A Mössbauer study of thermal decomposition of biotites

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SUMMARY. The effect of heat treatment in air at temperatures from 200 °C to 1000 °C of two Cornish biotites has been studied using the Mössbauer effect in ^{57}Fe. One of the micas was also studied after heating *in vacuo*.

Progressive changes in the Mössbauer spectra of the materials after heat treatment can be correlated with the following processes: Oxidation of Fe^{2+} ions in isolated octahedral sites to give Fe^{3+} in the co-ordination $Fe^{3+}(O_5OH)$; oxidation of Fe^{2+} ions in adjacent a-octahedral (*cis* OH^-) sites to give $Fe^{3+}(O_6)$; and oxidation of Fe^{2+} in adjacent a and b (trans OH^-) sites to give either $Fe^{3+}(O_5OH)$ or $Fe^{3+}(O_6)$ depending on whether a shared hydroxyl group remains intact or otherwise (these processes occur at temperatures below 500 °C). Also, at higher temperatures, dehydroxylation of $Fe^{3+}(O_5OH)$ to give more Fe^{3+} in the $Fe^{3+}(O_6)$ configuration. Finally, in the temperature range 900 to 1000 °C, structural breakdown yielding α-Fe_2O_3 as the iron-containing phase.

The results and interpretation are in good agreement with thermogravimetric data and with a previous infra-red study. The mechanism of charge diffusion in the lattice during oxidation is discussed in the light of the results.

ALTHOUGH much work has beend one on the thermal decomposition of hydrous silicates in general, there has been little published on biotites in particular, most of the mica work having been confined to muscovite. Brindley (1963) has summarized much of the work prior to that date and has emphasized the importance of X-ray techniques in elucidating the broader outlines of the various changes, but the more detailed mechanisms require other techniques for their elucidation. Hodgson, Freeman, and Taylor (1965a) have studied the thermal decomposition of crocidolite and amosite (1965b) by differential thermal analysis and thermogravimetry, and have interpreted their results in terms of the original detailed investigation of amphiboles by Addison *et al.* (1962). Gibb and Greenwood (1965) have also investigated these two amphiboles using the Mössbauer effect and their results generally support the results of previous workers. Vedder and Wilkins (1969) have studied the thermal decomposition of muscovites and biotites by infra-red spectroscopy, and the interpretation of the results to be presented here has been made along the lines of their arguments.

A Mössbauer study of high-temperature reactions in kaolinite and halloysite has been undertaken by MacKenzie (1969) and Mössbauer work on oxidation of biotite by weathering has been published by Rice and Williams (1969).

Instrumentation. The authors have previously published detailed Mössbauer work on a group of micas (Hogg and Meads, 1970) and the reader is referred to that paper for a description of the experimental technique and for the method of spectrum fitting and analysis.

Sample description and heat treatment. Two of the micas, of Cornish origin, Trelavour and Tregarden biotite, which were used in the previous work, were also used in the present work and were heated for 24 and 12 hours respectively in air at various temperatures between 200 °C and 1000 °C. The Tregarden biotite was also heated to two temperatures, 500 °C and 800 °C, *in vacuo* ($< 10^{-4}$ mm Hg).

Mössbauer experiments. After the heat treatment, the samples were mounted in perspex holders and Mössbauer spectra recorded at room temperature. The amount of material in each sample was adjusted to give an absorber thickness of about 5 mg cm^{-2} of natural iron.

