# Iron-57 Conversion-electron Mössbauer Spectroscopic Study of the Initial Stages of the Oxidation of Biotite

By **Michael J. Tricker** * and **Ann P. Winterbottom**, Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE
**Alan G. Freeman**, Department of Chemistry, University of Victoria, Wellington, New Zealand

The technique of $^{57}$Fe conversion-electron Mössbauer spectroscopy is shown to be a viable method for the study of the early stages of solid-state reactions which start in regions close to solid surfaces. In particular, increases in the $Fe^{3+}:Fe^{2+}$ ratio can be detected in a region confined to within 300 nm of the outer surfaces of a biotite flake which has been subjected to mild oxidation in air. These changes would have gone undetected if conventional transmission Mössbauer methods had been used alone. The reactions which occur in the surface regions of biotites during heat treatment in air are discussed.

THE use of $^{57}$Fe Mössbauer spectroscopy in the study of minerals and solid-state reactions is now well established.[1-3] Most Mössbauer spectra are accumulated by monitoring the $\gamma$-radiation transmitted through a 'thin' specimen and in this way information relating to bulk properties of the material under examination is obtained. In situations where the process of sample preparation and consequent alteration or destruction of the specimen is impracticable, 'thick' iron-containing specimens can be studied in a reflection geometry by monitoring the back-scattered $X$- or $\gamma$-ray photons which result from the decay of the $I = \frac{3}{2}$ nuclear spin state of $^{57}$Fe in the sample. This technique has been applied to mineral specimens including lunar samples [4-6] and in the study of corrosion products *in situ*.[7] More attractive to the surface chemist is the possibility of increasing the surface sensitivity of $^{57}$Fe Mössbauer spectroscopy by counting the back-scattered conversion and Auger electrons.[8-10] In this way the depth probed is limited to *ca.* 300 nm.[9,11] The sensitivity of the method is such that (using existing equipment) *ca.* 80 Å of natural iron (*ca.* 2% $^{57}$Fe) can be detected and, with enrichment, a monolayer or so of iron should be detectable.

The usefulness of conversion-electron Mössbauer spectroscopy (CEMS) in such areas as metallurgy,[12] oxidation,[11,13] and corrosion [8,9,11] of metals and ion implantation [14] has been demonstrated. The main purpose of this paper is to test the utility of CEMS in the study of the early stages of a solid-state reaction. To this end we have chosen to study the oxidation of biotite, a reaction which has already been studied by more conventional techniques such as weight loss and gas evolution,[15,16] infrared spectroscopy,[17] and recently transmission Mössbauer spectroscopy.[18]

## EXPERIMENTAL

Thin slices (*ca.* $30 \times 30 \times 0.5$ mm) of biotite single crystals (containing *ca.* 20% FeO) obtained from Gregory Bottley Ltd. were subjected to oxidation in a muffle furnace at 550 and 620 K. CEM and transmission spectra were recorded periodically at room temperature for each sample. The orientation of the crystals remained constant and the $\gamma$-radiation was perpendicular to the basal surface. During the heating processes no visible change occurred in the colouration of the biotite surfaces. Very long heating

---

[1] G. M. Bancroft, 'Mössbauer Spectroscopy, An Introduction for Inorganic Chemists and Geochemists,' McGraw-Hill, London, 1975.

[2] A. G. Maddock, 'Mössbauer Spectroscopy and its Applications,' I.A.E.E., Vienna, 1972.

[3] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman Hall, London, 1973, and refs. therein.

[4] L. D. Lafleur, G. D. Goodman, and E. A. King, *Science*, 1968, **162**, 1268.

[5] C. L. Herzenberg and D. L. Riley, 'Developments in Applied Spectroscopy,' Plenum Press, New York, 1970, vol. 8, p. 227.

[6] C. L. Herzenberg and D. L. Riley, *Proc. Apollo Lunar Sci. Conf.*, 1970, **3**, 2221.

[7] W. Meisal, *Werkstoffe Korros.*, 1970, **21**, 249.

[8] M. J. Tricker, J. M. Thomas, and A. P. Winterbottom, *Surface Sci.*, 1974, **45**, 601.

