Bancroft, Burns & Maddock, 1967; Heizenberg, Riley & Lamoreaux, 1968; Ghose & Hafner, 1967). For the case of the ferrous absorption in ilvaite, the isomer shifts are in the range characteristic of high-spin ferrous iron. They are a little smaller than is typical for high-spin

ferrous iron in octahedral coordination in the silicates, possibly because of less ionic bonding. The large ferrous electric quadrupole splittings are typical for high-spin ferrous iron octahedrally coordinated in the silicates. Our results for the ferrous absorption indicate that the ferrous iron is in the high-spin state, and the magnitudes of the parameters are compatible with octahedral coordination in an oxygen invironment. Two distinct sites for ferrous iron are present.

The absorption spectrum of the ferric iron in this crystal is rather unusual, and no previous Mössbauer measurements have been reported for a case of fivefold coordination of iron in silicate minerals with which these results can be compared. The observed isomer shift of the ferric absorption is typical for high-spin ferric iron in sixfold coordination to oxygen in the silicates, in agreement with what would be expected on the basis of the structure proposed by Belov & Mokeeva (1967). However, the electric quadrupole splitting is anomalously large. The magnitude of the electric quadrupole splitting is beyond the range containing most observed cases of high-spin ferric iron in silicates. This large value of the electric quadrupole splitting provides evidence that the Fe^{3+} is located in a site of low actual symmetry. To our knowledge, the only case of larger electric quadrupole splitting for high-spin ferric iron in a silicate mineral is in epidote, where the ferric ions are believed to occupy irregular, axially compressed oxygen octahedra (Bancroft, Maddock & Burns, 1967). The spectrum of the ferric iron in ilvaite thus appears to be compatible with the Fe^{3+} occupying an appreciably distorted octahedral site. However, in the absence of further information, fivefold coordination is not entirely ruled out by these results.

Estimates of the ratio of ferric to ferrous iron in the mineral sample, and of the proportion of ferrous ions in the two different ferrous sites, may be obtained from a comparison of the areas of absorption of the corresponding component spectra. Interpretation is complicated by a lack of knowledge of the values of the resonant fractions at the various sites and by the possible differences of intensity of the members of each doublet. Such estimates are therefore somewhat inaccurate, particularly in cases such as this where incompletely resolved peaks are present.

A comparison of the higher velocity members of the ferrous doublets indicates that the population ratio of the two distinguishable sites is approximately 0·8 to 1. Since it has been shown previously that the site population data obtainable by Mössbauer spectrometry in certain other minerals can be correlated with the temperatures and pressures of mineral formation (Bancroft & Burns, 1967; Ghose & Hafner, 1967), it is possible that this particular ratio in ilvaite may be indicative of its thermal history.

Comparison of the total higher velocity ferrous absorption to the higher velocity ferric absorption yields a ratio of about 1·6 to 1. This is considerably less than would be anticipated on the basis of the nominal chemical composition, and is probably accounted for by the partial substitution of Mn for Fe^{2+} in the mineral (Ito, 1950; Hey, 1955). Such a substitution is consistent with our interpretation of the relative intensities of the ferrous peaks.

The total absorption by the lower velocity superimposed peak is about ten per cent less than the total absorption by all of the higher velocity peaks. This suggests that relative intensity asymmetry effects are present but are minor, and therefore that the estimated ratios are roughly correct.

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Coherent neutron-scattering amplitudes. By THE NEUTRON DIFFRACTION COMMISSION*

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An up to date Table of coherent neutron scattering amplitudes is presented.

The following list of amplitudes is published on behalf of the Neutron Diffraction Commission. For brevity, references to the original sources of information are only given in the case of recently communicated data. The Chairman of the Commission* would be glad to hear from any readers who dispute the accuracy of any of these values and are able to provide new or improved information.

Table 1. *Coherent neutron scattering amplitudes*, b, *in units of* 10^{-12} cm

Complex amplitudes are for a wavelength of 1 Å.

