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THE AMERICAN MINERALOGIST, VOL. 55, MAY-JUNE, 1970

CHEMICAL DIFFERENCES AMONG THE SERPENTINE
"POLYMORPHS": A DISCUSSION

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ABSTRACT

Many of the serpentine mineral analyses treated statistically by Page (1968) do not conform to the standards he proposed for characterisation of the specimen or for completeness of analysis. When these unsatisfactory analyses are omitted the remainder are inconsistent with Page's conclusions that lizardite has relatively high SiO_2 and low Al_2O_3 contents and that antigorite has relatively large numbers of trivalent tetrahedral ions. They are consistent with his other conclusions that relative to one another chrysotile is low in Al_2O_3 , lizardite is low in Fe^{2+} and Fe^{3+} , and antigorite is high in SiO_2 and low in MgO and $\text{H}_2\text{O}+$. It is further shown that chrysotile and lizardite contain $\text{H}_2\text{O}+$ in excess of the ideal formula, antigorite has the highest $\text{FeO}/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ and lizardite the lowest. The extents of substitution by Fe and Al tend to be in the order chrysotile < lizardite < 6-layer serpentine, though the ranges overlap, and substitution in antigorite extends over the range of all the other species.

INTRODUCTION

In a recent paper under the above title, Page (1968) has examined statistically the possibility of differences between the chemical composi-

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tions of the serpentine minerals chrysotile, lizardite and antigorite. Such differences have been hinted at in the earlier studies of Bates (1959) and of Faust and Fahey (1962), but the problem is a difficult one because of the rather small compositional differences involved, the often extremely small grain size of the minerals which leads to difficulties of purification, and the fact that identification of specimens in the literature is very unreliable prior to the X-ray diffraction study of Whittaker and Zussman (1956). Page recognises these difficulties, and enunciates a number of criteria for reliability of data, which should ensure the reliability of his conclusions. At first sight Page's conclusions therefore seem to be the most reliable analysis to date of our knowledge of this subject. Unfortunately, a detailed examination of his paper shows that some of Page's conclusions are inconsistent with his own graphical and tabular presentations of his data, that some of these presentations are inconsistent with the analyses to which he refers, and worst of all that a substantial proportion of the analyzed specimens referred to do not meet either his own or any other reasonable criteria for purity, reliability of identification or adequacy of analysis.

In the present paper we re-examine the evidence that remains when only the more satisfactorily identified and analysed of the specimens are considered. The number of these is rather small for a statistical analysis and none has been attempted, but the results are clearly inconsistent with some of Page's conclusions and consistent with others.

QUALITY OF ANALYSES AND IDENTIFICATION

Page (1968) has chosen for his study 75 samples from those collected by Faust and Fahey (1962), plus 5 new analyses (Page, 1966). Since the chemical differences being examined for are very small, the question of how to evaluate analyses (particularly old analyses: the oldest is dated 1818 and a further 14 are older than 1900) is a problem open to considerable debate.

A far more difficult and more important problem is the classification of the minerals, from their original descriptions in the older literature, into the system of Whittaker and Zussman (1956) that is based on X-ray diffraction. A serpentine mineral described as green and macroscopically platy is probably antigorite, and a silky fibrous serpentine mineral is probably chrysotile, but there is certainly a reasonable doubt in many identifications.

Page states that a group of 52 analyses, marked with an asterisk in the Appendix, were classified as chrysotile, lizardite or antigorite, on the basis of "X-ray, DTA, or other information, but not on the basis of the chemical analysis", and these were subjected to a linear discriminant

analysis with the major oxides treated as variables. The result of the analysis was . . . "that out of 31 chrysotiles (originally grouped together) only two were included in other groups than chrysotile, for six lizardites only one was put in another group and for 15 antigorites only one was put into another group." (pp. 210–11). A check in the Appendix shows that only 44 analyses are marked with an asterisk and that 24 of these are chrysotiles, 9 are lizardites, and 11 are antigorites. Although these discrepancies may not affect the final results, it is difficult to know what to make of them.¹

Moreover, even some of the analyses marked with an asterisk cannot possibly be regarded as having had their identities established by "X-ray, D.T.A. or other information" unless the pre-1956 identifications of authors are regarded as suitable other information. An example of the problems of guessing mineral identities from their description is illustrated by samples 28 and 67. In the original description, 28 is described as "Commerical slip fiber with some brittle strands" (Keep, 1929, p. 114, sample G.33) and 67 is described as "Commerical quality slip fiber" (Keep, 1929, p. 114, sample G.62). These are listed in the Appendix (Page, 1968, pp. 214–5) as 28, probably lizardite, and 67, chrysotile. Sample 6 was originally described by Caillère (1936) as metaxite, from Moncaup, France. Page identifies it as probably lizardite, but Whitaker and Zussman (1956) found that metaxite from Reichenstein, Silesia was mainly chrysotile. Sample 102 described by Caillère as pseudocubic serpentine from the Tilly Foster Mine, New York, is identified by Page as "labelled antigorite, probably chrysotile". Faust and Fahey (1962) on strong X-ray and DTA evidence, identified a similar serpentine from the same locality as antigorite. The recent work of Aumento (1967), which unfortunately was not available to Page at his time of writing, presents further evidence that the Tilly Foster serpentine may be either a unique mineral or a mixture of chrysotile and antigorite. Certainly it cannot be used as a representative analysis of either chrysotile or antigorite. Sample 206 is listed in Dana (1892) as retinalite from Calumet Islands, Quebec, and is identified by Page as chrysotile. Faust and Fahey (1962) p. 6, discuss three retinalite samples. They found one to be clinochrysotile, one to be a mixture of chrysotile and lizardite, and noted that sample 206 appears to have contained slight impurities. All but the last sample discussed above were marked with an asterisk and used in the

¹ Contrary to what is stated in the Appendix of Page (1968): the samples numbered *10 and *102 were used as probably antigorite; *51 as probably chrysotile; 248 and 251 and the samples from Page (1967) should have asterisks added; and *249 of Faust and Fahey was omitted and should have been included (Page, personal communication).

statistical study. Some of Page's identifications may be correct, but there is certainly enough doubt about their reliability to exclude them from any statistical study.

A few of the analyses in the Appendix appear to contain impurities. Analysis 146 of lizardite from The Lizard, Cornwall, is described by Midgley (1951) as being contaminated with a talc impurity. Sample 194 was described by Faust and Fahey (1962) p. 45. . . "the analysis. . . is probably contaminated with the pyroxene from which the serpentine is derived." Sample F-41 is one of a number of specimens, originally named as deweylite, which are described by Faust and Fahey in the same paper (p. 37). . . "It has been observed in the DTA and X-ray studies that these same deweylite specimens were natural mixtures of serpentine and the magnesium end-member of the montmorillonite group, stevensite." The calculated structural formula for F-41 has a total of 5.56 for the octahedral sites, and 4.22 for the tetrahedral sites. The inclusion of analyses such as these in the average mineral composition calculations, particularly for lizardite in which only six analyses were used, cannot help but distort the final results.

