HYDROTHERMAL SYNTHESIS OF ANDALUSITE

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In a detailed investigation of the system Al_2O_3–SiO_2–H_2O, Roy and Osborn (1952) reported their failure to synthesize consistently and unequivocally the anhydrous aluminosilicates, sillimanite, andalusite and kyanite. Several earlier workers have reported the synthesis of sillimanite (Balconi 1941, Michel-Levy, 1949, Morey, 1942) but positive evidence that the product was sillimanite and not mullite has been lacking. Reports of the synthesis of andalusite (see Doelter, 1917, Baur, 1911, Lacy, 1952) are similarly open to question in view of the absence of evidence for positive identification of andalusite as a product of the reaction.

In the course of an investigation of equilibria in the system MgO–Al_2O_3–SiO_2–H_2O,* a phase with a powder *x*-ray diffraction pattern similar to andalusite was obtained. Although neglected at first as one of several "freak" occurrences, its repeated appearance made worthwhile further investigation. This phase has now been obtained consistently in many runs, using a variety of starting materials such as Langley kaolinite, Florida kaolinite, Macon (Georgia) kaolinite (*API* No. 3), 1:1 and 1:2 Al_2O_3:SiO_2 mixtures and gels, and mixtures in the system MgO–Al_2O_3–SiO_2–H_2O with the molar ratios 12:44:44 and 3:33:64 MgO:Al_2O_3:SiO_2. Representative runs are listed in Table 1. The techniques used for preparation of samples and hydrothermal reaction have been described in earlier papers from this Laboratory, Roy and Osborn (1952) Roy, Roy and Osborn (1950, 1952).

The identification of andalusite as a phase grown under hydrothermal conditions is based on the following criteria: (1) The crystals have the same mean refractive index as andalusite (1.635 ± 0.004) and low birefringence. Accurate determination of the three indices of refraction has not as yet been possible because of the small size of the crystals—maximum diameter about 20 microns. (2) The crystals grow on seeds of natural andalusite. The overgrowths form an interesting pattern, being always oriented at right angles to the seed. Thus seeds which are yellow under crossed-nicols with the gypsum plate are surrounded completely by a fringe of "blue" overgrowths. Thus the synthetic material when it does show any elongation (not pronounced) is length slow as compared to the length fast nature of natural andalusite in its usual habit. The *x*-ray

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TABLE 1. SUMMARY OF HYDROTHERMAL RUNS

Run No.	Starting Material Composition, Mol. %			Temp. (° C.)	Water Press. (psi)	Duration of run (hrs.)	Comments*	Phases Present*
	MgO	Al_2O_3	SiO_2					
5396		33	67	545	25,000	118		Hydralsite
5400		33	67	540	25,000	190	and. sds.	cor.+mull.+and.
5431		50	50	580	20,000	141	and. sds.	cor.+and.+1. mull.
5255	12	44	44	455	20,000	384		Hydral.+1. AS+1. and.
5213	12	44	44	530	20,000	432		and.+1.AS+1.cord. +1. cor.
5432	12	44	44	580	30,000	141	and. sds.	cord.+mull.+and.
5425	3	33	64	525	25,000	192	and. sds.	and.+Hydral.+cor. +1. qtz.
5433	3	33	64	580	20,000	141	and. sds.	mull.+1. cord.+and. +qtz.
5468	3	33	64	650	20,000	166	and. sds.	mull.+and.+1.cord.
218	Langley kaol.			450	10,000	192		Hydral.+pyroph. +and.
5435	Macon kaol.			505	20,000	141	and. sds.	pyroph.+Hydral. +and.+1. mull.
5436	Florida kaol.			505	20,000	141	and. sds.	pyroph+Hydral. +and.+mull.
5431	Langley kaol.			575	30,000	115		mull.+and.
5459	Langley kaol.			650	20,000	166	and. sds.	and.+mull.

* Abbreviations used: and.=andalusite, cor.=corundum, mull.=mullite, cord.=cordierite, qtz.=quartz, pyroph.=pyrophyllite, sds.=seeds, kaol.=kaoline, l=Little, AS=aluminum serpentine.

diffraction pattern is very similar to that of andalusite, particularly at low 2θ values (see Table 2). Since it has never been obtained as the only phase present, comparison at higher angles is somewhat difficult due to the overlapping of lines and the lack of distinct lines at higher angles. The 001 and 002 reflections are very pronounced and quite distinct from the spacings of any other phase appearing in this part of the system. Mullite, sillimanite, kyanite and all known alumina-silica hydrates are positively eliminated as alternatives by the *x*-ray diffraction pattern.