[9] K. R. Swanson and J. J. Spijkerman, *J. Appl. Phys.*, 1970, **41**, 3155.

[10] J. H. Terrel and J. J. Spijkerman, *Appl. Phys. Letters*, 1968, **13**, 11.

[11] J. M. Thomas, M. J. Tricker, and A. P. Winterbottom, *J.C.S. Faraday II*, 1975, 1708.

[12] H. K. Chow and R. L. Bogner, Applied Spectroscopy Symposium, Chicago, 1969.

[13] G. W. Simmons, E. Kellerman, and H. Leidheiser, jun., *Corrosion*, 1974, **45**, 227.

[14] M. J. Tricker, R. K. Thorpe, J. H. Freeman, and G. A Gard, *Phys. Stat. Solidi.* 1976, **A22**, 1597.

[15] A. D. White and J. H. Sharp, *J. Chem. Soc.* (*A*), 1971, 3062.

[16] P. G. Rouxhet, J. L. Gillard, and J. J. Fripiat, *Mineral. Mag.*, 1972, **38**, 583.

[17] W. Vedder and R. W. T. Wikins, *Amer. Mineral.*, 1969, **54**, 482.

[18] C. S. Hogg and R. E. Meads, *Mineral. Mag.*, 1975, **40**, 79.

times (*ca.* 50 d) produced some slight flaking of the surface and at this point the sample was discarded. In order to detect the conversion electrons a helium–methane flow proportional counter [8] was used together with a 50 mCi $^{57}$Co–Rh source. Normally CEM spectra were accumulated for 24 h resulting in *ca.* $10^6$ counts in each channel of a 256 multichannel analyser. Transmission spectra could be recorded simultaneously as previously described,[8] although shorter counting times were required.

TABLE 1

Summary of isomer shifts ($\delta$ rel. to $\alpha$-Fe), quadrupole splittings ($\Delta$), and full linewidths ($\Gamma$) obtained by transmission Mössbauer spectroscopy of the biotite studied before and after heat treatment for 700 h at 550 K. These parameters are in mm s$^{-1}$ and are thought to be accurate to $\pm 0.03$ mm s$^{-1}$. The iron(III) parameters quoted are 'averages' of the true parameters of the iron(III) sites present. The area ratios quoted are thought to be precise to $\pm 10\%$

| | $Fe^{2+}$ M1 | | | $Fe^{2+}$ M2 | | | | $Fe^{3+}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\delta$ | $\Delta$ | $\Gamma$ | $\delta$ | $\Delta$ | $\Gamma$ | $Fe^{2+}$ M1/M2 | $\delta$ | $\Delta$ | $\Gamma$ | $Fe^{3+}/Fe^{2+}$ |
| Unheated sample | 1.08 | 2.15 | 0.34 | 1.11 | 2.58 | 0.30 | 0.32 | 0.43 | 0.71 | 0.44 | 0.43 |
| Heated sample | 1.06 | 2.19 | 0.38 | 1.13 | 2.65 | 0.36 | 0.43 | 0.49 | 0.63 | 0.59 | 0.50 |

The spectra were computer fitted assuming Lorentzian lineshapes * using the 'least-squares' program of Stone.

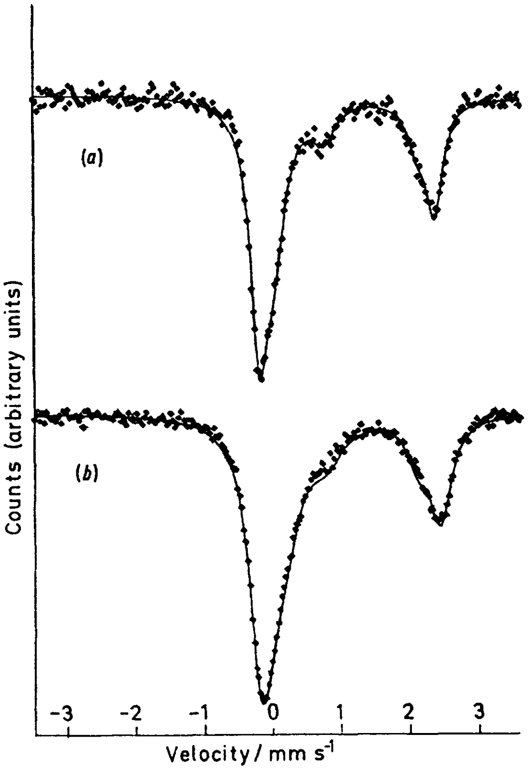

FIGURE 1 Transmission $^{57}$Fe Mössbauer spectra of biotite before (*a*) and after (*b*) heat treatment for 700 h at 550 K. Spectrum (*b*) shows a pronounced broadening, especially in the iron(III) region, relative to (*a*)

