

COMPOSITIONS OF NATURAL SILLIMANITES
FROM VOLCANIC INCLUSIONS
AND METAMORPHIC ROCKS

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ABSTRACT

Thirty-two sillimanites from numerous world-wide localities and geological environments were analyzed for Al, Si, Fe, and Ti by use of the electronmicroprobe. These sillimanites occur as fibrolitic, tabular, and granular crystals in middle almandine amphibolite (600°C, ± 5 kbar minimum ?) to granulite facies rocks and within inclusions in dacitic and olivine basaltic lavas (about 1150°C, ± 0.5 kbar pressure?). All the sillimanites analyzed were within very close limits pure Al_2SiO_5 indicating that the possibility of sillimanite-mullite solid solution in most natural environments need not be considered at values greater than the 3% level (the maximum error of measurement). This was even found true of corundum-bearing samples (Al_2O_3 -buffered), which occurred in high temperature-low pressure olivine basalts. The conclusion does not, of course, eliminate order-disorder effects in sillimanite nor slow kinetics as possible reasons for the too common occurrence of kyanite-sillimanite pairs.

INTRODUCTION

The problem involving the Al_2SiO_5 polymorphs is known to all petrologists and need not be elaborated upon here. Zen (1969), Pitcher (1965), and Fyfe (1969) give excellent reviews with newer ideas.

The possible influence of minor elements such as Fe, Ti, Mn, and Cr may, theoretically, produce a two phase area (Strens, 1968) but field studies have not substantiated this as being important (Albee and Chodos, 1969; Chinner *et al.*, 1966). The possible drastic effects of order-disorder in sillimanite at constant composition have been considered by a number of investigators (Zen, 1969; Greenwood, 1970), and some crystallographic evidence supports this hypothesis from experimental studies (Beger, Burnham, and Hays, 1970).

Theoretically, there is no reason why a solid solution series from sillimanite Al_2SiO_5 to pure Al_2O_3 should not exist (Burnham, 1964), and some evidence does exist for such a series between sillimanite and mullite (Aramaki, 1961; Aramaki and Roy, 1963). Aramaki (1961) found a fibrous sillimanite in a glassy inclusion from the Asama Volcano, Japan, which had an apparent $\text{Al}_2\text{O}_3:\text{SiO}_2$ molecular ratio of 52.4:47.6, lying compositionally and crystallographically between sillimanite and mullite. This raises the question as to whether the complete solid solution series exists.

As pointed out by Chinner (1961) and many other investigators, sillimanite is found both as large prisms and as fine mats of "fibrolite",

often together. The fibrolite is not usually analyzed (Zen, 1969, p. 304) and may well show limited mullite solid solution (or order-disorder effects). Moore and Best (1969) have crystallographically analyzed fibrolite from two pyroxene hornfels facies contact aureoles and have found no mullite, nor do the results suggest a solid solution series. Analysis of sillimanite in inclusions from low pressure-high temperature environments such as lavas are also scarce and should show the solid solution to the degree Aramaki's work suggests, especially if corundum occurs as a buffering phase.

ANALYTICAL RESULTS

All of the sillimanite samples from volcanic inclusions, most of the fibrolite, and most of the other samples were X-rayed and found to have a pure sillimanite pattern with no mullite reflections.

The chemical analyses were made on carbon-coated, polished thin-sections and grain mounts with a Norelco TPD low-angle (15°) electron microprobe. Wavelength scans were made on each sillimanite sample that did not fall within close limits (1.5 percent) of a 100 percent total, to see if other elements besides Al, Si, Ti, and Fe were present. Other elements were never detected above the 0.01 percent level and most of the variation is probably due to the orientation of the sample, to which analyses with the low-angle probe are sensitive.

The analytical conditions were 16.5 kV, 0.1 to 0.2 μ A for Fe and Ti and 17.5 kV for Al and Si at constant beam current. The standards used were kyanite from St. Gothard, Switzerland, Ti metal, and hematite (Fe_2O_3). The kyanite contained only 0.02 percent Fe_2O_3 (some of the Fe may have been Fe^{3+}), and no detectable Ti. The stoichiometry of the kyanite was independently checked by use of corundum and quartz standards and found to have essentially a 1:1 ratio of Al_2O_3 : SiO_2 (molecular proportion). In the samples and standards, sufficient counts were accumulated at each analyzed point to reduce statistical counting errors for Fe and Ti to less than 2 percent and for Al and Si to less than 0.3 percent. At least 5 grains were measured in each section, except in some fibrolites with insufficiently large crystals, where an area was measured. These areas gave an Al_2O_3 : SiO_2 ratio identical to the sillimanite occurring as crystals larger than 10 μ m.