Results. The Mössbauer parameters and percentage areas of spectrum components are given for both materials in Table I, together with data for the unheated samples taken from Hogg and Meads (1970). Figs. 1 to 6 show the experimental points and computer-fitted curves for the Tregarden biotite at several temperatures up to 800 °C. The spectrum after heating to 900 °C is shown in fig. 7. The spectra of Tregarden biotite, heated *in vacuo* at 500 °C and 800 °C, are shown in figs. 8 and 9 and those of the Trelavour biotite, heated in air at 900 °C and 1000 °C, in figs. 10 and 11. No detailed computer fitting of spectra of samples heated beyond 800 °C was attempted. The χ^2 values of the fitted spectra are, in general, satisfactory, for a system in which the number of degrees of freedom in fitting is 187. However, in certain cases, particularly those of the vacuum-heated Trelavour biotite, the χ^2 values and plots suggest that the spectra are more complicated than the model used to fit them, although the use of more complicated models did not give improvement. The original spectra (Hogg and Meads, 1970) were previously analysed into two quadrupole doublets, attributed to Fe^{2+} in octahedral sites with two OH^- groups in *cis* or *trans* positions, and one Fe^{3+} doublet also attributed to iron in octahedral sites. Between room temperature and 200 °C the spectrum of the Tregarden biotite shows little change. There has been a slight increase in the amount of ferric iron probably at the expense of ferrous iron in the outer doublet, and the quadrupole splitting of the ferric doublet has increased slightly, suggesting a slight increase in the ferric site distortion. At 300 °C there has been considerable increase in the ferric iron content, now clearly at the expense of the outer ferrous doublet. The quadrupole splitting of the ferric doublet is increasing as is the line width of the components, suggesting the formation of at least two unresolved ferric sites. At 350 °C only one ferrous doublet is resolvable, with parameters intermediate between the two doublets previously observed, as might be expected. However, two ferric doublets can now be distinguished, the more intense doublet having the larger quadrupole splitting, showing that most of the ferric iron formed is in a very asymmetric environment, but that a smaller amount is more symmetrically co-ordinated. At 400 °C the situation has changed only inasmuch as the amount of ferrous iron has decreased still further, and at 500 °C there is virtually no ferrous iron present at all. However, the area of the inner ferric doublet has now increased and

TABLE I. *Mössbauer parameters of biotites after heating to various temperatures (θ).*

Sample	θ	Fe²⁺ (outer)				Fe²⁺ (inner)				Fe³⁺ (outer)				Fe³⁺ (inner)				χ^2
		δ	Δ	Γ_{exp}	Area	δ	Δ	Γ_{exp}	Area	δ	Δ	Γ_{exp}	Area	δ	Δ	Γ_{exp}	Area	
Trelavour biotite	RT	1·41	2·51	0·50	89					0·66	0·80	0·46	11					181
	300	1·42	2·53	0·56	67					0·71	1·11	0·72	33					241
	400	1·37	2·42	0·66	30					0·67	1·45	0·72	48	0·69	1·03	0·44	22	217
	500	1·23	2·49	0·96	13					0·67	1·58	0·68	44	0·69	1·08	0·50	43	223
	800	—	—	—	—					0·64	1·83	0·62	47	0·67	1·18	0·44	53	294
Tregarden biotite	RT	1·39	2·61	0·32	44	1·39	2·18	0·46	32	0·65	0·85	0·64	24					215
	200	1·38	2·60	0·32	37	1·36	2·27	0·50	35	0·69	0·89	0·64	28					262
	300	1·40	2·60	0·32	25	1·39	2·24	0·48	30	0·68	1·16	0·78	45					244
	350	1·37	2·38	0·54	33	—	—	—	—	0·65	1·38	0·82	53	0·66	0·99	0·40	14	269
	400	1·31	2·38	0·60	20	—	—	—	—	0·66	1·39	0·74	61	0·68	0·96	0·40	19	200
	500	—	—	—	—	—	—	—	—	0·64	1·60	0·60	53	0·65	1·03	0·44	47	290
	600	—	—	—	—	—	—	—	—	0·63	1·62	0·68	48	0·64	1·08	0·50	52	193
	700	—	—	—	—	—	—	—	—	0·64	1·64	0·80	49	0·64	1·07	0·56	51	223
	800	—	—	—	—	—	—	—	—	0·64	1·67	0·76	47	0·63	1·06	0·60	53	246
Tregarden biotite (in vacuo)	500	1·36	2·37	0·46	36	1·31	1·95	0·64	19	0·77	1·15	0·90	45					276
	800	1·46	2·37	0·62	19	1·26	2·09	0·72	45	0·75	1·13	0·82	36					313

The isomer shift (δ), quadrupole splitting (Δ), and full-width at half-max. absorption (Γ_{exp}) are in mm s⁻¹. A precision of ±0·02 mm s⁻¹ is attributed to each value. Areas of resonances are given as percentages of the total resonance absorption with a precision of ±3 %. The δ values are relative to sodium nitroprusside. χ^2 values are to be compared with the number of degrees of freedom, 187. Values of parameters for unheated biotites are taken from Hogg and Meads (1970). Where a single set of values for Fe³⁺ or Fe²⁺ is given, no attempt to resolve two doublets has been made and the total area is implied.