In order to obtain convergence, constraints had to be imposed on the parameters. As the samples were single crystals the usual assumption that the peak areas of each arm of a quadrupole doublet are equal could not be made. Accordingly, for a given set of spectra of a crystal in the same orientation, the area ratios of the component quadrupole doublets were determined with positions sensibly fixed. These ratios were averaged and used as constraints in subsequent fits. For spectra with only weak iron(III) signals, six-line [two iron(II) and one iron(III) quadrupole doublets] fits were made. For spectra with higher iron(III) contents an extra iron(III) doublet was added making a total of eight lines per spectrum. $\chi^2$ Values were generally *ca.* 270 for 230 degrees of freedom.

## RESULTS

Transmission [Figure 1(*a*)] and CEM spectra [Figure 2(*a*)] of freshly cleaved unheated biotite crystals yielded essentially similar spectra. The material contains predominantly Fe$^{II}$ distributed over the two possible $Fe^{2+}(O^{2-})_4(OH^-)_2$ 'octahedral' sites within the biotite. The derived parameters (see Table 1) are in good agreement with previous

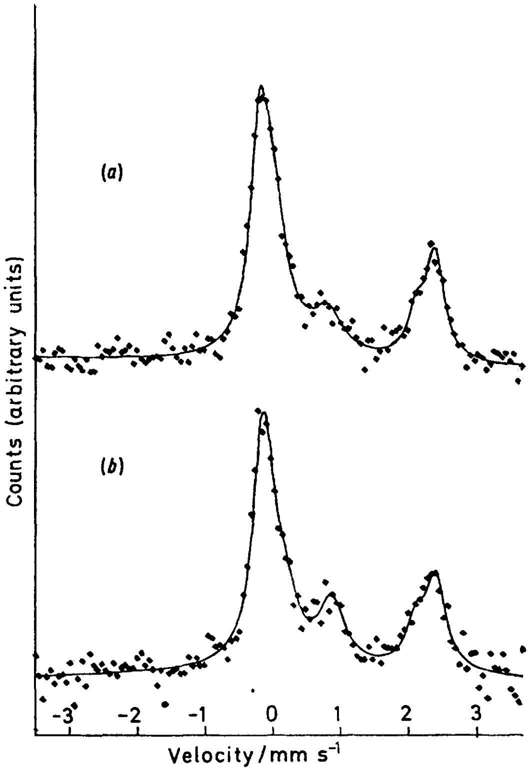

FIGURE 2 CEM spectrum of biotite before (*a*) and after (*b*) heat treatment at 550 K for 100 h. The increase in iron(III) content in spectrum (*b*) is to be noted

---

* This is a good approximation because the limited probing depth of CEMS means that all absorbers containing natural abundances of $^{57}$Fe can be taken to be effectively 'thin.' [19,20]

[19] T. E. Cranshaw, *J. Phys.* (*E*), 1974, **7**, 122.

[20] M. J. Tricker, A. G. Freeman, J. M. Thomas, and A. P. Winterbottom, *Nuclear Instr. Methods*, in the press.

