

The thermal decomposition of miscellaneous crocidolites

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Summary. Sixteen samples of crocidolite asbestos from weathered zones in mines in Cape Province, Transvaal, Western Australia, and Bolivia have been studied by thermal analysis methods and their characteristics are compared with those of fresh crocidolite from Koegas-Westerberg given by Hodgson, Freeman, and Taylor (1965). New chemical analyses of these samples are reported.

The effect of natural weathering on crocidolite tends to a removal of $\frac{1}{4}$ of the OH groups and an adjustment of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio to unity, but there are only minor changes in the physical characteristics of the fibre. The d.t.a. pattern of decomposition is not affected by weathering, but the endothermic peak corresponding to final decomposition is moved to higher temperatures as the Mg content of crocidolite increases. Mg-blocking of this decomposition is considered to be more important than Mg-blocking of the oxidation reaction at 400–450° C, suggested by Addison *et al.* (1962).

D.t.a. and other evidence shows that the Transvaal crocidolite contains intergrown amosite fibres, and suggests that the Bolivian crocidolite is admixed with anthophyllite.

SOUTH African amphibole asbestos occurs in metamorphosed sedimentary rocks, which contain up to 40 % of iron oxides by analysis. These ferruginous rocks, known as the Banded Ironstones, are part of the Transvaal System, a formation that is reputed to have a minimum age of nearly 2000 million years. The geological map of South Africa shows that the outcrop of the Transvaal System extends in a north-south line from the Orange River in Cape Province to the Bechuanaland border, where it disappears under the Kalahari sands, and thence from the western borders of the Transvaal to an area in Eastern Transvaal where it is bounded by the Drakensberg. In the country from which it takes its name, this formation has been intruded by the norite and granite of the immense Bushveld Igneous Complex, and as a result has been considerably metamorphosed.

Crocidolite, or blue asbestos, is mined extensively in Cape Province in the area from Koegas-Westerberg to Prieska along the Orange River, in Griqualand and the Kuruman Hills, and near the Bechuanaland border at Pomfret. Smaller deposits are worked in the Malips River area in the Transvaal. Large deposits of blue asbestos occur in the Wittenoom

Gorge in the Hamersley Range in Western Australia, in a formation that bears close similarity to the Banded Ironstones of South Africa. The Australian mines account for some 12 000 tons of the world's annual output of blue asbestos, the South African mines for some 90 000 tons, while in contrast the small but interesting deposit at Cochabamba in Bolivia produces less than 300 tons. The Bolivian asbestos, unlike the rest, is of metasomatic origin, and is a fine silky fibre of a paler blue colour than its South African counterpart.

The origin, geology, chemical composition, and thermal decomposition of crocidolite have been discussed recently in papers by Cilliers *et al.* (1961), Cilliers and Genis (1965), and Hodgson *et al.* (1965), all these making special reference to the fresh crocidolite from the Koegas–Westerberg area in Cape Province. Patterson (1965) has investigated the thermal decomposition of the Australian crocidolite by X-ray methods, and shown that fundamentally it is similar to the South African material.

It is useful to refer to the fresh crocidolite from Koegas–Westerberg for purposes of comparison, because not only is it representative of completely unweathered material, but it has a chemical composition, $\text{Na}_2\text{Fe}_3^{3+}\text{Fe}_2^{2+}\text{Mg}_{0.4}\text{Si}_8\text{O}_{22}(\text{OH})_2$, closer to a theoretical riebeckite formula than other known crocidolites, and it is available in quantity from the world's largest and deepest blue asbestos deposit.

In this present paper we are concerned with crocidolites that are not representative of fresh material or that in their origin differ from the Koegas material. The object of the investigation is to ascertain what effect weathering or chemical composition has had on the thermal decomposition of the fibre. Sixteen samples of crocidolite have been examined, these originating from weathered zones in the Westerberg reefs, from the Hounslow mine (near Koegas), the Kuruman Hills, Pomfret, Malipsdrift in the Transvaal, and from the Western Australian and Bolivian deposits. Thermogravimetric analysis, *d.t.a.*, and direct dehydration measurements in both oxidizing and inert atmospheres have been used to investigate the samples, these methods being identical to those previously used by Hodgson, Freeman, and Taylor (1965) on the fresh Koegas material. The investigation and results are described in detail by Hodgson (1963).