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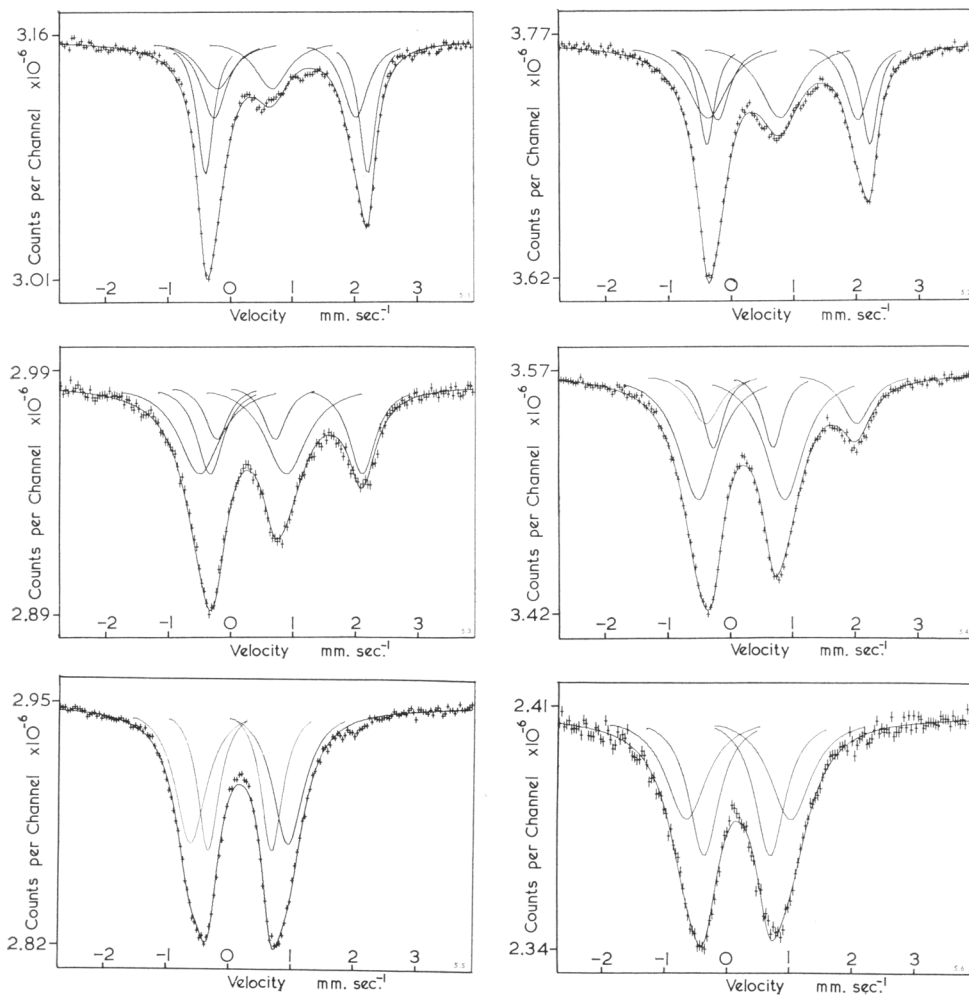
FIGS. 1 to 6: Mössbauer spectrum of Tregarden biotite after heating in air: FIG. 1 (top left) at 200 °C; FIG. 2 (top right) at 300 °C; FIG. 3 (middle left) at 350 °C; FIG. 4 (middle right) at 400 °C; FIG. 5 (bottom left) at 500 °C; FIG. 6 (bottom right) at 800 °C.
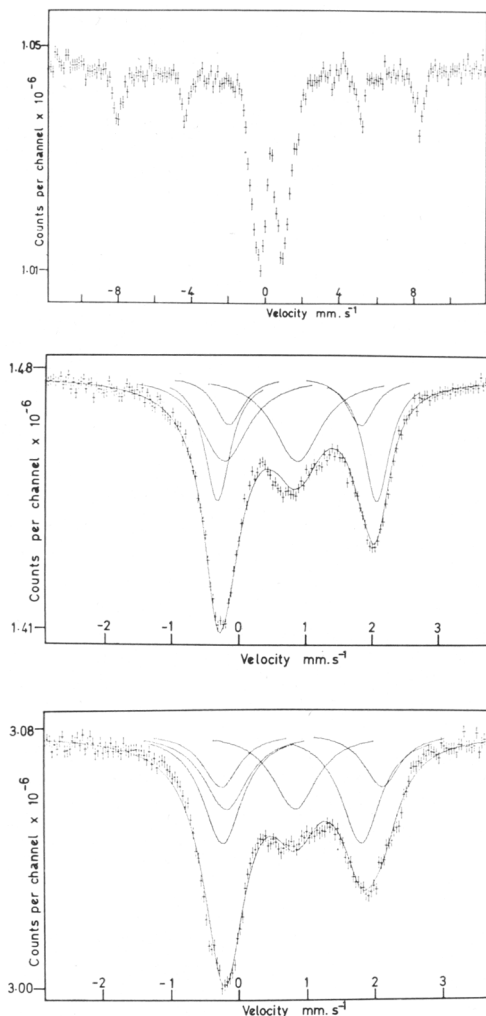
that of the outer doublet decreased, so that they are approximately equal in area. The isomer shifts of both doublets have decreased and their quadrupole splittings increased, indicating increased distortion of the lattice as the temperature is raised. The spectrum parameters now remain more or less constant up to 800 °C. At 900 °C structural decomposition has set in and the spectrum shows a six-line spectrum attributed to α-Fe_2O_3 with a hyperfine magnetic field of 503 ± 5 kOe, together with a residual Fe^{3+} quadrupole doublet. At 1000 °C complete breakdown of the structure has taken place, and the spectrum consists of a low-intensity ferric doublet and a well defined α-Fe_2O_3 spectrum. In parallel with these changes in the Mössbauer

