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SILLIMANITE AND CORDIERITE FROM VOLCANIC XENOLITHS

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ABSTRACT

Basement sedimentary rocks containing various minerals formed during pyrometamorphism have been ejected from the Asama Volcano. The physical properties of sillimanite and cordierite reflect the unusual conditions of their formation at higher temperatures and lower pressures.

INTRODUCTION

Asama Volcano is a composite stratovolcano with an active crater at the top. It is situated about 140 km. northwest of Tokyo, Japan, and is about 2500 m. above sea level. The volcano has been active throughout historic time, the largest known eruption being that in 1783. After this eruption, violent "Vulcanian" eruptions have occurred repeatedly from the top crater. Among the ejected blocks of such eruptions there are many kinds of sedimentary rocks which constitute the basement of the volcano. These sedimentary rocks contain sillimanite, andalusite, corundum, cordierite, osumilite, hypersthene, diopside, wollastonite, feldspars, iron oxides, etc., which were formed during the pyrometamorphism by the magma. Sillimanite and cordierite crystals were separated from the host rock and their chemical composition and physical properties were determined. The physical properties of both the sillimanite and cordierite were found to reflect the unusual conditons of their formation, *i.e.* the higher temperatures and lower pressures.

P-t conditons of pyrometamorphism

The andesite occurring as bombs of the recent eruptions and representing the host rock of the sedimentary xenoliths contains phenocrysts of augite, hypersthene, plagioclase, magnetite, and small amounts of olivine and is calc-alkali andesite in composition (Aramaki, 1956, 1957). T. Minakami of the Earthquake Research Institute measured the temperature of the lava pool at the bottom of the open crater-pit directly by a thermocouple and obtained a value of about 1000° C. (Minakami, personal communication). Hydrothermal experiments (Aramaki and Roy, in press)* showed that the glass formed by the partial fusion of the

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* Hydrothermal experiments on this glass were made as a part of the study on the system Al_2O_3—SiO_2—H_2O at the Department of Geochemistry, Pennsylvania State University. The glass was separated by a heavy liquid. The concentrate contained some cordierite and sillimanite crystals embedded in the glass. In the presence of excess water,

sediments becomes fluid at a temperature range between 945 and 1005° C. and water pressure of about 200 bars. The metamorphosed sediments appear to have been derived from shale, calcareous rocks, tuff, and other volcanic rocks. Such rocks occur among the Miocene to Pliocene formations which are exposed around the volcano and supposedly continue beneath it at a depth of about 1 to 3 km. from the crater. From these observations it is inferred that the metamorphism took place at a temperature between 945 and 1005° C. and under a solid pressure of 200–800 bars.

Sillimanite

The sillimanite occurs as needles up to 0.1×0.02 mm. in a transparent, colorless glass ($n=1.487$) which was formed by partial melting of clastic(?) sediment rich in Al_2O_3 and SiO_2. The glass occupies up to half the volume of the original rock and the remaining crystalline part contains cordierite, detrital quartz, magnetite, andalusite and corundum in a general order of decreasing amount.

Practically all the needles of sillimanite are confined in the glass and therefore crystallized directly from the liquid during the pyrometamorphism.

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the following results were obtained.

Run	Temperature	Pressure	Length of run	Result
A	680° C.	300 bars	773 hours	No crystallization. Glass did not become fluid.
B	945	200	280	No crystallization. Glass did not become fluid.
C	1005	200	2	No crystallization. Glass became fluid.
D	1070	300	50	No crystallization (?). Glass became fluid.

That the glass became fluid after heating was detected by observing that the original angular glass fragments were completely changed to a compact mass of glass cast into the shape of the platinum container. This happened in runs C and D whereas in runs A and B the powder remained incoherent and the shape of the original angular grains of glass remained unchanged.

The refractive index of the glass ($n=1.487\pm0.002$, including the heterogeneity of the glass) remained practically unchanged after the heating. In no case could any new product of crystallization of the glass during the treatment be detected except for possible formation of sillimanite or mullite as fine fibres with mottled extinction in run D.

