

REDOX BEHAVIOUR OF IRON IN HYDROXYLATED SILICATES

by

W. E. ADDISON and J. H. SHARP

The University, Nottingham, England

ABSTRACT

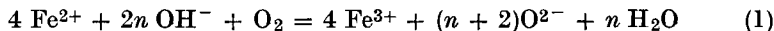
The oxidation and reduction of clay minerals, particularly chamosite and nontronite, are compared with those of the amphibole crocidolite. Oxidation is very similar, but differences in behaviour on reduction are described. These differences are interpreted in terms of the different environments of the oxygen atoms in the various structures. Mechanisms of the various processes are discussed in detail.

INTRODUCTION

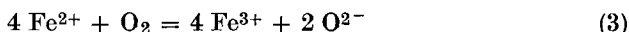
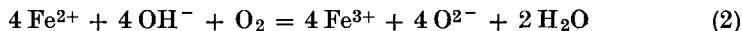
Quantitative data on the oxidation and reduction of iron-containing hydroxylated silicates are not extensive. Chamosite has been studied by Brindley and Youell (1953), gedrite by Francis (1955), and more recently crocidolite, the fibrous form of the amphibole riebeckite, by Addison *et al.* (1962a, b, c). The approach of these latter workers is extended here to samples of chamosite, nontronite and a montmorillonite.

Oxidation

The cited studies have established that the oxidation of iron(II) is accompanied by a simultaneous oxidation of hydroxyl, with elimination of water. Addison and Sharp (1962d) have proposed that when a mineral is heated in oxygen, or air, the behaviour can be represented by the general equation:



The value of n depends upon the relative proportions of three subsidiary reactions which can be represented by equations (2)-(4):



Equation (2) represents the simultaneous oxidation of iron(II) and hydroxyl, and is the primary reaction; no major change in the crystal lattice is caused by this reaction.

Equation (3) represents an alternative oxidation of iron(II) alone. It is considered that, when no hydroxyl ions are available, this reaction occurs on the surface only to form a superficial oxide layer where metal ions were exposed on the surface. This causes an extension of, but no major change in, the crystal lattice. The amount of iron(II) which can be oxidized as described above is dependent both upon the hydroxyl content of the mineral and also upon the extent to which the lattice can tolerate a surface gain of oxygen "oxide" ions. The oxidation of any residual iron(II) occurs only at a higher temperature when structural transformation takes place.

Equation (4) represents the elimination of structural hydroxyl groups which occurs independent of oxidation at a sufficiently elevated temperature.

Addison *et al.* (1962a, b) have extended the ideas of Brindley and Youell (1953) on the mechanism of oxidation. They postulate that reaction occurs only on the surface and that the oxidizable ions are regenerated on the surface by the migration through the crystal lattice of electrons and protons separately. The activation energy obtained for the oxidation of crocidolite was found to be 21 kcal/mole, and is in good agreement with that measured for the migration of electrons in that mineral under the influence of an applied electromotive force (Willis, 1961).

The presence of a layer of water adsorbed on the surface decreases the rate of oxidation and at low temperatures prevents it entirely. This is particularly important since water is formed as a reaction product during oxidation. An ion of iron(II) can remain unoxidized at elevated temperatures even in the presence of hydroxyl ions if no route is available for the migration of its outermost electron to the surface. These routes are blocked by ions such as magnesium and aluminium which cannot readily gain an electron. The probability of such blocking becomes less as particle size decreases and is less in a layer than in a chain silicate since an infinite two-dimensional sheet affords a larger number of possible routes for an electron to reach the surface than does a narrow ribbon. Hence this factor for the inhibition of oxidation is more important in amphiboles than in clay minerals.

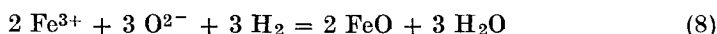
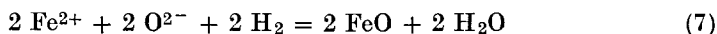
Reduction

Brindley and Youell (1953) attempted to restore oxidized chamosite to its original state by heating it in an atmosphere of hydrogen saturated with water vapour. Reduction was effected, but reaction was said to be slow, incomplete and accompanied by decomposition even at the optimum temperature of 460°. Barnes (1930) observed that brown oxidized hornblende could be restored to its original green colour by heating in hydrogen.

