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THERMAL AND MÖSSBAUER STUDIES OF IRON-CONTAINING HYDROUS SILICATES. VI. MINNESOTAITE

K.J.D. MACKENZIE, R.M. BEREZOWSKI and M.E. BOWDEN
Chemistry Division, D.S.I.R., Private Bag, Petone (New Zealand)

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ABSTRACT

Thermal analysis, X-ray diffraction, infrared spectroscopy and Mössbauer studies of minnesotaite, a ferrous mineral structurally similar to talc, show that when heated in air, oxidation to a ferric form without the loss of the minnesotaite structure is virtually complete by the onset of dehydroxylation at 600°C. Water loss continues over several hundred degrees, with the formation of amorphous silica and disordered hematite of small particle size, some of which subsequently transforms to a magnetite-like spinel under the influence of the residual water present. Under reducing conditions, $FeSiO_3$ is formed on dehydroxylation possibly by a mechanism analogous to that of talc. Further reduction forms α-Fe metal, and, at about 1150°C, some γ-Fe which may be stabilised by the silicate host lattice. At about 1150°C the $FeSiO_3$ transforms to olivine and the amorphous silica to cristobalite.

INTRODUCTION

Minnesotaite is a 2 : 1 hydrous iron-containing layer silicate which occurs in the iron formations of the Mesabi and Cuyuna Ranges, Minnesota, U.S.A., taking its name from its locality of origin. Although originally classified as an amphibole (presumably because of its slightly fibrous habit in the massive state), it was suggested by Gruner [1] to have a talc-like structure in which the magnesium ions are substantially replaced by Fe^{2+}. The ideal formula of such a phase is $Fe_6^{2+}Si_8O_{20}(OH)_4$. In naturally occurring samples, small amounts of Fe^{3+}, Al, Mg, Mn and alkalis are also found [2]. The extreme degree of misfit between the tetrahedral and octahedral layers which would occur in a true ferrous analogue of talc suggests that in minnesotaite some strain-relief mechanism must operate; a recent X-ray study [3] suggests that this may consist of a complex series of regular modulations along the three axes of both the tetrahedral and octahedral sheets rather than a simple curling of the sheets.

Little is known of the thermal decomposition chemistry of minnesotaite, despite its interest because of its relationship with talc. A published DTA trace of Cuyuna minnesotaite [2] indicates a dehydroxylation endotherm at about 750°C followed by an exotherm which appears to be related to the

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crystallization of magnetite (Fe_3O_4). At higher temperatures, an unidentified phase also appeared [2]. The IR spectrum of minnesotaite has been reported [4], as has a Mössbauer spectrum [5] which indicated that the ferrous ions were in the octahedral sites of the talc-like structure. The Mössbauer spectrum of that sample (No. 170M, Cuyuna Iron Range) also indicated considerable contamination by siderite ($FeCO_3$).

The aim of the present work was to investigate the thermal reactions of minnesotaite using techniques which have previously proved useful in such studies (thermal analysis, X-ray diffraction, IR and Mössbauer spectroscopy).

EXPERIMENTAL

Materials

Two minnesotaite samples were available for study. One, from the Virginia Mine, Mesabi district, was part of sample 115274 of the Smithsonian Institution collection, kindly supplied by Dr. J. Aren. This was found by X-ray diffraction (XRD) to contain quartz, estimated from the 4.26 Å X-ray reflection to be ~ 15%. The only other contaminant detectable by XRD was a very small trace of greenalite, a 1 : 1 iron layer silicate with a diagnostic basal spacing at 7.2 Å. Another sample, from the Cuyuna Iron Range (specimen 170M of the A.E. Seaman mineral collection, Michigan Technological University) was kindly supplied by Dr. J.P. Kemp and Dr. A.P. Ruotsala. This was found by XRD to contain appreciable siderite but only a trace of quartz. Attempts to remove the siderite by acid treatment [1] were not satisfactory; because this was to be a Mössbauer study, quartz was deemed to be a less undesirable impurity than siderite, and the present work was confined to the Virginia sample 115274. Chemical analysis of the whole material indicates the presence of 2–3% of Mn, Al and Ca, but an EDAX examination of the powdered sample reveals that these elements occur in a few small, discrete impurity grains. Some grains, of spherical morphology, contain only Mn and Ca, while other more angular grains contain Ca and Al. The quartz impurity is visible as large angular blocks, while the minnesotaite occurs in blocky tabular sheets of consistent composition (Table 1, column 1), corresponding to almost ideal minnesotaite with some octahedral substitution by Mg. The unit cell contents are shown in Table 1, together with data for two other reported minnesotaites for comparison.

Methods

Samples of minnesotaite 115274 were heated both in ambient air and in a dynamic reducing atmosphere (5% H_2, 95% N_2, 0.6 l min^{-1}) to various temperatures determined from the thermal analysis curves, using a serial

TABLE 1

Chemical analysis and unit cell contents of minnesotaites (on the basis of 24(O, OH))

	1		2		3		4	
SiO_2(%)	49.67		51.29		51.26		50.6	
Al_2O_3	2.7		0.61		1.52		–	
Fe_2O_3	–		2.00		0.52		–	
FeO	44.03		33.66		37.23		45.6	
MnO	–		0.12		0.77		–	
MgO	3.23		6.26		3.38		–	
Na_2O	–		0.08		–		–	
K_2O	–		0.03		–		–	
H_2O^+	3.1		5.54		5.29		3.8	
H_2O^-	–		0.24		0.03		–	
Total	100.0		99.87		100.00		100.0	
Unit cell contents								
Si	7.90	7.90	7.874	7.95	7.90	8.0	8.0	8.0
Al	–		0.074		0.10		–	
Fe^{2+}	5.83	6.59	4.323	6.00	4.80	5.92	6.0	6.0
Fe^{3+}	–		0.231		0.06		–	
Al	–		–		0.18		–	
Mg	0.76		1.432		0.78		–	
Mn^{2+}	–		0.016		0.10		–	
Na	–		0.024		–		–	
K	–		0.006		–		–	
OH	3.24		4.0		5.44		4	
O	20		20		20		20	