Before describing the results, it is convenient to define what is meant by the terms 'fresh' and 'weathered'. In the crocidolite fields in South Africa, three zones of strata are recognized from ground surface downwards to beneath the water table. The Fresh Zone lies below the latter, which is generally 50–200 ft below ground surface. The rock here is

finely laminated, hard, compact, and dark blue in colour. Above the water table there is an oxidized or leached zone, in which the rocks have become softened and partly oxidized to a yellowish-brown colour due to the normal agencies of weathering. Near the surface lies the Silicified Zone, where the rocks have become hardened owing to secondary silicification and carbonation. The asbestos seams are resistant to weathering and commonly persist to the surface without deterioration in quality.

Chemical Analyses are shown in table 1. The Silicified Zone is represented by RS. 18, which displays little evidence of silicification or oxidation in its fibre, though different parts of its associated rock are high in silica, iron oxides, and calcium carbonate. The remaining specimens show various degrees of weathering in the hand samples, and are considered to be representative of the Leached Zone. There is slight evidence of this in the analyses, the proportion of Fe_2O_3 in several of them being higher than that of FeO .

There is some variation of silica contents in the samples, the normal proportion of which is shown by samples RS. 1-4. RS. 17 contains excess silica as a secondary impurity, but the Malipsdrift samples contain an excess of primary silica intergrowth with the crocidolite fibres. Probably the most interesting feature in the analyses is the variation in MgO and Na_2O contents, the normal proportion of which is represented in the Westerberg Samples. Going northward through the localities from Westerberg, through Hounslow and the Kuruman Hills to Pomfret, there is a distinct increase in MgO content from 1.6 to 4.6 %. The Na_2O contents of most of the Hounslow, Kuruman, and Pomfret samples are lower than normal, and the lowest Na_2O contents are shown by the Malipsdrift samples. Even if the latter are corrected for a 10 % silica impurity the Na_2O is still low.

In most respects, the Bolivian crocidolite has a similar analysis to that published by Whittaker (1949). We find Na_2O to be higher and H_2O^+ lower than the previous analysis, and also find a high proportion of aluminium to be present.

Thermal analyses. All the samples examined give the expected pattern for d.t.a. in oxygen and argon, and figs. 1 and 2 show some typical examples. Fresh crocidolite has an exotherm between 400° and 450°C , and a marked endotherm just above 900°C , followed by an exotherm, in d.t.a. in oxygen. In some of these samples the low temperature exotherm is missing or much diminished, and in general the high temperature endotherm appears in the range 900 - 980°C . Among

TABLE I. Chemical analyses of crocidolites

	Westerberg			Houslow			Kuruman Hills			Pomfret			Malipsdrift			Western Australian		Bolivia
	<i>RS. 1</i>	<i>RS. 2</i>	<i>RS. 4</i>	<i>RS. 17.</i>	<i>RS. 18</i>	<i>RS. 19</i>	<i>L. 422</i>	<i>L. 440</i>	<i>Pom. 1</i>	<i>Pom. 2</i>	<i>Pom. V H</i>	<i>M. 4</i>	<i>M. 5</i>	<i>M. 9</i>	<i>L. 483</i>	<i>L. 433</i>		
SiO ₂	49.40	50.85	51.40	57.46	52.40	50.35	50.10	50.70	52.27	52.27	52.00	59.41	63.65	59.90	52.85	55.65		
FeO	18.25	19.55	19.95	14.87	17.05	19.45	17.65	17.50	17.18	16.50	17.65	15.11	9.20	13.03	14.95	3.84		
Fe ₂ O ₃	19.57	18.15	17.71	16.85	19.05	17.90	18.85	18.30	17.48	17.12	16.05	14.03	14.18	16.57	18.55	13.01		
Al ₂ O ₃	—	—	—	1.20	0.15	nil	0.20	0.70	nil	nil	nil	nil	nil	nil	0.18	4.00		
CaO	1.60	1.20	0.55	0.47	0.59	0.57	1.45	1.30	0.68	0.60	1.20	0.49	2.66	1.86	1.07	1.45		
MgO	1.60	1.80	1.32	1.15	2.00	2.19	2.90	3.05	3.68	4.63	4.28	3.53	4.47	2.86	4.64	13.09		
MnO	0.12	0.06	tr.	0.11	0.04	0.03	0.08	0.06	tr.	tr.	tr.	tr.	0.05	0.05	tr.	tr.		
Na ₂ O	6.28	6.25	6.20	5.38	5.59	6.26	5.70	5.30	5.89	5.80	6.21	4.63	4.71	4.50	5.97	6.91		
K ₂ O	0.18	0.37	0.15	tr.	tr.	tr.	tr.	tr.	tr.	tr.	0.06	0.28	0.15	0.21	0.05	0.39		
H ₂ O+	2.75	2.26	2.20	2.61	2.26	2.82	2.35	2.53	2.71	2.63	2.43	2.07	1.70	1.78	2.77	1.78		
H ₂ O-	0.23	0.11	0.25	0.17	0.30	0.37	0.35	0.29	0.33	0.27	0.26	0.14	0.07	0.04	0.22	tr.		
CO ₂	1.00	0.08	0.20	0.40	0.82	0.44	0.97	0.45	0.16	0.12	0.09	0.09	tr.	tr.	0.23	tr.		
Total	100.98	100.68	99.93	100.67	100.25	100.38	100.60	100.18	100.38	99.94	100.23	99.78	100.84	100.80	100.48	100.35*		
Depth below ground surface ft.	100	167	163	49		71	approx. 200	approx. 200	80	160	approx. 200	approx. 100	approx. 100	approx. 100	—	—		
Reef	Main	Main	Main	Bottom			—	—	Upper	Lower	Violet	White	Prinsloo	IC	—	—		
											Horlizon	Cap	Bands	Bands				