The reduction of crocidolite has been studied quantitatively by Addison and Sharp (1962c), and the course of reaction found to differ according to the experimental conditions. These authors analysed each sample before and after each reduction and expressed their data by means of "apparent reduction ratios" and molar yields of water formed. The former term represents the number of ions of iron(III) reduced to iron(II) per mole of hydrogen. Since

zerovalent iron is formed as a reaction product and after solution titrates as iron(II), a reduction ratio less than 2.0 is always obtained. In general, the lower the apparent reduction ratio the greater the amount of zerovalent iron formed. The relevant data are given in Table 1.

A number of different equations must be used to describe the various reactions:



The reduction of fresh crocidolite follows equation (8); that of oxidized material follows equation (5) as the main reaction with (6) and (8) as subsidiary; that of the dehydroxylated material at 450° follows (5) and (7) with the former predominant in the early stages and the latter in the final stages, whereas at 615° when hydroxyl groups are not stable in the lattice, equation (5) is replaced by (6); equation (6) can be derived by a combination of (5) and (4).

It is proposed that the mechanism for reduction again involves a surface reaction, with the reaction being sustained by the migration of electrons and protons in the opposite direction to that required during oxidation. In accordance with this, good agreement with the activation energy of oxidation is seen in the value of 21 kcal/mole obtained for the initial stages of the reduction of oxidized crocidolite (Addison and Sharp, 1962e). These are the only conditions under which no breakdown of the structure occurs as an additional process thus rendering direct comparison with oxidation difficult.

To explain the different behaviour under the various conditions, it is postulated that initially a proton adds on to an oxygen atom which is three-coordinate—four-fold coordination produces more complete shielding—and that there is a simultaneous gain of an electron by an adjacent ion of iron(III).

TABLE 1.—REDUCTION OF CROCIDOLITE

State of crocidolite	Range of temperature	Molar water yield	Apparent reduction ratio
Fresh	350–500	1.0	0.67
Oxidized	350–500	0→1.0	2.0→06.7
Dehydroxylated	615	1.0	2.0→06.7
Dehydroxylated	450	0→0.7	2.0→06.7

(Dehydroxylation effected by heating at 615° *in vacuo*; where a range of values are indicated, the direction is with increase in hydrogen uptake.)

There is only one oxygen of such a nature in the unit cell of crocidolite, whereas both oxidation and dehydroxylation introduce a second such atom, and hence the reduction after such pretreatment can follow different courses. In crocidolite, a deficiency of positive charge is seen to be associated invariably with these three-coordinate oxygen atoms. It was suggested that this would favour the addition of a proton, but that an excessive positive charge would result leading to structural breakdown at that point.

Some experiments on the oxidation and reduction of samples of the clay minerals chamosite, nontronite, and an iron-containing montmorillonite are now described to allow comparison with the amphibole.

ACKNOWLEDGMENTS

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EXPERIMENTAL

The mineral samples were not subjected to any particular cleaning-up process since the materials were believed to be of reasonable purity and the presence of small amounts of most likely impurities, particularly those not containing iron, would not affect the validity of the results to be presented. The nontronite and montmorillonite have been analysed (see Table 2), and

TABLE 2.—CHEMICAL ANALYSES OF CLAY SPECIMENS

	Montmorillonite	Nontronite	Chamosite
SiO ₂	50.4	50.9	23.81
Al ₂ O ₃	8.7	—	23.12
Fe ₂ O ₃	5.1	27.7	0.23 (3.57)
FeO	1.7	—	39.45 (37.19)
MgO	1.6	4.7	2.72
CaO	0.9	—	—
Na ₂ O	3.9	0.3	—
K ₂ O	0.7	0.1	—
H ₂ O	25.5	16.2	10.62
	98.5	99.9	100.0

(The Al₂O₃ and SiO₂ analyses of nontronite and montmorillonite were determined by Maureen Dowlman, the remaining elements by W. E. Addison. The chamosite analysis is taken from Brindley and Youell (1953) and only the FeO and Fe₂O₃ in parenthesis apply to the present material.)

the I.R. spectra compared with literature. Only the iron content of the chamosite has been determined, but the analysis of the material used by Brindley and Youell is quoted with the present iron analysis for comparison.

