# 716. *Amphiboles. Part III.*[1] *The Reduction of Crocidolite.*

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Crocidolite loses all, or nearly all, of its hydroxyl groups, without structural breakdown, when heated at 615° *in vacuo*. The reductions of fresh, dehydroxylated, and oxidised crocidolite follow different mechanisms, but in each case zero-valent iron is formed as a reaction product. Calculation of the electrostatic potentials at the various oxygen atoms suggests that there is only one centre of reaction in the reduction of fresh crocidolite, whereas there are two competing centres in the reduction of both dehydroxylated and oxidised crocidolite. These centres are invariably three-co-ordinated oxygen atoms. It is suggested that the initial step in each reaction is the addition of a proton to such an oxygen atom with the simultaneous reduction of a ferric ion by an electron.

CROCIDOLITE is a fibrous amphibole, $Na_2Fe^{III}_2(Fe^{II},Mg)_3Si_8O_{22}(OH)_2$, where normally $Fe^{II} \gg Mg$. The effect of heating various samples of crocidolite in oxygen at temperatures $<500°$ has been described;[1,2] on oxidation the amphibole structure remains essentially unchanged, although a small decrease in cell dimensions accompanies the oxidation of ferrous to ferric iron and the change of hydroxide to oxide. The effect of heating both fresh and oxidised crocidolite in hydrogen at different temperatures is now described.

## EXPERIMENTAL AND RESULTS

The techniques and apparatus used are described in Part I.[2] The cold trap to remove water formed during reaction was maintained at liquid-nitrogen temperature. The sample of crocidolite was that described previously as R.S.13 (see ref. 2 for analysis); this was not fiberised before use since fiberisation is known to cause partial oxidation. The oxygen and hydrogen used were supplied spectroscopically pure by the British Oxygen Co. Ltd.

To terminate a reduction run, the excess of hydrogen was pumped off, the water yield measured, the weight change in the sample determined, and the material analysed for its ferrous and ferric content. In some experiments a small portion of the sample was used to obtain an *X*-ray powder photograph and/or infrared spectrum. The former were obtained by using a Raymax 60 tube with filtered Cu-$K_\alpha$ radiation, and the latter by using a Unicam S.P. 100 spectrophotometer over the range 375—3700 cm.$^{-1}$.

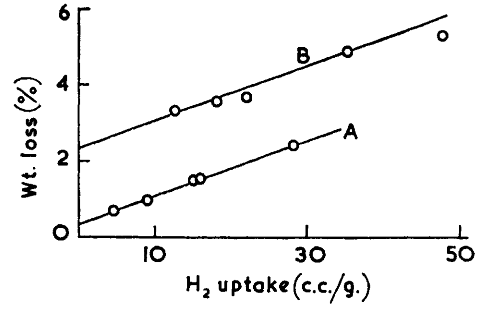

FIG. 1. The percentage weight lost by crocidolite when heated in hydrogen at (A) 450° and (B) 615°.

The reduction of crocidolite has been followed under various experimental conditions, as follows: (*a*) outgassed and reduced at 450° (Table 1A), (*b*) outgassed and reduced at 615° (Table 1B), (*c*) outgassed at 615° and reduced at 450° (Table 1A, last entry only), and (*d*) outgassed, oxidised, and reduced at 450° (Table 1C). The entries marked * in the Tables represent the maximum volume of hydrogen taken up at the appropriate temperature, whereas in the

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[1] Part II, Addison, Addison, Neal, and Sharp, *J.*, 1962, 1472.
[2] Part I, Addison, Neal, and Sharp, *J.*, 1962, 1468.

other runs reaction was stopped before completion. It was necessary to use a different sample for each run.

The percentage weight losses quoted in Tables 1A and B are shown graphically in Fig. 1.

TABLE 1.

