THE RELATIONSHIP BETWEEN TETRAHEDRAL ALUMINUM AND THE MAXIMUM POSSIBLE OCTAHEDRAL ALUMINUM IN NATURAL CALCIFEROUS AND SUBCALCIFEROUS AMPHIBOLES

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ABSTRACT

Critical examination of a plot of 936 available analyses of calciferous and subcalciferous amphiboles leads to the conclusion that the maximum possible Al⁶ increases regularly as the Al³ increases. The maximum allowed Al⁶ at any Al³ value is empirically obtained. New chemical analyses, together with new optical determinations, are given for three previously described amphiboles, from Madras and North Carolina, which appeared to contain more than the maximum allowed Al⁶. The new analyses show that the two Madras amphiboles contain much less than the maximum possible Al⁶, whereas the North Carolina sample contains the most Al⁶ allowed for its Al³ content.

INTRODUCTION

It is well-known that temolite and actinolite are poor not only in tetrahedrally coordinated aluminum but also in octahedrally coordinated aluminum, whereas the silica-poor pargasite, hastingsite and the hypothetical tschermakite are rich in both tetrahedral and octahedral aluminum. It seems therefore that in these amphiboles increasing amounts of tetrahedral Al permit increasing amounts of octahedral Al and it follows that at any one value of Al³ there is certain maximum amount of Al⁶ which is feasible. This paper tries to show what the maximum possible amount of Al⁶ is for each Al³ value of natural calciferous and subcalciferous amphiboles. Calciferous amphiboles are defined as those with at least 1.50 Ca in the half unit cell, referred to 24 (O, OH, F, Cl), while subcalciferous amphiboles contain more than 1.00 and less than 1.50 Ca in the half unit cell.

Obviously the maximum allowable Al⁶ will only be obtained in amphiboles whose host rocks have a suitable chemistry and which have crystallized under the most propitious physical conditions. It has been argued elsewhere (Leake, 1965) that the most suitable conditions are those of high pressures and moderate, not high, temperatures, for igneous amphiboles generally have low amounts of Al⁶ whereas amphiboles with the highest Al⁶ values are often associated with kyanite, jadeite or glaucophane, which are often considered indicative of high pressure conditions. This agrees with the general view formed from other mineral groups that high Al⁶ is favoured by high pressures during crystallization. Examples include clinopyroxenes (LaBas, 1962), orthopyroxenes (Boyd and
England, 1960,) and the $\text{Al}_2\text{SiO}_5$ polymorphs, while it is significant that
the only amphibole which contains really large amounts of $\text{Al}^6$ is glauco-
phane, which is excluded from this account as it is neither calciferous
nor subcalciferous.

**Previous Analyses**

In Fig. 1 936 post-1890 chemical analyses of calciferous and subcal-
ciferous amphiboles have been plotted. Those which lie above the line
drawn across the figure are believed to be unreliable analyses and so the
line shows the maximum amount of $\text{Al}^6$ at each $\text{Al}^4$ value assuming that
the relationship is linear. While further analyses will undoubtedly
slightly modify the precise position of the line there seem to be enough
reliable analyses immediately below the line to ensure that it is substan-
tially correct.

It is important to appreciate that a plot of $\text{Al}^4$ against $\text{Al}^6$ for amphi-
boles is hypersensitive to analytical error. It is now well-known that by
both classical methods of chemical analysis and by the more recent
colorimetric methods, the accuracy of alumina determination is among
the poorest of the major constituents of rocks and minerals. The accuracy
of combined water determinations is also very poor when, as with amphi-
boles, the material being analyzed does not part with all its water below
1000°–1200° C. Most determinations of combined water have been, and
still are, made by the Penfield method (Penfield, 1894) and this is known
to give low results (Riley, 1958a) unless a silica tube and a temperature
in excess of 1000° C is used. (Glass tubes melt at such a temperature).
A great many amphibole analyses are therefore seriously deficient in
water. Low OH in the cell content calculation results in spurious excessive
oxygen, a situation aggravated by the common absence of F and
Cl determinations. This excessive oxygen is the cause of erroneously
high cation values, especially high Si and Al. As $\text{Al}^6$ is obtained by sub-
tracting 8(Si+Al) from the total Si+Al, when the calculation is on the
basis of 24(O, OH), the resulting $\text{Al}^6$ is often grossly excessive. It is
therefore necessary to appraise critically those analyses which have high
contents of $\text{Al}^6$ for their $\text{Al}^4$ value.