The mineral sample, contained in a small bulb, was sealed on to a system containing a manometer and burette. The system also contained a detachable trap which was cooled in liquid nitrogen during oxidation and reduction runs to remove from the gas phase any water vapour formed during reaction, and to allow its determination. Each sample was pumped out at 10^{-6} mm at the temperature of the experiment before being exposed to oxygen or hydrogen; the chemisorption of oxygen or hydrogen was then followed by normal volumetric methods. Analysis for iron(II) and iron(III) was carried out by normal titrimetric methods before and after each run. A static weight loss determination was made on each material under conditions of high vacuum and the infrared spectrum of each sample was determined before and after each run. Further experimental details are given in the cited references.

RESULTS AND DISCUSSION

The main data to be described in this section relate to the oxidation of chamosite, and the reduction of both nontronite and chamosite.

Oxidation of Chamosite

The data obtained for the oxidation of fresh chamosite are presented in Table 3, whereas the oxidation of reduced chamosite is referred to in the section relating to its reduction. From a supplemental determination of weight loss, it appeared that loss of structural hydroxyl groups becomes significant at temperatures above 340°C , corresponding to the amorphous region referred to by Brindley and Youell. It is clear that in two of the runs referred to in Table 3 the chamosite has been grossly broken down.

The structure of chamosite is not destroyed by outgassing at 300°C , and

TABLE 3.—OXIDATION OF CHAMOSITE

Outgassing/ oxidation temperatures	FeO content			Molar water yield	Comment on I.R. spectrum†
	Original	Final*	Time		
$^{\circ}\text{C}$	%	%	hr		
290/285	37.2	24.8	25	1.82	Very similar
300/280	37.2	23.0	72	1.76	Very similar
425/425	37.2	8.0	1.3	Nil	Much altered
450/193	37.2	17.2	5.0	Nil	Much altered

* Experiments were normally stopped when further reaction was very slow, but not complete.

† Compared with fresh material.

such a preliminary treatment is necessary to ensure that the water yield obtained from an oxidation run is formed only as a product of oxidation. The water yields of 1.82 and 1.76 obtained during the oxidation of material which has not been heated above 300°C agree closely with values in the range 1.80–1.90 obtained for crocidolite (see Addison *et al.*, 1962a), and indicate accordance with equation (2) as the main reaction and equation (3) as a subsidiary. As had been observed by Brindley and Youell, oxidation of the iron(II) in these experiments was not complete and it is now suggested that this can be explained by the blocking action of the aluminium ions. Complete oxidation to iron(III) chamosite could not be accomplished at 400°, although obtained by Brindley and Youell using a different procedure, as the preliminary outgassing causes structural breakdown. These authors obtained their product by heating iron(II) chamosite in air rather than in vacuo and thus produced the more stable iron(III) form before structural breakdown could occur.

Oxidation of chamosite which has been dehydroxylated can yield no water and the rate and extent of its oxidation compared with that of the fresh material (see Table 3) is evidence that complete structural breakdown has taken place during the preliminary outgassing. This is in contrast to crocidolite, the dehydroxylated form of which is stable and resistant to other than surface oxidation even at 600°, (Addison and Sharp, 1962d).

Some preliminary experiments on the oxidation of montmorillonite appear to show behaviour similar to that described above, and a similar comment applies to its reduction.

Reduction of Nontronite

A weight loss experiment indicated that nontronite lost no structural hydroxyl groups at temperatures up to 450°. Samples were outgassed at 370° before reductions. Complete reduction of iron(III) to iron(II) requires 38.9 cc/g of hydrogen. Data are given in Table 4.