TABLE 2

Summary of the data obtained from CEM spectra of a biotite heated at 620 K. Parameters are in mm $s^{-1}$ and are accurate to $\pm 0.03$ mm $s^{-1}$. Area ratios are thought to be precise to $\pm 10\%$

| Time heated/h | $Fe^{2+}$ M1 |  | $Fe^{2+}$ M2 |  | $Fe^{2+}$ | $Fe^{3+}$ (1) |  |  | $Fe^{3+}$ (2) |  |  | $Fe^{2+}$ M1/M2 | $Fe^{3+}$ (1)/ $Fe^{3+}$ (2) | $Fe^{3+}/Fe^{2+}$ | $\alpha$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $\delta$ | $\Delta$ | $\delta$ | $\Delta$ | $\Gamma$ | $\delta$ | $\Delta$ | $\Gamma$ | $\delta$ | $\Delta$ | $\Gamma$ |  |  |  |  |
| 24 | 1.05 | 2.09 | 1.10 | 2.61 | 0.35 | 0.52 | 1.16 | 0.34 | 0.54 | 0.62 | 0.46 | 0.51 | 0.58 | 0.60 | 0.0061 |
| 43 | 1.07 | 2.12 | 1.11 | 2.70 | 0.35 | 0.50 | 1.20 | 0.36 | 0.50 | 0.65 | 0.40 | 0.60 | 1.0 | 0.62 | 0.075 |
| 60 | 1.09 | 2.18 | 1.11 | 2.64 | 0.36 | 0.50 | 1.15 | 0.40 | 0.48 | 0.70 | 0.37 | 0.53 | 1.6 | 0.86 | 0.19 |
| 78 | 1.07 | 2.18 | 1.13 | 2.67 | 0.36 | 0.51 | 1.17 | 0.46 | 0.50 | 0.74 | 0.42 | 0.40 | 1.6 | 0.91 | 0.20 |
| 90 | 1.06 | 2.13 | 1.11 | 2.63 | 0.47 | 0.48 | 1.19 | 0.51 | 0.45 | 0.73 | 0.50 | 0.54 | 1.5 | 0.96 | 0.24 |
| 114 | 1.06 | 2.11 | 1.10 | 2.63 | 0.36 | 0.51 | 1.13 | 0.46 | 0.49 | 0.78 | 0.37 | 0.47 | 2.0 | 1.03 | 0.25 |

work [21-25] and in accordance with the majority of workers we assign the outer iron(II) doublet to the M2 site with *cis*-hydroxides and the inner iron(II) doublet to the M1 site with *trans*-hydroxides.[18,21-25] As the iron(III) content of the unheated samples was low, only a single doublet could be fitted to the central regions, although some workers have fitted this region to two doublets corresponding to iron(III) in the M1 and M2 sites.[22-24] Fortunately the $Fe^{2+}$ : $Fe^{3+}$ ratios in biotites and related minerals seem to be little changed by using a six-line or eight-line total fit.[24]

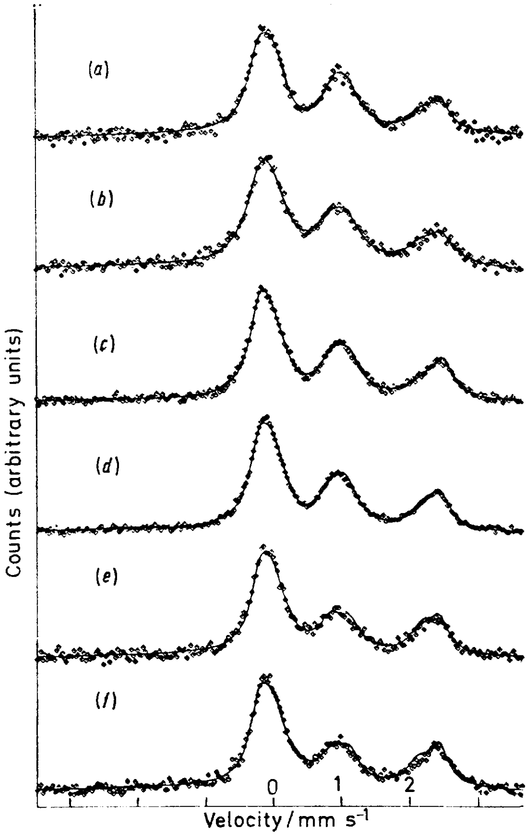

FIGURE 3 CEM spectra of biotite heated at 620 K. The total time of heat treatment was 114 (*a*), 90 (*b*), 78 (*c*), 60 (*d*), 43 (*e*), and 24 h (*f*)