spectra the samples showed characteristic changes in appearance. Up to about 350 °C

the powders were brownish grey in colour, the brownish tinge increasing with temperature. Above 400 °C a sharp colour change takes place, to light brown, and by 900 °C the colour is quite orange brown. At 1000 °C the sample melted into small spherules with a metallic grey lustre, which, on grinding, gave the cherry red colour usually associated with hematite, α-Fe_2O_3.

None of the spectra show any evidence for the formation of significant quantities of α-Fe_2O_3 below 900 °C. Hellner and Euler (1957) suggest that the formation of hematite starts at about 350 °C. A small quantity, particularly if in microcrystalline form, well-dispersed in the material, would be difficult to detect, because it would probably be superparamagnetic at room temperature and show only a doublet spectrum.

The spectra and behaviour of the Trelavour biotite, heated in air, showed very similar features to those described above. The ferrous iron persisted to a slightly higher temperature in this biotite, despite the fact that it received the longer heat treatment. In general, there appeared to be no great difference between samples heated for twelve or twenty-four hours.

In the case of the Tregarden biotite, heated in vacuo, the sample heated to 500 °C is not so very

FIGS. 7 to 9: Mössbauer spectrum of Tregarden biotite after heating: FIG. 7 (top) in air at 900 °C; FIG. 8 (middle) in vacuo at 500 °C; FIG. 9 (bottom) in vacuo at 800 °C.

different from the original mica. There has been some oxidation of ferrous iron probably by adsorbed oxygen, and some changes in the parameters, but not the large changes seen in the air-heated sample. At 800 °C there is still a large amount of ferrous iron present, and the ratio of the intensities of the two ferrous doublets has been reversed, the inner doublet being now much the larger.

Discussion and interpretation. In both biotites and amphiboles, two distinct pro-
cesses occur during heating. Dehydroxylation takes place in biotite at temperatures
above 500 °C. Vedder and Wilkins (1969) have shown that the dehydroxylation of
biotite occurs via a similar process to that in muscovite, by condensation across
vacant octahedral sites, preferentially *b*-sites, that is with hydroxyls on opposite
corners of the octahedron. Hydroxyls not associated with vacancies remain stable
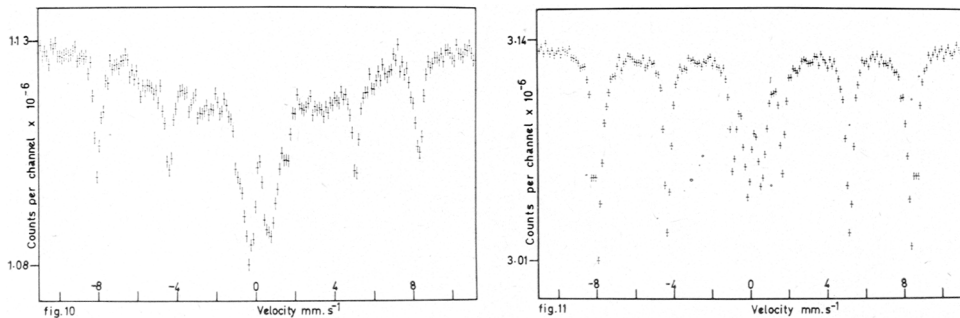
FIGS. 10 and 11: Mössbauer spectrum of Trelavour biotite after heating in air: FIG. 10 (left) at 900 °C;
FIG. 11 (right) at 1000 °C.