Z	Element or isotope	b	Z	Element or isotope	b
1	^{1}H	-0.372[1]	19	K	0.37[14]
	^{2}H	0.621[2]		^{39}K	0.37[15]
	^{3}H	0.471[9]	20	Ca	0.49
2	^{4}He	0.30		^{40}Ca	0.49
3	Li	-0.194[3]		^{44}Ca	0.18
	^{6}Li	$0.18+0.025i$[4]	21	^{45}Sc	1.18
	^{7}Li	-0.21[5]	22	Ti	-0.34
4	^{9}Be	0.774		^{46}Ti	0.48
5	B	$0.54+0.021i$[4]		^{47}Ti	0.33
	^{11}B	0.60[6]		^{48}Ti	-0.58
6	^{12}C	0.665[1]		^{49}Ti	0.08
	^{13}C	0.60		^{50}Ti	0.55
7	^{14}N	0.94	23	V	-0.05
8	^{16}O	0.577	24	Cr	0.352
	^{17}O	0.578[7]		^{52}Cr	0.490
	^{18}O	0.600[8]	25	^{55}Mn	-0.36
9	^{19}F	0.55	26	Fe	0.95[16]
10	Ne	0.46[9]		^{54}Fe	0.42
11	^{23}Na	0.35[1]		^{56}Fe	1.01
12	Mg	0.52[10]		^{57}Fe	0.23
13	^{27}Al	0.35	27	^{59}Co	0.25[17]
14	Si	0.42	28	Ni	1.03
15	^{31}P	0.51[11]		^{58}Ni	1.44
16	^{32}S	0.28[12]		^{60}Ni	0.30
17	Cl	0.96[1]		^{61}Ni	0.76[18]
	^{35}Cl	1.18[13]		^{62}Ni	-0.87
	^{37}Cl	0.26[13]		^{64}Ni	-0.037[18]
18	^{40}A	0.20			

Table 1 (cont.)

Z	Element or isotope	b	Z	Element or isotope	b
29	Cu	0.76[15]	52	^{124}Te	0.55
	^{63}Cu	0.67		^{125}Te	0.56
	^{65}Cu	1.11	53	^{127}I	0.52
30	Zn	0.57[15]	54	Xe	0.47[30]
	^{64}Zn	0.55[15]	55	^{133}Cs	0.75[15]
	^{66}Zn	0.63[15]	56	Ba	0.52
	^{68}Zn	0.67[15]	57	^{139}La	0.83
31	Ga	0.72[20]	58	Ce	0.46
32	Ge	0.84		^{140}Ce	0.47
33	As	0.64[20]		^{142}Ce	0.45
34	Se	0.78[21]	59	^{141}Pr	0.44
35	Br	0.67	60	Nd	0.72
36	Kr	0.74[22]		^{142}Nd	0.77
37	Rb	0.85		^{144}Nd	0.28
	^{85}Rb	0.83		^{146}Nd	0.87
38	Sr	0.656[24]	62	^{152}Sm	-0.5
39	^{89}Y	0.79[25]		^{154}Sm	0.8
40	Zr	0.694[2]	63	Eu	0.55[32]
41	^{93}Nb	0.69	64	Gd	1.5[33]
42	Mo	0.66	65	Tb	0.76[34]
43	Tc	0.68[26]	66	Dy	1.69[35]
44	Ru	0.73		^{160}Dy	0.67[35]
45	Rh	0.59		^{161}Dy	1.03[35]
46	Pd	0.60[27]		^{162}Dy	-0.14[35]
47	Ag	0.61		^{163}Dy	0.50[35]
	^{107}Ag	0.83		^{164}Dy	4.94[35]
	^{109}Ag	0.43	67	^{165}Ho	0.85
48	Cd	$0.37+0.16i$[4]	68	Er	0.79
	^{113}Cd	$-1.5+1.2i$[28]	69	^{169}Tm	0.69[36]
49	In	0.39[20]	70	Yb	1.26[37]
50	Sn	0.61	71	Lu	0.73[37]
	^{116}Sn	0.58[29]	72	Hf	0.78[38]
	^{117}Sn	0.64[29]	73	^{181}Ta	0.70
	^{118}Sn	0.58[29]	74	W	0.46[6]
	^{119}Sn	0.60[29]	75	Re	0.92
	^{120}Sn	0.64[29]	76	Os	1.07
	^{122}Sn	0.55[29]		^{188}Os	0.78[39]
	^{124}Sn	0.59[29]		^{189}Os	1.10[39]
51	Sb	0.54		^{190}Os	1.14[39]
52	Te	0.56		^{192}Os	1.19[39]
	^{120}Te	0.52	77	Ir	1.06[40]
	^{123}Te	0.57	78	Pt	0.95
			79	Au	0.76

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