* Includes F, 0.23%.

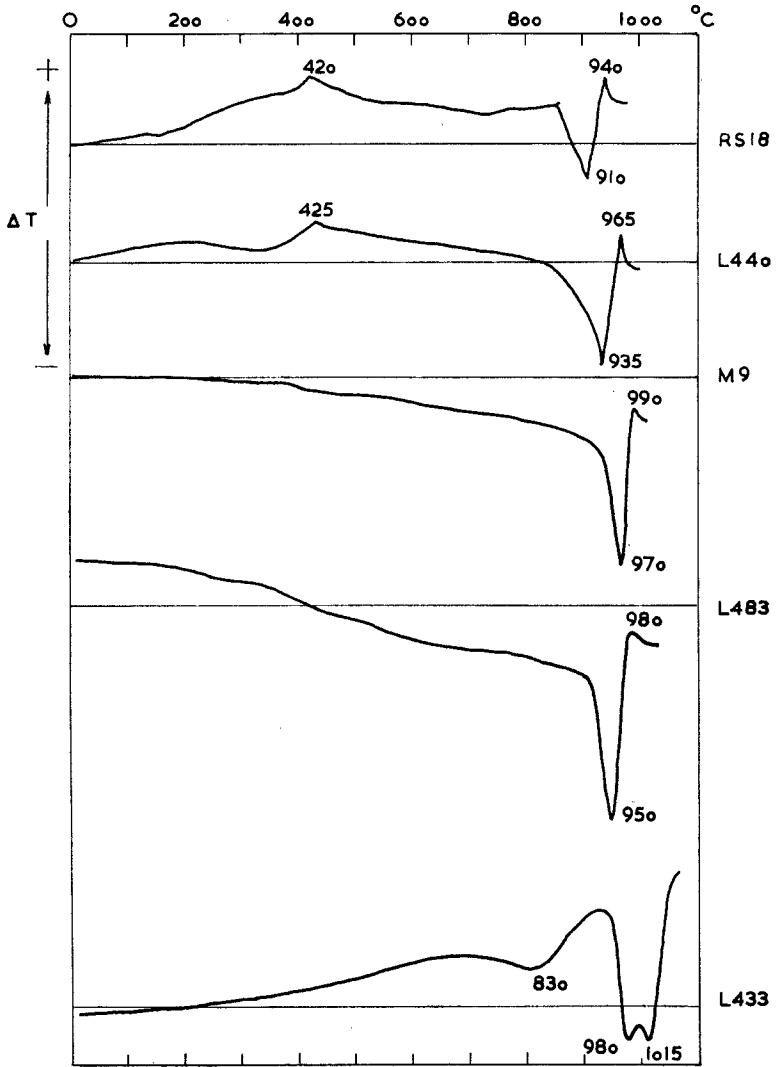


FIG. 1. Differential thermal analyses of crocidolite in oxygen: RS. 18, Hounslow; L. 440, Kuruman Hills; M. 9, Malipsdrift; L. 483, Western Australia; L. 433, Bolivia.