up to the onset of structural breakdown. The second process, oxidation of ferrous
iron, takes place at lower temperatures. It is accepted by the above authors that
ferrous iron co-ordinated by oxygen and one or more hydroxyls oxidizes to ferric
iron co-ordinated by one less hydroxyl group with the release of hydrogen, which
diffuses to the surface and is oxidized to water. The precise mechanism of this diffusion,
whether as a separate proton and electron via a hopping mechanism, or as atomic
hydrogen diffusing through the lattice, is uncertain.

In biotites, Vedder and Wilkins (1969) have pointed out three possible routes that
oxidation can follow, depending on the location of ferrous ions relative to one another.
Isolated ferrous ions in either *a*- or *b*- octahedral sites will oxidize to give ferric iron
co-ordinated by five oxygens and one hydroxyl group $Fe^{3+}(O_5OH)$. Ferrous ions in
adjacent *a*-sites, that is, sharing two hydroxyl ions, will both oxidize to give two
ferric ions co-ordinated by six oxygen ions, $Fe^{3+}(O_6)$. Ferrous ions in adjacent *a*-
and *b*-sites with three hydroxyl groups between them, sharing one, may yield two
$Fe^{3+}(O_5OH)$ if the shared hydroxyl remains intact, or one $Fe^{3+}(O_5OH)$ and one
$Fe^{3+}(O_6)$ if not. Thus one would expect to get substantial amounts of $Fe^{3+}(O_5OH)$
and lesser amounts of $Fe^{3+}(O_6)$ on heating.

The Mössbauer spectra of the heated biotites can be explained in terms of the two
main processes described above, dehydroxylation and oxidation. Below 500 °C it
can be seen that oxidation of ferrous iron is the main process. It would seem reason-
able to assume that the two ferric doublets resolvable above 350 °C are attributable
to the two types of ferric iron produced. The larger quadrupole split doublet is
attributed to the less symmetric $Fe^{3+}(O_5OH)$ species, while the inner doublet is
attributable to the more symmetric $Fe^{3+}(O_6)$ species. It can be seen that, initially,

the majority of the ferric iron produced is of the former type. Whether it is produced at the expense of ferrous iron in the a or b sites depends on how one assigns to these sites the inner and outer ferrous quadrupole doublets in the spectrum of the original mica. In the case of dioctahedral micas, Hogg and Meads (1970) have assigned the outer doublet to the $trans$-OH^- b-sites. They have assumed that this is also true of biotites, although the evidence is admittedly less firm. Yassoglou et $al.$ (1972) reached the same conclusion. Goodman and Wilson (1973), Annersten (1974), and Häggström et $al.$ (1969) have concluded that the larger quadrupole splitting should be ascribed to the cis a-sites. The last-mentioned authors base their conclusion on the result that, for a biotite sample very rich in iron, the intensity of the outer doublet corresponds to the occupation of more than two sites per formula unit by Fe^{2+}. The chosen formula unit contains four cis-OH^- sites and two $trans$-OH^- sites. Bancroft (1973) has pointed out the difficulty of making the assignment with certainty in trioctahedral micas where the X-ray evidence shows little difference in site size and distortion, unlike the dioctahedral case.