To check the supposition that matrix effect corrections are unimportant when the standard (kyanite) is essentially identical in composition to the sample (sillimanite), corrections were done on a number of samples using the method of Springer (1967). These corrections generally were within 0.2 weight percent of the particular oxides of the samples and are well within the uncertainty of the total measurement. Some of the sillimanite crystals measured were very small (10–15 μ m), and surface effects (orientation) play a significant part in the uncertainties of the analysis.

Tables 1 and 2 show respectively the pertinent geological and analytical data. As can be seen, the variation of the Al_2O_3 : SiO_2 ratios (molecular proportions) are small. Sample 9 has a high value of Al_2O_3 approaching that of Aramaki's. The reason for this is unknown, but this sample and 13, which has a high SiO_2 proportion, both have relatively large uncertainties of analysis. It must also be remembered that the uncertainties are calculated from the variation of the radiation readings and include problems of orientation as mentioned earlier. Samples 1, 3, 5, 9, 19, 21, 28, and 32 contain between 0.34 and 0.88 weight percent of calculated Fe_2O_3 and samples 1, 7, 26 and 28 between 0.25 and 0.81 weight percent of calculated TiO_2 . These relatively low values may have a limited effect on the sillimanite

TABLE 1. GEOLOGICAL INFORMATION ABOUT THE ANALYZED SILLIMANITE SAMPLES AND SOME INTERPRETTED P-T CONDITIONS

| Number | Location | General geology | T-P (approx) interpretation | Assemblage | Form and size of crystals | Petrographic association of Si | Collector & collection number of source |
|---|--|---|-----------------------------|---------------------------|---------------------------|--------------------------------|---|
| <i>Almandine amphibolite facies—quartz bearing (buffered)</i> | | | | | | | |
| 1 | Northern Naxos, Greece | Between Ky isograd and begin of migmatization | ~650°C ~6 kbar | BMQP | Fib.; fine | Intergrown with B | Nax. 73, R. D. Schulling V.M.L. |
| 2 | * | Unknown | Unknown | Q | Fib.; fine | Fib. vein in B schist | Ben Jansen, V.M.L. |
| 3 | * | Between Ky isograd & begin of migmatization | ~550°C ~6 kbar | Ky BPQM | Fib.; fine | From border of Ky Q vein | Nax. 260, R. S. Schulling V.M.L. |
| 4 | Grenville Prov, Dill township near Sudbury, Ont. | Above Ky and M isograds; below granulite facies | ~550 to 750°C ~6 kbar | GPBKQRMg | Fib.; fine | No specific relationships | T-296, T. Kwak, V.M.L. |
| 5 | * | * | * | * | Gran; medium | * | T-293, * |
| 6 | * | Above Ky isograd below M isograd | * | GPBKQRMgM | * | * | T-249, * |
| 7 | * | Same as 4 | * | GPBKQRMg | * | * | T-292, * |
| 8 | * | Between S and K (+M) isograds | * | MGPBKyQRMg | Fib.; fine | Intergrown mainly with B | T-232-1c * |
| 9 | * | * | * | MGPBKyQRMg | * | * | T-156-1B * |
| 10 | * | * | * | MGPBKyQRMg ^(S) | * | * | T-232-1B * |
| 11 | * | * | * | MGPBKyQRMg | * | * | T-150-1B * |
| 12 | * | * | * | MGPBKyQRMg ^(S) | * | * | T-120-1A * |

TABLE 1.—(Continued)