Reduction of crocidolite.

| $H_2$ uptake (c.c./g.) | Wt. loss (%) | Molar ratio of $H_2O$ formed per $H_2$ taken up | Apparent no. of oxidn. states reduçed per mole of $H_2$ | |
|---|---|---|---|---|
| | | | *ex* Fe(II) analysis | *ex* Fe(III) analysis |
| (A) At 450°. | | | | |
| 4·56 | 0·66 | 0·85 | 0·55 | 0·49 |
| 9·00 | 0·96 | 1·04 | — | — |
| 15·08 | 1·45 | 1·02 | 0·70 | 0·71 |
| 15·98 | 1·53 | 1·02 | 0·81 | 0·61 |
| 18·78 | — | 0·90 | 0·55 | 0·60 |
| 28·07 * | 2·40 | 1·01 | 0·54 | 0·56 |
| 33·62 *† | 3·75 | 0·61 | 1·01 | 1·00 |
| (B) At 615°. | | | | |
| 12·72 | 3·30 | 0·99 | 1·69 | 1·68 |
| 18·01 | 3·53 | 1·21 | 1·56 | 1·54 |
| 22·07 | 3·63 | 0·98 | 1·55 | 1·54 |
| 35·27 | 4·82 | 1·01 | 1·39 | 1·39 |
| 41·97 | — | 0·98 | — | — |
| 47·77 * | 5·21 | 0·95 | 1·02 | 1·02 |

(C) Oxidised crocidolite at 450°.

| $O_2$ uptake (c.c./g.) | $H_2$ uptake (c.c./g.) | Molar ratio of $H_2O$ formed per $H_2$ taken up | *ex* Fe(II) analysis | *ex* Fe(III) analysis |
|---|---|---|---|---|
| 6·12 | 10·28 | 0·17 | 1·58 | 1·45 |
| 12·20 | 11·93 | 0·24 | | |
| | 23·84 | 0·25 | | |
| | 34·62 | 0·43 | 1·40 | 1·38 |
| 12·67 | 25·36 | 0·21 | — | — |
| 11·26 | 18·80 | 0·22 | | |
| | 47·60 | 0·58 | 1·22 | 1·24 |

* See text. † This sample was outgassed at 615° before being reduced at 450°.

Crocidolite, reduced at 450° develops a paler shade of blue; reduced at 615° it becomes black; reduction restores the blue colour to crocidolite previously turned brown by oxidation.

The infrared spectrum obtained for fresh crocidolite showed the characteristics of an amphibole.[3,4] Two sharp peaks, at 3623 and 3640 cm.$^{-1}$, are assigned to the hydroxyl groups. The spectra of crocidolite which has been variously treated as follows show loss of definition, but retention of the amphibole structure: (i) outgassed and reduced at 450°; (ii) outgassed only at 615°; (iii) outgassed at 615° and reduced at 450°. In (ii) the absorption due to hydroxyl is absent and in (iii) it is diminished. The spectrum of crocidolite which has been reduced at 615° shows diffuse absorption and none of the characteristics of an amphibole. The *X*-ray powder photograph of this material showed it to be amorphous, whereas photographs of the other materials were closely similar to that of the fresh unheated material. Similar observations have been made previously by Freeman (personal communication).

## DISCUSSION

*Water Yield and Weight Loss.*—The water formed on the reduction of fresh crocidolite, both at 450 and 615°, is seen from Tables 1A and B to be one mole per mole of hydrogen taken up, within the limits of experimental error. It is appreciably less on the reduction of oxidised material (Table 1C).

The percentage weight losses quoted in Tables 1A and B are expressed with reference

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[3] Saksena, *Trans. Faraday Soc.*, 1961, **57**, 242.

[4] LeCompte, " Handbuch der Physik," Springer Verlag, Leipzig, 1958, Vol. XXVI, 839.

to the fresh sample, and hence include the loss of non-essential water, loss (if any) of structural hydroxyl, and loss of oxygen from the lattice in combination with hydrogen effecting reduction. In Fig. 1 are plotted the experimental points for weight losses as given in Tables 1A and B. The lines drawn are theoretical, having the slope required for an equimolar formation of water; the intercepts on the weight-loss axis differ by an amount corresponding with the hydroxyl content of the crocidolite, and the higher value corresponds with the total water content reported in the analysis, *i.e.*, essential plus non-essential water.

The agreement between experiment and theory indicates that all non-essential water, but no hydroxyl group, is removed during outgassing at 450°, and that all, or almost all, the hydroxyl groups are eliminated at 615°. It is concluded from *X*-ray and infrared evidence that the amphibole structure is not appreciably altered by such outgassing. Similar behaviour has been observed for pyrophyllite [5] and muscovite [6] which are not too different in structure.

