

## NOTES AND NEWS

A PRELIMINARY NOTE ON THE RELATIVE STABILITY OF  
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## INTRODUCTION

In recent years there has been considerable interest in the stability relations of the polymorphic modifications of  $\text{Al}_2\text{SiO}_5$  and their high-temperature breakdown products, mullite+silica. Clark, Robertson, and Birch (1957) synthesized sillimanite from kyanite at  $1,340 \pm 30^\circ \text{C}$ . and  $18,600 \pm 100$  bars in  $7\frac{3}{4}$  hours. They converted sillimanite to kyanite in  $2\frac{3}{4}$  hours at  $1,220 \pm 50^\circ \text{C}$ . and  $23,000 \pm 200$  bars. From syntheses based on various other starting materials the same authors established a phase boundary between the two polymorphs in the range  $900\text{--}1,300^\circ \text{C}$ . and  $18,000\text{--}24,000$  bars. This boundary was extrapolated back to lower temperatures and pressures within the metamorphic range. The only certain deduction that can be drawn from a synthesis is that the products have a lower chemical potential than the reactants. It is obvious that if the kinetics of reversibility of a polymorphic transition are highly unfavorable, a synthesis from other phases having much higher free energy than either polymorph can lead to a misleading version of the equilibrium phase diagram. The reversibility between kyanite and sillimanite established by Clark, Robertson, and Birch, *ibid.*, in relatively short runs indicates that their equilibrium curve is well founded in the high temperature and pressure range. Extrapolation back to metamorphic conditions may be less reliable for it is based largely on results of syntheses at conditions where the polymorphic transitions were too slow to observe. Moreover there are no reliable experimental data on the stability relations between sillimanite, andalusite, and mullite+silica.

In an attempt to provide further data at lower temperatures and pressures, the writers made more than a dozen runs starting with various mixtures of andalusite, kyanite, sillimanite, and water as a solvent, in the range  $700\text{--}900^\circ \text{C}$ . and  $700\text{--}2,000$  bars. It was hoped that the most stable phase would be augmented at the expense of the less stable phases, thus overcoming the difficulty of nucleation which must certainly be significant in the kinetics of conversion. In experiments of over four weeks duration no hint of conversion was obtained. Clearly, in this range reversibility is difficult to establish, and syntheses might therefore be correspondingly unreliable.

In a further effort to overcome the difficulty, the indirect method of

measuring the solubilities of the polymorphs in a suitable solvent has been attempted. The results obtained to date are set out below.

### Experimental

Fused cryolite ( $\text{Na}_3\text{AlF}_6$ ) is well known as a solvent of alumina, in which capacity it has long been used for the electrolytic preparation of aluminum. Preliminary experiments indicated that it is also a powerful solvent of aluminosilicates.

Various mixtures in the  $\text{Al}_2\text{SiO}_5$ - $\text{Na}_3\text{AlF}_6$  system were sealed in

TABLE I. COMPOSITIONS OF MELTS IN EQUILIBRIUM WITH CORUNDUM AND ANDALUSITE, KYANITE, AND SILLIMANITE AT  $1010^\circ\text{C}$ ., 1 ATMOSPHERE (FIGURES FOR KYANITE ARE ONLY LIMITING VALUES DUE TO THE GROWTH OF MULLITE). ANDALUSITE FROM MINAS GERAIS, BRAZIL; KYANITE FROM BUNCOMBE COUNTY, N. CAROLINA; SILLIMANITE FROM BENSON MINES, N. Y.

Poly-morph	Solution					
	$\text{SiO}_2/\text{Na}_3\text{AlF}_6$ wt. ratio	Component	Composition wt. %		Composition mole %	
Andalusite	$2.19 \pm 0.09$	$\text{Al}_2\text{O}_3$	14.0	17.0	$11.0 \pm 0.1$	$13.5 \pm 0.1$
		$\text{SiO}_2$	$59.0 \pm 0.8$	$57.0 \pm 0.7$	$78.8 \pm 0.4$	$76.5 \pm 0.5$
		$\text{Na}_3\text{AlF}_6$	$27.0 \pm 0.8$	$26.0 \pm 0.7$	$10.2 \pm 0.4$	$10.0 \pm 0.5$
Kyanite	$3.17 \pm 0.17$	$\text{Al}_2\text{O}_3$	14.0	17.0	$10.3 \pm 0.1$	$12.7 \pm 0.1$
		$\text{SiO}_2$	$65.3 \pm 0.8$	$63.1 \pm 0.8$	$82.3 \pm 0.5$	$80.1 \pm 0.5$
		$\text{Na}_3\text{AlF}_6$	$20.7 \pm 0.8$	$19.9 \pm 0.8$	$7.4 \pm 0.4$	$7.2 \pm 0.5$
Sillimanite	$1.75 \pm 0.06$	$\text{Al}_2\text{O}_3$	14.0	17.0	$11.4 \pm 0.1$	$14.1 \pm 0.1$
		$\text{SiO}_2$	$54.7 \pm 0.7$	$52.8 \pm 0.7$	$76.1 \pm 0.4$	$73.9 \pm 0.5$
		$\text{Na}_3\text{AlF}_6$	$31.3 \pm 0.7$	$30.2 \pm 0.7$	$12.5 \pm 0.4$	$12.0 \pm 0.5$