Thus the statements (p. 205) "analyses of serpentines for which there is not sufficient X-ray, optical and textural, DTA and infrared evidence to determine the mineral species are not considered here" and "for the present study, analyses (Appendix) made on material apparently free of mineralogical impurities and identified as to mineral type, were chosen" simply do not represent the facts.

Two 6-layer serpentines, 33 and 112, are listed by Page (1968, 214-215) but there is no indication in which mineral group, if any, they are included.

Some of the analyses used are also unsatisfactory on account of their incompleteness, and this again extends to those marked with an asterisk and used in the statistical analysis and for the calculation of the mean compositions in Page's Table 1. Since the chemical formulae given in that Table are calculated on a basis which uses the value of H_2O+ , it is particularly obscure how the analyses that only give total water were used. The incorporation of these analyses in Page's Figures 2 and 3, where total H_2O is treated as H_2O+ whenever H_2O- is not available, must certainly obscure the true facts. There are also quite a large number of analyses in which Fe_2O_3 and FeO were not determined separately, which must again undermine confidence in the interpretations of Page's Figure 3 and Table 1.

Table 1 of this paper indicates the analyses which we regard as questionable on grounds of identification, impurity or incompleteness. We have considered the identification of a mineral doubtful unless it has been identified by X-ray diffraction, or, in the case of antigorite, by

TABLE 1. LIST OF ANALYSES CHOSEN BY PAGE (1968) WITH COMMENTS ON THEIR RELIABILITY

Page's sample numbers	Incomplete analysis	Doubtful identification	Impurities present	Analyses accepted for this study
*6		×		
*10	×	×		
*12		×		
13		×		
*15	×			
*20	×	×		
*28		×		
29	×	×		
*30	×	×		
33				×
*35	×			
*37		×		
42			×	
43		×		
*45				×
*49				×
50		×		
*51	×	×		
53	×			
54	×	×		
63		×		
*64			×	
*65			×(?)	
*67		×		
70	×			
71	×			
75	×			
76	×			
*78	×	×		
79	×			
*86		×		
89	×			
*91			×	
*94	×			
*96		×		
97	×			
100	×	×		
101	×			
*102	×	×		
111	×			
112				×
115	×		×	
*120				×
*121	×			
*129	×			

TABLE 1.—(Continued)

Page's sample numbers	Incomplete analysis	Doubtful identification	Impurities present	Analyses accepted for this study
*132	×	×		
*136	×	×		
*137	×	×		
*146	×		×	
*147	×	×		
152	×			
*194	×		×	
*197	×			
203	×			
204	×			
205	×			
206	×	×	×	
212	×		×	
217	×			
*222			×(?)	
243	×	×		
248	×			
*250	×			
251	×			
*260	×			
*F-1				×
*F-15				×
*F-20				×
*F-22				×
*F-23				×
*F-24				×
*F-41	×		×	
*F-43			×	
*F-46				×
*F-47				×
19NI-63A				×
38NZ62-5				×
94NZ-62				×
19NI-63B				×
14NI-63A				×

D.T.A. The exceptions to this statement are chrysotiles from known asbestos areas. We have accepted these identifications as correct, although even here with no X-ray data, some doubt about their identity and their purity must remain. The questionable analyses comprise 57 out of the total of 80, and include 33 out of the 44 marked with an asterisk and used for the statistical study. Since no statistical study can be any

better than its original data, we feel that Page's results cannot be accepted without further examination.

OTHER INCONSISTENCIES

Apart from the validity of some of Page's results there are also inconsistencies in his statements as to what his results are. Such discrepancies arise on p. 212 in statements (1), (2) and (6) of the conclusions. According to the data in his Table 1: (a) the weight percent SiO_2 is not higher for both lizardite and antigorite, but only for antigorite, contrary to statement (1); (b) lizardite does not have a low Al_2O_3 content, contrary to statement (2); and (c) antigorite does not contain a large number of trivalent ions in tetrahedral coordination, contrary to statement (6). Also the average weight percent Al_2O_3 and Fe_2O_3 in lizardite given in his Table 1 are inconsistent with the corresponding histograms in his Figure 1(b) and (c).

METHOD OF CALCULATING CHEMICAL FORMULAE

Before examining the analytical data in detail it is desirable to consider the relative usefulness of the two methods that have been proposed for calculating the chemical formulae of serpentine minerals. The so-called "hydrogen equivalent method" used by Page involves the assumption that the $\text{H}_2\text{O}+$ analysis correctly represents the amount of structural water in the mineral, and that any excess of H above (or shortfall below) the ideal value (8) is replacing or replaced by other ions. Therefore all the oxides (including $\text{H}_2\text{O}+$) are scaled to give 18(O, OH). The so-called 28 negative charge method assumes that any excess of H above (or shortfall below) the ideal value will be accompanied by a corresponding excess (or deficiency) of $\frac{1}{2}\text{O}$. Therefore all the oxides except $\text{H}_2\text{O}+$ are scaled to give 14 O, and then a theoretical water content is added. (This description of the method is in line with that used in other mineral groups, *e.g.*, the 23 O method in the amphiboles). For a material of idealized formula the two methods give the same result, but they give different results if the analysis does not correspond to the idealized serpentine formula $(\text{A}_{1-2x}^{2+} \text{B}_{2x}^{3+})_6 (\text{BS}_x^{3+} \text{Si}_{1-x})_4 \text{O}_{10}(\text{OH})_8$, either because the true formula is different or because of impurities.

The likely effects are as follows:

Cause	Calculation to 18(O, OH)	Calculation to 14 O
1. High $\text{H}_2\text{O}+$ due to strongly adsorbed water.	Si and Mg low	Si and Mg correct
2. High $\text{H}_2\text{O}+$ due to highly hydrous impurity	Si low	Si low, but less so

like brucite or brugnatellite.	Mg high	Mg even higher
3. Low H ₂ O+ due to less hydrous high Si, low Mg impurity like talc, tremolite, enstatite, diopside.	Si high Mg low	Si high, but less so Mg even lower
4. Low H ₂ O+ due to less hydrous low Si, high Mg or Fe impurity like magnesite, dolomite, forsterite, magnetite, hematite.	Si low or high depending on impurity. (Mg, Fe) high	Si low, (Mg, Fe) high, but both lower than 18(O, OH) method
5. Mineral slightly dehydrated O ²⁻ replacing 2(OH) ⁻ .	Si and Mg high	Si and Mg correct
6. Mineral contains 4H ⁺ substituting for Si.	Si and Mg high	Si and Mg high
7. Antigorite structure with systematic omission of Mg and (OH) at Mg-bridges.	Si and Mg high	Si and Mg high, but less so.