The small amount of $Fe^{3+}(O_6)$ formed at 400 °C and below would be the result of the latter part of the third oxidation route described above. Between 400 °C and 500 °C there is a marked increase in the amount of $Fe^{3+}(O_6)$ and a decrease in the amount of $Fe^{3+}(O_5OH)$. Although it is possible to argue that the remaining ferrous iron has all been oxidized to sixfold oxygen-co-ordinated ferric iron, this seems unlikely in view of the results up to this temperature, and it will be recalled that at this temperature dehydroxylation starts to take place. It therefore seems reasonable to suggest that most of the $Fe^{3+}(O_6)$ has been produced by dehydroxylation of $Fe^{3+}(O_5OH)$ across neighbouring vacancies. It is interesting to note that at the higher temperatures the amounts of ferric iron in both sites is nearly equal in the two micas. At first sight this suggests that in the original samples half the ferrous ions in the unit cell are adjacent to vacancies. This could just be true in the Trelavour biotite, where calculations from the analysis show 0·97 vacancies and 1·84 ferrous ions per unit cell. However, the argument is too simple as there is some ferric iron present initially that contributes to the inner doublet, and some $Fe^{3+}(O_6)$ ions will be formed directly from ferrous iron. Thus one would expect somewhat less than half the ferrous iron to be adjacent to vacancies, which is probably more realistic. Unfortunately, total analysis figures for the Tregarden biotite are not available, so a similar comparison cannot be made.

As previously stated, for the Tregarden biotite, heated in $vacuo$, reversal of the intensities of the two ferrous doublets has occurred between the temperatures 500 °C and 800 °C, the inner doublet being more intense in the sample heated to the higher temperature. This means that the ferrous iron is in a very distorted environment as one might expect if one is forming $Fe^{2+}(O_5OH)$ by condensation of hydroxyl groups across vacancies. It is interesting to note that in the air-heated samples, this condensation has apparently all taken place by about 500 °C but has barely started in the sample heated in $vacuo$ at this temperature. This rather suggests that the oxidation reaction catalyses the dehydroxylation process, perhaps by providing protons that are already mobile.

It should be noted that, as in the authors' previous work on micas (Hogg and Meads, 1970), the Mössbauer spectra are interpreted in terms of iron substitution in octa hedral sites only in the structure. There is some evidence that Fe^{3+} can substitute in tetrahedral sites in phlogopite (Hogarth et al. (1970)) but the results obtained by Annersten et al. (1971) indicate that the isomer shift for tetrahedral Fe^{3+} in a syn- thetic phlogopite is very much smaller ($\approx$ 0·3 mm s^{-1}) than the values ($\approx$ 0·7 mm s^{-1}) obtained in the present work. Some further tentative evidence for tetrahedral sub- stitution of Fe^{3+} in phlogopite has been given by Kemp (1972) in interpreting some weak Fe^{3+} electron-spin resonances in a mica of this type. The suggestion of Rice and Williams (1969) that low-spin Fe^{3+} occurs in biotites seems very unlikely. Their spectra are not very different from ours, and it seems likely that an alternative inter- pretation based on high-spin octahedral sites only is possible.

The *mechanism of oxidation* of ferrous iron and the concomitant release of hydrogen has been discussed in some detail by Addison et al. (1962), who studied the thermal oxidation of crocidolite fibres in air at 450 °C. They concluded that oxidation of ferrous iron within the lattice by oxygen is unlikely, as oxygen molecules are far too big to diffuse through the lattice. The mechanism they propose is that of surface oxidation of ferrous ions and hydroxyls fed from within the lattice by migration of electrons and protons by a hopping process: $Fe^{2+}_{(in\ lattice)} - e^-_{(mobile)} \rightarrow Fe^{3+}_{(in\ lattice)}$; $e^-_{(mobile)} + Fe^{3+}_{(surface)} \rightarrow Fe^{2+}_{(surface)}$; $OH^-_{(in\ lattice)} - H^+_{(mobile)} \rightarrow O^{2-}_{(in\ lattice)}$; $H^+_{(mobile)} + O^{2-}_{(surface)} \rightarrow OH^-_{(surface)}$. The process by which ferrous ions arrive at the surface is the same as positive-hole conduction, involving transfer of an electron from ferrous iron to a neighbouring ferric ion. Thus ferric ions 'diffuse' from the surface into the lattice. In amphiboles the cations are arranged in ribbons, and it was suggested that electron transfer takes place along these ribbons. The presence of magnesium in the ribbon blocks the transfer process, and amphiboles with high magnesium contents tend to be oxidation-resistant. In biotites the cations are arranged in sheets and, while the electron transfer processes will be confined to these sheets, there is much less likelihood of its being blocked by magnesium ions. Proton migration is by a similar process to electron migration, that is, by hopping between the O^{2-} ions until an OH^- ion appears on the surface to be oxidized. Vedder and Wilkins (1969) have questioned this hop- ping mechanism, arguing on the basis of diffusion constants that it is unlikely that the proton and electron will separate by any great distance. They argue for the dif- fusion of atomic hydrogen or a proton and electron in close association. If this were the case, one would expect oxidation to occur even *in vacuo*, the hydrogen atoms uniting to form molecules at the surface and being removed. Clearly this does not happen to any great extent. Further, in the analogous situation of the thermal de- composition of $Fe(OH)_2$ one might expect Fe_2O_3, H_2O, and H_2 as decomposition products by Vedder and Wilkins's argument, but Bernal et al. (1959) have shown that $Fe(OH)_2$ dehydrates to FeO at 200 °C and on further heating disproportionates to metallic iron and Fe_3O_4. Thus the original mechanism proposed by Addison et al. (1962) would seem most acceptable.

