

COMPOSITIONS OF NATURAL SILLIMANITES
FROM VOLCANIC INCLUSIONS
AND METAMORPHIC ROCKS

TEUNIS A. P. KWAK, *Vening Meinesz Laboratorium,
Rijksuniversiteit te Utrecht, Utrecht, The Netherlands*

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-170-1A

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	*	*	*	MGPBKyQRMz (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	*	*	QBPKG	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	*	KPBQI	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. Poortier
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
<i>Granulite facies—corundum bearing</i>							
23	Haldummula, Uva Prov., Ceylon	Unknown	"	CBP	Tab., large	85% Si; in sub-parallel sheaths	R.G.M.
<i>Volcanic Inclusions—quartz bearing</i>							
24	Finkenbergl, Eifel Mts. W. Germany	6 cm long equant inclusion in olivine—pyroxene lava	~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	"	FQ 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 "
<i>Volcanic Inclusions—neither quartz nor corundum bearing</i>							
28	Cerro del Hoyazo, S.E. Spain	"clot" of fib. & 1 large crystal in BCP dacite lava	~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	"	ABCGPSp("Sp-Co hornfels")	"	A partly altered to Si; Si also around relict A crystal	Zo 9, "
<i>Volcanic Inclusions—corundum bearing</i>							
30	Finkenbergl, Eifel Mts. W. Germany	6 cm long elliptical inclusion in olivine-pyroxene lava	"	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

Sp = spinel
B = biotite
K = K-feldspar
R = rutile

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

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

() = 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

VML = Vening Meinesz Laboratory, Utrecht, Neth.

MGIU = Mineralogisch-Geologisch Instituut, Utrecht

RGM = Rijksmuseum van Geologie and 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.

TABLE 2. CHEMICAL ANALYSIS OF SILLIMANTITE SAMPLES IN WEIGHT PERCENT AND MOLECULAR PROPORTIONS OF $Al_2O_3:SiO_2$

	Almandine amphibolite facies samples - quartz bearing													
	1	2	3	4	5	6	7	8	9	10				
Al_2O_3	62.78	62.72	62.37	61.17	61.91	64.37	62.28	63.95	63.48	61.72				
SiO_2	37.28	36.57	37.53	36.93	35.88	36.88	37.54	37.95	35.77	36.28				
TiO_2	0.34	0.01	0.00	0.01	0.01	0.01	0.81	0.01	0.01	0.01				
Fe_2O_3	0.35	0.01	0.75	0.21	0.34	0.10	0.15	0.09	0.40	0.17				
total	100.75	99.31	100.65	98.32	98.14	101.36	100.78	102.00	99.56	98.18				
$Al_2O_3:SiO_2$	69.9:50.1	50.3:49.7	49.5:50.5	49.4:50.6	50.4:49.6	50.7:49.3	49.4:50.6	49.8:50.2	51.1:48.9	50.1:49.9				
molecular ratio	± .3	± .1	± 0.1	± 0.2	± 0.2	± 0.3	± 0.2	± 0.3	± 0.6	± 0.2				
	11	12	13	14										
Al_2O_3	62.01	59.86	63.75	62.44										
SiO_2	36.56	38.03	36.75	37.36										
TiO_2	0.01	0.01	0.01	0.07										
Fe_2O_3	0.03	0.13	0.06	0.16										
total	98.61	97.3	100.57	100.03										
$Al_2O_3:SiO_2$	50.2:49.8	48.1:51.9	50.6:49.4	49.6:50.4										
molecular ratio	± 0.3	± 0.6	± 0.2	± 0.1										
					Granulite facies - quartz bearing									
					15				16 17 18					
Al_2O_3					64.05				61.64 62.92 61.87					
SiO_2					36.99				36.86 36.57 36.74					
TiO_2					0.00				0.00 0.17 0.00					
Fe_2O_3					0.00				0.12 0.00 0.29					
total					101.04				98.72 99.66 98.91					
$Al_2O_3:SiO_2$					50.5:49.5				49.6:50.4 50.3:49.7 49.8:50.2					
molecular ratio					± 0.4				± 0.2 ± 0.2 ± 0.1					
									Granulite facies - corundum bearing					
					23									
Al_2O_3					62.14									
SiO_2					36.10									
TiO_2					0.00									
Fe_2O_3					0.17									
total					98.41									
$Al_2O_3:SiO_2$					50.4:49.6									
molecular ratio					± 0.1				± 0.2 ± 0.3					

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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