The analyses which plot above the line in Fig. 1 have been numbered
with the same numbers as they have in a compilation of amphibole
analyses, which it is hoped are to be published shortly. Accordingly these
analyses are not reproduced here and only their sources are given to-
gether with brief notes on the analyses to indicate why they are regarded
as unreliable. Obviously many, but not all, of the analyses which plot
below the line are also unreliable but they are not of interest at present.
A few of the numbered points, above the line are analyses which have
Fig. 1. Plot of octahedral aluminum in the half unit cell against tetrahedral aluminum (or silicon) for 936 analysed calciferous and subcalciferous amphiboles. The numbered analyses are discussed in the text. The suggested maximum possible Al₆ is shown by the line drawn across the figure. Analyses with Si greater than 8.00 are excluded from the plot as they are obviously erroneous.
no certain deficiencies and although they are believed to be erroneous, it has not been possible to conclusively show this. These are also listed below. It is generally accepted that amphibole compositions calculated from a chemical analysis of a rock and its modal constitution are not reliable unless the amphibole forms a very large proportion of the rock and so such compositions are not discussed in detail. Some of the analyses which plot just below the line and which are considered to be trustworthy are numbered and brief notes on these are given separately.

Analyses which plot above the line in Fig. 1.

43 Peltola, E. (1960) Bull. Comm. Geol. Finlande 192, 53. Analysed material contained 3.95% C. as graphite, 0.21% S as pyrrhotite and 1.64% CO₂ as calcite. Analysis was re-calculated to 100% to remove these impurities. OH + F + Cl in cell contents is low, being only 0.88.

45 Yen, T. P. (1959) Bull. Geol. Surv. Taiwan 11, 23. H₂O + is far too low, being only 0.17.

46 Andreott, C. and R. Pirani (1950) Min. Abst. 11, 330. H₂O + is rather low (1.24%) especially as only a trace of Fe₂O₃ is reported and the host rock is a serpentine.

47 Rondolino, R. (1936) Min. Abst. 7, 26. TiO₂ and FeO not reported; Fe₂O₃ said to be a trace, analysis total, 99.14, is low.

48 Dolar-Mantani, L. and Gr. Gagarin (1936) Min. Abst. 7, 256. OH + F in cell contents is low, being only 0.90.

49 Krenner, A. (1900) Neues Jahrb. f. Min. 41, 341. Old analysis with TiO₂ and MnO not determined, Fe₂O₃ is low, being 0.51, analysis total, 100.97, is high.

50 Parsons, A. L. (1936) Univ. Toronto Studies, Geol. Ser. 29, 31. OH in cell contents is low, being only 0.98.


53 Novotny, M. (1949) Min. Abst. 11, 199. Recalculated to 100% to remove impurities; TiO₂ and Fe₂O₃ not reported.


55 Heron, A. M. (1924) Rec. Geol. Surv. India 56, 192. OH + F in cell contents is low being only 0.77.

56 As 121.

57 Jones, W. A. (1930) Univ. Toronto Studies, Geol. Ser. 29, 68. OH in cell contents is low, being 0.92.


60 Yen, T. P. (1939) Bull. Geol. Surv. Taiwan 11, 23. Although the CaO is rather low and the Fe₂O₃ is greater than the FeO, it is not certain that this is a poor analysis.