Column 1: present sample, Smithsonian 115274, Virginia Mine, Mesabi Range, Minnesota. EDAX analysis by G.D. Walker.
Column 2: E. Mesabi Range, analyst J. Gruner, 1944 [1].
Column 3: sample BM 131, Cuyuna Iron Range, analyst E.H. Oslund, 1965 [2].
Column 4: ideal minnesotaite.

heating technique [6]. After each stage of the heating, the sample was examined by X-ray diffraction (XRD), IR spectroscopy and Mössbauer spectroscopy, using an Elscint AME50 spectrometer with a Co/Rh source and soft iron as the reference material. These techniques are described in greater detail elsewhere [6]. Evolved gas analyses (EGA) were carried out using an Extranuclear Corp. quadrupole mass spectrometer with He carrier gas (0.04 $l\ min^{-1}$) at a heating rate of $10°C\ min^{-1}$.

RESULTS AND DISCUSSION

(a) Thermal analyses

The thermal analysis curves are shown in Fig. 1. The principal difference between the present DTA curves (Fig. 1A, B, C) and those reported for talcs

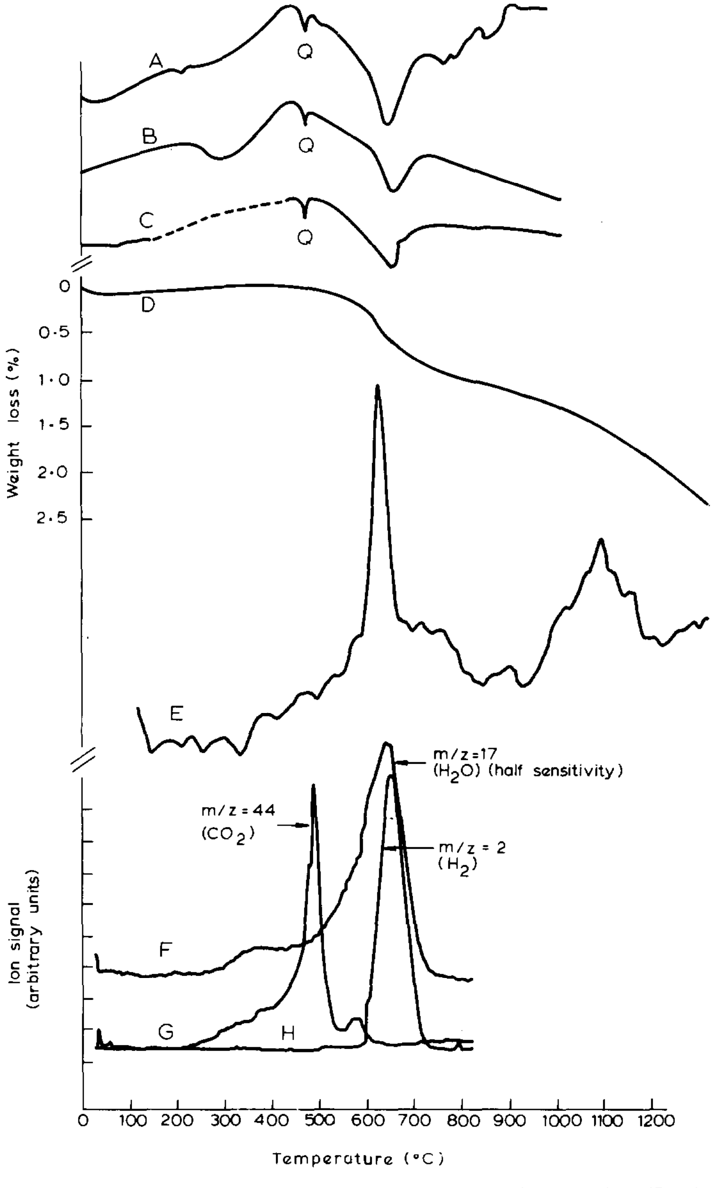

Fig. 1. Thermal analysis curve of Virginia Mine minnesotaite. Heating rate, 10°C min^{-1}. (A) DTA in static air; (Q) quartz peak; (B) DTA in oxygen-free N_2; (C) DTA in H_2/N_2 (5% : 95%); (— — —) region where baseline was corrected for adsorption of hydrogen on the platinel thermocouples; (D) TG in static air; (E) DTG; (F), (G), (H) evolved gas analysis in He carrier gas.

[7] is that under all atmospheres, the dehydroxylation of minnesotaite occurs at least 200°C lower than in talc. In this respect, the present sample agrees reasonably well with the one published DTA trace of Cuyuna minnesotaite [2]. The TG and DTG curves (Fig. 1D, E) indicate that the brisk weight loss

at ~ 600°C is followed by a more gradual loss which continues to at least 1200°C. The EGA curves indicate that the small initial weight loss at about 500°C is associated with the decomposition of a carbonate impurity, the concentration of which is too small for detection by XRD. The main dehydroxylation event at about 680°C is accompanied by the evolution of a small amount of hydrogen as shown by a mass 2 peak (Fig. 1H). This interesting phenomenon can be explained by intralattice oxidation of Fe^{2+} by a so-called "dry" reaction

$$Fe^{2+} + OH^- \rightarrow Fe^{3+} + O^{2-} + H^\cdot \qquad (1)$$

The $H^\cdot$ thus produced may either react with surface oxygen to form water, or, under conditions of low oxygen partial pressure (as in the present case with He carrier gas), forms H_2. Unfortunately the temperature of the EGA experiment was limited to 800°C by the heating arrangements, precluding the identification to the evolved species responsible for the higher-temperature weight loss; this seems likely, however, to be due to the gradual loss of further water.