platinum tubes, taken to  $1010^\circ\text{C}$ . at atmospheric pressure, held under these conditions for 200-1,000 hours, quenched and examined under the polarizing microscope and with  $x$ -ray diffraction with a view to obtaining the composition of the solution. The composition of the mixture at which the  $\text{Al}_2\text{SiO}_5$  polymorphs just disappeared into the melt could be easily determined in this fashion. These compositions are in the range 80-90%  $\text{Al}_2\text{SiO}_5$  by weight. The  $x$ -ray diffractometer technique is sensitive to 5% or even less  $\text{Al}_2\text{SiO}_5$ . The compositions thus measured are accurate to better than 1%. Microscopic examination yields an even closer tolerance. The dissolution process is incongruent resulting in the formation of corundum and liquid, so that our measurements give only the  $\text{SiO}_2/\text{Na}_3\text{AlF}_6$  ratio in the liquid phase resulting from the melting of each

of the polymorphs. The composition of the liquid phase in equilibrium with each of the polymorphs was then determined by taking mixtures in the  $\text{SiO}_2\text{-Na}_3\text{AlF}_6\text{-Al}_2\text{SiO}_5$  system (using the  $\text{SiO}_2/\text{Na}_3\text{AlF}_6$  ratios previously determined) and observing at which composition corundum completely disappeared into the melt. Runs varying in duration from 200–1,000 hours gave consistent results. Since the region studied is at the  $\text{Al}_2\text{O}_3$ -poor corner of the ternary system, the accuracy of these latter determinations is no better than  $\pm 1.5\%$ . According to Rolin (1960) the  $\text{Al}_2\text{O}_3$  liquidus in the  $\text{Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6$  system at  $1,010^\circ\text{C}$ . lies at 13–14%  $\text{Al}_2\text{O}_3$  by weight. This is within 2 to 3 per cent of that measured in this study at  $\text{SiO}_2/\text{Na}_3\text{AlF}_6$  weight ratios varying from 1.7 to 3.3. The addition of  $\text{SiO}_2$  in the ternary system seems to have very little effect on the weight percentage of  $\text{Al}_2\text{O}_3$  in the melt in equilibrium with corundum. It follows that in comparisons of the equilibrium melt compositions for the three polymorphs, the  $\text{Al}_2\text{O}_3$  content cannot vary the full range (14–17%) given in Table I.  $\text{SiO}_2$  and  $\text{Na}_3\text{AlF}_6$  content are therefore given for each of the limiting values of  $\text{Al}_2\text{O}_3$  content.

#### DISCUSSION

The thermodynamics of the incongruent solution may be approached as follows. For andalusite (A) in equilibrium with melt:

$$\mu^{(A)} = \mu_{\text{SiO}_2}^0 + RT \ln \frac{a_{\text{SiO}_2}^{(\text{sol A})}}{a_{\text{SiO}_2}^0} + \mu_{\text{Al}_2\text{O}_3}^{(\text{sol A})} \quad 1.$$

Similar expressions may be written for kyanite (K) and sillimanite (S). Corundum is in equilibrium with the melt in each case so that:

$$\mu_{\text{Al}_2\text{O}_3}^{(\text{sol A})} = \mu_{\text{Al}_2\text{O}_3}^{(\text{sol K})} = \mu_{\text{Al}_2\text{O}_3}^{(\text{sol S})} \quad 2.$$

Subtracting expressions of type 1 from each other and making use of 2, the free energy relations between the polymorphs are summarized as follows:

$$\mu^{(A)} - \mu^{(K)} = RT \ln \frac{a_{\text{SiO}_2}^{(\text{sol A})}}{a_{\text{SiO}_2}^{(\text{sol K})}}; \mu^{(A)} - \mu^{(S)} = RT \ln \frac{a_{\text{SiO}_2}^{(\text{sol A})}}{a_{\text{SiO}_2}^{(\text{sol S})}}; \text{ and } \mu^{(K)} - \mu^{(S)} = RT \ln \frac{a_{\text{SiO}_2}^{(\text{sol K})}}{a_{\text{SiO}_2}^{(\text{sol S})}} \quad 3.$$

