

*The oxidation of Bolivian crocidolite*By W. E. ADDISON¹ and A. D. WHITE²

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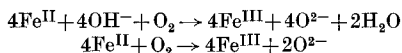
Summary. A hypothesis has previously been advanced to account for the termination of the dehydrogenation process for the oxidation of South African crocidolite: it was postulated that the presence of magnesium ions would block the electronic migration required for complete oxidation of iron(II) in the temperature range 400° to 500° C. In view of criticism of the validity of the evidence for this hypothesis, new data for the oxidation of Bolivian crocidolite, which has a much higher magnesium content than the South African material, is presented; this is more satisfactory evidence of the validity of the hypothesis.

IN a recent paper, Addison and Sharp (1968) discussed the oxidation of amosite (fibrous grunerite of composition approximately $\text{Fe}_{5.5}^{\text{II}}\text{Mg}_{1.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$), including therein a reappraisal of earlier work by Addison *et al.* (1962) on the oxidation of crocidolite (fibrous riebeckite) of South African origin and of composition approximately



In this earlier paper a hypothesis was advanced to explain why, in the temperature range 400° to 450° C, the oxidation of crocidolite terminated while leaving unoxidized approximately one-fifth of the original ferrous iron content. The validity of this hypothesis had been questioned by Taylor (1964; see also Hodgson *et al.*, 1965). Addison and Sharp (1968) suggest that the hypothesis can be applied more satisfactorily to interpret the oxidation of amosite and further that it would apply also to the oxidation of Bolivian crocidolite, in which the relative atomic proportions of ferrous iron and of magnesium are the inverse of those found in the South African mineral.

The arguments of the hypothesis and its criticism will first be summarized. The oxidation of ferrous iron in an amphibole can proceed by two different processes, which have been termed by Hodgson *et al.* (1965) dehydrogenation and oxygenation respectively:



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In the original paper analytical data were presented to show that dehydrogenation was the principal process; however, the yields of water obtained were always less than the theoretical yield expected if dehydrogenation were the only process, and the number of ferrous ions oxidized was always in excess of that permitted by the hydroxyl content, again on that assumption. It was estimated that oxygenation in the temperature range 400° to 450° C accounted for 5 to 10 % of the oxidation of ferrous iron. Addison and Sharp (1968) have also reported that about 12 % of the ferrous iron of crocidolite anhydride can be oxidized at 450° C; dehydrogenation is not, of course, a mechanism possible for this material.

Addison and White (1968) have recently produced further inferential evidence that oxygenation can occur at still lower temperatures. They have found that carbon monoxide reduces some of the ferric iron content of crocidolite to ferrous iron by a mechanism whereby the ferric ions must be at the surface, and also that the extent of this reduction is the same whether the crocidolite be 'fresh' or after oxidation at 450° C. From this it is concluded that the surface iron content of even 'fresh' crocidolite is completely oxidized. It has been shown by Addison *et al.* (1966) that the adsorption of ammonia by crocidolite can be interpreted satisfactorily only if hydroxyl ions are assumed to be present on the surface, which would not be so if the surface layer of 'fresh' crocidolite had been oxidized by a dehydrogenation mechanism.

The mechanism postulated for the oxidation requires that the ferrous iron should be regenerated at the mineral surface in place of ferric iron by an electron-switch mechanism along the ribbon of cations (the complementary hydrogen ion migration need not be considered in this discussion). It was postulated further that magnesium ions would block this migration, and that two such blocks within a fibre should render the ferrous ions between these blocks unoxidizable (this would not apply, however, if the temperature were high enough to allow ionic migration and hence the removal of the blocks). Two lines of evidence were advanced for this postulate: in a series of crocidolites, the higher the magnesium content, and hence the probability of blocking, the higher is the amount of ferrous iron unoxidized; fiberization before oxidation allowed a larger amount of iron to be oxidized. Blockage would be less probable in fibres of shorter length but of the same magnesium content.