Of the causes listed, (1) is known from thermogravimetric data to be prevalent for chrysotile, and we have found (2) to occur commonly in chrysotile and lizardite. In Table 2 we show the results calculated by the two methods for the "average serpentine compositions" given by Page. It is notable that for both chrysotile and lizardite the 18(O, OH) method gives Si and Mg lower than does the 14 O method, which suggests causes (1), (2) or (6). Since it is impossible to discount the high probability of cause (1) we consider that the 14 O method is rather more likely to give a structurally significant formula. Cause (6) would in any case require the assignment of the excess H to tetrahedral positions, which Page does not do. For antigorite the 18(O,OH) method leads to the higher results for Si and Mg, suggesting causes (3), (4), (5) and (7). The fact that the high results slightly exceed the ideal values of both 6 for octahedral cations and 4 for Si, again suggests that the 14 O method is the more satisfactory, especially as the crystal structure determinations of Zussman (1954) and Kunze (1956, 1958) have suggested that there are structural reasons why Mg, as well as OH, should be below the ideal value in antigorite. For this reason neither method of calculation is entirely satisfactory for antigorite.

Our comparison of formulae calculated by the two methods obviously tends to confirm that at least some of the analyses included in Page's work relate to somewhat impure materials.

It is to be noted that the number of octahedral cations, calculated by the 14 O method, in Page's average lizardite is closer to the antigorite value than the chrysotile value. This is not true of the best lizardite analyses, and is probably due to the inclusion of poor data in the small group of analyses from which the average is derived.

There would seem to be an error on p. 212 of Page (1968) where 5.65 is given as the number of octahedral cations in his average antigorite calculated by the 14 O method.

TABLE 2. A COMPARISON OF MINERAL FORMULAE CALCULATED BY THE 18(O, OH) AND 14 O METHODS FROM THE AVERAGE SERPENTINE COMPOSITIONS GIVEN BY PAGE (1968)

18(O, OH) method	Chrysotile	Lizardite	Antigorite
Tetrahedral ions			
Si	3.897	3.834	4.010
Al	0.079	0.154	—
Σ	3.976	3.988	4.010
Octahedral ions			
Al	—	—	0.184
Fe ³⁺	0.051	0.288	0.083
Fe	0.049	0.033	0.297
Mg	5.724	5.494	5.443
Σ	5.824	5.815	6.007
Anions			
O ²⁻	9.524	9.717	10.320
(OH) ⁻	8.476	8.283	7.680
14O method			
Tetrahedral ions			
Si	3.966	3.874	3.965
Al	0.034	0.126	0.035
Σ	4.000	4.000	4.000
Octahedral ions			
Al	0.046	0.029	0.146
Fe ³⁺	0.052	0.291	0.083
Fe ²⁺	0.049	0.034	0.294
Mg	5.823	5.549	5.380
Σ	5.970	5.903	5.903
Anions			
O ²⁺	10.0	10.0	10.0
(OH) ⁻	8.0	8.0	8.0

ANALYSES SELECTED

In order to have a basis for comparison with Page's results we have chosen the analyses of the samples listed in Table 3. All but a few of these analyses can be found in Faust and Fahey (1962), but the papers in which the analyses were originally published are also listed in Table 3.

TABLE 3. SAMPLE NUMBERS, LOCATIONS, AND REFERENCES FOR ANALYSES OF SAMPLES USED IN THIS STUDY

Sample No.	Page (1968)	Location	Reference
Chrysotile			
C-1	F-20	Gila County, Ariz., U.S.A.	Faust and Fahey (1962)
C-2	F-22	Montville, N.J., U.S.A.	Faust and Fahey (1962)
C-3	F-24	Montville, N.J., U.S.A.	Faust and Fahey (1962)
C-4	F-56	Balmat Corners, N.Y., U.S.A.	Faust and Fahey (1962)
C-5	45	Transvaal, Union of South Africa	Brindley and Zussman (1957)
C-6	14NI-63B	New Idria, Calif., U.S.A.	Page (1966)
C-7	19NI-63A	New Idria, Calif., U.S.A.	Page (1966)
Lizardite			
L-1	F-23	Dognacska, Hungary	Faust and Fahey (1962)
L-2	F-46	Bellow Fall, Vt., U.S.A.	Faust and Fahey (1962)
L-3	F-47	Tyrol, Austria (?)	Faust and Fahey (1962)
L-4		Transvaal, Union of South Africa	Deer, Howie and Zussman (1962)
L-5	19N163A	New Idria, Calif., U.S.A.	Page (1966)
6-Layer			
S-1	33	Shetland Islands, United Kingdom	Brindley and von Knorring (1954)
S-2	112	Shetland Islands, United Kingdom	Brindley and von Knorring (1954)
S-3		Thompson Lake, Quebec, Canada	Olsen (1961)
Antigorite			
A-1	F-1	State Line Pits, Low's Mine, Pa., U.S.A.	Faust and Fahey (1962)
A-2	F-8	Smithfield, R.I., U.S.A.	Faust and Fahey (1962)
A-3	F-15	Val Antigorio, Piedmont, Italy	Faust and Fahey (1962)
A-4	49	Mikonui, New Zealand	Zussman (1954)
A-5	120	Vicinity of Caracas, Venezuela	Hess, Smith and Dengo (1952)
A-6	38NZ62-5	Milford South, New Zealand	Page (1966)
A-7	94NZ-62	Griffin Range, Westland, New Zealand	Page (1966)

We have selected only those samples which have been identified by X-ray diffraction and for which the chemical analyses included determinations of Al_2O_3 , Fe_2O_3 , FeO , $\text{H}_2\text{O}+$ and $\text{H}_2\text{O}-$ as well as the other major oxides. All analyses that did not meet these requirements were disregarded. It is

somewhat of a shock to realise how few analyses of pure, properly identified serpentine mineral exist. The largest source is that of Faust and Fahey (1962) from which we quote ten analyses for serpentine minerals identified by X-ray diffraction and DTA. However, they only regard even these samples as consisting of 90% or more of a single serpentine phase. Page (1966) gives five analyses of samples identified by X-ray diffraction. There are two analyses not listed by Faust and Fahey, namely a lizardite sample from Transvaal given in Deer, Howie and Zussman (1962) and a 6-layer serpentine analysed by Olsen (1961). The remaining five samples were also quoted by Faust and Fahey.

We have carried three 6-layer serpentine mineral analyses through our discussion as a separate group, although it appears that they are very closely related to lizardite.