Andalusite occurs with sillimanite in most of the rock specimens examined. In the specimen No. AS2X10 from which the sillimanite was separated, idiomorphic andalusite crystals (up to 1×0.2 mm.) are found under the microscope. They occur sporadically in the portion where the glass formed by pyrometamorphism is apparently absent. In another specimen small andalusite prisms (up to 0.5×0.1 mm.) occur more abundantly in the glass. In this case the crystals are honeycombed, suggesting resorption. Parallel growth or a replacement relation between andalusite and sillimanite is never observed.

The rock powder was treated with cold HF for a week to ensure the decomposition of minerals other than sillimanite. The residue was washed with a concentrated mixture of $1HCl \cdot 3HNO_3$, then with a dilute mixture of the same. Sillimanite was then concentrated by Clerici solution and the proportion of the three minerals was carefully measured with an integration table (Table 1).

TABLE 1. CHEMICAL COMPOSITION OF SILLIMANITE FROM ASAMA VOLCANO: SAMPLE No. AS2X10
Chemical analysis by H. Haramura

	No. 1	No. 2
SiO_2	32.72	31.6
Al_2O_3	64.69	65.6
TiO_2	0.12	—
Fe_2O_3	0.86	—
FeO	0.71	—
MnO	0.02	—
MgO	0.00	—
CaO	0.00	—
$H_2O(+)$	0.18	—
$H_2O(-)$	0.05	—
Total	99.81	
Amount of sample analyzed	1.2g	0.13g
Mineral composition of sample analyzed (wt%)		
sillimanite	93.7	92.6
andalusite	2.6	3.1
corundum	3.7	3.8
unidentified impurity	0.0	0.5
	100.0	100.0
Molecular ratio of SiO_2 and Al_2O_3 in sillimanite (corrected for andalusite and corundum)		
SiO_2	47.6	46.4
Al_2O_3	52.4	53.6

The chemical composition of the mixture of the three minerals is given in Table 1 (No. 1). When corrected for the andalusite and corundum, the $Al_2O_3:SiO_2$ ratio is 52.4:47.6. This is appreciably higher than the ideal ratio 1:1 for sillimanite. TiO_2, Fe_2O_3, and FeO may be considered to substitute for Al^{3+} in the octahedral position in the sillimanite structure rather than Si^{4+} in the tetrahedral position. Therefore, even if all three oxides reported in the analysis are taken into account as essential constituents in the sillimanite structure, they will not decrease the ratio $R_{\text{octahedral}}:R_{\text{tetrahedral}}$ as represented by the ratio $Al_2O_3:SiO_2$ but will increase it.

In order to check the above result, another batch of sillimanite concentrate was prepared. Partial analysis (No. 2, Table 1) again indicates the excess of alumina over silica. According to H. Haramura who undertook the analysis, the error in the analysis is probably less than $\pm 0.5\%$ by weight. Therefore the amount of excess alumina over silica is far greater than the analytical error.

There are still other possibilities for getting an incorrect $Al_2O_3:SiO_2$ ratio. They are: 1) incorrect estimation of the amount of the corundum, 2) possible persistence of amorphous alumina as decomposition product in the residue of the HF-treated sample and 3) differential leaching of SiO_2 from the sillimanite during the treatment.

The first possibility is rather unlikely, for in order to reduce the ratio to 50:50 it would be necessary to have about 12% corundum by weight in the batch instead of about 4% as actually measured. A glance under the microscope reveals that even the total amount of the impurities is far less than 10%. For the same reason it is difficult to conceive that there was present about 10% amorphous alumina in the concentrate. The possibility of leaching SiO_2 from the sillimanite during a week's treatment might be admitted, for the action of HF on sillimanite is not well known. However, the following evidences appear to be against the leaching hypothesis: 1) under the microscope, the sillimanite shows no abnormal appearance indicative of leaching or decomposition—the sillimanite prisms are clear throughout without any marring of their sharp outlines, 2) the refractive indices show no appreciable variation in different fractions, and 3) the *x*-ray powder pattern shows sharp peaks giving well-defined spacings.