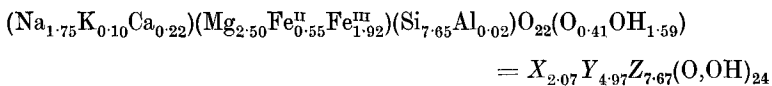
Taylor (1964) has pointed out that the data of Addison *et al.* (1962) show that the oxidized samples contain no residual hydroxyl ions and

hence that dehydrogenation must have gone to completion. It follows that reaction must have terminated because oxygenation could proceed no further under the conditions. Oxygenation adds oxide ions as a surface layer and requires that cations should redistribute themselves by ionic migration to balance this added negative charge. Such a process cannot be affected by magnesium blocking of electronic migration. It is well known that the substitution of magnesium for ferrous iron increases the temperature at which a solid state reaction takes place (see, for example, Freeman, 1966), and it is a corollary of this that the higher the proportion of magnesium in a ferromagnesian mineral the less will be the extent of a reaction at a given temperature. This argument affords an explanation of the first line of experimental evidence quoted above. The process of fiberization increases the available surface and hence the extent to which oxygenation can occur, and thus the second line of evidence can also be accounted for by an alternative argument.

Addison and Sharp (1968) suggest that the oxidation of amosite proceeds by both mechanisms, and give evidence that dehydrogenation is complete by 550° C.

The composition of this oxidized material is approximately, $\text{Fe}_{3.9}^{\text{II}}\text{Fe}_{1.6}^{\text{III}}\text{Mg}_{1.5}\text{Si}_3\text{O}_{22}(\text{OH})_{0.8}$; since this material contains residual hydroxyl the dehydrogenation process must have terminated for some reason other than the absence of hydroxyl ions. The magnesium content of this amosite is appreciably higher than that of the South African crocidolite, so that the magnesium blocking hypothesis can readily explain the termination of dehydrogenation in amosite. Fiberization of the amosite increased the extent of the oxidation of ferrous iron, and this observation can also be explained by magnesium blocking.

Experimental. Bolivian crocidolite was first described by Ahlfeld (1943), since when its crystal structure has been determined by Whitaker (1949), and its thermal decomposition described by Hodgson (1965). The material used in this investigation came from the Cochabamba mine and was supplied by Dr. A. A. Hodgson; its analysis (analyst A. D. W.) is as follows: SiO_2 55.15 %, Al_2O_3 0.12, Fe_2O_3 18.41, FeO 4.72, MgO 12.07, CaO 1.48, Na_2O 6.51, K_2O 0.58, H_2O^+ 1.72, H_2O^- trace, Total 100.76 %. The ionic formula based on $\text{O} = 24$ is as follows:



The analyses of the various Bolivian crocidolites show agreement in most of their features but two points of variation are noteworthy. Firstly, the figures for Al_2O_3 are either very low as in the above analysis and that quoted by Whittaker, or are of the order of 4 %. In view of this variation the above analysis was carefully checked. Secondly, the figures for H_2O^+ are variable; Whittaker reported difficulty in obtaining consistent values and used a theoretical value in his calculations; the values quoted by Ahlfeld are very low. Hodgson (1965) has drawn attention to the very high temperature required to remove all the water, an observation confirmed in the present work. There is close agreement between the above figure and that quoted by Hodgson of 1.78 %. Ahlfeld's values may be too low for this reason.

It will be seen that in contrast to the South African crocidolites, the Bolivian crocidolites, like amosite, contain a higher atomic proportion of hydroxyl ion than of ferrous ion and thus afford a suitable test for the magnesium blocking theory in crocidolite.

Measurement of the infra-red spectrum of the Bolivian material showed it to be similar to that of South African crocidolite, such differences as occur, for example, in the relative heights of the peaks assigned to hydroxyl groups (see Strens 1966), being attributable to the different proportions of magnesium and iron(II). In the authors' opinion there is no evidence to support the suggestion made by Hodgson (1965) that the crocidolite is mixed with anthophyllite.