The selected analyses all give reasonable formulae when calculated by Faust and Fahey (1962) or by their method. Chrysotiles fall within the limits $\sum_{\text{oct}} = 5.96$ (except one at 5.86) – 6.07, $\sum_{\text{tet}} = 3.98$ – 4.09; lizardite within $\sum_{\text{oct}} = 5.91$ – 6.04, $\sum_{\text{tet}} = 4.00$; 6-layer within $\sum_{\text{oct}} = 5.94$ – 6.11, $\sum_{\text{tet}} = 4.00$; and antigorites within $\sum_{\text{oct}} = 5.80$ – 5.94, $\sum_{\text{tet}} = 4.00$ – 4.09.

COMPOSITIONAL RELATIONSHIPS

The analyses of the specimens listed in Table 3 were calculated on the basis of weight percent and plotted on the ternary diagrams,

- (1) MgO-SiO₂-H₂O+, (2) MgO-FeO-SiO₂, (3) MgO-Al₂O₃-SiO₂,
 (4) MgO-FeO-H₂O+, (5) Al₂O₃-Fe₂O₃-FeO, (6a) MgO-Al₂O₃-Fe₂O₃
 (6b) MgO-Fe₂O₃-FeO, (6c) MgO-FeO-Al₂O₃.

It is to be noted that in (2) and (4) FeO represents total Fe calculated as FeO. The following diagrams were also plotted from the chemical formula calculations: (7) frequency of various degrees of Si⁴⁺ occupancy of tetrahedral sites and (8) $(\text{Mg}^{2+} + \text{Fe}^{2+}) / (\text{Fe}^{3+} + \text{Al}^{3+})$ vs. H₂O+.

It is to be noted that in diagrams 1–6 the contents of the three vertex components are in each case scaled up to make their sum equal to 100. In discussing each diagram the corresponding relative proportions of the components are described as “values” to distinguish them from the true “contents”.

The MgO-SiO₂-H₂O+ diagram, Figure 1, shows a distinct separation between antigorites on the one hand and chrysotiles, lizardites and 6-layer

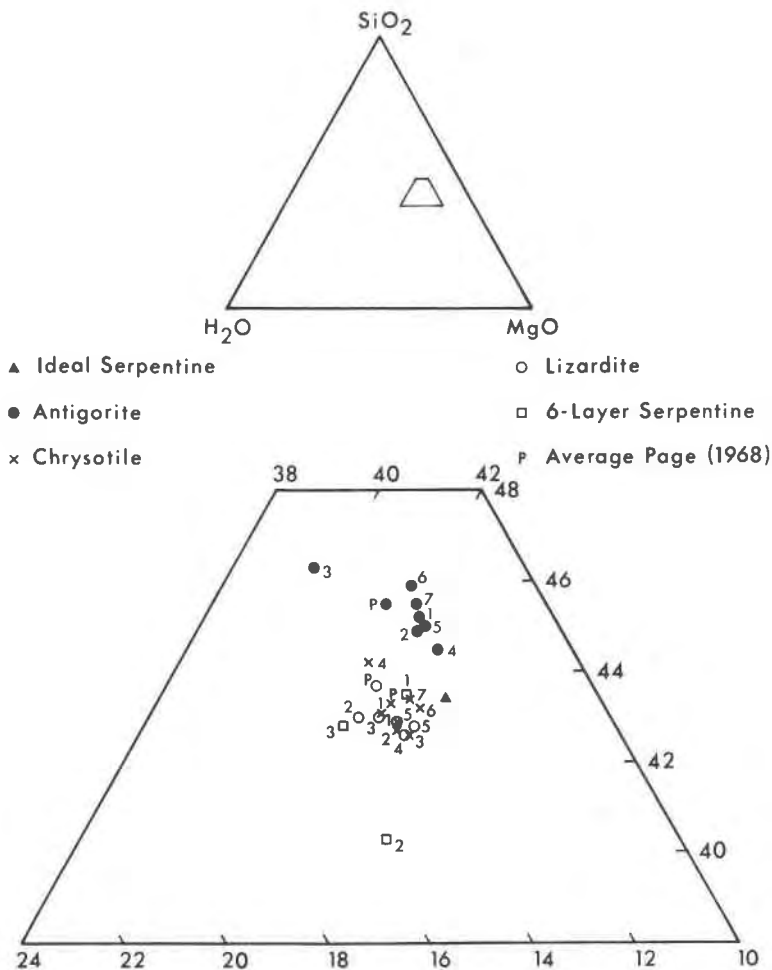


FIG. 1. Selected serpentine analyses plotted on the ternary diagram $MgO-SiO_2-H_2O+$.

serpentines on the other. The chrysotiles, with one exception, and the lizardites are tightly grouped about the approximate MgO and SiO_2 values of ideal serpentine but at a slightly higher H_2O+ value. Two of the three 6-layer serpentines lie on the outer edges of this group, but the third lies at higher MgO and H_2O+ and lower SiO_2 values. Antigorites lie at higher SiO_2 , lower MgO , and (with the one exception of A-3) fall slightly below the H_2O+ value of the ideal serpentine composition. It is to be noted that a high H_2O+ value on this plot does not necessarily correspond to a high H_2O+ content in the analysis. Thus A-3 has a slightly

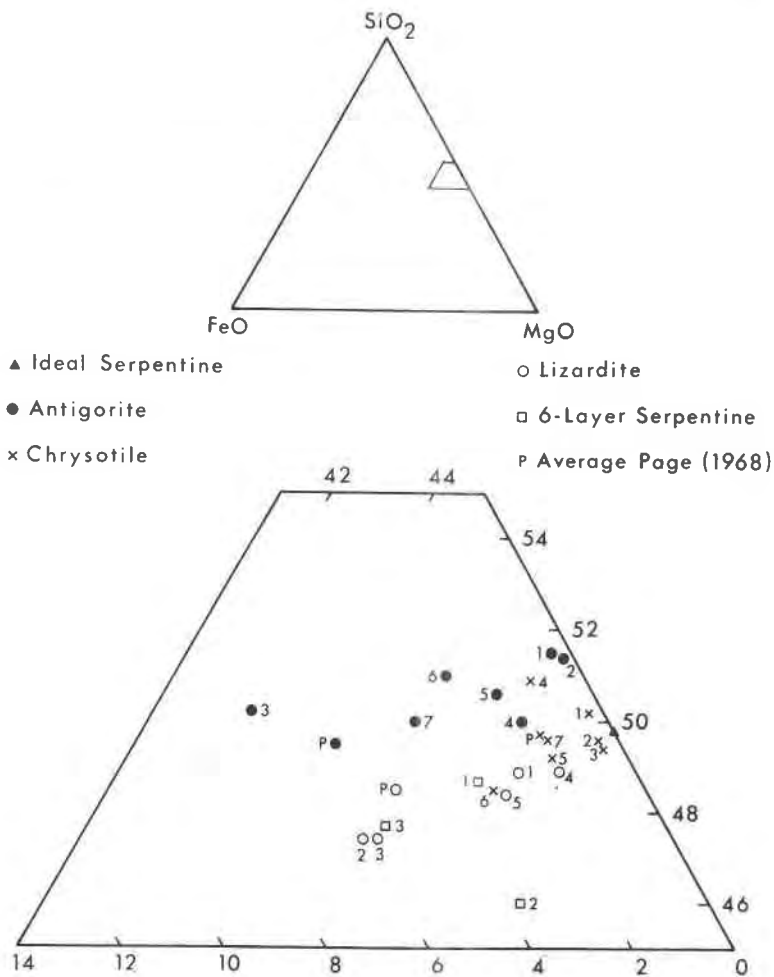


FIG. 2. Selected serpentine analyses plotted on the ternary diagram MgO-FeO-SiO₂. Note that FeO represents the total iron calculated as FeO.

lower H₂O+ content than A-2, but the value on the plot is raised as a result of its high iron and alumina contents, and its resulting low MgO content.