(b) X-ray powder diffraction

The X-ray trace of the unheated material contains, in addition to the sharp, intense peaks of well-crystallized minnesotaite, weak diffuse bands at 5.3–5.6, 4.6 and 3.5–3.8 Å. The peak at 4.6 Å has been indexed by Guggenheim and Bailey [3] as a reflection of the supercell lattice. On heating, these diffuse reflections disappear at the same temperature as the sharp minnesotaite peaks suggesting that all these features arise from the minnesotaite structure, possibly associated with the supercell lattice. Even though oxidation of Fe^{2+} is essentially complete when the sample is heated in air at 600°C (see Section d), the minnesotaite reflections survive this heat treatment without loss of intensity or significant change in the lattice parameters, calculated from measurements of twelve indexed reflections, for which the quartz impurity was used as an internal angular calibration standard.

Above 600°C, the intensity of the minnesotaite pattern progressively decreases, being completely lost by about 1100°C. The two small peaks corresponding to the major reflections of the 7 Å impurity phase (greenalite) are completely destroyed by heating to 400°C in air (but this phase persists for another 100°C or so in reducing atmospheres). In air, the progressive loss of the minnesotaite reflections is accompanied by the appearance of hematite (Fe_2O_3) at about 600°C and magnetite (Fe_3O_4) at about 800°C, with a small amount of cristobalite (SiO_2) appearing at > 1100°C. Thus, by contrast with talc, which transforms sharply to enstatite ($MgSiO_3$) immediately on dehydroxylation [8], the reaction of minnesotaite is more gradual, consistent with the continuous water loss observed by thermal analysis. Although dehydroxylation results in the immediate formation of crystalline iron oxide, there is

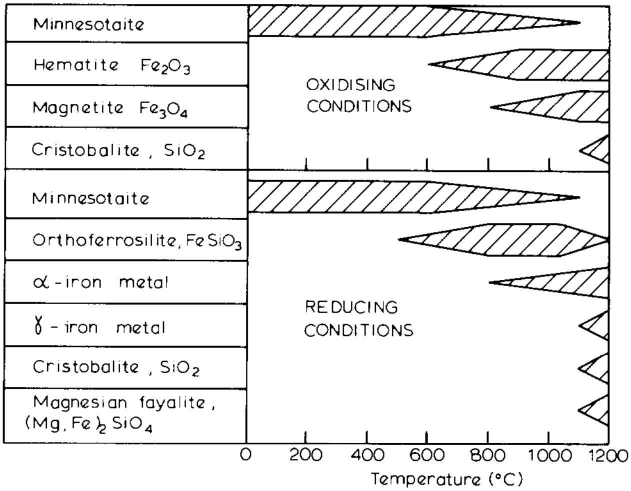

Fig. 2. Semi-schematic diagram of phase development in minnesotaite heated under oxidising and reducing conditions.

no simultaneous appearance of a new crystalline silica phase, suggesting that the silica which separates on dehydroxylation is initially amorphous, recrystallizing to cristobalite only at about 1150–1200°C. The sequence of phase formation is shown semi-schematically in Fig. 2.

As with the air-fired samples, heat-treatment under reducing conditions up to about 600°C produces no significant change in the intensities of the X-ray peaks nor in the cell parameters. Gradual dehydroxylation again begins at about 600°C, the initial product being orthoferrosilite ($FeSiO_3$), analagous to be formation of enstatite from talc [8]. Further heating results in the reduction of some of the iron to α-Fe metal, while at 1200°C, small amounts of cristobalite and fayalite (Fe_2SiO_4) are also observed, the X-ray parameters of the latter suggesting the incorporation of some Mg in this phase. Samples reduced at 1200°C also contain another phase with a major reflection at 2.060 Å, consistent with the X-ray pattern of γ-Fe metal. This is a face-centred cubic form which although normally stable between 910 and 1390°C [9], has been reported in iron-containing clay minerals reduced at $>$ 1000°C [10]. The room-temperature occurrence of γ-Fe in these materials has been attributed to stabilization by impurities [10]. Careful measurements of the X-ray trace of the present material, again using quartz as the angular calibrant, indicate a cell parameter of 3.573 Å, in excellent agreement with the value obtained by extrapolating the high-temperature cell constant data [9] to room temperature. Confirmation of the formation of γ-Fe was also provided by Mössbauer spectroscopy (see Section d). The phases developed on heating under reducing conditions are shown in Fig. 2.

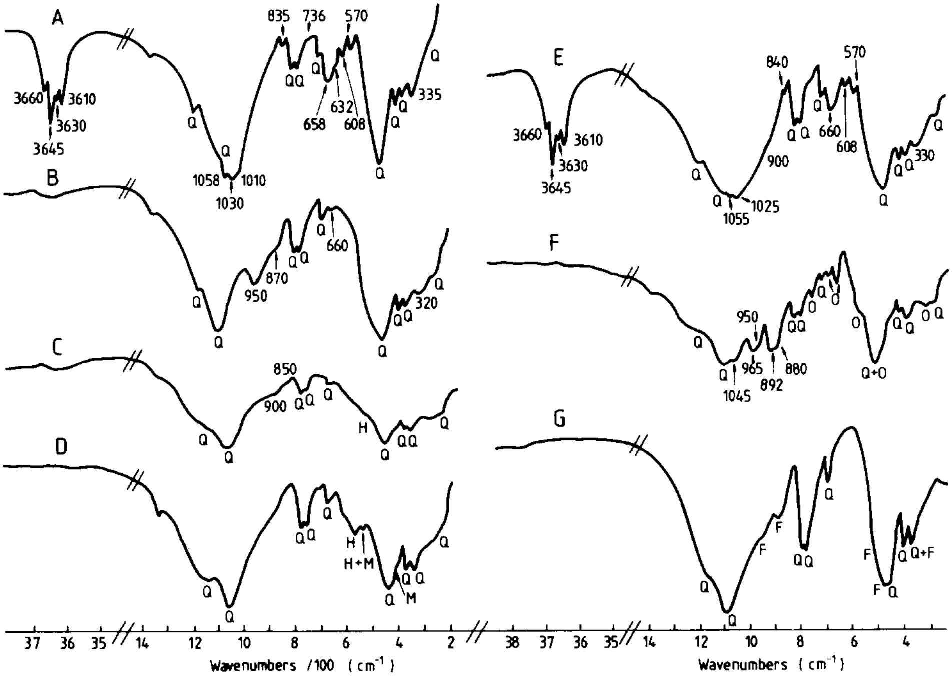

Fig. 3. Typical IR spectra of minnesotaite, unheated and heated to various temperatures in oxidising and reducing atmospheres. (A) Unheated and heated to 200–400°C in air and H_2/N_2. (B) 600°C, air. (C) 800°C, air. (D) 1000–1200°C, air. (E) 375–600°C, H_2/N_2. (F) 800–1000°C, H_2/N_2. (G) 1200°C, H_2/N_2. Q = quartz, H = hematite, M = magnetite, O = orthoferrosilite, F = fayalite.