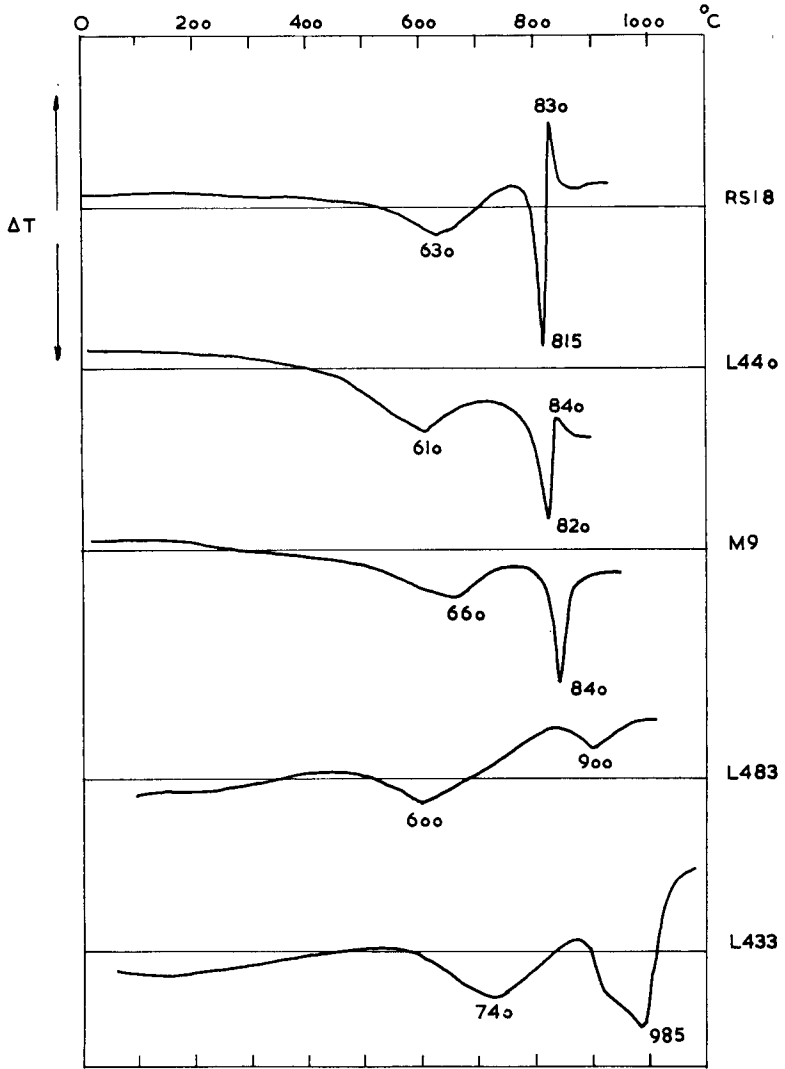


FIG. 2. Differential thermal analyses of crocidolite in argon.⁵ Samples as fig. 1.

the d.t.a.s in argon there is a variation in peak temperatures according to source of sample, the dehydroxylation endotherm taking place between 610° and 680° C, and the decomposition endotherm between 800° and 880° C.

The Bolivian crocidolite (L. 433) has such curious d.t.a.s that it is doubtful if it can be classified as a true crocidolite or riebeckite. While it is probable that the endotherm at 980° C in oxygen can be attributed to a crocidolite decomposition, this d.t.a. has additional endotherms at 830° and 1015° C, and the corresponding supposed crocidolite peak at 985° C on the d.t.a. in argon does not show the usual depression to a lower peak temperature found in the remaining crocidolites. The Australian crocidolite shows the usual high temperature pattern in oxygen, but its d.t.a. in argon is quite abnormal above 800° C (this abnormality has been confirmed on other samples of Australian crocidolite that have been examined).

Thermogravimetric analysis curves in argon and dehydration curves in argon and oxygen all show the patterns obtained previously for the fresh Koegas-Westerberg crocidolites. Table II summarizes the more important quantitative data obtained in these measurements. Generally these show that the uncombined water loss between 100° and 600° C (in argon) may be up to over 1.0 % and that the combined water loss has a lower limit of 1.5 %. There is some overlapping of the uncombined and combined water losses on dehydration measurement. The dehydroxylation losses of the Malipsdrift samples are distinctly lower at 1.37–1.41 % than the rest by weight loss measurement and are correspondingly higher by 0.2–0.3 % by direct dehydration measurement in oxygen.

Thermogravimetric analyses (t.g.a.) in oxygen of all these samples have been made, but these are generally unsatisfactory for interpretative purposes. Roughly the normal pattern for crocidolite is followed, with a weight loss of 0.5–1.0 % up to 600° C, and a weight gain of nil to 0.5 % between 600° and 950° C. The usual sharp oxidation gain of about 0.25 % at 850–950° C is missing from most of these samples, and where it can be observed it is about 0.05 %. It is fairly clear that since these samples have been subjected to some degree of natural weathering they would not be expected to give the same t.g.a. pattern in oxygen as the fresh material.