The MgO-FeO-SiO₂ diagram, Figure 2, indicates that chrysotiles, with one exception, and lizardites have MgO and SiO₂ values close to the theoretical serpentine composition. The lizardites appear to extend into larger total iron values than the chrysotiles, and two of the 6 layer serpentines lie at the high iron end of the lizardite trend. The third has high

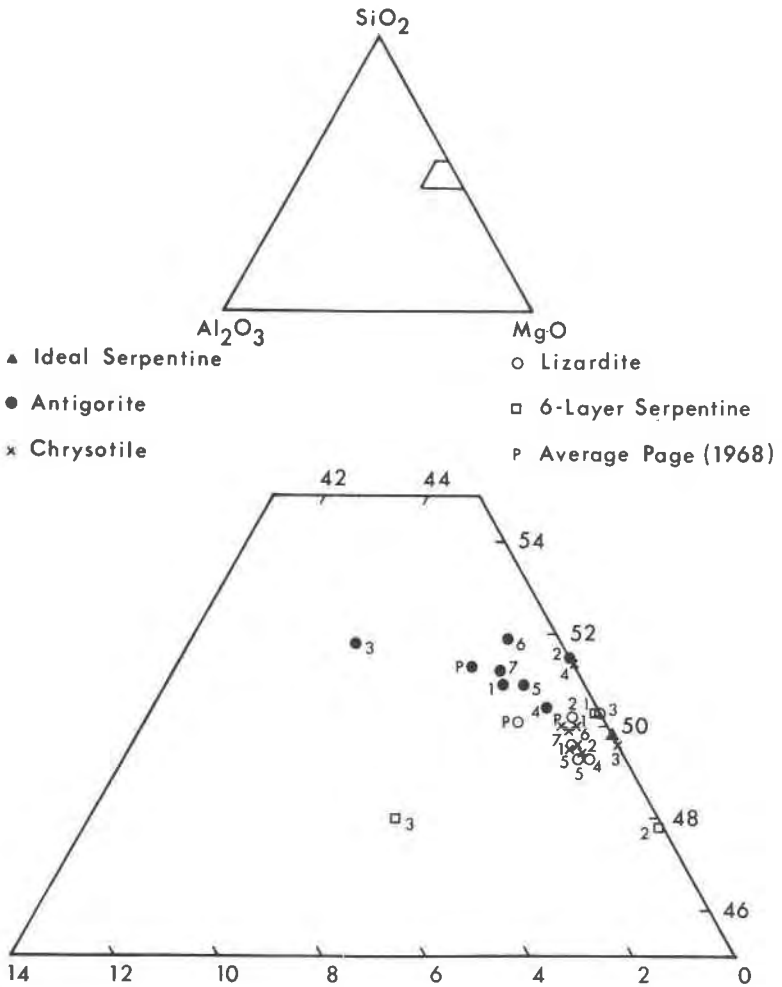


FIG. 3. Selected serpentine analyses plotted on the ternary diagram $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

total iron but is on the low SiO_2 side of the lizardite trend. Antigorites tend to have SiO_2 values higher and MgO values lower than theoretical serpentine.

The $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ diagram, Figure 3, shows features similar to the previous diagram. Antigorites tend to have SiO_2 values above, and MgO values below ideal serpentine. Chrysotiles and lizardites tend to cluster about the ideal serpentine composition. One of the 6-layer serpentines lies within the chrysotile-lizardite cluster, and one lies opposite the cluster

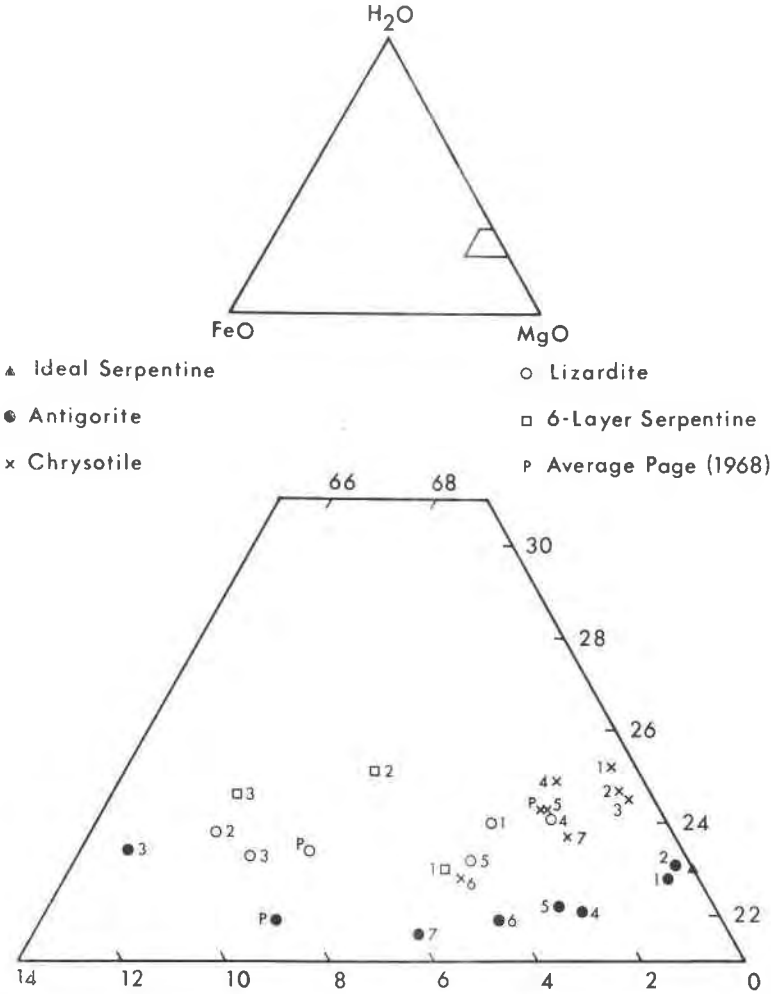


FIG. 4. Selected serpentine analyses plotted on the ternary diagram MgO-FeO-H₂O+. Note that FeO represents the total iron calculated as FeO.

at a higher Al₂O₃ value. The third 6-layer serpentine lies on the high MgO, low SiO₂ side of the ideal serpentine. The Al₂O₃ content of all but one of the 6-layer serpentines and one of the antigorites is low (<2%).