(c) Infrared spectroscopy

Figure 3 shows typical IR spectra of minnesotaite, both unheated and heated to various temperatures under oxidising and reducing conditions.

The IR spectrum of unheated minnesotaite (Fig. 3A) shows, in addition to the impurity quartz bands, more fine structure than in the only previously published spectrum [4], particularly in the hydroxyl stretching region (3500-4300 cm^{-1}). By comparison with the single –OH stretching band reported by Stubican and Roy [4], four bands can be distinguished in the present material (Fig. 3A). Four –OH stretching bands have been noted in synthetic substituted talcs [11], the relative intensities of which depend on the degree of octahedral substitution. The principal –OH stretching frequency in talc (at 3676 cm^{-1}) pertains to hydroxyls directly bonded to three octahedral magnesiums, and is not observed here. Substitution of one, two and three Fe^{2+} ions for these octahedral magnesiums results in bands at 3663, 3646 and 3624 cm^{-1}, respectively [11], in good agreement with the three highest wavenumber bands in the present spectrum. However, this simple explanation does not correctly predict the relative intensities of these bands, nor does it account for the peak at 3610 cm^{-1} (Fig. 3A). This lower frequency peak cannot be explained in terms of substitution of manganese for octahedral iron as suggested by the structural formula (Table 1), since the –OH frequencies of synthetic Mn-substituted talc are not significantly different from the iron analogue [11]; neither would the presence of octahedral Al be expected to give rise to this peak, since in the aluminium analogue of talc (pyrophyllite) the hydroxyl bands occur at *higher* wavenumbers [12].

By analogy with talc and related 2 : 1 trioctahedral minerals, the lower wavenumber bands of unheated minnesotaite may be assigned as follows.

1058, 1030 and 1010 cm^{-1}: Si–O stretching vibrations, the lower two probably corresponding to the a', and e', modes, respectively [12].

835 cm^{-1}: tetrahedral Al–O [12].

736 cm^{-1}: Al–O–Si [4] (two other Al–O–Si bands which would be expected at 800 and 780 cm^{-1} [4] are obscured by quartz peaks, as is the Si–O band noted in minnesotaite by Stubican and Roy at 695 cm^{-1} [4]).

658 cm^{-1}: –OH libration [12].

632, 608 and 570 cm^{-1}: –OH vibrations in the 2 : 1 layers (chlorites of high Fe content typically absorb in this region [12]).

460 cm^{-1}: Si–O bend, corresponding to a similar quartz vibration. This is also the region in which Si–O–Fe^{2+} vibrations occur [4].

On the basis of this spectral interpretation, conversion of Fe^{2+} to Fe^{3+} by heating should produce the following spectral changes:

(a) replacement of the Si–O–Fe^{2+} vibration at < 400 cm^{-1} by an Si–O–Fe^{3+} vibration at 530–550 cm^{-1} [4];

(b) the appearance of a new octahedral Fe^{3+}–OH band at 800–900 cm^{-1} [4].

In practice, the spectra of samples heated to 400°C in both oxidising and reducing conditions were identical to the unheated material, even though Mössbauer spectroscopy (Section d) indicates the occurrence of some oxidation in both atmospheres by 400°C. However, the spectra of samples heated in air at 600°C (Fig. 3B) show both the above oxidation changes; the Si–O–Fe^{2+}, band at 335 cm^{-1} broadens and loses intensity with the concomitant appearance of a broad Si–O–Fe^{3+} shoulder at about 540 cm^{-1}, and a new shoulder also appears at about 870 cm^{-1}. Consistent with the virtual disappearance of the hydroxyl stretching bands in this sample, the lattice vibrations at 632, 608 and 570 cm^{-1}, all involving –OH groups, have disappeared, as has the -OH libration at 658 cm^{-1}, which is barely evident at 600°C. By contrast, all these hydroxyl-related bands are still present in samples heated at 600°C under reducing conditions (Fig. 3E), in which the small amount of Fe^{3+} formed at 400°C by auto-oxidation has been re-reduced at 600°C (see Section d).

A feature of the oxidised spectrum (Fig. 3B) is the shift of the Si–O stretching vibration at 1010–1030 to 950 cm^{-1}. The 950 cm^{-1} peak may be similar to a diagnostic band found in freshly precipitated silica gels and opaline silicas which has been attributed to the Si–O stretch of Si–OH groups [13]. Such a band could arise here if the onset of dehydroxylation resulted in the separation of amorphous silica sufficiently reactive to re-absorb some of the evolved water, the progressive loss of which on further heating could explain the gradual weight loss observed between 700 and 1200°C (Fig. 1D). The broad hump at 3450 cm^{-1} characteristic of molecular water (Fig. 3C) eventually disappears by 1200°C, leaving only the quartz peaks and broad features corresponding to hematite and magnetite (Fig. 3D).

Under reducing conditions, dehydroxylation results in the immediate appearance of a number of new bands attributable to orthoferrosilite [14]; additional bands at 892 and 960 cm^{-1} are precursors of the diagnostic fayalite vibrations. Between 1000 and 1200°C the orthoferrosilite transforms to fayalite, with a correspondingly simpler spectrum (Fig. 3G).