Davidson and Yoffe (1968) have studied electrical conduction in micas as a function of temperature between 4·2 and 520 K but have interpreted the increased conductivity

at high temperatures in classical terms of conduction in insulators. It is doubtful whether any effects due to dehydroxylation would be seen at 520 K anyhow. However, it would be interesting to observe the change in conductivity in the region 300 °C to 600 °C in biotite. A marked increase in the conductivity would imply the liberation of protons and electrons by the Addison mechanism. Littler and Williams (1965) have interpreted the electrical conductivity of crocidolite at room temperature in terms of proton and electron hopping mechanisms.

Correlation of Mössbauer and thermogravimetry results. Analysis by thermogravimetry (TG) of the Trelavour biotite gives results in excellent agreement with the broad outlines of the Mössbauer analysis, supporting the conclusions reached here and elsewhere. The curve of percentage weight loss versus temperatu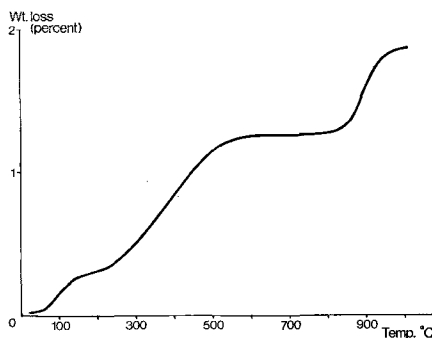re is shown in fig. 12. It can be seen that up to 150 °C there is a small loss in weight due to desorption of moisture. Between 200 °C and 550 °C there is a 1 % weight loss. It is in this region that the Mössbauer spectra show oxidation and dehydroxylation. Between 550 ° and 800 ° there is little change in weight, as expected from the spectra in this region, but from 850 ° to 1000 ° there is a second large weight loss corresponding in the Mössbauer spectra to the destruction of the biotite lattice and formation of Fe_2O_3.

FIG. 12: Weight loss *v.* temperature for Trelavour biotite.

Conclusions. The Mössbauer spectra of biotites heated in air at various temperatures can be interpreted in terms of two main processes. Substantial oxidation of ferrous iron takes place at temperatures below 400 °C and dehydroxylation occurs at slightly higher temperatures. Between 500 ° and 900 ° no great changes are apparent and the spectra consist of two ferric doublets of similar isomer shift but different quadrupole splittings. The inner doublet is attributed to ferric iron co-ordinated by six oxygen ions, the outer doublet to ferric iron co-ordinated by five oxygens and one hydroxyl ion. At 900 °C structural breakdown commences, and α-Fe_2O_3 becomes the principle iron-bearing phase. This interpretation agrees well with the effects observed in micas and amphiboles by other workers using other techniques. Spectra of biotite heated *in vacuo* show the mica to have suffered much less oxidation, and the onset of dehydroxylation would appear to be delayed relative to the samples heated in air. The lack of oxidation *in vacuo* tends to support the theory of Addison *et al.* (1962) of oxidation by a hopping mechanism rather than that of Vedder and Wilkins (1969) suggesting hydrogen atom formation. The Mössbauer results correlate well with those of thermogravimetry.

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