The relationship between MgO and H₂O+ in Figure 4 (the MgO-FeO-H₂O+ diagram) illustrates some important relationships between the H₂O+ content and the octahedral sheet of the various serpentine minerals. The antigorites, with one exception, plot approximately opposite

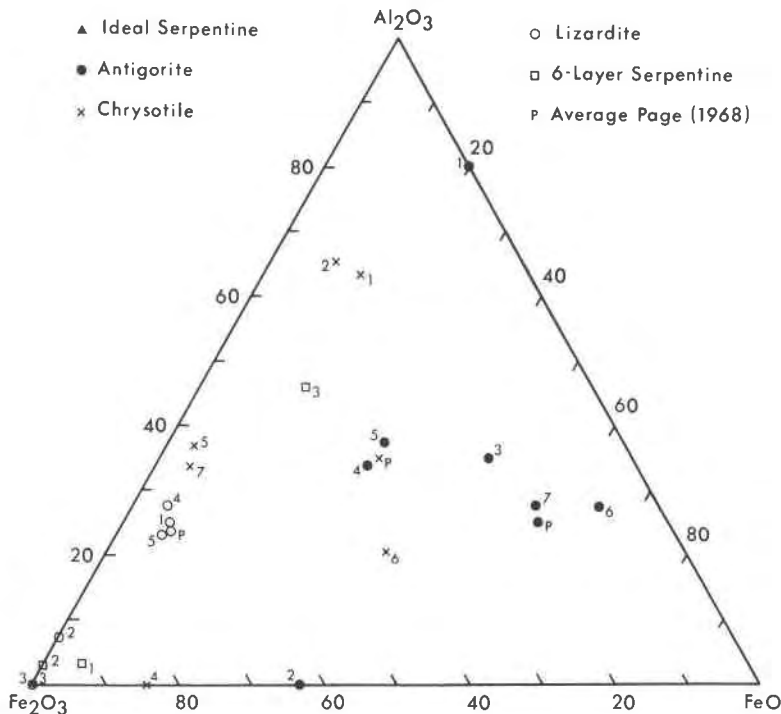


FIG. 5. Selected serpentine analyses plotted on the ternary diagram FeO-Fe₂O₃-Al₂O₃.

the theoretical serpentine composition. Thus, although antigorites tend to have lower H₂O+ (Fig. 1) and MgO contents (Figs. 1, 2 and 3) than do chrysotiles and lizardites, the ratio of MgO to H₂O+ is the same, or close to, that of ideal serpentine. This is a reflection of the feature that both Mg and OH are omitted at the bridge points in the wave structure of antigorite. The antigorite sample, A-3, that does not follow this trend has a high amount of Al₂O₃ substituting for MgO, which would account somewhat for its anomalous position in this diagram. The chrysotiles, lizardites and 6-layer serpentines, all plot on the high H₂O+ side of the theoretical serpentine composition. Since they contain approximately the same amount of MgO as the theoretical serpentine, this high H₂O+ position indicates that they contain a surplus of H₂O+ over that which is needed in the octahedral sheet. The variation in total iron content in this diagram is similar to that in Figure 2.

The Al₂O₃-Fe₂O₃-FeO diagram, Figure 5, is one that was used by Page (1966) but was not included in Page (1968). This was an unfortunate omission because the diagram illustrates important distinctions between

the minerals that are not evident in the previous diagrams. The $\text{FeO}/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3) \times 100$ ratio of antigorites appears to be restricted to more than 20–25%, whereas for lizardites and the 6-layer serpentines it appears to be less than 10–15%. The Fe_2O_3 and Al_2O_3 ratios of antigorites appear to extend across the full range but the Al_2O_3 ratio tends to be slightly higher than the Fe_2O_3 ratio. Most of the lizardites, and two of the 6-layer serpentines lie towards a high Fe_2O_3 ratio, and only two lizardites and one 6-layer serpentine lie at or above the 50% point of $\text{Al}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3) \times 100$. However, it is known that the lizardite from the Lizard, Cornwall, (Midgley, 1951) and the aluminous 6-layer serpentines described by Gillery (1959) and Bailey and Tyler (1960) would plot in the Al_2O_3 corner of the diagram although analyses of these specimens could not be included in the general discussion. Thus it seems probable that lizardites and 6-layer serpentines give a complete series from high Fe^{2+} to high Al^{3+} . The chrysotiles in this diagram tend to plot close to, and along the Fe_2O_3 - Al_2O_3 boundary, but it appears that they can occur elsewhere in the diagram so that no unique pattern applies to their Fe_2O_3 - Al_2O_3 - FeO ratios.

In Figure 6 there are shown portions of all the three faces of the MgO - Al_2O_3 - Fe_2O_3 - FeO tetrahedron which meet at the MgO vertex, and on each face are represented the projections of the analyses from the opposite vertex. It therefore shows the substitutions of Al, Fe^{3+} and Fe^{2+} for Mg. Not all the Al, and possibly not all of the Fe^{3+} , will actually be substituting for Mg in these minerals, as some will undoubtedly be substituting for Si. However, this diagram was chosen because it serves to illustrate the trends in substitution. Also, it was easy to calculate from the weight percent of oxides and probably is no less arbitrary or inaccurate than a plot based on one or other of the methods of calculating chemical formulae. The diagram shows that the chrysotiles tend to have less substitution than the other minerals, although there is overlapping between the chrysotiles with the greatest substitution and the lizardites with the least substitution. Some lizardites have an appreciable amount of substitution, as do all of the 6-layer serpentines. The preference of the lizardites and 6-layer serpentines for Fe_2O_3 and, to a lesser extent, Al_2O_3 is illustrated. Antigorites also appear capable of significant substitution and the trend toward FeO and, to a lesser extent, Al_2O_3 is illustrated.

In the previous diagrams, only the weight percent of the various oxides from the analyses was used, so that the problem of what method to use for the calculation of structural formulae was avoided. The following diagrams, Figures 7 and 8, are based on the formula calculations of Faust and Fahey (1962) or the application of their 14 O method.