These recent data suggest that andalusite is a stable phase between 450° and 650° C. at water pressures between 10,000 and 30,000 psi. Roy and Osborn (1952) have decomposed andalusite in the presence of water up to about 425° C., the chief decomposition products being either kaolinite or pyrophyllite. The data also suggest the possible importance of the presence of slightly larger cations such as Mg^{++} or Ca^{++} in aiding

TABLE 2. X-RAY DATA ON SYNTHETIC ANDALUSITE; COMPARISON WITH MULLITE AND NATURAL ANDALSUITE

Natural Andalusite (USNM)		Synthetic Andalusite +Mullite			Mullite (Corhart electrically fused)	
d (A°)	I/I_0	d (A°)	I/I_0	Identification*	d(A°)	I/I_0
5.57	10	5.60	5	A		
		5.45	1.5	M	5.50	7
4.56	6	4.55	3	A		
3.94	3	3.99	2	A		
3.53	6	3.53	3	A		
		3.43	7	M	3.44	10
					2.89	1.5
2.78	10	2.79	10	A		
		2.71	2	M	2.71	5
		2.56	2	M	2.56	3
2.47	9					
					2.44	4
					2.30	1.5
2.28, 2.26	3					
		2.22	2	M	2.22	7
2.17	5					
		2.13	1	M	2.13	4

* A = andalusite, M = mullite.

the formation of andalusite. Pure gels or alumina-silica mixtures did not yield andalusite except as growth on seeds (or in the presence of seeds) whereas mixtures in the $MgO–Al_2O_3–SiO_2$ system did so readily. This fact may be connected with the five-fold coordination of one Al^{3+} ion in andalusite; Mg^{2+} entering such a structure would certainly strive for a higher coordination than four. The Macon (Georgia) kaolinite contains .47% MgO and .52% CaO, and the others probably also contain significant amounts of these cations which, although perhaps not essential, may aid greatly in the growing of crystals of andalusite.

REFERENCES

BAUER, E. (1912), Hydrothermal Silicates: *Zeit. Elektrochem.*, **17**, 739; and *Zeit. Anorg. Chem.* **72**, 119 (1911).

BALCONI, M. (1941), Synthesis of sillimanite: *Rend. Soc. Min. Ital.*, **1**, 77.

DOELTER, C. (1927), Handbuch der Mineralchemie. Steinkopf, Leipzig.

LACY, E. D. (1951), Minerals and magmas: Studies at high temperatures and pressures: *Nature*, **168**, 537.

MICHEL-LEVY, M (1950), Reproduction artificielle de la sillimanite: *Compt. Rend.*, **230**, 2213.

Morey, G. W. (1942), Solubility of solids in water vapor: *Proc. A.S.T.M.*, **42**, 986.

Roy, R., Roy, D. M., and Osborn, E. F. (1950), Stability and compositional relationships among the lithium aluminosilicates, eucryptite, spodumene and petalite: *J. Am. Ceram. Soc.*, **33**, 152.

Roy, D. M., Roy, R., and Osborn, E. F. (1953), The system MgO–Al_2O_3–H_2O: *Am. J. Sc.*, **251**, 337.

Roy, R., and Osborn, E. F. (1952), The system Al_2O_3–SiO_2–H_2O: *Am. Mineral.*, **37**, 300 (Abstract).

Roy, R., and Osborn, E. F. (1952), Some simple aids in the hydrothermal investigation of mineral systems: *Econ. Geol.* **47**, 717.

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COBALT IN KIMBERLITES

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Nickel has been reported as a constituent of Jagersfontein kimberlite in quantities from 0.08 to 0.14%, and as a component of nodules of eclogite, pyroxenite, phlogopite, and chrome diopside found in kimberlites, in amounts from a trace to 0.26% (4). We have not, however, been able to find a reference to cobalt in kimberlite or its associated minerals.

In the course of complete chemical analyses of the ten different types of kimberlite found in Premier Mine, Transvaal, South Africa, we have found cobalt ranging from 0.003 to 0.008%. Cobalt was determined by the accurate and convenient colorimetric procedure using nitroso-R-salt (5). The results for cobalt, together with those for iron and nickel, are given in Table 1.

Some investigators have seen an analogy between the forces of tem-

Table 1. Content of Cobalt, Iron, and Nickel in Premier Mine Kimberlites

Kimberlite Type	*Percentage*		
	Co	Fe	Ni
1	0.005	5.86	0.10
2	0.003	5.41	0.11
3	0.007	7.32	0.11
4	0.006	6.36	0.12
5	0.007	6.90	0.13
6	0.006	8.73	0.10
7	0.006	7.00	0.09
8	0.008	7.35	0.11
9	0.005	9.35	0.15
10	0.006	7.05	0.11