From these considerations, it was concluded that the sillimanite has a composition intermediate between ideal sillimanite and ideal mullite.

It has been almost established (Agrell and Smith, 1960, Aramaki and Roy, in press) that a continuous solid solution exists between mullites of compositions $3Al_2O_3 \cdot 2SiO_2$ and $2Al_2O_3 \cdot SiO_2$. As is shown by Agrell and Smith (1960) for the mullite solid solution, it is possible for the sillimanite structure to substitute Al for an equal amount of Si with a corresponding falling off of oxygen from the structure (one oxygen per two Si-Al replacements). As the structure of mullite is essentially the same as that of sillimanite—Al-O octahedral chains cross-linked by tetrahedral Si and Al—there is good reason to believe there exists a continuous solid solution between sillimanite and $3Al_2O_3 \cdot 2SiO_2$ mullite.

Almost all the reliable analyses of sillimanites in the literature show the ratio $Al_2O_3:SiO_2$ as close to 1:1, but these are from rocks formed by low temperature metamorphism. The Asama sillimanite may owe its abnormal composition to the unusually high temperature and low pressure of its formation.

Kennedy (1960) reported the synthesis of a part of the solid solution between sillimanite and mullite by breaking down kaolinite at high temperature and pressure, although he did not state how these phases were identified.

Accurate measurement of the unit cell dimensions of the sillimanite was carried out by means of the North American Philips Geiger-counter diffractometer (Table 2), using silicon as the internal standard. The method of measurement is described by Aramaki and Roy (in press). According to Agrell and Smith, mullites and sillimanites fall into two separate groups in the plottings *a–c*, *b–c*, and volume-*c* of the unit cell (Agrell and Smith, 1960), thus making the identification quite unequivocal. The unit cell volume-*c* plotting is reproduced schematically in Fig. 1. They also found that four specimens of natural sillimanites have very similar unit cell dimensions, the total range being $a = 7.4876–7.4839$ Å, $b = 7.6758–7.6718$ Å, $c = 5.7728–5.7692$ Å, and volume $= 331.24–331.62$ Å^3.

A fibrolite from an eastern Pennsylvania metamorphic rock and a xenocrystic sillimanite in granite porphyry from Japan also fall close to this range (see Fig. 1 and the analysis and *x*-ray data by Aramaki and Roy, in press). In the plottings *a–c* and *b–c*, the Asama sillimanite falls on the points reasonable for the sillimanite group and not for mullite, although the *b*-spacing of the Asama mineral is closer to mullite than to sillimanite. In the plotting unit cell volume-*c* (Fig. 1), the Asama sillimanite falls on a point rather apart from either the field of six sillimanites mentioned above or that of mullite without Fe^{3+} and Ti.

According to Agrell and Smith, the entrance of Fe^{3+} and Ti into the structure of mullite increases the *c*-edge considerably while the change in *a*- and *b*-edges is less conspicuous. They showed that while pure mullite irrespective of $Al_2O_3:SiO_2$ ratios has a *c*-edge of about 2.885 Å, TiO_2(0.55wt%) and Fe_2O_3(5.93wt%) increase the *c*-edge of a natural mullite to 2.8952 Å. The presence of Ti and Fe in the Asama sillimanite may reasonably explain the difference in *c*-spacings between the Asama