| Number | Location | General geology | T-P (approx) interpretation | Assemblage | Form and size of crystals | Petrographic association of Si | Collector & collection number or source |
|--------|---|----------------------|------------------------------|---|---------------------------|---|---|
| 13 | * | * | * | MGPBK _y QRMg (S) | * | * | T-290-1A * |
| 14 | Custer, N. Dak. | Unknown | Unknown | With Q in vein in B schist | Fib., fine | No specific relationships | 70-Sil-1 V.M.L. collection (from Wards) |
| 15 | Rohrsdorf near Chemnitz, Saxony, W. Germ. | Pyroxene granulite | Beyond M isograd | Granulite facies—quartz bearing (buffered) QPKBG(Ky) | Fib. and tab.; fine | Formed from Ky | 72-1882, M (G.I.U. collection) |
| 16 | Waldheim, Sax., W. Germany | * | * | QRPKG | Tab.; fine | Longate masses of crystals parallel to layering | 372-1884 * |
| 17 | Rohrsdorf, Sax. W. Germany | * | * | KKyGPBQ | Tab.; fine | * | 47-1880 * |
| 18 | Waldheim, Sax. W. Germany | * | * | KPQGB | Gran.; fine | "Clots" after Ky? | 375-1884 * |
| 19 | Saxony, W. Germany | Hornblende granulite | * | KFPQI | Fib.; fine | Intergrown mainly with B | 163 * |
| 20 | Adirondack Mts. N. Y. | Granulite facies | * | BQP(K?) | Tab.; large | Mainly in Q-P masses | AD8, R. D. Schulling V.M.L. |
| 21 | S. Rogaland near Moi, Norway | Pyroxene granulite | Beyond orthopyroxene isograd | KQPGI | Tab.; large | No specific relationships | R. Poorter |
| 22 | Khasia, India | Unknown | Unknown | QKR | Tab.; large | Radiation and Interlocking aggregates | 70-Sil-2, VML collection (from Wards) |

TABLE 1.—(Continued)

| Number | Location | General geology | T-P (approx) interpretation | Assemblage | Form and size of crystals | Petrographic association of Si | Collector & collection number of source |
|--------|------------------------------------|---|---|--------------------------|-----------------------------------|---|---|
| 23 | Haldummula, Uva Prov., Ceylon | Unknown | <i>Granulite facies</i> —corundum bearing | CBP | Tab., large | 85% Si; in sub-parallel sheaths | R.G.M. |
| 24 | Finkenbergl, Eifel Mts. W. Germany | 6 cm long equant inclusion in olivine—pyroxene lava | <i>Volcanic Inclusions</i> —quartz bearing ~1150°C? ~0.5 kbar | Sp Gl QP | Tab., medium | Equant Q-S bodies in Sp-Gl matrix | H. M. E. Schürmann |
| 25 | " | 10 cm-long equant inclusion in olivine-pyroxene lava | " | I Q Mg (+altered glass) | Fib. and gran.; fine and large | 2 types of Si crystals | 59-1908, MGIU |
| 26 | Cerro del Hoyazo, S.E. Spain | Large inclusion in BCP dacite lava | ~1000°C? ~0.5 kbar? | BCGQ "G-B-Si gneiss" | " | Clots of Si commonly n & around B | Z 73 Ho, " |
| 27 | " | " | " | BCGQ "Q-Co rock" | " | " | Z 46 Ho * |
| 28 | Cerro del Hoyazo, S.E. Spain | "clot" of fib. & 1 large crystal in BCP dacite lava | <i>Volcanic Inclusions</i> —neither quartz nor corundum bearing ~1000°C? ~0.5 kbar? | Only Si in clot | Fib.; fine | As under general geology | Z 208 A, H. P. Zeck, U. of A. |
| 29 | " | Large inclusion in BCP dacite lava | " | ABCQPSp "Sp-Co hornfels" | " | A partly altered to Si; Si also around relict A crystal | Zo 9, " |
| 30 | Finkenbergl, Eifel Mts. W. Germany | 6 cm long elliptical inclusion in olivine-pyroxene lava | <i>Volcanic Inclusions</i> —corundum bearing | PCMg (+altered glass) | Fib.; large crystals to 2 cm long | Fibrolite in form but much larger size crystals | Fink 412, H. M. E. Schürmann |

TABLE 1.—(Continued)

| Number | Location | General geology | T-P (approx) interpretation | Assemblage | Form and Size of crystals | Petrographic association of Si | Collector & collection number of source |
|--------|----------|---|-----------------------------|------------|---------------------------|--------------------------------|---|
| 31 | * | 5 cm long elliptical inclusion in olivine-pyroxene lava | * | * | * | * | Fbg 57, * |
| 32 | * | 3 cm long elliptical inclusion in olivine-pyroxene lava | * | * | * | * | 71-1908, MGIU |

Explanation

* Probably granulite facies but possibly high grade contact metamorphism.

Minerals.