In summary, the IR spectra indicate:

(i) spectral changes due to oxidation of Fe^{2+} only become evident when the thermal reactions have progressed to the point of dehydroxylation;

(ii) dehydroxylation is accompanied both by the loss of hydroxyl-related peaks and the appearance of a new Si–O stretching peak at 950 cm^{-1} which may be due to the separation of amorphous hydrated silica which progressively loses water on further heating;

(iii) the IR spectra of samples heated at higher temperatures are consistent with the phase assemblages indicated by XRD.

(d) Mössbauer spectroscopy

The room-temperature Mössbauer spectra taken after heating samples to various stages of reaction under oxidising and reducing conditions are shown in Figs. 4 and 5, respectively. The spectrum of unheated minnesotaite (Fig. 4A) indicates the presence of only Fe^{2+} but can only be satisfactorily computer-fitted by postulating two Fe^{2+} doublets. The only previously reported spectrum [5] also contains two Fe^{2+} doublets, one with a quadrupole splitting (QS) of 2.6 mm s^{-1} similar to the present doublet B. The other previously reported doublet (QS = 1.85 mm s^{-1}) was identified with a ferrous carbonate impurity [5], not detected here. The present Fe^{2+} doublet A was not resolved in the previous spectrum which was not computer-fitted.

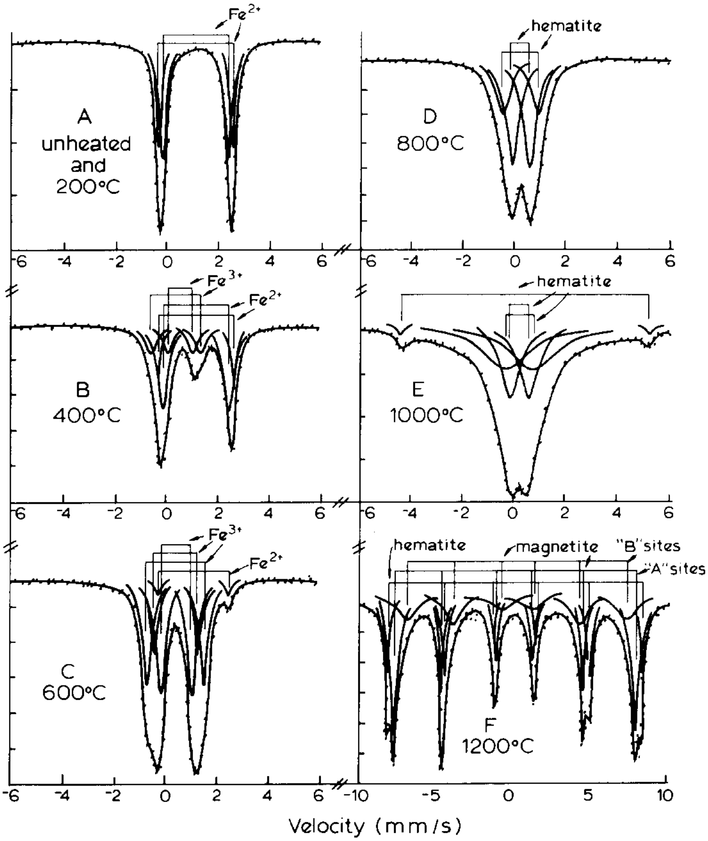

Fig. 4. Room-temperature Mössbauer spectra of minnesotaite, unheated and heated to various temperatures in air.

The present observation of doublets A and B is consistent with findings for other iron-rich 2 : 1 layer silicates, in which the doublet of larger QS is generally assigned to the M2 octahedral site (hydroxyl groups in *cis*-configuration), the smaller QS doublet being associated with M1 (*trans*-hydroxyl) octahedral sites [15]. Annersten and Olesch [16] and Hogg and Meads [17] reverse this assignment, ascribing the smaller QS doublet to the *cis*-sites; in the case of Annersten and Olesch, this seems to be a nomenclature problem, since they describe these *cis*-sites as M1 [16]. The present unheated spectrum differs from that reported for talc [17], which contained only one Fe^{2+} doublet (QS = 2.60, IS = 1.13 mm s^{-1}, recalculated relative to natural iron). Evidently only one of the available octahedral sites in talc is occupied by iron, or alternatively the M1 and M2 sites in talc are indistinguishable by Mössbauer spectroscopy.

On heating in air to 400°C, oxidation of the Fe^{2+} begins, the higher QS (*cis*) site being the less thermally stable. By 660°C, both the *cis*- and *trans*-Fe^{2+} have been almost fully oxidised; on the basis of the X-ray data

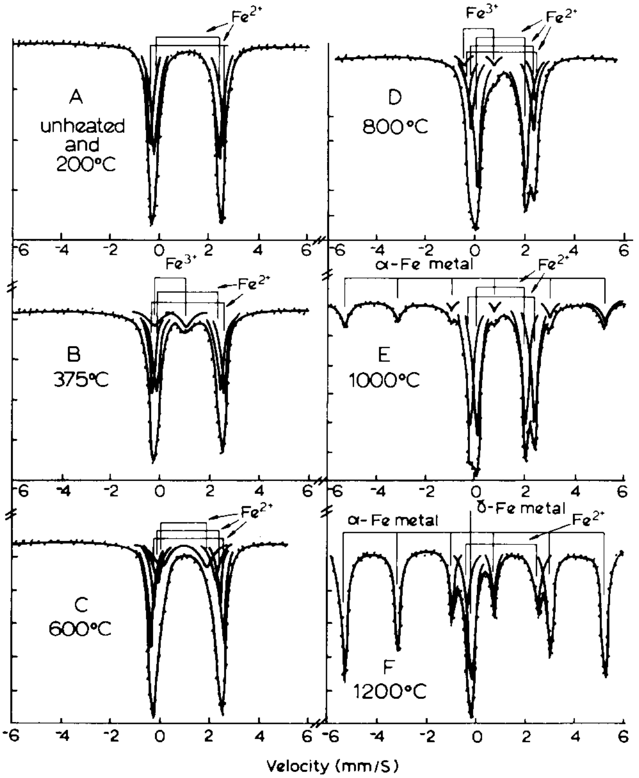

Fig. 5. Room-temperature Mössbauer spectra of minnesotaite heated to various temperatures in H_2/N_2.