61 As 121, also the total, 99.30, is low.


63 Foslie, S. (1945) Norsh Geol. Tid. 25, 83. Calculated from a rock analysis and a mode with 55% hornblende.

64 Lacroix, A. (1942) Min. Abst. 9, 274. May contain some glaucophane impurity like 186.

65 As 121.


67 Van der Plass, L. (1959) Leidse Geol. Meded. 24, 457. Excellent analysis but the material is zoned and heterogeneous with glaucophane cores.


69 Kreutz, S. (1908) Sitz. ber. Akad. Wiss., Wien 117, Abt I, 918. Analysis mostly by Rammelsberg (1858) and is rather old. Total, 99.04 and OH + F in cell contents of 0.39, are both low.

70 As 172.


72 As 176 but the rock contains 66% hornblende.

73 Palmunen, M. K. (1925) Fennia 45, 9. 9. H₂O + 0.16, is far too low.


75 As 176 but the rock contains 61% hornblende.

76 As 176 but the rock contains 54% hornblende.


APPARENTLY RELIABLE ANALYSES FOR THE PRESENT PURPOSE

Of particular interest in Fig. 1 are those analyses which have very large amounts of Al. There is no doubt that 441 is an erroneous analysis (see above) whereas 256, 324 and 285, which are calculated from rock and modal analyses, are highly dubious. Two analyses marked “Previous value of 776 and 816” in Fig. 1 have had an interesting history. Both these amphiboles come from Madras State, India, and were originally described by Naidu (1960, p. 18) who gave the analyses reproduced in Table 1 as I and IV. Somewhat curiously changed figures were later

NEW ANALYSES
Table 1. Chemical Analyses of Re-Investigated Amphiboles

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
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<td>43.91</td>
<td>42.78</td>
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<td>Al₂O₃</td>
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<td>18.35</td>
<td>14.30</td>
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<td>19.04</td>
<td>11.40</td>
<td>18.66</td>
<td>15.96</td>
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<td>0.05</td>
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<td>0.11</td>
<td>0.89</td>
<td>1.35</td>
<td>0.02</td>
<td>0.04</td>
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<td>Fe₂O₃</td>
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<td>FeO</td>
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<td>10.43</td>
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<td>CaO</td>
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<td>15.92</td>
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<tr>
<td>H₂O⁺</td>
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<td>2.50</td>
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<tr>
<td>H₂O⁻</td>
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<tr>
<td></td>
<td>Total</td>
<td>98.30</td>
<td>99.54</td>
<td>99.58</td>
<td>97.76</td>
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Number of Ions on the Basis of 24(O, OH)

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<th>Al³⁺</th>
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<th>Fe²⁺</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
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<td>0.71</td>
<td>0.01</td>
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<td>2.31</td>
<td>0.09</td>
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<td>(2.00)</td>
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<tr>
<td>II</td>
<td>6.61</td>
<td>1.39</td>
<td>1.72</td>
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<td>0.73</td>
<td>0.01</td>
<td>2.60</td>
<td>2.46</td>
<td>0.09</td>
<td>0.00</td>
<td>(2.00)</td>
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<tr>
<td>III</td>
<td>6.32</td>
<td>1.68</td>
<td>0.72</td>
<td>0.00</td>
<td>0.26</td>
<td>0.02</td>
<td>3.41</td>
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<td>0.45</td>
<td>0.00</td>
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</tr>
<tr>
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<td>6.18</td>
<td>1.82</td>
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<td>0.36</td>
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<td>0.03</td>
<td>(2.00)</td>
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<tr>
<td></td>
<td>6.29</td>
<td>1.71</td>
<td>0.27</td>
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<td>1.64</td>
<td>0.47</td>
<td>0.10</td>
<td>(2.00)</td>
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<td>6.31</td>
<td>1.69</td>
<td>1.37</td>
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<td>0.01</td>
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<td>1.82</td>
<td>0.33</td>
<td>0.03</td>
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<td></td>
<td>6.52</td>
<td>1.68</td>
<td>1.13</td>
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<td>0.00</td>
<td>3.69</td>
<td>1.74</td>
<td>0.33</td>
<td>0.02</td>
<td>1.90</td>
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</table>