Gl = glass
Mg = magnetite
P = plagioclase
I = ilmenite
() = metastable—partly altered to another mineral or only enclosed ("armoured") in a particular mineral

Grain shapes—of sillimanite

fib. = fibrolite—maximum to minimum length ratio > 10:1
tab. = tabular—maximum to minimum length ratio 3:1 to 10:1
gran. = granular—maximum to minimum length ratio < 3:1

Grain size

fine = < 30 μ wide
medium = 30 μ to 500 μ (0.5 mm) wide
large = > 500 μ wide

AML = Vening Meinesz Laboratory, Utrecht, Neth.
MGIU = Mineralogisch-Geologisch Instituut, Utrecht
RGM = Rijksmuseum van Geologie en Mineralogie, Leiden, Neth.
U of A = Universiteit van Amsterdam, Amsterdam, Neth.
Dr. H. M. E. Schürmann = Ph.D. thesis materials (1914), 149 Waalsdorperweg, The Hague, Neth.

Si = sillimanite
Q = quartz
S = staurolite
C = cordierite

A = andalusite
M = muscovite
Co = cordierite
Ky = kyanite

TABLE 2.—(Continued)

| | Volcanic Inclusions - quartz bearing | | | Volcanic Inclusions - neither quartz nor corundum bearing | | |
|--|---|-----------------|-----------------|---|-----------------|-----------|
| | 24 | 25 ⁺ | 26 ^x | 27 ^x | 28 ^x | 29 |
| Al ₂ O ₃ | 63.50 | 62.78 | 62.14 | 61.59 | 61.20 | 61.49 |
| SiO ₂ | 37.15 | 37.43 | 38.70 | 37.01 | 38.50 | 36.79 |
| TiO ₂ | 0.00 | 0.00 | 0.49 | 0.03 | 0.27 | 0.01 |
| Fe ₂ O ₃ | 0.10 | 0.19 | 0.17 | 0.23 | 0.72 | 0.09 |
| total | 100.75 | 100.40 | 101.50 | 98.86 | 100.69 | 98.38 |
| Al ₂ O ₃ :SiO ₂ | 50.2:49.8 | 49.7:50.3 | 48.6:51.4 | 49.5:51.5 | 48.4:51.6 | 49.6:50.4 |
| molecular ratio | +0.3 | +0.2 | +0.6 | +0.5 | +0.6 | +0.5 |
| | Volcanic Inclusions - corundum bearing | | | | | |
| | 30 | 31 | 32 | Average of Almandine Amphibole samples (14) | | |
| Al ₂ O ₃ | 63.31 | 62.69 | 61.91 | --- | --- | --- |
| SiO ₂ | 36.52 | 37.37 | 35.66 | --- | --- | --- |
| TiO ₂ | 0.00 | 0.00 | 0.00 | --- | --- | --- |
| Fe ₂ O ₃ | 0.10 | 0.05 | 0.60 | --- | --- | --- |
| total | 99.97 | 100.11 | 98.17 | --- | --- | --- |
| Al ₂ O ₃ :SiO ₂ | 50.5:49.5 | 49.7:50.3 | 50.6:49.4 | --- | --- | --- |
| molecular ratio | +0.3 | +0.3 | +0.2 | --- | --- | --- |
| | Average of Almandine Amphibole samples (14) | | | | | |
| | = 49.9:50.1 | | | | | |
| | Granulite samples (9) | | | | | |
| | = 50.1:49.9 | | | | | |
| | Volcanic inclusion samples (9) | | | | | |
| | = 49.6:50.4 | | | | | |
| | Corundum bearing samples (4) | | | | | |
| | = 50.3:49.7 | | | | | |
| | Quartz bearing samples (22) | | | | | |
| | = 50.0:50.0 | | | | | |
| | Quartz and Corundum free samples (2) | | | | | |
| | = 49.0:51.0 | | | | | |

^x measurement of fibrolite mass and not individual crystals

+ both fibrolite and granular sillimanite gave essentially identical values

The proportions were calculated to 100% and do not include TiO₂ or Fe₂O₃. The uncertainty stated is the maximum positive or negative deviation of the raw probe data, either the SiO₂ or the Al₂O₃ analysis; taking whichever is the largest. Averages of analyses of sillimanites are given for various metamorphic conditions as well as corundum-bearing (Al₂O₃-buffered), quartz-bearing (SiO₂-buffered) and corundum- and quartz-free assemblages. Some of the deviation from 100% total (weight percent) is probably due to the orientation of the sample and is not described by the uncertainties stated.

stability, but, as mentioned in the introduction, such minor amounts have not been found to be a major factor.