(Section b) this phase corresponds to ferric minnesotaite. The onset of dehydroxylation is accompanied by the appearance of two new broad Fe^{3+} doublets which replace the previously formed Fe^{3+} of oxidised minnesotaite (Fig. 4D). The parameters and widths of the new doublets are consistent with poorly ordered hematite of small crystallite size (J.H. Johnston, personal communication, 1985). The identification of these doublets with hematite was strengthened by re-running the Mössbauer spectrum at 77 K, which resulted in the partial resolution of the six-line magnetic hematite spectrum. On further heating, the hematite particle size and crystallinity improves, reflected by the development of a magnetic six-line hematite spectrum (Fig. 4E, F). At 1200°C, the spectrum is resolvable into three six-line magnetic spectra, one of which has an internal field of 507 kG, in good agreement with the room-temperature internal field reported for hematite (490–517 kG) [18]. The other two six-line spectra have internal fields of 486 and 438 kG, and have therefore been assigned respectively to the A and B sites of magnetite, for which the room-temperature internal fields are reported as 490 and 458 kG, respectively [18]. The changes in site occupation under oxidising conditions are plotted as a function of firing

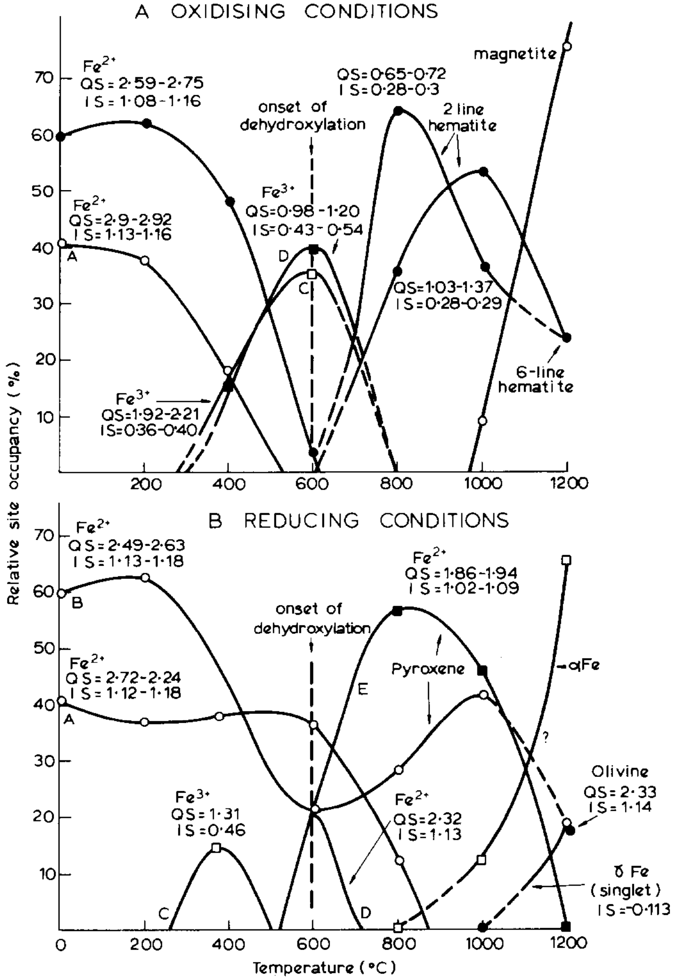

Fig. 6. Change in relative iron site occupancy in minnesotaite as a function of heating temperature in (A) oxidising and (B) reducing conditions, deduced from computer-fitted peak areas. Isomer shifts relative to natural iron.

temperature in Fig. 6, on the basis of computer-fitted peak areas, assuming the recoil-free fractions of Fe^{2+} and Fe^{3+} to be approximately equal.

When heated under reducing conditions to about 400°C, slight transitory internal oxidation of the smaller QS Fe^{2+} site occurs (Fig. 5B). Dehydroxylation at about 600°C is accompanied by a decrease in the occupancy of the original larger QS Fe^{2+} site and the appearance of two new Fe^{2+} sites of smaller QS (sites D and E, Fig. 6B). Between about 700 and 1000°C the predominant Fe^{2+} resonances are the original resonance B (QS = 2.49–2.63 mm s^{-1}) and the new resonance E (QS = 1.86–1.94 mm s^{-1}). These parameters are identical to those reported for the M1 and M2 Fe^{2+} sites of synthetic ferrosilite (QS = 2.490 and 1.906 mm s^{-1}) [19], in agreement with the XRD

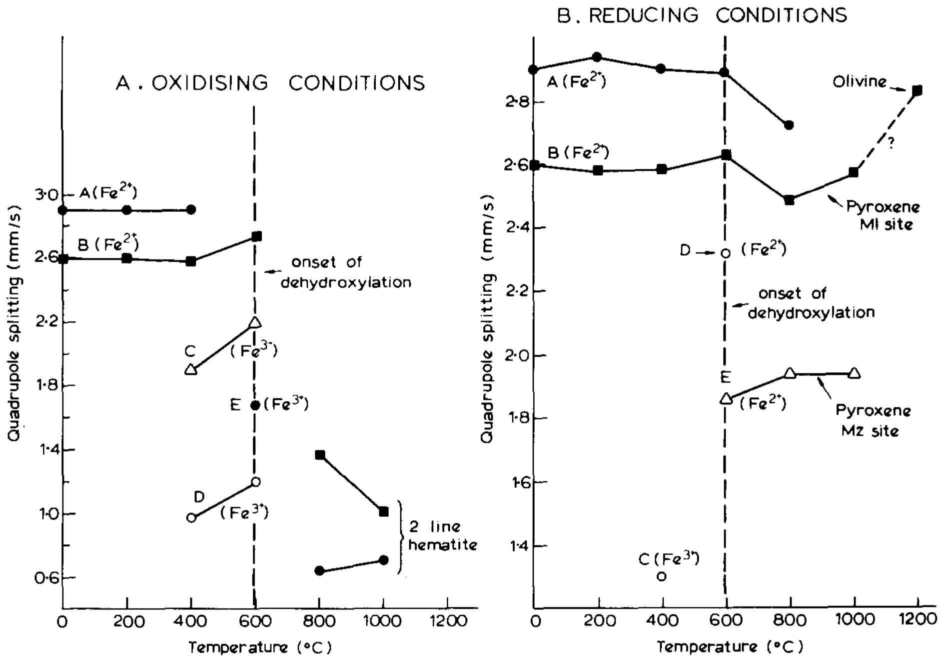

Fig. 7. Change in quadrupole splittings of room-temperature Mössbauer spectra of minnesotaite as a function of heating temperature in (A) oxidising and (B) reducing conditions.