The Bolivian crocidolite gives chemically combined water contents of 1.69 % by weight loss in argon and 1.61 % by dehydration measurement in argon. The dehydration measurement in oxygen gives an almost stepless curve and the separation into two phases of dehydration

above and below 740° C is only approximate. Unlike any other crocidolite examined, the Bolivian material has a weight loss curve in oxygen that gives 0.14 % loss from 100° to 760° C and 1.44 % loss from 760° to 940° C, a reaction similar to that of the high-magnesium amphiboles, such as tremolite and anthophyllite.

TABLE II. Summarized data for thermogravimetric analysis in argon and dehydration in oxygen

Sample	First loss	Temp. limits	Second loss	Temp. limits
<i>Thermogravimetric analysis in argon</i>				
Westerberg				
RS. 1, 2, 4	0.46-0.77 %	100-590° C	1.66-1.73 %	560-700° C
Hounslow				
RS. 17, 18, 19	0.67-0.79 %	100-600° C	1.50-1.56 %	560-680° C
Kuruman Hills				
L. 422, 440	1.35-1.42 %	100-600° C	1.52-1.58 %	600-720° C
Pomfret				
Pom. 1, 2, VH	0.53-0.77 %	100-620° C	1.52-1.90 %	600-730° C
Malipsdrift				
M 4, 5, 9	0.33-0.40 %	100-660° C	1.37-1.41 %	620-820° C
W. Australia				
L. 483	0.63 %	100-580° C	2.14 %	580-730° C
Bolivia				
L. 433	0.09 %	100-680° C	1.69 %	680-930° C
<i>Dehydration in oxygen</i>				
Westerberg				
RS. 1, 2, 4	0.48-1.16 %	100-550° C	1.30-1.72 %	450-640° C
Hounslow				
RS. 17, 18, 19	0.67-0.70 %	100-470° C	1.57-1.71 %	460-540° C
Kuruman Hills				
L. 422, 440	0.33-0.75 %	100-370° C	1.78-1.95 %	350-720° C
Pomfret				
Pom. 1, 2, VH	0.36-0.59 %	100-430° C	1.61-2.04 %	340-600° C
Malipsdrift				
M. 4, 5, 9	0.23-0.40 %	100-430° C	1.60-1.70 %	350-860° C
W. Australia				
L. 483	0.30 %	100-330° C	2.14 %	350-500° C
Bolivia				
L. 433	0.50 %	200-740° C	1.37 %	740-940° C

Discussion

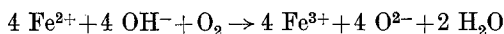
Weathering. Examination of the analyses of the samples indicates that the amount of oxidation and leaching in weathered crocidolite is quite limited. The analyses of the Westerberg and Hounslow samples show that only in certain instances is the proportion of ferrous iron reduced, that silica may if anything be increased, and that there is no definite evidence that Na₂O is removed. The thermal analysis data

indicates that a limited amount of combined water is removed, leaving a residual content of 1.50 %; that the total water content is only slightly greater than in fresh crocidolite; and that in a number of examples part of the normal amount of ferrous iron remains to be oxidized above 600° C. It therefore appears that the amount of oxidation sustained by these crocidolites is limited almost to a quantitative degree, and that the mineral resists any further decomposition under normal conditions of sub-surface leaching.

If we take the ionic ratios of Fe^{2+} to Fe^{3+} in the samples RS. 1 to RS. 19 and compare these with the combined water contents, the following figures are obtained. (Sample RS. 23 is included to provide comparison with a deep mined fresh fibre—see Cilliers *et al.*, 1961, for analysis.)

	$\text{Fe}^{2+}/\text{Fe}^{3+}$	Combined H_2O	Depth
RS. 1	1.04	1.73	100 ft.
RS. 2	1.20	1.66	167
RS. 4	1.25	1.68	163
RS. 17	0.98	1.56	49
RS. 18	1.00	1.50	1
RS. 19	1.21	1.54	71
RS. 23	1.46	1.96	1330

As the combined water falls to 1.50 %, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio tends to unity. In terms of the double cell for crocidolite, this implies that since one quarter approximately of the total combined water content is lost in the process of weathering one (OH) group in four is more susceptible to oxidation than the remaining three. Also if there are 6 Fe^{2+} and 4 Fe^{3+} in the double cell, and one Fe^{2+} is oxidized in accordance with the oxidation equation for crocidolite:



(Addison *et al.*, 1962), then a proportion of 5 Fe^{2+} to 5 Fe^{3+} , a ratio of unity will be left. The facts do not completely fit, because there is a small amount of Mg substituting for Fe^{2+} , but in view of the difficulties in dealing with the quantitative examination of weathered fibre, which is somewhat variable in its composition in the mass, the evidence gives reasonably good support to this suggestion of limited oxidation under natural conditions.