As can be seen in table 2, the samples from the three different environments—almandine amphibolite facies, granulite facies, and from inclusions in lava show no important variations. The samples from corundum-bearing, quartz-bearing, and quartz- and corundum-free assemblages are also fairly similar, although the latter have a higher SiO_2 content. The reason for this is unknown, and the average is only of two analyses, both of which are themselves highly uncertain. The corundum-bearing samples have an average $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio that is highest but well within the uncertainties of measurement, and no conclusion can be drawn.

DISCUSSION

Some of the sillimanites from inclusions in volcanic lavas (Finkenberg) must have been subjected to temperatures near or greater than those of Aramaki's (1961) sillimanite; and, like Aramaki's sillimanite, have corundum as a buffering Al_2O_3 phase, but show no significant excess of Al_2O_3 over the ideal composition. The olivine-bearing basalts at Finkenberg probably were quenched at temperatures near 1150°C and a few bars pressure and, if Aramaki's sillimanite is a metastable phase, these should theoretically also have persisted. A pre-existing mullite *may* have reacted as follows,



but this seems unlikely in the Finkenberg samples in view of the coarse grain (averaging 2 cm long and 1 mm wide) that can hardly be attributed to quench conditions. No reason is known for the differing conclusions of Aramaki (1961) and the present study, but it appears that possible mullite-sillimanite solid solutions at values greater than the 3 weight percent (the maximum error of measurement) in nearly all geological materials need not worry the petrologist.

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REFERENCES

- AGRELL, S. O., AND J. V. SMITH (1960) Cell dimensions, solid solution, polymorphism and identification of mullite and sillimanite. *Amer. Ceram. Soc. J.*, **43**, 69-76.
 ALBEE, A. L., AND A. A. CHODOS (1969) Minor element content of coexisting Al_2SiO_5 polymorphs. *Amer. J. Sci.* **267**, 310-316.

- ARAMAKI, S. (1961), Sillimanite and cordierite from volcanic xenoliths. *Amer. Mineral.* **46**, 1154-1165.
- , AND R. ROY (1963) A new polymorph of Al_2SiO_5 and further studies in the system Al_2O_3 - SiO_2 - H_2O . *Amer. Mineral.* **48**, 1322-1347.
- BEGER, R. M., BURNHAM, C. W., AND HAYS J. F. (1970) Structural changes in sillimanite at high temperature (abstr.) *Geol. Soc. Amer. Meet., Milwaukee, Wisconsin.* 490-491.
- CHINNER, G. A. (1961) The origin of sillimanite in Glen Cova, Angus. *J. Petrology* **2**, 312-323.
- , C. R. KNOWLES, AND J. V. SMITH (1966) Iron content of aluminum silicate polymorphs (abstr.) *Int. Mineral. Assoc. Meet., Cambridge.*
- KWAK, T. A. P. (1968) *Metamorphic Petrology and Geochemistry Across the Grenville Province, Southern Province Boundary, Dill Twp., Sudbury, Ontario.* Ph.D. thesis, McMaster University.
- MOORE, J. M., AND M. G. BEST (1969), Sillimanite from two contact aureoles. *Amer. Mineral.* **54**, 975-979.
- PITCHER, W. S. (1965) The aluminum silicate polymorphs. In W. S. Pitcher and G. W. Flinn, eds. *Controls of Metamorphism.* Oliver Boyd, Edinburgh, 119-139.
- SCHULLING, R. D., AND M. G. OOSTEROM (1967) The metamorphic complex on Naxos (Greece) and the strontium and barium content of its carbonate rocks. *Proc. Kon. Ned. Akad. Wetensch.* **B 70**, 165-175.
- SPRINGER, G. (1967) Die Berechnung für die quantitative Elektronenstrahl-Mikroanalyse. *Fortschr. Mineral.* **45**, 103-124.
- STRENS, R. G. J. (1968) Stability of Al_2SiO_5 solid solutions. *Mineral Mag.* **36**, 839-849.
- WONES, D. R., AND H. P. EUGSTER (1965) Stability of biotite: experiment, theory and application. *Amer. Mineral.* **50**, 1228-1272.
- ZECK, H. P. (1968) *Anatectic Origin and Further Petrogenesis of Almandine Bearing Biotite-Cordierite-Labradorite-Dacite and Many Inclusions of Reshite and Basaloid Material; Cerro del Hoyazo, S. E. Spain.* Ph.D. thesis, Univ. of Amsterdam, 1-161.
- ZEN, E-AN. (1969) The stability relations of the polymorphs of aluminum silicate: a survey and some comments. *Amer. J. Sci.* **267**, 297-309.

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