Since it has been seen from the discussion of the behaviour of crocidolite that the apparent reduction ratio is important for an understanding of the process, values of this were calculated from the analytical data, and were

TABLE 4.—REDUCTION OF NONTRONITE

Temperature °C	Hydrogen uptake cc/g	Total water yield	
		Obs. mg.	Calc. mg*
270	7.9	6.6	4.3
310	28.2	10.3	13.2
345	29.1	11.7	11.1
360	33.7	17.4	16.3
360	34.8	18.8	19.9

* The calculated yield is based on a molar yield of 0.67, see discussion.

found to be approximately 1.4 in each run, compared with the value of 2.0 expected for reduction of iron(III) to iron(II). Two explanations of this low value are possible. Either there is formation of iron(0), or some iron(II) is reoxidized when the sample is exposed to air before analysis. The former explanation applies to the case of crocidolite, but the latter has now been shown to explain the behaviour of nontronite. Thus chemisorption occurs when samples of nontronite which have been reduced previously at a high temperature are exposed to oxygen at 25°C. After correction for this measured extent of reoxidation, values for the reduction ratio are obtained which are always very close to 2.0. It is concluded that the reduction of nontronite proceeds only as far as the iron(II) state.

Reduction of Chamosite

A sample of chamosite, outgassed at 305°C, was heated in hydrogen at 300°C. The volume of hydrogen taken up was only slightly less than that required to reduce all the iron(III) to iron(II)—(observed 4.3 cc/g, calculated 5.0 cc/g); a small amount of water was also formed, but this was insufficient to weigh with accuracy. The reduced material chemisorbed oxygen at 25°C as did reduced nontronite. When correction is made for this, a reduction ratio of 2.0 is again obtained.

Another sample of chamosite was extensively oxidized at 300°C before treatment with hydrogen. On reduction, this also yielded a very small amount of water and a reduction ratio of 2.0. The infrared spectrum and the colour of this product were closely similar to those of fresh chamosite. This reduction has been effected under milder conditions and with less evidence of structural breakdown than Brindley and Youell observed when carrying out a reduction with hydrogen saturated with water vapour.

Activation energies have been calculated from various reduction data for initial rates of reaction, in a manner similar to that described for the oxidation of crocidolite by Addison, Neal and Sharp (1962b). These values are listed in Table 5, and can be compared with 21 kcal/mole obtained for the reduction of oxidized crocidolite.

TABLE 5.—ACTIVATION ENERGIES FOR REDUCTION REACTIONS

	kcal/mole
Reduction of fresh chamosite	21
Reduction of oxidized chamosite	17
Reduction of fresh nontronite	21
Reduction of fresh montmorillonite	17

CONCLUSIONS

The features which characterized the oxidation of the amphibole crocidolite are to be found also in the oxidation of the clay mineral chamosite. Oxidation produces water in slightly less than the yield required by equation (2), the slight deficiency being attributed to a surface gain of oxide ions formed by

equation (3). Although there is a contraction in unit cell dimensions as noted by Brindley and Youell for chamosite, and by Freeman and Taylor (1961) for crocidolite, the structure is not profoundly changed as shown by the I.R. spectra and the reformation of the original material by the action of hydrogen.

There is close agreement between the activation energies for the oxidation of fresh crocidolite and the reduction of oxidized crocidolite, on the one hand, and those for the reduction of the clay minerals (as quoted in Table 5), on the other. This is strong evidence that the mechanism for the reduction of clay minerals, like that of crocidolite, involves electron and proton migration.

Whereas the apparent reduction ratios obtained for crocidolite are always less than 2.0 (Table 1), the reduction of clay minerals was found to yield a ratio of 2.0 invariably. The mechanism of reduction can be considered further for both the dioctahedral and the trioctahedral case.