A point of further interest is that the loss of hydroxyl water in weathered crocidolite is balanced by an increase in the proportion of uncombined water. This is not loose moisture that may be driven off at 100° C, but on the contrary is lost in the range 100–600° C. It is

apparently retained as physically combined water tightly bound in the interstices of the fibrils.

Weathered crocidolite is generally softer and more flexible in the fiberized state than its deep-mined counterpart. It is probable that the very limited amount of physically combined water in fresh fibre allows for close contact between individual fibrils, so that inter-molecular forces bind them tightly together. Fresh crocidolite is thus stiff and springy. In weathered crocidolite the amount of interstitial water appears to force the fibrils apart, without leading to their actual separation. The interstitial water appears also to provide some lubrication between fibrils which helps to give rise to its softer and more flexible nature.

Thermal decomposition. A survey of all the d.t.a. results shows that the high temperature endotherm in crocidolite is always present, and that it varies over a range of about 100°C from sample to sample; the higher the temperature at which it occurs in oxygen, the higher the temperature in argon. Since the samples examined have certain differences in chemical composition, it seemed possible that a relation between composition and the high temperature endothermic reaction might exist. This has been examined by comparing the endothermic temperatures, both in argon and oxygen, with the corresponding Na_2O , MgO , FeO , and Fe_2O_3 contents of the samples, and particularly with the ratios total Fe/Mg and Fe^{2+}/Mg . At first sight there is an indication that the endotherms take place at progressively higher temperatures as the Na_2O contents diminish, but although this is plainly so when the data for the Malipsdrift materials are compared with those for the Westerberg materials, the relationship is by no means clear in general. A more definite relationship can be found by considering iron/magnesium ratios, and fig. 3 shows the result of a plot of Fe^{2+}/Mg ratio against endothermic reaction temperatures. Although there is some scatter of points the graph indicates that the endothermic temperature tends to a minimum figure of about 900°C in oxygen and 800°C in argon at Fe^{2+}/Mg ratios of above 5/1; below this ratio the endothermic temperatures move up by some 80°C as the ratio approaches 2/1. A similar, though not quite so clear, plot can be obtained by taking total Fe/Mg ratios, and it seems certain that magnesium has an important influence on the temperature of the final decomposition of crocidolite.

Addison *et al.* (1962) have suggested that the oxidation of crocidolite at $400\text{--}450^{\circ}\text{C}$ is subject to magnesium blocking and it is inferred that

higher proportions of magnesium in the amphibole will drive the oxidation reaction to increasingly higher temperatures. There is, however, no clear relationship between the Mg contents of the samples and the