Increases in the iron(III) content of biotite could be detected by CEMS after treatment at 550 K for 100 h [Figure 2(*b*)]. No change in the transmission spectra occurred indicating that the oxidation is confined to the outermost regions of the biotite. Longer heat treatments at 550 K resulted in increasing iron(III) content at the surface as indicated by CEMS but the $Fe^{2+}$ : $Fe^{3+}$ ratio remained unaltered in the bulk. Very long heating times, 700 h at 550 K, eventually caused a broadening of the transmission spectra [Figure 1(*b*)] especially in the iron(III) region where considerable resolution was lost. The results of a more detailed study at 620 K are summarised in Table 2. The CEM spectra revealed an increase in $Fe^{3+}$ in the surface regions which levelled off after 120 h (Figure 3). No changes in the transmission spectra were observed during heat treatment at 620 K. The CEM spectra were computer fitted to two iron(II) and two iron(III) doublets (see Experimental section). The fractional decomposition, $\alpha$, of the iron(II) content is shown in Figure 4, where it can be seen that there is an induction period followed by an acceleration period before the reaction effectively ceases, in the region probed, at $\alpha = 0.25$.* It can also be seen from Table 2 that there is no preferential oxidation of $Fe^{2+}$ in M1 or M2 sites as the ratio of $Fe^{2+}$ in the two sites is constant at *ca.* 0.5 : 1 throughout the heat treatment.

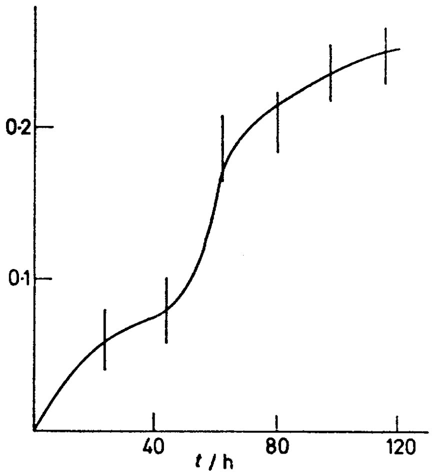

FIGURE 4 Fractional decomposition of biotite to oxybiotite as a function of time

---

* The $Fe^{2+}$ : $Fe^{3+}$ ratios were determined directly from the spectral areas. This assumes that the recoil-free fraction of the iron is similar in all the sites and that the distribution of $Fe^{3+}$ relative to $Fe^{2+}$ is constant in depth. As $Fe^{3+}$ may be concentrated closer to the surface, the values of $\alpha$ may be systematically too small for the reactive region.

[21] C. S. Hogg and R. E. Meads, *Mineral. Mag.*, 1970, **37**, 606.

[22] H. Annersten, *Amer. Mineral.*, 1971, **59**, 143.

[23] B. A. Goodman and M. J. Wilson, *Mineral. Mag.*, 1973, **39**, 448.

[24] G. M. Bancroft and J. R. Brown, *Amer. Mineral.*, 1975, **60**, 265.

[25] L. Haggstrom, R. Wappling, and H. Annersten, *Chem. Phys. Letters*, 1969, **4**, 107.

The trend of the data (Table 2) suggests that the iron(III) site with the larger quadrupole interaction is the main product of the oxidation. These iron(III) parameters are similar to those assigned to $Fe^{3+}(O^{2-})_6$ species by Hogg and Meads,[18] using transmission methods in more heavily oxidised biotites. The iron(III) parameters can be associated with the production of mainly $Fe^{3+}(O^{2-})_6$ moieties at the surface of the biotite. The interpretation of the iron(III) region of the spectra is complicated by the undoubted presence of other ion species such as $Fe^{3+}(O^{2-})_5(OH^-)$ and $Fe^{3+}(O^{2-})_4(OH^-)_2$ (*cis* and *trans*) within the clay. Further more detailed interpretation of the 'averaged' fit is therefore not warranted, although the relative $Fe^{3+} : Fe^{2+}$ ratios are expected to be meaningful.[24]

The inequality of the area ratios of the individual arms of the iron(III) quadrupole doublets is in small part due to the inadequacy of a four-line fit to the iron(III) regions, but more importantly asymmetry is expected as the product is orientated with respect to the parent lattice and no loss of crystallinity is expected following mild heat treatment.