*Iron Content of Reduced Material.*—After reduction, the ferrous and ferric contents were determined and compared with the analysis of fresh material. The apparent number of oxidation states of iron reduced per hydrogen molecule, referred to hereafter as the " apparent reduction ratio," is calculated from the increase in ferrous content, the decrease in ferric content, and the volume of hydrogen taken up. Theoretically this value should be 2·00, but experimentally such a value is never attained (see Tables). (Allowance is made in Table 1C for the effect of the preliminary oxidation.)

The invariably low values for this ratio are attributed to the presence of zero-valent iron as a reaction product. When this is dissolved during analysis it is oxidised to the ferrous state and is titrated as such. Values for the " apparent reduction ratio " corresponding with possible reactions are: Fe(III)-Fe(II), 2·00; Fe(III)-Fe(0), 0·67; Fe(II)-Fe(0), 0·00. The values in Table 1A are scattered, with a mean value of 0·61, whereas those in Table 1B are appreciably higher and show a regular trend. Extrapolation of the observed ratio to zero uptake of hydrogen gives a value close to 2·00.

*Possible Equations for Reactions.*—The fundamental reaction on the oxidation of crocidolite was shown to be:

$$4Fe^{II} + 4OH^- + O_2 \longrightarrow 4Fe^{III} + 4O^{2-} + 2H_2O \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

and the analogous reduction is:

$$4Fe^{III} + 4O^{2-} + 2H_2 \longrightarrow 4Fe^{II} + 4OH^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Since water is always formed during reduction, the latter cannot be the only process. Possible reactions for the three reduction steps quoted above, producing one molecule of water per molecule of hydrogen, are:

$$4Fe^{III} + 2O^{2-} + 2H_2 \longrightarrow 4Fe^{II} + 2H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$2Fe^{II} + 2O^{2-} + 2H_2 \longrightarrow 2Fe^0 + 2H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$2Fe^{III} + 3O^{2-} + 3H_2 \longrightarrow 2Fe^0 + 3H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Reaction (3) can be derived by a combination of (2) with the reaction:

$$4OH^- \longrightarrow 2O^{2-} + 2H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

Whereas reaction (2) does not require structural breakdown, reactions (3)—(5) necessitate at least local disruption of the lattice. Agreement with the experimentally observed " apparent reduction ratios " is obtained if reaction (5) occurs at 450°, and if reaction (3) is the primary reaction accompanied by (4) or (5) as a subsidiary at 615°.

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[5] Parmelee and Barrett, *J. Amer. Ceram. Soc.*, 1938, **21**, 388.
[6] Roy, *J. Amer. Ceram. Soc.*, 1949, **32**, 202.

*Mechanisms of Reaction.*—Transport of molecules through the crystal lattice is unlikely on account of the closeness of packing of the oxygen atoms. It is considered that, as on oxidation, reaction is sustained by the migration of electrons and protons.

Mechanisms of reaction are to be considered for the different conditions detailed in the Experimental section. To determine likely centres of instability and structural breakdown, electrostatic potentials have been calculated, following Pauling.[7] These electrostatic potentials are given in Table 2, for fresh crocidolite, and for crocidolite under various conditions as indicated. The atoms are described by Whittaker's notation[8] (see Fig. 2). It has been assumed in accordance with Whittaker's arguments[9] that the $M_4$ sites are occupied by sodium ions, $M_2$ by ferric ions, and $M_1$ and $M_3$ by the bivalent magnesium and ferrous ions. It is fortunate that in this particular crocidolite the numbers of sodium (1·89) and ferric ions (2·02) correspond closely with the ideal value of 2·00.

TABLE 2.

Calculated positive electrostatic potentials for various oxygen atoms in crocidolite under different conditions.

Electrostatic potential

| | 1 | 2 | 3 | 4 | 5 | | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $O_1$ ......... | 2·17 | 2·38 | 2·00 | 2·30 | 2·13 | $O_3$ ......... | 2·00 * | 1·32 | 2·00 * | 1·20 | 2·20 * |
| $O_2$ ......... | 1·96 | 2·06 | 1·79 | 2·03 | 1·86 | $O_4$ ......... | 1·63 | 1·63 | 2·46 * | 1·63 | 1·46 |

Key to columns 1—5. Atoms marked * are bonded to hydrogen. 1, Fresh crocidolite. 2, Oxidised crocidolite. 3, Gain of one proton and one electron by crocidolite (suggested transition state). 4, Crocidolite outgassed at 615°, *i.e.*, dehydroxylated. 5, Gain of one proton and one electron by dehydroxylated crocidolite (suggested transition state).

