

278. *Amphiboles. Part I. The Oxidation of Crocidolite.*

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The oxidation of crocidolite at 450° has been shown to involve simultaneous oxidation of ferrous and hydroxyl ions, and to follow mainly the equation,  $4\text{Fe}^{2+} + 4\text{OH}^- + \text{O}_2 \longrightarrow 4\text{Fe}^{3+} + 4\text{O}^{2-} + 2\text{H}_2\text{O}$ , with a secondary surface reaction,  $4\text{Fe}^{2+} + \text{O}_2 \longrightarrow 4\text{Fe}^{3+} + 2\text{O}^{2-}$ . The reaction takes place on the surface and is maintained by the migration of electrons and protons through the crystal. The incomplete nature of the oxidation at this temperature is attributed, not to a deficiency of hydroxyl ions, but to a blocking action by magnesium ions.

THE mineral crocidolite (blue asbestos) is the fibrous form of the amphibole riebeckite and can be represented by the idealised formula  $\text{Na}_2\text{Fe}^{\text{III}}_2(\text{Fe}^{\text{II}}, \text{Mg})_3\text{Si}_8\text{O}_{22}(\text{OH})_2$ . It has considerable commercial importance but little or no quantitative information about its oxidation is available. Study has been concentrated on differential thermal analysis (D.T.A.) experiments<sup>1</sup> and a structure determination of a sample of Bolivian origin.<sup>2</sup>

## EXPERIMENTAL

The samples of crocidolite used in this study are described by Cilliers *et al.*<sup>3</sup> as R.S. 8, 10, and 13 and came from the Koegas district of South Africa. Their analyses are given in Table 1.

TABLE 1.  
Analyses of crocidolite samples.\*

	R.S. 8	R.S. 10	R.S. 13		R.S. 8	R.S. 10	R.S. 13		R.S. 8	R.S. 10	R.S. 13
$\text{SiO}_2$ ...	51.40	51.40	51.20	MnO ...	—	—	0.07 †	$\text{H}_2\text{O}^{+105}$	2.37	2.22	2.20
$\text{Fe}_2\text{O}_3$ ...	17.70	19.07	17.40	CaO .....	0.78	0.90	1.11	$\text{H}_2\text{O}^{-105}$	0.20	0.20	0.17
FeO ...	19.00	19.15	20.40	$\text{Na}_2\text{O}$ ...	6.27	6.30	6.31				
MgO ...	2.05	1.40	2.21	$\text{CO}_2$ .....	0.33	0.10	0.06	Total	100.10	100.74	101.03

\* The analyses are by W. Bennis, except for the FeO and  $\text{Fe}_2\text{O}_3$  figures which were determined by W. E. Addison on each individual sample in its precise condition before and after oxidation on account of the ease of superficial oxidation.

† This small amount of manganese has been neglected in subsequent calculations based on this analysis.

Their interpretation to yield atomic ratios is not entirely straightforward. As will be discussed below, crocidolite is very easily oxidised, at least superficially, water is a product of its oxidation, and weight-loss determinations<sup>4</sup> and work described below indicate that some water is held tenaciously on the surface; it is thus inadvisable to use the  $\text{H}_2\text{O}^{+105}$  figure as an indication of the hydroxyl content, as is sometimes done for minerals of this type. The atomic ratios are given in Table 2, columns marked A, two assumptions having been made in their derivation. First, that the carbon dioxide is present as calcite (the calcium content of the crocidolite has been modified accordingly); secondly, for fresh materials, that the oxygen lattice of what can be regarded as an approximately close-packed structure is complete, and that the metal and silicon atoms fill the fifteen sites per twenty-four oxygen atoms available to them. Aluminium is absent, and the closeness of the values obtained for silicon to the theoretical value of 8.0 supports these assumptions.

*Oxidations.*—Samples of crocidolite were contained in a small bulb within an electric furnace and attached to a system containing a manometer and a burette with a levelling device to enable the pressure in the system to be maintained approximately constant, if required.

<sup>1</sup> Vermaas, *Trans. Geol. Soc. South Africa*, 1953, **55**, 199.

<sup>2</sup> Whittaker, *Acta Cryst.*, 1949, **2**, 312.

<sup>3</sup> Cilliers, Freeman, Hodgson, and Taylor, *Econ. Geol.*, 1961, **56**, 1421.

<sup>4</sup> Freeman and Taylor, personal communication.

A cold trap was added at a point as near to the sample as possible and separated from the rest of the system by a tap. The samples were pumped out at the oxidation temperature and  $10^{-6}$  mm. overnight before being oxidised. Spectroscopically pure oxygen was then admitted and a pressure of 30—40 cm. maintained by adjusting the levelling device; the whole was then left until no further uptake of oxygen was detected in 24 hr.; 7—10 days were required for this. Variation of pressure was shown not to affect the extent of oxidation. Oxidations were studied at  $450^{\circ}$ , *i.e.*, appreciably above the temperature range ( $410$ — $420^{\circ}$ ) found to correspond to an exotherm on the D.T.A. experiments and normally attributed to oxidation.<sup>1,2</sup> Slight increase in temperature did not produce a detectable increase in the amount of oxidation.