Figure 7 shows the silica occupancy of the tetrahedral sites. It sug-

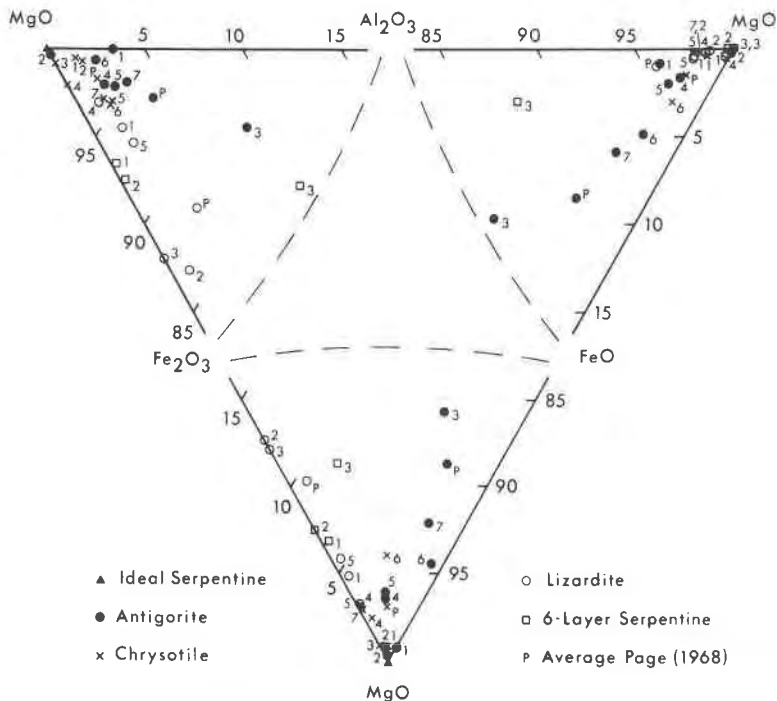


FIG. 6. Selected serpentine analyses projected on the faces of the tetrahedron $\text{MgO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ near the MgO vertex.

gests a tendency for little substitution to occur in the tetrahedral sites of antigorite, though this may be slightly exaggerated by the method of calculation. In chrysotiles, some substitution for silicon does occur, but in some cases there is none. Substitution for silicon appears to be more appreciable for lizardites, and greatest for some of the 6-layer serpentines

The plot of $(\text{Mg}^{2+} + \text{Fe}^{2+}) / (\text{Fe}^{3+} + \text{Al}^{3+})$ vs. weight percent H_2O is one used by Page (1968) Figure 3, p. 210. From his diagram Page concluded (p. 209) . . . "Figure 3 demonstrates that antigorite and lizardite contain less water than chrysotile and that lizardite and antigorite differ chemically from chrysotile by having lower ratios of $(\text{Fe}^{2+} + \text{Mg}^{2+})$ to $(\text{Fe}^{3+} + \text{Al}^{3+})$ ", although in fact his diagram does not suggest any difference between the water content of chrysotile and lizardite. Page used both $\text{H}_2\text{O} +$ and total H_2O values in his plot, so that the H_2O relationships are in any case inevitably obscured. He did not state whether he used only octahedral cations or the total number of cations for the ratio $(\text{Mg}^{2+} + \text{Fe}^{2+}) / (\text{Fe}^{3+} + \text{Al}^{3+})$. We have chosen to use the total number of cations because this allows a greater number of analyses to be plotted.

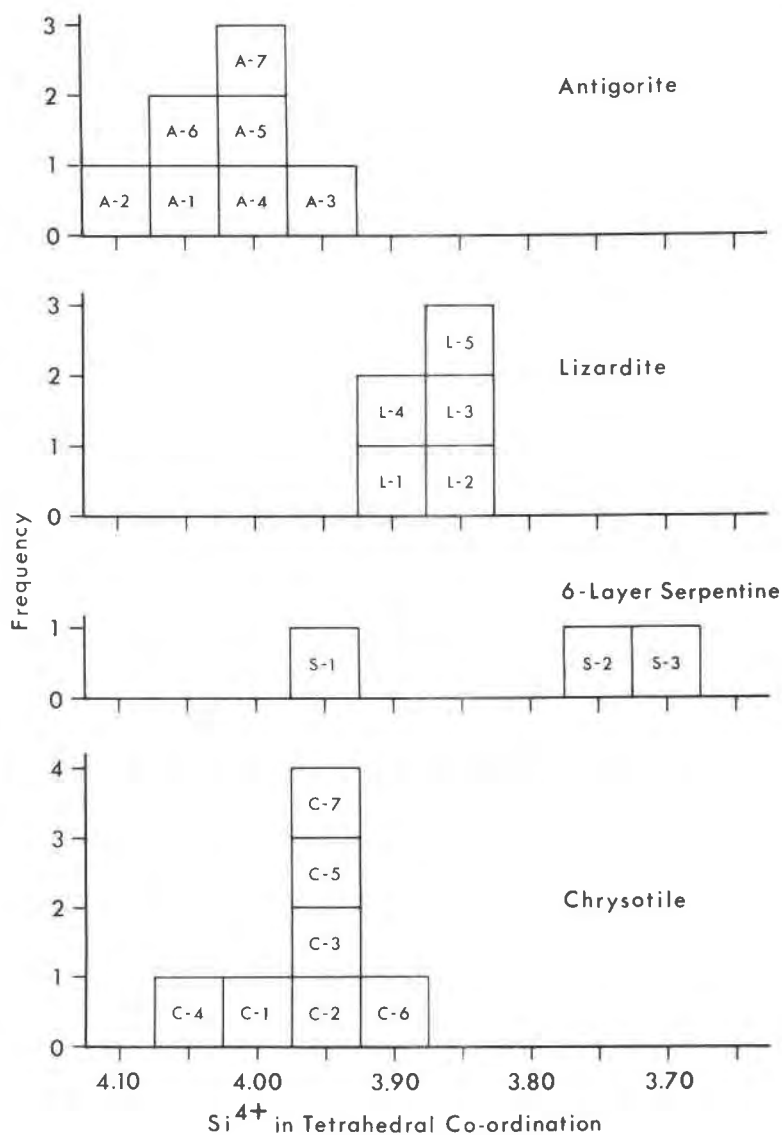


FIG. 7. Frequency of occupancy of the tetrahedra by Si⁴⁺ for various serpentine minerals.