$O_7$ is co-ordinated to two silicon atoms only, so that the electrostatic potential at that point is 2·00; both $O_5$ and $O_6$ are co-ordinated to two silicon atoms and to a sodium ion at $M_4$, which produce an electrostatic potential of 2·13. None of these oxygen atoms is adjacent to an iron atom, nor is any situated at a point where there is a deficiency of positive charge such as would attract a proton; they are accordingly omitted from further consideration. The remaining oxygen atoms are more closely associated with the octahedrally co-ordinated metal ions and the electrostatic potential at these points must change as reduction proceeds. $O_1$ is co-ordinated to one silicon atom and two bi- and one ter-valent metal ion. $O_2$ is co-ordinated to one silicon atom and to one uni-, one bi-, and one ter-valent metal ion. $O_3$ is co-ordinated to a hydrogen atom and to three bivalent metal ions. $O_4$ is co-ordinated to a silicon atom and to a uni- and a ter-valent metal ion; thus it is unique among the oxygen atoms co-ordinated to octahedral metal ions since it is only three-co-ordinate. A similar observation was made by Ghose when discussing the structure of a cummingtonite.[10]

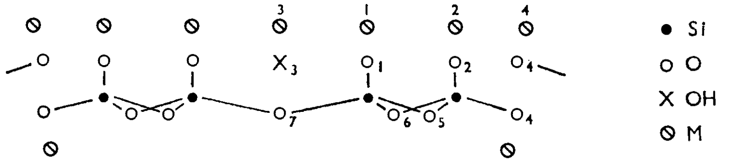

FIG. 2. Diagrammatic representation of the structure of crocidolite.

(*a*) *Crocidolite outgassed and reduced at* 450°. Under these conditions crocidolite

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[7] Pauling, " Nature of the Chemical Bond," 3rd edn., Cornell University Press, New York, 1961, p. 547.

[8] Whittaker, *Acta Cryst.*, 1960, **13**, 291.

[9] Whittaker, *Acta Cryst.*, 1949, **2**, 312.

[10] Ghose, *Acta Cryst.*, 1961, **14**, 622.

maintains all its hydroxyl groups. Reference to Table 2 shows that there is a deficiency of positive charge at $O_4$, and this atom has been seen to be three-co-ordinate. These circumstances lead to the postulate that the first step in reduction is the gain of a proton by $O_4$. Even if the neighbouring iron(III) at $M_2$ simultaneously gains an electron, thus becoming iron(II), this results in an " over-compensation " and produces an excess of positive charge at $O_4$ (see Table 2, column 3). It is suggested that this is a nucleus of structural breakdown, which is completed by the withdrawal of electrons from $M_2$, leaving iron(0) and the elimination of oxygen from the lattice as water. Since this corresponds to a change from iron(III) to iron(0) in one $M_2$ site, this corresponds to reaction (5) above. The average experimental value of 0·61 for the " apparent reduction ratio " is close to the value of 0·67 required for this reaction.

The maximum uptake of hydrogen under these conditions corresponds to the reduction of approximately one-third of the iron(III) to the zero-valent state. Much of the structure would be maintained, including the hydroxyl groups, thus explaining the agreement of the infrared and *X*-ray evidence. At this temperature it is unlikely that iron atoms can migrate and so they would remain dispersed throughout the lattice, undetectable by *X*-rays.

(*b*) *Crocidolite outgassed and reduced at* 615°. Under these conditions crocidolite loses all, or nearly all, its hydroxyl groups, without collapse of the lattice. It is impossible to determine which oxygen atoms are eliminated as water, and unnecessary that all should originally have borne hydrogen atoms, particularly as some redistribution of oxygen atoms may be possible at this temperature. There must, however, be vacancies in the oxygen lattice so that some metal ions become 5- instead of 6-co-ordinate. For convenience it is assumed that one hydroxyl group is completely removed and that the adjacent $O_3$ position retains its oxygen atom which is rendered three-co-ordinate by the loss of hydrogen. Calculation of electrostatic potentials for this structure (Table 2, column 4) shows deficiency of positive charge at $O_3$ and $O_4$—greater deficiency at $O_3$; both atoms are three-co-ordinate and hence alternative sites for the addition of a proton.

