

A mineral phase intermediate in composition between sillimanite and mullite

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Abstract

A member of the sillimanite–mullite solid solution series with a chemical composition midway between that of sillimanite and 3 : 2 mullite occurs in a metamorphosed lithomarge from Rathlin Island, Northern Ireland. Its diffraction pattern displays weak but sharp *l*-odd maxima, characteristic of sillimanite.

Introduction

Crystallographically, there is no reason why solid solution should not be complete between sillimanite and mullite (Burnham, 1964). The most aluminous sillimanite reported so far, however, contains 48.6 mole percent SiO₂ and the most siliceous natural mullite 43.0 mole percent SiO₂ (Aramaki, 1961; Cameron and Ashworth, 1972). The writer considers that these have crystallized from a liquid formed by partial melting of pelitic material, probably within the temperature range 900–1100°C. Sillimanites occurring in accidental xenoliths or as xenocrysts in volcanic rocks have been found to be stoichiometric (Al,Fe)₂SiO₅ within experimental error (Kwak, 1971; Cameron, in preparation), in accordance with the large activation energy for mullitization (Wilson, 1969). A third mode of formation, dehydration of gibbsite–halloysite mixtures resulting from the lateritic weathering of basalts (Eyles, 1952) yielded mullite at Tievebulliagh (Agrell and Langley, 1958) but at Brockley, Rathlin Island, County Antrim, a more siliceous phase is found.

Occurrence

The aluminosilicate forms the major component in segregations about 5 mm in diameter in a contact-metamorphosed basaltic lithomarge, now a hercynite–magnetite–cordierite(Fe₇₃)–tridymite–‘mullite’ rock (specimens 70846, 70848¹). In thin section the pale yellow segregations look like devitrified glass, but after acid treatment² they may be seen under the electron microscope to consist of tiny prisms up to

0.2 × 0.2 × 1.0 μm. No contrast attributable to domain structure or exsolution was apparent.

Composition

Pure separated material was analyzed by XRF (method of Norrish and Hutton, 1969) using the most Fe-rich stoichiometric sillimanite the writer has found (specimen 94191 from the Benson Mine, New York), mullite from Rubh’ a Chroman, Mull, Scotland (specimen 76398), and a synthetic glass, FS45, as standards. ‘Accepted’ values for specimens 94191 and 76398 were obtained by EPMA (method of Sweatman and Long, 1969), as were analyses of specimen S18001a³ (Bailey *et al.*, 1924, p. 274) near the Al-rich limit for natural mullites, and the oft-quoted Brandywine Springs sillimanite (Bell and Nord, 1974). Reproducible results on finer-grained material could be obtained only when the acid-treated powder had been separated from insoluble impurities by heavy liquids and mounted in Araldite on a glass slide. Analyses were carried out only on inclusion-free single crystals, the estimated error being ± 1 percent (*cf.* Kwak, 1971).

Structural evidence

Cell dimensions were computed from average positions relative to a Si standard of the 11 strong powder lines between 56–77° 2θ using CuKα radiation. The effect of substituting Fe for Al is seen by comparing the first two results and those of specimens 70846 and 70848 (Table 1). Taking a set with roughly equivalent Fe + Ti contents: specimens 94191, 100622, 70846, 76398, and S18001a, it may be shown that *a* and *V*

¹ Catalog numbers in the Harker Collection, Cambridge.

² 20 percent HF followed by warming in 1 : 1 HCl.

³ Provided by the Institute of Geological Sciences, London.

TABLE 1. Chemical compositions and cell parameters of sillimanites, mullite, and the intermediate phases

	SILLIMANITE				MULLITE		
	Brandywine Springs	Benson 94191	Asama 100622	Rathlin 70846	Rathlin 70848	Mull 76398	Mull 818001a
Al ₂ O ₃	62.9	61.8	61.5	64.8	64.1	67.6	68.9
SiO ₂	36.7	36.8	35.6	32.9	32.8	30.6	29.5
Fe ₂ O ₃	0.16	1.6	2.6	2.0	2.8	0.6	0.5
TiO ₂	0.02	0.02	0.08	0.28	0.24	0.7	1.0
Total	99.8	100.2	99.8	100.0	99.9	99.5	99.9
Mol% SiO ₂	49.6 ± 0.5	49.6 ± 0.5	48.6 ± 0.5	45.4 ± 0.5	45.6 ± 0.5	43.0 ± 0.5	41.6 ± 0.5
a (Å)	7.4831 (4)*	7.4883 (4)	7.4963 (4)	7.5080 (6)	7.5088 (8)	7.5260 (3)	7.5384 (4)
b (Å)	7.6710 (4)	7.6783 (4)	7.6851 (4)	7.6881 (4)	7.6934 (6)	7.6882 (3)	7.6933 (4)
c (Å)	2.8850 (2) [†]	2.8872 (2) [†]	2.8882 (2)	2.8880 (2)	2.8893 (3)	2.8882 (2)	2.8884 (2)
V (Å) ³	165.61 (3)	166.01 (3)	166.39 (3)	166.70 (4)	166.91 (4)	167.11 (3)	167.52 (3)

* Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 7.4831(4) indicates an esd of 0.0004.
[†] half *c*_{true}. Use of the pseudo-repeat facilitates comparison with mullite.

increase smoothly with decreasing mole percent SiO₂. The *b* and *c* dimensions are rather more sensitive to variation in minor element contents.

Selected area electron diffraction patterns of the Rathlin phases show weak, sharp *l*-odd reflections consistent with the space group *Pbnm*, that of sillimanite. No diffuse reflections are present. As a somewhat subjective judgment, the ratio of the average intensity of the *l*-odd to *l*-even reflections appeared slightly less than that for stoichiometric sillimanite and the Asama sample, 100622.

The infrared spectrum of specimen 70848 was found to be very similar to that of the Asama sillimanite (trace B, Fig. 2, Cameron and Ashworth 1972), both in the positions and shapes of absorption maxima.

Discussion

The phase described is best termed an aluminous sillimanite, with the implication that the change to the mullite domain structure is at a greater Al/Si ratio. A simple hydrothermal reaction either of a highly specific gibbsite-halloysite bulk composition or over a narrowly defined temperature range, or both, could account for the rarity of intermediate phases. Alternatively, iron may provide the stabilizing effect, since no intermediate compositions in the binary system Al₂O₃-SiO₂ have yet been described, except perhaps those synthesized at high pressures by Hariya *et al.* (1969) where chemical compositions were inferred from cell dimensions. Synthetic Fe-mullites containing excess silica have been reported (Muan, 1957). The writer's repetition of his experiments, but followed by HF treatment of the products, yielded mullites (by E.M. and I.R.) with (Al + Fe): Si ratios close to 3:2. The absence of low Fe + Ti intermediate phases in sanidinite-facies rocks which have involved large-scale diffusion of Al and Si hints

at possible metastability relative to a sillimanite with a small amount of excess Al, e.g. specimen 100622, coexisting with a silica-rich mullite, e.g. 76398.

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