The techniques used in studying the reaction between Bolivian crocidolite and oxygen have been described by Addison *et al.* (1962). The sample of the mineral is first heated overnight at somewhat above the reaction temperature and at a pressure of 10^{-6} mm Hg. Oxygen is then admitted to the system which contains a liquid nitrogen trap to remove the water vapour formed, and the progress of the reaction is followed volumetrically. Each sample was taken off and analysed for its iron content only when no further uptake of oxygen could be detected after a further period of 24 hours. Both fiberized and unfiberized samples were used in the investigation, the results being shown in table I. Runs 1 to 3 will be seen to show three characteristic features of the oxidation, as described previously for South African crocidolite: Oxidation of iron(II) is incomplete; in runs 1 and 2 only 37 and 48 % respectively of that available was oxidized, whereas an average figure for samples of South African crocidolites in the same temperature range is 80 %. At comparable temperatures, a fiberized sample is oxidized to a greater extent than is an unfiberized sample. The yield

of water formed is very close to that expected from the dehydrogenation reaction, and the loss in weight of the sample is also in accordance with that mechanism of oxidation.

A further feature is the gradual increase in the extent of oxidation with increase in reaction temperature. Measurement of the infra-red spectra after oxidation was completed for those samples used in runs 1 to 3 showed absorption characteristic of the presence of hydroxyl

TABLE I. Oxidation of Bolivian crocidolite

Run	Condition of crocidolite	T (° C)	Oxygen uptake 10 ² × moles/ formula weight	Change in Fe (II) composition	Water yield %	Weight change*
1	Unfiberized	420	6.09	0.54—0.34	~ 100	Decrease
2	Unfiberized	440	7.04	0.54—0.28	~ 100	Decrease
3	Fiberized	429	8.98	0.51—0.19†		
		545	10.84	0.51—0.12	~ 100	Decrease
4	Fiberized and appreciably dehydroxylated	450	2.44	—	0	Increase

* After correction for the change caused by outgassing.

† Calculated value.

groups, though the bands were less sharp than those of the untreated crocidolite. A further sample was heated in oxygen at 450° C until reaction had ceased, after which it was heated *in vacuo* to 600° C. A pressure developed in the system equal in magnitude to that of saturated water vapour at the temperature of the surrounding atmosphere; the gas formed was completely condensable. Such formation of water can result only from the condensation of residual hydroxyl groups, $2 \text{OH}^- = \text{O}^{2-} + \text{H}_2\text{O}$.

Discussion and conclusions. The evidence presented in table I supports the view that the oxidation of Bolivian crocidolite, in the temperature range 420° to 550° C, like that of South African crocidolite, proceeds primarily by dehydrogenation; the possibility that oxygenation also occurs to a small extent is not ruled out, and is supported by the data of run 4. Further, the process of oxidation in runs 1 to 3 stopped (or became infinitely slow) when, according to the analytical evidence, a significant amount of iron(II) remained and, according to spectroscopic evidence and the subsequent liberation of water as described above, a significant amount of hydroxyl ion also remained. It must be concluded that the termination of reaction under these conditions should

be accounted for by the theory of magnesium blocking proposed previously to account for the behaviour of South African crocidolite on evidence that in view of the above discussion was inadequate. The greater extent to which a sample can be oxidized after fiberization (run 3) can be accounted for by this hypothesis also or by the alternative mechanism discussed above, namely that the larger surface area would enable oxidation by the oxygenation process to proceed to a greater extent.

It is possible to explain the outstanding observation made for Bolivian but not for South African crocidolite, i.e. that the extent to which reaction proceeds before further reaction is undetectable increases with temperature, by the assumption that the increased mobility of the magnesium ions with temperature gradually removes the blockages to electron migration.

The effect of such increased mobility will affect the oxidative behaviour of the crocidolites differently since termination of reaction in the temperature range 400–500° C occurs with the iron-rich material when oxygenation is the only possible process (since all the hydroxyl groups have been eliminated) whereas with the magnesium-rich Bolivian material both dehydrogenation and oxygenation are possible.

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