The environments of the different oxygen atoms in crocidolite, and in a di- and a tri-octahedral layer silicate are given in Table 6. It has been assumed in the calculation that the dioctahedral mineral contains a statistical distribution of M^{III} ions and that the trioctahedral mineral contains only M^{II} ions in the octahedral layer; no allowance is made for the presence of tetrahedral aluminium. Nontronite is dioctahedral and chamosite trioctahedral.

TABLE 6.—COORDINATION OF OXYGEN ATOMS IN PERTINENT STRUCTURES

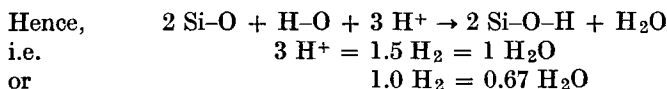
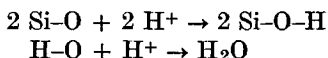
Atom neighbours		Coordination	Electrostatic potential
Crocidolite			
O ₁	Si, 2 M ^{II} , M ^{III}	4	2.17
O ₂	Si, M ^I , M ^{II} , M ^{III}	4	1.96
O ₃	H, 3 M ^{II}	4	2.00
O ₄	Si, M ^I , M ^{III}	3	1.63
Dioctahedral			
O ₁	Si, 2 M ^{III}	3	2.00
O ₂	H, 2 M ^{III}	3	2.00
Trioctahedral			
O ₁	Si, 3 M ^{II}	4	2.00
O ₂	H, 3 M ^{II}	4	2.00

Whereas in crocidolite there is a deficiency in the positive electrostatic potential at the three-coordinate oxygen atom, this is not so in the other cases; the presence of tetrahedral aluminium, however, decreases the value of the electrostatic potential for O₁ in both the di- and tri-octahedral cases from 2.0 to 1.75.

Mechanism for Dioctahedral Minerals

It was noted in Table 4 that the yield of water obtained in the reduction of nontronite is 0.67 mole/mole of hydrogen. This differs from the behaviour of crocidolite. It can be seen from Table 6 that in nontronite all the oxygen

atoms enclosing the octahedral layer are three-coordinate. The ratio of "hydroxyl" oxygens (O_2) to "oxide" oxygens (O_1) is 1:2. As electrons add to iron(III) ions causing reduction to iron(II), protons add to both O_1 and O_2 . An "oxide" oxygen is converted to a "hydroxyl" oxygen *without* elimination of water, thus forming a Si-O-H grouping, whereas a "hydroxyl" oxygen is converted to a water molecule and eliminated as such. Since the ratio of $O_1:O_2$ is 2:1, a water yield of 0.67 can be explained, thus:



It can be appreciated that the reduction of iron(III) in a dioctahedral mineral of the kaolinite type should proceed by the same mechanism but give a water yield of 1.3 mole/mole of hydrogen since $O_2:O_1$ is 2:1.

Mechanism for Trioctahedral Minerals

Provided that the octahedral layer in chamosite is complete and that no hydroxyl groups have been lost, there are no three-coordinate oxygen atoms available. The small amount of iron(III) in the sample investigated was reduced with the formation of a small yield of water, in contrast to the reduction of both crocidolite and the dioctahedral nontronite, but similar to the relatively low yields obtained from oxidized crocidolite.

Freshly reduced chamosite has been shown to undergo oxidation even at room temperature. It is suggested that the iron(III) content of the chamosite used in this investigation was formed by oxidation of a mineral that contained originally iron(II) only. This oxidation produces the three-coordinate oxygen atoms necessary to initiate reduction. Since oxidation follows equations (2) and (3) reduction will proceed by the complementary processes represented by (5) and (6). Reaction (5) yields no water, whereas the reduction of the small proportion of surface oxide formed by (3) and reduced by (6) will account for the low water yield observed. The reduction of iron(III) in a 2:1 trioctahedral layer silicate should be analogous.

Further evidence in favour of this hypothesis is provided by the reduction of oxidized chamosite, since in this case also, only a small yield of water is obtained.

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104 ELEVENTH NATIONAL CONFERENCE ON CLAYS AND CLAY MINERALS

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