TABLE 2. X-RAY POWDER DATA OF SILLIMANITE FROM ASAMA VOLCANO: SAMPLE NO. AS2X10
CuK$_{\alpha}$ Radiation

I	*hkl*	$2\theta_{\mathrm{obs}}$	$2\theta_{\mathrm{calc}}$
(3	andalusite	15.97)	
32	110	16.51	16.52
(2	andalusite	19.45)	
9	200	23.71	23.73
(3	andalusite corundum	25.63)	
100	120	26.04	26.06
96	210	26.43	26.44
5	002	30.96	30.95
(2	andalusite	32.20)	
43	220	33.39	33.38
17	112	35.25	35.26
13	130	37.07	37.07
3	202	39.38	39.35
22	122	40.88	40.87
19	230	42.72	42.72
(4	corundum	43.2)	
5	400	48.53	48.52
2	312	49.67	49.63
3	330	51.00	51.02
(2	corundum	52.51)	
7	240	53.54	53.57
8	420	54.39	54.41
9	042	57.57	57.59
2	402	58.64	58.66
13	332	60.86	60.87
2	422	63.92	63.92
2	004	64.47	64.47
3	250	65.60	65.61
2	014	65.78	65.75
3	520	66.95	66.92
3	440	70.11	70.09
5	152	70.49	70.49
4	252	74.31	74.29
3	224	74.55	74.57
3	522	75.56	75.54
2	600	76.12	76.09
1	161	77.33	77.32

$a=7.498\pm0.003$ Å
$b=7.690\pm0.003$
$c=5.797\pm0.003$

TABLE 3. OPTICAL PROPERTIES OF SILLIMANITE AND CORDIERITE FROM ASAMA VOLCANO

Sillimanite (AS2X10)	Cordierite (AS297)
$\alpha=1.659\pm0.003$	$\alpha=1.537\pm0.002$
$\beta=1.664\pm0.003$	$\beta=1.542\pm0.002$
$\gamma=1.681\pm0.001$	$\gamma=1.546\pm0.002$
$\gamma-\alpha=0.022$	$\gamma-\alpha=0.009$
	2V(+)=83, 82, 82, 80°

and other sillimanites, the latter supposedly very low in Ti and Fe contents, while the abnormal increase in unit cell volume may be ascribed to the increase in $Al_2O_3:SiO_2$ ratio.

The refractive indices of the Asama sillimanite (Table 3), after having been corrected for the amount of Fe^{3+} and Ti according to the curves given by Bowen, Greig, and Zies (1924), fall very close to a point representing an imaginary sillimanite free from impurities.

Only a preliminary discussion will be given in the following on the for-

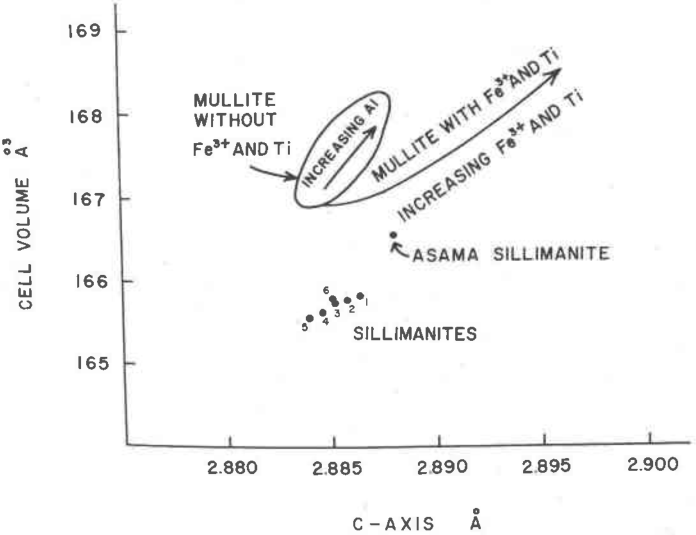

FIG. 1. Variation of cell volume with the cell edge *c* for mullite and sillimanite (after Agrell and Smith, 1960; Aramaki and Roy, in press). Sillimanites are: Nos. 1, 2, 3, and 4 from Agrell and Smith, No. 5 fibrolite from eastern Pennsylvania, No. 6 xenocrystic sillimanite in granite porphyry, central Japan. Oval area represents the mullite solid solution of the composition from $3Al_2O_3\cdot2SiO_2$ to $2Al_2O_3\cdot SiO_2$.

mation and stability relations of sillimanites, leaving the full arguments to the paper by Aramaki and Roy on the Al_2O_3-SiO_2-H_2O system.