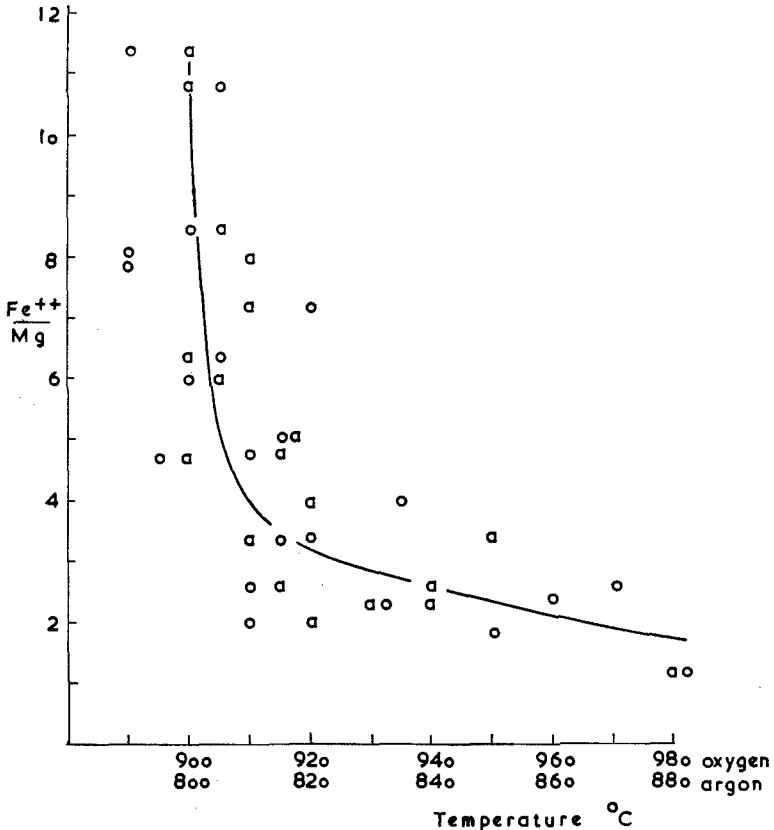


FIG. 3. Relation between the ratio Fe²⁺/Mg and the high-temperature endotherm for crocidolite. a, in argon; o, in oxygen.

dehydration temperatures of the main or second loss in oxygen (table II), which should be coincident with the oxidation mechanism. Excluding the Malipsdrift samples, all dehydration temperatures fall within the same range irrespective of MgO contents, which vary from 1.6 to 4.6 %, and indeed there are several examples where the onset of dehydration occurs at temperatures lower than usual despite a higher MgO content.

On the other hand, the present investigation suggests that magnesium exerts a blocking effect on the decomposition of crocidolite, with higher magnesium contents forcing the final decomposition to higher temperatures. It may well be, then, that the effect of magnesium on oxidation is a corollary to a more important effect of magnesium in the structure. We do not know where the magnesium will end up among the decomposition products; it may be in an iron-rich pyroxene or in an Fe-Mg spinel. In either event it appears that the ease with which magnesium is transferred into the end product is inhibited as the proportion of magnesium present increases.

The Malipdrift and Bolivian crocidolites

The Malipdrift crocidolite is intimately associated with amosite; seams of amosite and crocidolite occur in the same reef and crocidolite seams themselves often have a thin selvage of amosite, usually at one edge of the seam only. Fig. 4 shows this effect in a hand sample from Malipdrift, and compares the material with the fresh rock from Koegas. The microscopic examination of crocidolite from this area reveals that crocidolite passes into amosite without a break at such a selvage, and that both amosite and silica fibres may be found in intermingled parallel growth with the crocidolite (amosite is the long-fibred ash-grey-coloured amphibole asbestos mined at Penge in the Transvaal and also at Malipdrift. It approximates to $\text{Fe}_{5.5}^{2+} \text{Mg}_{1.5} \text{Si}_8 \text{O}_{22} (\text{OH})_2$). The chemical analyses of the Malipdrift crocidolite invariably give high silica contents of 60 % or more (this also applies to the Malipdrift amosite), but there is nothing in the analyses to indicate that amosite could be present as well. However, there are certain interesting characteristics in the thermal analyses of this crocidolite. There is no endotherm about 400° C on the d.t.a. in oxygen, as would be expected for crocidolite, and the corresponding dehydration in oxygen takes place over a wide range of some 500° C, instead of the usual narrow range of about 150° C. The dehydration in oxygen shows two steps, one between 400° and 600° C and a further smaller one between 750° and 850° C. Furthermore, the dehydration in oxygen is consistently higher by 0.2 to 0.3 % than the dehydration in argon. All these are features of dehydration that have been found in investigations of amosite (Hodgson, 1963).

Although the similarities between amosite and these characteristics of the Malipdrift crocidolite are by no means exact, there is certainly an amosite influence in the latter. Mixed fibres of amosite and crocidolite can be found in thin sections, and mixed crystals of grunerite and