When oxidation was complete, the amount of water formed was determined. First, the cold trap was isolated and the rest of the system evacuated; then the gaseous oxygen in the trap was very rapidly pumped off (2—3 sec.), and the oxidised crocidolite left in system with a tared tube immersed in a trap containing liquid nitrogen for at least 12 hr. It was shown that a shorter period did not yield all the water, which illustrates the strong retention of some surface water by oxidised crocidolite. Finally, the oxidised crocidolite was reweighed after cooling and then analysed for ferrous and ferric iron. The results, converted into atomic ratios, are given in Table 2 for each sample of crocidolite, both in the massive form as obtained (unfiberised) and after being ground by means of a hack-saw blade in order to break up the bundles of fibres and decrease the average fibre length (fiberised).

### RESULTS AND DISCUSSION

*Stoichiometry of Reaction.*—The atomic compositions of the fresh unfiberised, fiberised, and oxidised materials are given in Table 2, together with information ( $x$ ,  $y$ ) about the oxidation. The average number of atoms of ferrous iron oxidised per mole of oxygen

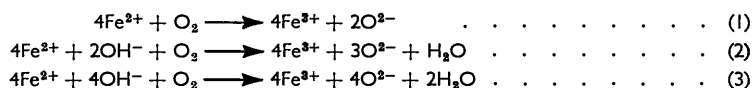
TABLE 2.  
Atomic ratios in fresh unfiberised (A), fiberised (B), oxidised unfiberised (C), and oxidised fiberised (D) crocidolite.

	R.S. 8				R.S. 10				R.S. 13			
	A	B	C	D	A	B	C	D	A	B	C	D
Na ...	1.89	1.89	1.89	1.89	1.90	1.90	1.90	1.90	1.88	1.88	1.88	1.88
Ca ...	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.16	0.16	0.16	0.16
Mg ...	0.48	0.48	0.48	0.48	0.32	0.32	0.32	0.32	0.51	0.51	0.51	0.51
Fe <sup>2+</sup> ...	2.46	2.27	0.44	0.24	2.49	2.36	0.34	0.19	2.63	2.36	0.64	0.41
Fe <sup>3+</sup> ...	2.12	2.31	4.15	4.37	2.23	2.35	4.37	4.54	2.02	2.35	3.99	4.21
Si .....	7.97	7.97	7.97	7.97	7.98	7.98	7.98	7.98	7.89	7.89	7.89	7.89
O .....	22.17	22.36	24.11	24.19	22.29	22.39	24.20	24.31	22.10	22.37	24.01	24.12
OH ...	1.83	1.64	—	—	1.71	1.61	—	—	1.90	1.63	—	—
$x$ .....			3.92	3.97			4.14	4.04			3.91	3.74
$y$ .....			11.57	11.54			11.61	12.09			11.34	11.41

$x$  = No. of Fe atoms oxidised per mole of O<sub>2</sub>.  $y$  = Vol. of O<sub>2</sub> (l. per formula wt. of crocidolite) used in oxidation.

is 3.95, close to the required value of 4.00. In addition there is given the volume of oxygen used in the oxidation per formula weight of crocidolite.

Various equations can be suggested to describe the oxidation:

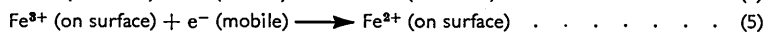
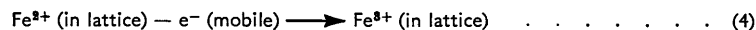


Three lines of evidence are available to differentiate them and each is in accord with reaction (3). First, the oxidation of crocidolite is always accompanied by a slight weight loss, whereas reactions (1) and (2) should result in a gain in weight. Secondly, water is liberated during reaction and the yield obtained in a large number of experiments averaged 90—95% of that required by reaction (3) (the significance of the yield's being below 100%

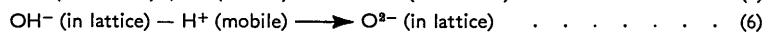
is referred to below). Thirdly, Freeman and Taylor<sup>4</sup> have shown that oxidised samples have an identical *X*-ray pattern with that of fresh material, apart from a slight lattice contraction commensurate with the change from ferrous to ferric iron. Some change in structure and hence in *X*-ray pattern would be expected if reactions (1) or (2) were of importance in describing the reaction. It is concluded that reaction (3) is basic for the reaction and that oxidation of ferrous to ferric iron is thus accompanied by oxidation of hydroxyl to oxide ion, leaving as product an oxo-amphibole.

The extent to which crocidolite is oxidised on fiberisation can be seen by comparing the ferrous contents of each of the three specimens in the unfiberised and the fiberised condition. Fiberisation was effected at room temperature under relatively mild conditions and for a short time only, so that it seems reasonable to conclude that any sample of the mineral which has been exposed to the air will be, at least superficially, oxidised, and hence be slightly deficient in hydroxyl, since this oxidation must be the oxidation of fresh surfaces. This is in accord with the hydroxyl contents of fresh materials shown in Table 2. Fiberisation does not alter the colour of the material, whereas extensively oxidised crocidolite has a rich brown colour.