The Asama sillimanite may be considered as a variety stable at high-temperatures, *i.e.* at 1000° C., and low pressures. If this holds true and the well-known occurrence of mullites in the Hebridian province (Agrell and Langley, 1958; Agrell and Smith, 1960) also represents stable conditions, the sillimanite$\rightleftharpoons$mullite+silica mineral boundary goes beyond a temperature a little above 1000° C., probably not far above 1200° C., at a relatively low pressure. It follows then that the boundary curve sillimanite$\rightleftharpoons$mullite+silica mineral given tentatively by Clark, Robertson, and Birch (Fig. 3, p. 638, 1957) should be shifted towards the high-temperature side and cross the temperature axis at 1000° C. or a little higher. The fact that andalusite occurs with the sillimanite in Asama might indicate that the sillimanite$\rightleftharpoons$andalusite boundary curve is steeper with respect to pressure in the phase diagram than that given by Clark, *et al.*, and crosses the temperature axis at a higher temperature. The known occurrences of volcanic sillimanite and mullite appear to be consistent with the postulated temperatures for the sillimanite$\rightleftharpoons$mullite+silica mineral boundary. The mullites which have been distinguished from sillimanites with certainty are all products of pyrometamorphism found in basalt and dolerite including picritic varieties, whereas sillimanites are found in andesite and trachyte.

It is possible, however, that the Asama sillimanite has been crystallized metastably from the liquid produced by the partial fusion of the xenoliths. The fact that sillimanite is easily synthesized by a simple squeezer in the *p-t* range well within the supposed stability field of kyanite (Kennedy, 1959, and Aramaki and Roy, in press) might indicate its ready formation in a metastable state.

Cordierite

The high-temperature polymorph of cordierite was first proposed by Miyashiro, Iiyama, Yamasaki, and Miyashiro (1955). The basis of distinction between high- and low-temperature forms of cordierite was the difference in refractive indices for the same $Fe^{2+}+Mn/Mg+Fe^{2+}+Mn$ ratio, the high-temperature form having lower refractive indices than the low-temperature form. Later Miyashiro (1957) found all gradations of structural ordering from hexagonal indialite through "subdistortional cordierite" to "perdistortional cordierite." Systematic measurements of optical properties and unit cell dimensions were made on the cordierite and indialite series by Iiyama (1956). Cordierite from Asama was identified as a typical high-temperature (and perdistortional) cordierite in all of the papers mentioned above where its various properties, except its chemical composition, were already described.

An ejected block of silicic tuff(?) of the basement rock now pyrometamorphosed into a compact porcelain-like mass (which has been called by previous Japanese petrologists "ceramicite"; Koto, 1916) contains quartz, cordierite, and sillimanite, in order of decreasing amounts, with very small amounts of acid plagioclase, K-feldspar and glass. As is described in detail by Hussak (1883) the cordierite crystals occur in aggregates a few millimeters across which can be seen as purple spots in a hand specimen.

About 30 kg. of the rock were crushed, the cordierite was separated by heavy liquid and magnetic separators, and about 1.2 grams of comparatively pure material were finally obtained. The impurity is estimated as less than 0.2% by volume. Its chemical composition is given in Table 4. The structural formula is fairly well satisfied for cations with remarkably low contents of Na, K, and H_2O. A very high content of TiO_2 may also be noticed.

