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SOME HIGH-PRESSURE HYDROTHERMAL EXPERIMENTS ON SEVERELY GROUND KYANITE AND SILLIMANITE

ROBERT C. NEWTON

Department of Geophysical Sciences,
University of Chicago, Chicago, Illinois 60637

ABSTRACT. Prolonged severe fine-grinding of an initially lightly-ground kyanite-sillimanite mixture greatly decreased its hydrothermal reactivity. Pressures required for kyanite growth relative to sillimanite at 750°C in runs of a few days duration were substantially raised for the severely ground starting mix over the pressures needed to produce kyanite at the expense of sillimanite in the lightly ground mix. This effect is due to preferential degradation of kyanite in grinding. Sillimanite nucleated in runs on degraded kyanite at 750°C as much as 2 kb above the stability limit of sillimanite determined from runs on the lightly ground mix. The faster degradation rate of kyanite may be sufficient to explain the relatively high pressure location of the kyanite-sillimanite boundary deduced by Althaus (1967) in experiments on severely ground minerals.

A number of recent experimental determinations of the kyanite-sillimanite equilibrium pressure-temperature boundary in the Al_2SiO_5 system are in considerable accord as to the pressure of the equilibrium in the temperature range 650° to 850°C. For instance, at 750°C, Newton (1966), gives 8.1 ± 0.4 kb; Richardson, Bell, and Gilbert (1968), give $8.6^{+0.7}_{-0.2}$ kb; Weill (1966), gives 9.2 kb; and very recently, P. Anderson and O. J. Kleppa (personal commun.), found a value of 7.8 ± 1.5 kb. The last two studies are particularly valuable in that they are indirect determinations based on measurements of thermodynamic properties. The value of Weill was based on measurements of the relative solubilities of kyanite and sillimanite in fused cryolite at atmospheric pressure, and the result of Anderson and Kleppa was based on measurements of the heats of solution of the minerals in a fused-salt calorimeter at 1 atm.

An apparent exception to the general accord is the work of Althaus (1967), which places the kyanite-sillimanite boundary above 11 kb at 750°C. Although this study is quite extensive and seemingly straightforward, it differs from the other investigations in that severely ground natural minerals were used as starting materials. The kyanite and sillimanite used by Althaus were ground in an automatic tungsten carbide mortar until there was "remarkable" broadening of the X-ray diffraction peaks. The desired effect was greatly augmented reaction rates by virtue of highly activated starting material. The possibility of perturbing the equilibrium by introducing considerable surface and strain energy into the reactants was not considered by Althaus. This point deserves attention, however, because of the small enthalpy change of the equilibrium and hence its susceptibility to perturbing energy effects and because of Althaus' somewhat unique experimental results.

In the present investigation, a few runs were made repeating those of Newton (1966). The starting materials, natural kyanite and sillimanite, were the same as those used in the 1966 study. The starting mix, consisting of about 50 percent each mineral, was very lightly ground, so that homo-

geneity could be achieved without introducing structural degradation. The 1 in. diameter piston-cylinder apparatus was used, and the direction and degree of reaction deduced by comparing X-ray diffraction peak heights of the quenched charges and the starting material. The results or lightly-ground starting materials reinforced the earlier work (table 1).

TABLE 1

Hydrothermal experiments at 750°C

"Standard Mix" is natural kyanite and sillimanite, 1:1

No.	Starting material	Pressure (kb)	Time (hr)	Results
1	Std Mix lightly ground	10.5	2	Complete conversion to kyanite*
2	Std Mix lightly ground	9.5	50	Complete conversion to kyanite
3	Std Mix lightly ground	9.0	48	Kyanite gained over sillimanite
4	Std Mix lightly ground	8.0	41½	Sillimanite gained over kyanite
5	Std Mix ground 3¼ hr	11.5	48	Both phases recrystallized Kyanite gained over sillimanite
6	Std Mix ground 3¼ hr	10.5	43	Sillimanite and kyanite recrystallized somewhat. Possible slight gain of kyanite
7	Std Mix ground 3¼ hr	9.5	47	Sillimanite and kyanite recrystallized slightly. No apparent change in amounts **
8	Severely ground kyanite	11.5	26	Kyanite recrystallized Trace of sillimanite present
9	Severely ground kyanite	10.5	20	Kyanite recrystallized Sillimanite appeared (5%)
10	Severely ground kyanite	9.5	52	Kyanite recrystallized somewhat Sillimanite appeared (20%)
11	Std Mix ground 3¼ hr Quartz added	10.5	47	All phases recrystallized. Evidence for kyanite growth after regrinding (see text)

* All quenched charges had small amounts of corundum and pyrophyllite. See Newton (1966).