1. Amphibole from anorthite gneiss, Tiruchengodu, Sittampundi, Madras State, India. P. R. K. Naidu (1960) p. 18, 2V₉,95°. Total includes Cr₂O₃ 0.05.
2. Same amphibole as I. P. R. J. Naidu (1963) p. 212, 2V₉, 85–90°. This is plotted on Fig. 1 as the 'Previous value of 776.'
3. Same amphibole as I. Analyst, A. Kemp, Jr. 6.37, 8.1 6 4 8, 2V₉,92±3°. Associated feldspar, An₇. Plotted on Fig. 1 as 'New value of 776.'
5. Same amphibole as IV. P. R. J. Naidu (1963) p. 121, 2V₉, 72–78°. This is plotted on Fig. 1 as the 'Previous value of 776.'
6. Same amphibole as IV, analysts A. Kemp and B. E. Leake. Jr. 6.61, 1.684, 2V₉,68±2°. Associated feldspar, An₇. Plotted on Fig. 1 as 'New value of 816.'
7. Amphibole from Clay County, North Carolina, U.S.A. H. Kaufman (1963) p. 152, 6.626, 1.643, 2V₉, 96. Total includes Cr₂O₃ 0.22, NiO 0.11, Li₂O 0.01, V₂O₅ 0.00, F 0.00. Cell contents include Cr 0.03, Ni 0.01, Li 0.00, V 0.00, F 0.00.
8. Same amphibole as VII. Analyst, B. E. Leake. Jr. 6.626, 1.646, 2V₉, 96. Associated with anorthite, An₇ and vesuvianite. Total includes Cr₂O₃ 0.22, NiO 0.11, Li₂O 0.01, V₂O₅ 0.00 and F 0.00 determined by C. O. Ingamells. Cell contents include Cr 0.02, Ni 0.01, Li 0.00, V 0.00, F 0.00.
published (Naidu, 1963, p. 121) and these are also reproduced in Table 1 (II and V). While the original analyses have extraordinarily high Al\textsuperscript{6}, the revised analyses, which are plotted in Fig. 1, have even more Al\textsuperscript{6}. It therefore seemed advisable to re-investigate these two amphiboles especially as one of the amphiboles was said to be associated with anorthite, and as this is the most aluminous plagioclase it therefore seemed feasible that this amphibole might be unusually aluminous. Professor Naidu kindly sent some of the analyzed amphiboles to the writer.

After purification of the powders new chemical analyses were carefully carried out in triplicate and appreciably different results were obtained (Table 1, III and VI) using the methods of Riley (1958b). The new analyses are plotted on Fig. 1 as “New values of 776 and 816.” The new H\textsubscript{2}O, Fe\textsubscript{2}O\textsubscript{3}, CaO and Al\textsubscript{2}O\textsubscript{3} values are much more satisfactory. It is apparent that both amphiboles contain less than the suggested maximum amount of Al\textsuperscript{6}.

New 2V measurements on the amphiboles have been made and the refractive indices determined. The associated feldspar of 776 has \(\gamma-1.582\), indicating An\textsubscript{35} using the curves of Smith (in Hess, 1960) whereas the felspar with 816 has \(\gamma-1.555\), indicating An\textsubscript{38}.