TABLE 4. CHEMICAL COMPOSITION OF CORDIERITE FROM ASAMA VOLCANO: SAMPLE NO. AS297

Chemical analysis by H. Haramura

SiO_2	47.67	O (excluding O in H_2O)	18.00	
Al_2O_3	31.12	Si	4.93	6.00
TiO_2	2.05	Al	1.07	
Fe_2O_3	1.18			
FeO	11.53	Al	2.72	4.97
MnO	0.41	Ti	0.16	
MgO	6.14	Fe^{3+}	0.09	
CaO	trace	Fe^{2+}	1.00	
Na_2O	0.12	Mn	0.04	
K_2O	0.03	Mg	0.95	
$H_2O(+)$	0.05	Na	0.01	
$H_2O(-)$	0.05	K	0.00	
Total	100.35			
		$H_2O(+)$	0.02	
		$H_2O(-)$	0.02	

$$\frac{Fe^{2+}+Mn}{Mg+Fe^{2+}+Mn} = 0.52$$

Iiyama (1958) has shown that the difference between the so-called high- and low-temperature cordierites is due to the difference in the H_2O content. According to his hydrothermal experiments a natural cordierite with refractive indices of the "low-temperature" variety was found to decrease its refractive indices when heated above a certain temperature. This change is reversible and the transition temperature is strongly pressure-dependent, varying from 600° C.* at very low water pressure to 800° C.* at 600 bars. Iiyama concludes that this change is due to the

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* Values corrected by the original author.

hydration-dehydration of cordierite and the so-called high-temperature polymorph has a lower content of H_2O than the so-called low-temperature polymorph.

It is of interest that the Asama cordierite contains a lower amount of H_2O than any of the analyzed natural cordierites reported by Miyashiro, Iiyama, Yamasaki, and Miyashiro (1955), Miyashiro (1957) and Iiyama (1956). The *p-t* conditions of the formation of the Asama cordierite fall within the stability field of the high-temperature form of Iiyama's diagram, and its low water content is therefore in accord with the general scheme.

However, it is noted that although the difference between the so-called high- and low-temperature polymorphs of cordierite exactly corresponds to the difference in H_2O content, such a pair of varieties of cordierite cannot be called a polymorphic pair because of the necessary difference in the chemical composition.

TABLE 5. *X*-RAY POWDER DATA OF CORDIERITE FROM ASAMA VOLCANO:
SAMPLE NO. AS297
CuK_α radiation

I	*hkl*	$2\theta_{obs}$	$2\theta_{calc}$*
77	200	10.34	10.30
76	110	10.43	10.42
11	310	17.95	17.95
11	002	19.02	19.05
73	112	21.76	21.76
100	312	26.31	26.27
73	022	26.44	26.42
53	511	29.18	29.14
50	421	29.27	29.27
37	131	29.49	29.49
27	422	33.75	33.77
9	620	36.34	36.33
7	040	36.77	36.77
21	004	38.66	38.63
9	?	39.35	
11	622	41.31	41.33
11	242	43.08	43.09
11	?	48.0	
5	350	49.20	49.23
9	334	50.74	50.72
11	10.00	53.25	53.26
24	624	54.05	54.07

$a = 17.18_6$ Å*
$b = 9.76_9$
$c = 9.31_5$

* Calculated by T. Iiyama (1956, Table 8).

X-ray powder diffraction data are given in Table 5 together with calculated 2θ values for another sample of cordierite from Asama given by Iiyama (1956, Table 8). Iiyama's calculated 2θ values fit very closely the observed 2θ of the analyzed cordierite and therefore the same unit cell dimensions may be assigned to Iiyama's and the chemically analysed cordierites. Coincidence in refractive indices of the two cordierites also suggests the close similarity in chemical composition.

The ratio $Fe^{2+}+Mn/Mg+Fe^{2+}+Mn$ of the Asama cordierite is 0.52 (Table 4). If this value is plotted in Iiyama's diagrams (Figs. 1, 2, and 5; 1956) it is apparent that the Asama cordierite has anomalous *a*-spacing and refractive indices compared to those of artificially heated and dehydrated cordierites of various ratios of $Fe^{2+}+Mn/Mg+Fe^{2+}+Mn$. This tendency has been already noted by Iiyama, though he had no exact value of the ratio $Fe^{2+}+Mn/Mg+Fe^{2+}+Mn$ at the time his paper was written. It appears possible, as Iiyama pointed out, that natural volcanic cordierites belong to a polymorph different from that to which artificially dehydrated cordierites would belong.

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