From the data in Table I we conclude that

$$a_{\text{SiO}_2}^{(\text{sol K})} > a_{\text{SiO}_2}^{(\text{sol A})} > a_{\text{SiO}_2}^{(\text{sol S})}$$

and therefore at  $1,010^\circ\text{C}$ ., 1 atm.

$$\mu^{(K)} > \mu^{(A)} > \mu^{(S)}$$

so that the most stable polymorph is sillimanite. This does not mean that sillimanite necessarily is stable relative to mullite+silica. It should be

noted also that kyanite dissolved in cryolite was rapidly converted to well crystallized mullite, indicating the potential of fused salts for silicate synthesis. Entropy data for andalusite and sillimanite according to Kelley (1950 and 1960) show that in the range 127–1,327° C.,  $S_A > S_S$ . Since  $(\partial\mu/\partial T)_P = -S$  we conclude from the solubility and entropy data that andalusite is metastable with respect to sillimanite in this temperature range. According to  $x$ -ray measurements made by the writers from calibrated Weissenberg photographs:  $V_A = 51.43 \pm 0.10$  cc/mole and  $V_S = 49.78 \pm 0.10$  cc/mole. The thermal expansion of the phases in question would be most anomalous if the sign of  $\Delta V$  were to change over the range of metamorphic temperatures. Thus if the compressibility is neglected, from  $(\partial\mu/\partial P)_T = V$  we might conclude that andalusite has no true stability field with respect to sillimanite at metamorphic pressures and temperatures.

It must be stressed that the preceding treatment is valid only for the phases which do not deviate appreciably from the ideal composition  $\text{Al}_2\text{SiO}_5$ . The effect of compositional variations on the stability fields of the three minerals cannot be discounted.

While more data at lower temperatures are essential, the possibility that andalusite is metastable in nature need not be considered improbable because of the common geological occurrence of the mineral. The persistence of unstable phases in geologic environments is well established (e.g. order-disorder in feldspars, cristobalite, boehmite, etc.). In fact the lack of reactivity of the polymorphs makes such metastable persistence probable.

Estimates of the free energy differences between the three polymorphs of  $\text{Al}_2\text{SiO}_5$  could be made if the nature of the species in solution as well as their activity coefficients were known. It is hoped that the accumulation of more data will make such a quantitative approach possible.

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NATROLITE FROM HOUDAILLE INDUSTRIES QUARRY  
BOUND BROOK, SOMERSET COUNTY, N. J.

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Compared to other quarries in the first Watchung sill of Northern New Jersey, the Houdaille Industries Quarry located 1.7 miles north-west of Bound Brook, Somerset County, New Jersey, produces few specimens of interest to the collector. A visit to the quarry in early summer of 1960 in company with Mr. Gene Vitali of North Haledon, N. J., produced specimens of ordinary calcite and, unexpectedly, natrolite crystals of unusual size and transparency. The latter are quite unlike any hitherto reported from New Jersey localities.

The Houdaille Quarry, commonly called the Chimney Rock quarry, is an oval opening approximately one third mile in length penetrating the thick basalt sill of the First Watchung Mountain. An excellent map of basalt and diabase outcrops, including the Watchung sills, plus descriptions of New Jersey trap minerals, appears in Mason (1). Current quarrying is confined (1960) to the west wall where enormous slopes of broken basalt are searched for minerals by local collectors. The exposed section of sill is divided by parallel, vertical joints, the most prominent of which are oriented in a north-south direction. Thin calcite-filled veins are emplaced in joints, and, in favorable sites, open into lenticular cavities lined with good crystals of calcite and occasionally other minerals.

Due to chloritization of wall rock, vein material separates readily from basalt and entire sections may be found in the blast rubble. One such mass revealed several small cavities lined with large rhombohedral crystals of calcite with open spaces criss-crossed by prismatic crystals of natrolite as shown in Fig. 1. Natrolite prisms were found coated almost completely by very small scalenohedral crystals of calcite of uniform size and habit. Underneath each such coating was found a layer of minute colorless gypsum crystals, simple in habit, and perfectly transparent except for a slight pearly luster upon the  $b(010)$  faces. Beneath this layer and immediately in contact with the natrolite was found more gypsum as a white spongy inner layer consisting of numerous