Amphibole 840 (Hashimoto, 1961, p. 118) also appears to contain more than the allowed amount of Al\textsuperscript{6}. The host rock is an epidote-An\textsubscript{35} amphibolite with minor magnetite and comes from Kyushu, Japan. The remaining piece of the hand specimen from which the amphibole was separated was kindly sent to the writer by Dr. Hashimoto as none of the originally analyzed powder was left. Unfortunately, despite several days work on this rock it has proved impossible to completely separate the hornblende from the epidote. There is a considerable overlap of density, magnetic, and shape characteristics of the two minerals. A grain mount of the purest amphibole fraction obtained gave about 8% epidote by point-counting and analysis of this powder gave 16.86% Al\textsubscript{2}O\textsubscript{3} compared with 19.26% reported previously. Since epidotes usually contain between 20 and 30% Al\textsubscript{2}O\textsubscript{3} and epidotes with less than 20% Al\textsubscript{2}O\textsubscript{3} are distinctly unusual (Deer et al. 1962, p. 199) it seems that the epidote impurity will enhance the Al\textsubscript{2}O\textsubscript{3}, and thus it can be deduced that the hornblende must contain less than 16.86% Al\textsubscript{2}O\textsubscript{3}. Probably the high alumina previously reported was at least partly the result of epidote contamination. Certainly, if the amphibole contains less than 16.86% Al\textsubscript{2}O\textsubscript{3} then it will plot below the line drawn across Fig. 1.

Analysis 751, from Clay County, North Carolina, was recently published by Kaufman (1963, p. 152) and this plots well above the line in Fig. 1. As this analysis was made by C. O. Ingamells (Table 1, VII) it seemed unlikely that it would be significantly erroneous. Nevertheless,
a number of disquieting features suggested a re-examination of this amphibole was necessary. The recorded refractive indices and birefringence of this amphibole, and several others published with it, seemed impossible for the compositions recorded. The mineral assemblage in the rock from which this amphibole came was not recorded but the analyzed powder was reported (Kaufman, 1963, p. 140) to contain “0.3% inclusions of actinolite, tremolite and hornblende (?)”

A piece of the rock was kindly sent to the writer by Professor W. R. Phillips. Thin sections of the rock show that only one, apparently homogeneous, amphibole is present associated with vesuvianite and anorthite and with a trace of chromite. The anorthite has \( \alpha-1.573, \gamma-1.585 \), indicating \( \text{An}_{34} \), a surprisingly calcic composition. A new chemical analysis (Table 1, VIII) of carefully purified material shows significant differences from the previous result. These differences are consistent with the view that the originally analyzed powder was appreciably contaminated with anorthite, and possibly vesuvianite in addition, for this would explain the slightly increased \( \text{SiO}_2, \text{TiO}_2, \text{Fe}_2\text{O}_3, \text{FeO}, \text{H}_2\text{O} \) and the considerably increased \( \text{MgO} \) while also explaining the lower \( \text{Al}_2\text{O}_3 \) and \( \text{CaO} \). The new analysis plots exactly on the line of maximum possible \( \text{Al}^6 \) (Fig. 1) which is not surprising in view of the aluminous nature of the rock, combined with what must be a low alkali content. The original powder was not pure simply because the rock was not crushed finely enough to separate the constituent minerals, for Kaufman (1963, p. 137) ground only to 60 mesh, whereas at least 120 mesh is essential to separate this amphibole.

New determination of \( \gamma \) gives 1.646, which agrees with the composition satisfactorily and also gives a reasonable birefringence.

It seems therefore that there are substantial reasons to believe that the maximum possible \( \text{Al}^6 \) at each \( \text{Al}^1 \) value is fairly well shown by the line drawn on Fig. 1. It remains a matter of very serious concern that so many amphibole analyses are not reliable. From Fig. 1 it is apparent that there are no amphiboles known which even approach the composition of the hypothetical tschermakite. The conclusions drawn certainly do not apply to amphiboles with less than 1.00 Ca in the half unit cell (e.g. glaucophane) and may not be valid for those containing just a little more than 1.00 Ca.

**Acknowledgments**

I wish to thank Professor Naidu and Phillips and Dr. Hashimoto for kindly supplying me with the material re-studied. Mr. A. Kemp analysed most of the Madras amphiboles while Mr. G. Plant revised the manuscript.
AL IN AMPHIBOLES

REFERENCES


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