## DISCUSSION

The results clearly demonstrate that CEMS is capable of revealing information on the surface and subsurface regions of biotites which would have gone undetected if transmission Mössbauer spectroscopy had been used alone. Previous estimates [11] of the probing depth of CEMS indicate that the changes monitored occur within 300—500 nm of the outermost surface.

A number of reactions, (1)—(3), occur when biotites are heated in the presence of oxygen.[15] When biotites are heated in air in the range 770—870 K reaction (3) and, to a lesser extent, (2) occur in the bulk.[15] Reaction (3) is favoured as this can be sustained by diffusion of protons and electrons to surface regions thereby continually exposing $Fe^{2+}$ and $OH^-$ to oxygen.[26]

$$\text{Dehydroxylation, } 2OH^- \longrightarrow O^{2-} + H_2O \qquad (1)$$

$$\text{Oxygenation, } 4Fe^{2+} + O_2 \longrightarrow 4Fe^{3+} + 2O^{2-} \qquad (2)$$

$$\text{Dehydrogenation, } 4Fe^{2+} + 4OH^- + O_2 \longrightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O \qquad (3)$$

At the surface we may expect $Fe^{3+}$ to be produced by both reactions (2) and (3). Reaction (3) clearly leads to the production of $Fe^{3+}(O^{2-})_5(OH^-)$ and $Fe^{3+}(O^{2-})_4(OH^-)_2$ moieties compatible with the observed CEMS results. However, oxygenation is expected to be facilitated and may even predominate at the surface because there, in contrast to in the bulk, direct reaction of $Fe^{2+}$ with oxygen may occur at basal surfaces and at exposed prismatic edges at steps on the basal surfaces. Moreover, the ability of oxygen to gain access to the internal structure by diffusion into cracks associated with grain and sub-grain boundaries is enhanced close to the surface. Following oxygenation, two new $O^{2-}$ anions per $O_2$ have to be accommodated in the structure. These anions could be incorporated by reaction of oxygen with five-(or less)co-ordinate $Fe^{2+}$ exposed at prismatic edges following removal of adsorbed species during heat treatment. It is also possible that dehydroxylation [reaction (1)] occurs in the surface regions. This reaction involves the removal of an $OH^-$ but the resulting incomplete co-ordination shell could be rapidly made good by oxygenation.

Transmission methods indicate that there is a small increase in the iron(III) content in the bulk of the specimen treated for 700 h at 280 °C (Figure 1 and Table 1), although the quality of the fit is not good especially in the iron(III) region. This increase could result from reactions (1) and (2) and could in part lead to the observed broadening of the lines relative to the unheated sample (Table 1). The broadening of this transmission spectrum may also be associated with dehydroxylation in the bulk. Although this process is generally thought to occur readily at higher tempertures,[15,17] the water molecules produced would be trapped in the bulk at these low temperatures and remain undetected by weight-change or gas-evolution experiments. As the broadening is especially pronounced in the iron(III) region it appears that, as suggested by Veddar and Wikins,[17] dehydroxylation of an iron(III) hydroxide with a neighbour across an octahedral vacancy associated with $Fe^{3+}$ takes place readily. As oxygenation would not be possible in the bulk at such low temperatures, the distortion of the lattice, due to the presence of $O^{2-}$ and trapped water molecules, would yield a range of iron sites and lead to the observed spectral broadening.

In conclusion, it is clear that CEMS will prove to be a valuable technique in the elucidation of the early stages of a variety of solid-state reactions which cause nucleation in the surface regions. Information relating to the nature of the product, its rate of growth, and, for single-crystal studies, the orientation of the product with respect to the parent should be obtainable.

We thank Professor J. M. Thomas for stimulating discussion, J. R. Brown for a preprint of ref. 24, the S.R.C. for support, and the British Steel Corporation for an award of a fellowship (to M. J. T.).

[6/039 *Received, 7th January*, 1976]

[26] C. C. Addison, W. E. Addison, G. H. Neal, and J. H. Sharpe, *J. Chem. Soc.*, 1962, 1468.