It is postulated that the first step in the reduction is the addition of a proton to the more deficient $O_3$, and that an atom of iron(III) is simultaneously reduced to iron(II) by an electron. This produces a slight excess of positive charge at $O_3$ but an even greater deficiency at $O_4$ (Table 2, column 5). Attack on $O_4$ by a further proton must be a subsequent step with a reduction of iron(II) to iron(0) in the adjacent $M_2$ position. Reduction of one atom from iron(III) to iron(0) is therefore associated with the addition of two protons, and not one as in (*a*) above.

All the hydrogen atoms introduced in this process must be eliminated as water since the lattice cannot tolerate hydroxyl groups at this temperature, and hence the structure breaks down at different points and in a more drastic way than during reduction at 450°, which is in accordance with the lack of amphibole character shown by the *X*-ray and infrared spectra.

The two reduction steps iron(III)–iron(II) and iron(II)–iron(0) correspond to " apparent reduction ratios " of 2·00 and 0·00, respectively. The experimentally observed values (Table 1B) lie between these and indicate that the former is predominant in the initial stage of reduction and that the latter becomes more important as reaction proceeds. In accordance with this conclusion analyses of samples where the uptake of hydrogen exceeded 35 c.c./g. (Table 1B) showed a complete absence of ferric iron. The various analytical results have been used to demonstrate the balance between the two processes as reaction proceeds, and these are shown in Table 3.

(*c*) *Crocidolite outgassed at* 615° *and reduced at* 450°. The electrostatic potentials are the same as for (*b*) above since the material has been outgassed at 615°. The mechanism is similar to that described under (*b*) except that elimination of the hydroxyl re-formed at $O_3$ does not occur at the lower temperature of reduction. Hence the structural breakdown is less drastic and will correspond to (*a*) above, the water yield is less than in (*a*) and (*b*), and the infrared spectrum of the product shows that hydroxyl groups have been re-formed. The " apparent reduction ratio " is closer to that observed under (*b*) than under (*a*) since two points of attack are available to the hydrogen; the difference may be due to a different balance between the two reactions due to the presence of regenerated hydroxyl groups.

(*d*) *Crocidolite outgassed, oxidised and reduced at* 450°. Oxidation removes the hydrogen atom from $O_3$, making it three-co-ordinate but, in contrast to the effect of outgassing at 615°, no loss of oxygen occurs. A further consequence of oxidation is that ~63% of the metal ions at $M_1$ and $M_3$ become iron(III). The electrostatic potential at $O_3$ after oxidation is again deficient (Table 2, column 2).

TABLE 3.

Relative extent of competing reactions in the reduction of crocidolite at 615°.

| Apparent reduction ratio | Hydrogen uptake | | Atoms of iron changing | |
|---|---|---|---|---|
| | | moles/formula weight | (III)–(II) | (II)–(0) |
| $x$ | c.c./g. | $y$ | $xy$ | $\frac{1}{2}(2y - xy)$ |
| 1·69 | 12·72 | 0·52 | 0·89 | 0·08 |
| 1·56 | 18·01 | 0·74 | 1·16 | 0·16 |
| 1·55 | 22·07 | 0·91 | 1·41 | 0·20 |
| 1·39 | 35·27 | 1·46 | 2·02 | 0·44 |
| 1·02 | 47·77 | 1·97 | 2·01 | 0·96 |

On the reduction of oxidised crocidolite at 450° a proton can add either to $O_3$ or to $O_4$. In the former case a hydroxyl group is regenerated in its normal position, and the simultaneous addition of an electron to a neighbouring ion converts iron(III) into iron(II) as in the fresh unoxidised material. Such a reaction is the direct analogue of oxidation and is reaction (2) above. No water is liberated during this process and the " apparent reduction ratio " is 2·00. Alternatively, a proton can add to $O_4$ as under (*a*) above, after reaction (5) and liberating water, and with an " apparent reduction ratio " of 0·67. The experimental data of Table 1C show that the water yield is ~0·2 mole per mole of hydrogen taken up so long as the volume of hydrogen remains less than or equal to twice the volume of oxygen used in the pre-oxidation. Attack on $O_3$ is therefore the predominant reaction since attack on $O_4$ results in a molar yield of water. When the hydrogen uptake exceeds the oxygen equivalence point the water yield increases since attack must then be on $O_4$. The observed " apparent reduction ratios " decrease with increase in hydrogen uptake and lie between the theoretical values of 2·00 for attack on $O_3$ only and 0·67 for attack on $O_4$ only, and thus confirm the evidence of the water yield.

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