However, the use of only the octahedral cations for the ratio does not significantly alter the relationships. Figure 8 is the plot of our chosen analyses on the same diagram. There is an even more marked separation of antigorite and chrysotile based on weight percent H₂O than noted by

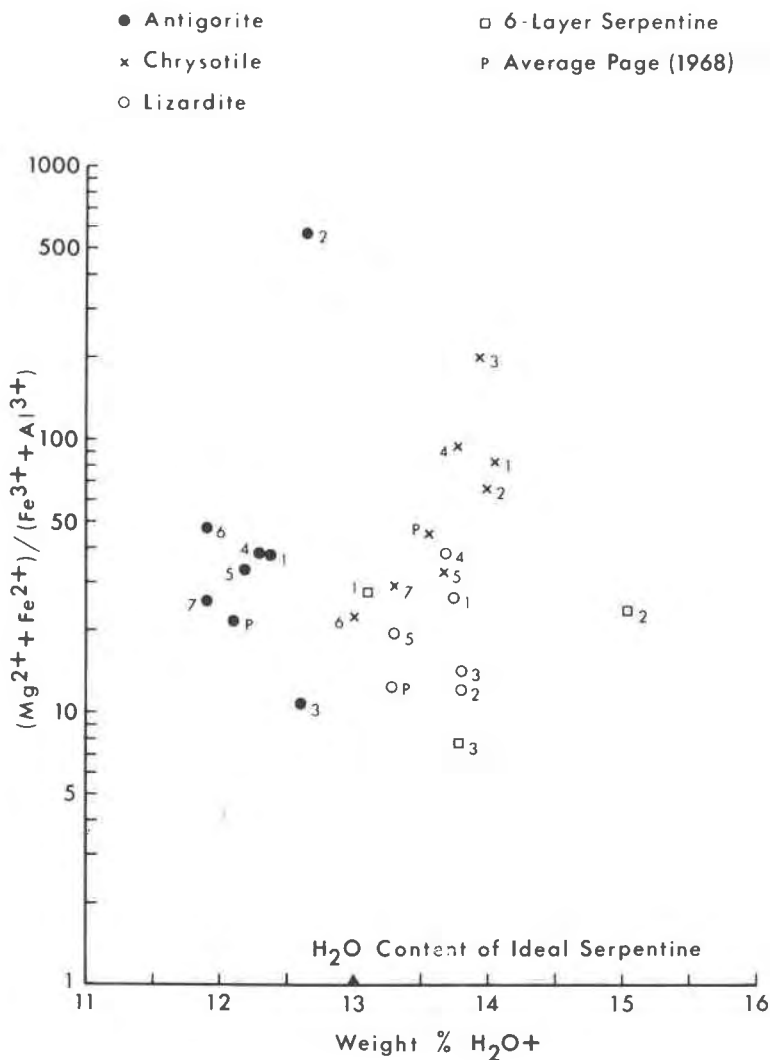


FIG. 8. $(Mg^{2+} + Fe^{2+}) / (Fe^{3+} + Al^{3+})$ versus percent H₂O+ for selected serpentine analyses.

Page. However, contrary to Page's statement, the range of water contents of chrysotile (and the 6-layer serpentines) completely overlaps that of the lizardite. Also, the sharp break at approximately 40 on the ordinate between chrysotile, and antigorite and lizardite as illustrated by Page's Figure 3, does not appear to exist.

CONCLUSIONS

The "average" compositions of the three serpentine minerals, chrysotile, lizardite and antigorite, as given by Page (1968) Table 1, page 211, have been plotted on all the diagrams, Figures 1-8. In some of the figures these "average" values fall within the apparent trends of the analyses plotted. In others they are close to but not within the apparent trends. In none of the diagrams are these "average" composition representative of the samples plotted. If these "average" compositions are to be used at all they must be used with caution.

The apparent chemical differences shown by the previous figures can be summarized as follows:

(1) Antigorites have higher SiO_2 and lower MgO and $\text{H}_2\text{O}+$ contents than the ideal serpentine composition. The range of substitution of iron and aluminium in the antigorite structure appears to extend from almost nil to the greatest amounts of substitution observed in any of the serpentine minerals. Since the substitution for Si in the tetrahedral sheet appears to be low, most of the iron and aluminium must be replacing magnesium in the octahedral sheet. The valence state of the iron in antigorite appears to be critical. FeO never appears to be less than 20-25 percent of the three oxides FeO , Fe_2O_3 and Al_2O_3 and is usually greater than this value. There may be a slight tendency for Al, rather than Fe^{3+} , to make up the balance of the substituting cations.

(2) Chrysotiles have MgO and SiO_2 contents close to those of ideal serpentine but their $\text{H}_2\text{O}+$ contents are higher. The substitution of iron and aluminium in the chrysotile structure tends to be the lowest of the serpentine minerals. Substitution for Si in the tetrahedral sheet appears to be low, and it follows that substitution for Mg in the octahedral sheet should also be low. There appears to be a tendency for Fe^{3+} and Al ions to be the most abundant, but some samples also contain appreciable Fe^{2+} .

(3) Lizardites also have MgO and SiO_2 contents close to those of theoretical serpentine, but $\text{H}_2\text{O}+$ contents that are higher, very much like the chrysotiles. Substitution of iron and aluminium in the lizardite structure appears to be moderate to substantial. The lizardites with the least substitution overlap somewhat with those chrysotiles which display larger amounts of substitution. The lizardites that display the greatest substitution almost equal the antigorites with the greatest substitution. The substitution for Si in the tetrahedral sheet appears to be greater in lizardites than in most chrysotiles and antigorites. The valence state of the substituting cations appears to be critical for lizardites. FeO makes up less than 7% of the total of the three oxides $\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$. The

lizardites considered ranged from high to moderate Fe^{3+} lizardites, and no high Al lizardites were included. However, high Al lizardites have been found in nature (Midgley, 1951) and produced synthetically (Gillery, 1959), and therefore a complete range from high Fe^{3+} to high Al^{3+} lizardites probably exists.

(4) One of the 6-layer serpentines, S-2, has a $\text{H}_2\text{O}+$ content much higher, and a SiO_2 content much lower than the ideal serpentine composition, and, as a result, tends to plot somewhat anomalously. The problems of interpreting this analysis have been discussed by Brindley and von Knorring (1954), McConnell (1954) and Zussman (1956). McConnell has suggested that $(\text{H}^+)_4$ substitutes for Si^{4+} in the tetrahedral sheet. If this unusual composition is momentarily overlooked, it can be seen that this sample and the other two 6-layer serpentine samples have similarities to those lizardites with the greatest degree of substitution. All contain significant amounts of Fe^{3+} and/or Al^{3+} and low amounts of Fe^{2+} . (Two samples have $\text{FeO}/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3) \times 100$ ratios of 5% or less and the third has a somewhat higher ratio of 15%). 6-layer serpentines with high Al contents (and low Fe^{3+} and Fe^{2+}) have been described by Bailey and Tyler (1960) and produced synthetically by Gillery (1959) so that it appears that both high Fe^{3+} and high Al^{3+} 6-layer serpentines exist.

Comparison of these conclusions with those reached by Page (1968, p. 212) shows the following discrepancies.

- (a) lizardite does not have a high weight percent SiO_2 ;
- (b) lizardite does not have a low Al_2O_3 content;
- (c) antigorite does not have large numbers of trivalent ions in tetrahedral coordination.

The present analysis of the data is, however, consistent with his other conclusions, namely:

- (d) antigorite has a high weight percent SiO_2 ;
- (e) chrysotile has low Al_2O_3 content;
- (f) lizardite has a large ratio of Fe_2O_3 to FeO ;
- (g) antigorite has low MgO and H_2O weight percents;
- (h) lizardites are low in Fe^{2+}

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