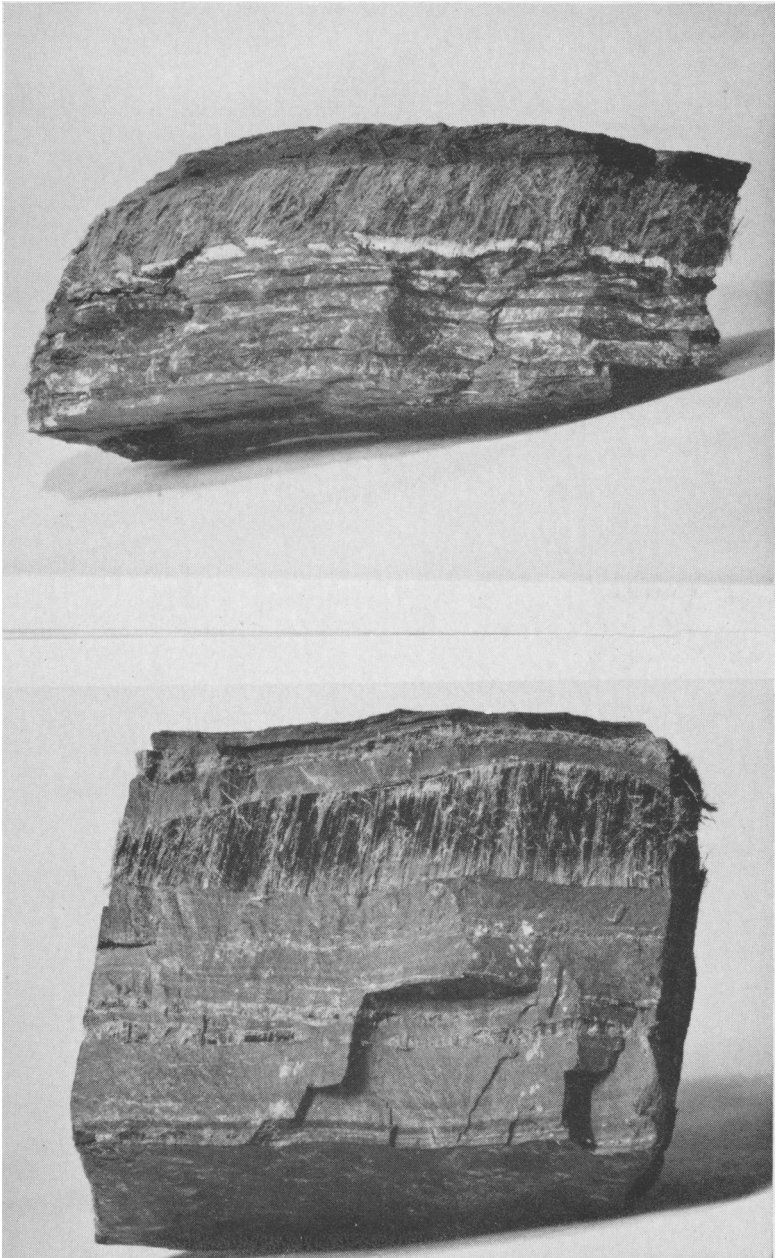


FIG. 4. Top: crocidolite in banded ironstone from Malipsdrift, Transvaal, showing fibre seam with a white selvedge of amosite. Bottom: crocidolite seam in banded ironstone from Koegas, Cape Province.

riebeckite can be found in the rocks, adjacent to the fibre seams. These admixtures would undoubtedly have an effect on the thermal analyses, and indeed may account for the elevation of the decomposition temperatures of this crocidolite.

The same possibilities for an association of two amphiboles can be suggested for the Bolivian crocidolite. The d.t.a. in oxygen has an endotherm at 1015° C, reminiscent of tremolite or anthophyllite, and the d.t.a. in argon has a high-temperature endotherm at 985° C quite unlike that normally found in crocidolite. In comparison the high temperature decomposition of anthophyllite in d.t.a. is almost independent of the surrounding atmosphere. The weight loss and dehydration curves for the Bolivian crocidolite are not of the usual pattern for crocidolite generally, and in particular this applies to the weight loss in oxygen, which is little different from that in argon. The curves so obtained show some resemblance to those for anthophyllite, where the main dehydroxylation occurs in the range 800–1000° C, independently of the surrounding atmosphere, though of course the magnitude of such a loss in anthophyllite is up to 2.5 % (Hodgson, 1963).

The Bolivian crocidolite has been compared with crocidolite from Lusaka, Northern Rhodesia. The two types have similar chemical analyses and are classified as magnesio-riebeckites (Drysdall and Newton, 1960). Their origin is metasomatic and the soda required for their formation is supposed to be derived] from soda-rich solutions that invaded the host rocks. Hand samples of the Bolivian crocidolite ore are composed of crudely rectangular fibrous bundles up to 1 in. across, the bundles being oriented in all directions with respect to each other. These samples bear a close similarity in appearance to ore samples of the Finnish anthophyllite, which is also a product of high grade metamorphism. It does not seem improbable therefore, that magnesio-riebeckites, such as the Bolivian crocidolites, may be distinctly different from crocidolites as they are defined here. They appear to have close affinities with anthophyllite both in mode of formation and on the grounds of d.t.a. evidence, and the possibility of a mixed crocidolite-anthophyllite cannot be excluded.

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