results (Section b). On heating to 1200°C both these ferrosilite peaks decrease in intensity, being replaced by α-Fe metal, and, at 1200°C by a singlet peak (IS = -0.11 mm s^{-1}) which can be identified with γ-Fe both from XRD evidence (Section b) and by analogy with other reduced iron-containing clays [20]. The parameters of the small Fe^{2+} doublet remaining at 1200°C (QS = 2.83, IS = 1.14 mm s^{-1}) are in good agreement with the room-temperature parameters reported [21] for various olivines (QS = 2.80–3.02, IS = 1.16–1.18 mm s^{-1}, recalculated with respect to natural iron). This supports the XRD results that the orthoferrosilite converts to olivine at > 1000°C (Section b) and is consistent with the finding of Sueno et al. [22] of the topotactic conversion of orthoferrosilite to fayalite at 1060°C. The changes in iron site occupancy under reducing conditions are shown in Fig. 6B. Changes in the quadrupole splittings with various heat treatments are shown in Fig. 7.

Figure 7 indicates that the Fe^{2+} QS values (and hence the Fe^{2+} environments) are relatively unchanged until the onset of oxidation; thereafter under oxidising conditions (Fig. 7A) the QS values of the resulting Fe^{3+} sites increase upon dehydroxylation, indicating a concomitant increase in octahedral distortion. The immediate product (disordered hematite) is fitted by two broad doublets which should not necessarily be taken to indicate two discrete sites but rather a continuum of sites with a range of energies and distortions (J.H. Johnston, personal communication, 1985).

Under reducing conditions (Fig. 7B), little change occurs in the Fe^{2+} QS values until dehydroxylation, when two new Fe^{2+} resonances of lower QS appear, followed by a decrease in the QS values of the original Fe^{2+} resonances. Such QS decreases in Fe^{2+} doublets generally indicate increasing site distortion (a possible exception being the 1 : 1 layer silicates [23]). Immediately after dehydroxylation, the original *cis*-OH site and one of the newly formed Fe^{2+} sites disappear, the remaining Fe^{2+} sites becoming identifiable with the M1 and M2 sites of orthoferrosilite. On conversion of the latter to fayalite at > 1000°C, only one Fe^{2+} site can be resolved, consistent with a previous finding attributed to similarities in the formal electrostatic charge on the M1 and M2 sites of olivine [21].

(e) Mechanistic implications

The thermal transformations of minnesotaite in air may be summarised as follows.

(a) At about 480°C, oxidation of lattice Fe^{2+} occurs, without significant change in the minnesotaite lattice parameters or structural breakdown.

(b) At about 600°C, dehydroxylation sets in, the structure decomposing to a disordered hematite of small particle size and an amorphous silica-rich phase which may contain some of the molecular water produced. Dehydroxylation continues slowly to about 1000°C.

(c) At about 700°C, magnetite appears and the crystallinity of the hematite improves. Cristobalite recrystallizes at about 1150°C.

A different reaction sequence occurs under reducing conditions, due to the persistence of Fe^{2+} throughout (apart from the transitory appearance at about 400°C of some Fe^{3+} formed by internal oxidation). On dehydroxylation, $FeSiO_3$ immediately forms, with the separation of an amorphous silica-rich phase. This reaction is apparently analogous to the formation of enstatite ($MgSiO_3$) from talc, for which an inhomogeneous mechanism has been postulated [8], involving the migration of eight protons per unit cell to "donor" regions where they combine with hydroxyls to form water. Charge balance is preserved by counter-migration of $4Mg^{2+}$ from the "donor" to "acceptor" regions, where only slight cation rearrangement within a fixed oxygen framework is required to form enstatite [8]. The Mg-depleted "donor" regions constitute the silica-rich phase. Although the present study of minnesotaite has not established that the formation of $FeSiO_3$ is topotactic, a plausible inhomogeneous reaction scheme can be written by analogy with talc. This is shown schematically in Fig. 8.

On further reduction, α-Fe metal is formed at about 800°C, with some γ-Fe appearing at about 1150°C, possibly stabilized by the silicate lattice in which it forms [20]. At about the same temperature, $FeSiO_3$ transforms to an

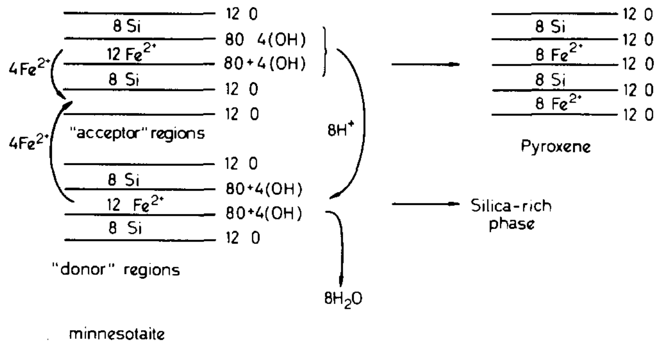

Fig. 8. Schematic representation of the proposed inhomogeneous reaction mechanism in minnesotaite under reducing conditions. Horizontal lines represent planes of oxygen atoms in approximately close packing.

olivine by the reaction

$$2FeSiO_3 \rightarrow Fe_2SiO_4 + SiO_2 \qquad (2)$$

(Although these reactions are written in terms of the purely ferrous minerals, they will contain other substituent elements, particularly Mg.)