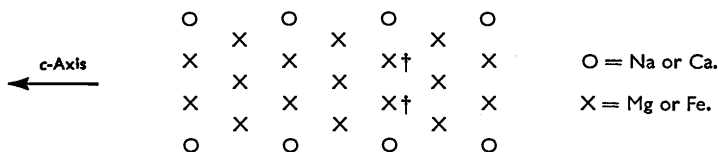
*Mechanism of Reaction.*—Reaction between gaseous oxygen and ferrous and hydroxyl ions is most unlikely to occur within the crystal lattice as the oxygen molecule is too large to penetrate it. For reaction to proceed on the surface to the extent indicated in Table 2, both ferrous and hydroxyl ions must be available on the surface continuously, and this requires transport of both types of ion or, more simply, migration of both electrons and protons through the crystal. This can be represented schematically by the reactions:



and



This process, by which a ferrous ion is produced on the surface, is the same as in positive hole conduction and involves transfer of an electron from one ferrous ion to a neighbouring ferric ion and the continuance of this process until there is a ferrous ion on the surface. The cations in an amphibole are arranged in a ribbon-like manner parallel to the *c* (fibre) axis, so that any electron transfer should be along the ribbon, whereas movement from one ribbon to another is unlikely on account of the greater distance involved and because the outermost ions in the ribbon are the larger sodium and calcium ions<sup>5</sup> which could not participate in the electron transfer (see diagram).



The migration of a proton is similar to that of an electron and there are adequate  $\text{O}^{2-}$  ions in the structure for the proton to be able to move in single jumps until a hydroxyl ion is produced at the surface.

If reaction (3) represents the reaction completely oxidation should stop when the hydroxyl ions have been oxidised, since in the samples used the number of ferrous ions is greater than the number of hydroxyl ions. The results in Table 2 indicate that reaction does not stop at this point, and the more extensive oxidation of fiberised material in each case cannot be reconciled with such a mechanism. It is suggested, therefore, that when no hydroxyl ions remain, oxidation follows reaction (1), producing a superficial layer

<sup>5</sup> Whittaker, *Acta Cryst.*, 1960, **13**, 291.

approximating to ferric oxide in composition; such a layer could not be detected by means of X-ray diffraction, but the partial obedience to reaction (1) can explain the low yields of water referred to above.

If two positions  $X\ddagger$  are occupied by magnesium ions, the migration of an electron through this ribbon, as discussed above, becomes blocked; and if two such blocks occur within one fibre, those ferrous ions which are trapped between the two blocks cannot be oxidised in this way. That would explain the inability to achieve complete oxidation of ferrous iron at 450° by a combination of reactions (1) and (3). When the material is fiberised there is less likelihood that any fibre will be sufficiently long for two blocks to occur, and hence the oxidation of fiberised material will be more extensive, as was found (see Table 2).

Further evidence in favour of this hypothesis is that the higher the magnesium content of the sample, and hence the greater the probability of blockage, the higher is the residual ferrous iron content when oxidation at 450° has reached its limit. The analytical figures given in Table 3 amplify this point.

TABLE 3.

Sample	R.S. 13	R.S. 8	R.S. 10
MgO (%) in fresh material .....	2.21	2.05	1.40
FeO (%) in oxidised, fiberised material.....	3.23	1.86	1.48
FeO (%) in oxidised, unfiberised material .....	4.85	3.34	2.64

A sample of Bolivian crocidolite was very kindly supplied by Dr. E. J. W. Whittaker; this has a much higher magnesium content than African crocidolite (see ref. 2 for a typical analysis) and a correspondingly lower ferrous-iron content. After oxidation at 450°, this material also contained an appreciable amount of ferrous iron, which could not be attributed to a deficiency of hydroxyl ion. Preliminary experiments indicate that amosite, an amphibole which is much richer than crocidolite in magnesium, is oxidised appreciably less than the latter at 450°. In addition Francis<sup>6</sup> found that less than half the ferrous content of gedrite, MgO 9.59%, is oxidised below 500°.

The residual ferrous iron which is prevented by magnesium from being oxidised at 450° will become available for oxidation only at much higher temperatures, where structural transformation of the amphibole occurs. This oxidation could well account for the exotherm in D.T.A. experiments in the range 920—960°, and such an interpretation has already been suggested.<sup>1</sup>

The oxidation of metals and of such metal oxides as have been studied is always accompanied by addition of new layers to the crystal lattice. The oxidation of crocidolite, apart from a superficial layer added perhaps during later stages of the oxidation, does not show this characteristic, and consequently some kinetic studies are being carried out (cf. the following paper).

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<sup>6</sup> Francis, *Mineralog. Mag.*, 1955, **30**, 709.