A reaction scheme such as that in Fig. 8 does not occur in air; since analogous ferric silicates do not exist, dehydroxylation results in the immediate appearance of the component oxides without the intervention of an X-ray amorphous state such as found in the more Al-rich silicates, e.g., aluminous berthierine [24]. The subsequent formation of magnetite, although curious at first sight, is consistent with the finding of Johnson et al. [25] that in the presence of water vapour, hematite transforms at > 300°C to a magnetic spinel which may be either magnetite or maghemite (γ-Fe_2O_3). The present cubic phase has $a = 8.38$ Å, by comparison with 8.37 Å for Johnson's spinel and 8.394 Å for magnetite [26]; since its Mössbauer spectrum is reasonably consistent with magnetite and it lacks the diagnostic maghemite X-ray reflection at 2.78 Å, it has been described as magnetite, although it could contain other ions, such as Mn. Its formation can be accounted for in terms of the findings of Johnson et al. [25] by the persistence to high temperatures of water in the system.

CONCLUSIONS

Where minnesotaite is heated in air to 400°C, octahedral Fe^{2+} in the *cis*-OH sites begin to oxidise. By the onset of dehydroxylation at 600°C, oxidation of both *cis*- and *trans*-OH Fe^{2+} is virtually complete, but with no significant change in the lattice parameters. Loss of the minnesotaite structure resulting from dehydroxylation occurs progressively over several hundred degrees and is accompanied by the formation of disordered hematite of small particle size, and amorphous silica which possibly retains molecular water. At higher temperatures, the presence of this water may initiate the transformation of some hematite to a spinel resembling magnetite, but possibly containing other ions, e.g. Mn.

In reducing atmospheres, some transitory internal oxidation occurs at about 400°C. On dehydroxylation, $FeSiO_3$ and an amorphous siliceous phase is formed, possibly by an inhomogeneous mechanism analogous to talc, but extending over several hundred degrees, as in air. Further reduction at about 1000°C results in the formation of α-Fe metal and, at about 1150°C, some α-Fe (a metastable face-centred cubic form of iron which may be stabilized here by the silicate host lattice). At about 1150°C the $FeSiO_3$ pyroxene forms olivine, $(Fe,Mg)_2SiO_4$, the excess silica recrystallizing as cristobalite.

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REFERENCES

1 J.W. Gruner, Am. Mineral., 29 (1944) 363.
2 R.L. Blake, Am. Mineral., 50 (1965) 148.
3 S. Guggenheim and S.W. Bailey, Can. Mineral., 20 (1982) 579.
4 V. Stubican and R. Roy, J. Am. Ceram. Soc., 44 (1961) 625.
5 G.L. Taylor, A.P. Ruotsala and R.O. Keeling, Clays Clay Miner., 16 (1968–1969) 381.
6 K.J.D. MacKenzie and M.E. Bowden, Thermochim. Acta, 64 (1983) 83.
7 R.C. MacKenzie (Ed.), The Differential Thermal Investigation of Clays, Min. Soc. Monograph, London, 1957, p. 180.
8 M. Nakahira and T. Kato, Clays Clay Miner., 12 (1964) 21.
9 W.B. Pearson, Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 1, Pergamon, London, 1958, p. 625.
10 J. Van Wonterghem, S. Mørup and C.J.W. Koch, J. Mater. Sci. Lett., 3 (1984) 1080.
11 R.W.T. Wilkins and J. Ito, Am. Mineral., 52 (1967) 1649.
12 V.C. Farmer (Ed.), The Infrared Spectra of Minerals, Min. Soc. Monograph 4, London, 1974, Ch. 15.
13 M. Hino and T. Sato, Bull. Chem. Soc. Jpn., 44 (1971) 33.
14 P.A. Estep-Barnes, in Physical Methods in Determinative Minerology, J. Zussman (Ed.), 2nd edn., Academic Press, London, 1977, p. 567.
15 a L. Haggstrom, R. Wappling and H. Annersten, Chem. Phys. Lett., 4 (1969) 107.
b I. Rozenson and L. Heller-Kallai, Clays Clay Miner., 25 (1977) 94.
c J.D. Russell, B.A. Goodman and A.R. Fraser, Clays Clay Miner., 27 (1979) 63.
d L. Heller-Kallai and I. Rozenson, Clays Clay Miner., 28 (1980) 355.
e O. Ballet and J.M.D. Coey, Phys. Chem. Miner., 8 (1982) 218.

16 H. Annersten and M. Olesch, Can. Mineral., 16 (1978) 199.
17 C.S. Hogg and R.E. Meads, Mineral. Mag., 37 (1970) 606.
18 C.W. Childs and J.G. Baker-Sherman, N.Z. Soil Burea Report 66, D.S.I.R., Wellington, 1984, p. 8.
19 E. Dowty and D.H. Lindsley, Am. Mineral., 58 (1973) 850.
20 K.J.D. MacKenzie, I.W.M. Brown, M.E. Bowden and W.J. Cousins, React. Solids, in press.
21 G.M. Bancroft, A.G. Maddock and R.G. Burns, Geochim. Cosmochim. Acta, 31 (1967) 2219.
22 S. Sueno, C.T. Prewitt and M. Ohmasa, Kobutsugaku Zasshi, 14 (1980) 339.
23 K.J.D. MacKenzie, M.E. Bowden and R.M. Berezowski, in G.J. Long and J.G. Stevens (Eds.), Industrial Applications of the Mössbauer Effect, Plenum, in press.
24 K.J.D. MacKenzie and R.M. Berezowski, Thermochim. Acta, 74 (1984) 291.
25 H.P. Johnson, H. Kinoshita and R.T. Merrill, Nature (London), Phys. Sci., 239 (1972) 151.
26 I. David and A.J.E. Welch, Trans. Farad. Soc., 52 (1956) 1642.