** Relative to severely ground mix. Evidence for sillimanite growth relative to lightly ground mix.

Another starting mix was prepared with severely ground minerals. The 1:1 mixture of kyanite and sillimanite powder was ground by hand in an agate mortar for 3¼ hours, with periodic halts to prepare diffractograms in order to monitor progressive damage to the minerals as indicated by progressive peak-broadening. About 3 g of material were ground. The mortar had a bowl 4 in. across. The pestle was ¾ in. in diameter. No great amount of force was applied in grinding. Figure 1 shows the effect of grinding time on the major peaks. A significant effect was revealed in the grinding experiments, that of preferential degradation of kyanite. The kyanite peaks were greatly weakened relative to those of sillimanite after 3¼ hours of grinding. This is probably due to the superior cleavage of kyanite and hence swifter comminution.

Runs at 11.5, 10.5, and 9.5 kb at 750°C for about 48 hours were made with the degraded kyanite-sillimanite starting material (table 1). A most surprising result was encountered. Instead of augmenting the reaction rates, the grinding treatment dramatically decreased reactivity. The 10.5

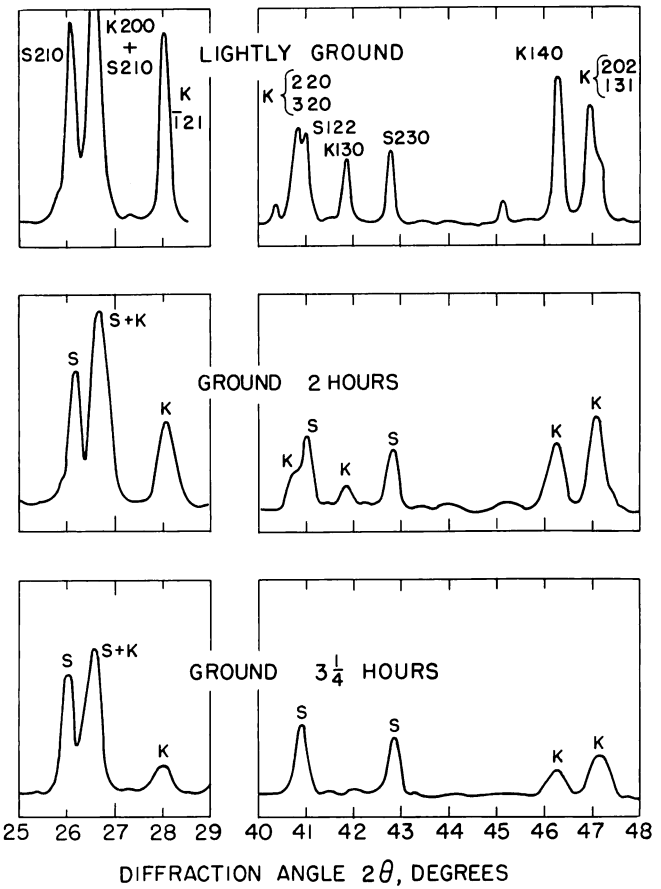

Fig. 1. Effect of grinding time on the x-ray diffraction pattern of a 1:1 kyanite-sillimanite mixture. The preferential degradation of kyanite is evident.

kb run showed very slight relative increase of kyanite in 2 days, with both phases recrystallizing somewhat, as deduced by slimming of the X-ray peaks, whereas the lightly ground starting mix showed complete reaction to kyanite at the same conditions in two hours. The 9.5 kb run on highly ground material showed no discernible reaction when its diffractogram was compared to that of the highly ground starting mix. If one were to use the criterion of comparing the diffractogram of the quenched charge to that of the lightly ground starting material, one would have deduced a considerable reaction toward sillimanite. Apparently the presence of viable seeds of the phases is much more effective in producing good reaction rates than extreme activation of the starting material.

Runs at 9.5, 10.5, and 11.5 kb were made on a kyanite powder that had been ground for ¾ hour by hand in an agate mortar. The peak-broadening was comparable to that of the kyanite in the kyanite-sillimanite

mix ground 3¼ hours. The faster degradation was due to a smaller amount of material ground. The 9.5 and 10.5 kb runs on the degraded kyanite produced sillimanite spontaneously. The sillimanite was detected both optically and with X-rays. It was not possible to establish that the volunteering phase was not in reality mullite, because of the small amount and crystal form of very thin needles. The fibrous habit and relatively siliceous bulk composition of the charge make sillimanite seem more likely. The necessity of carefully specifying the state of aggregation in experiments on this system should be evident from this result.

A run at 10.5 kb was made in an attempt to simulate the experiment of Althaus at 750°C. Althaus used quartz as an internal amount indicator. About 40 percent of quartz was present in his highly ground starting mix. During his runs, all phases recrystallized, including the quartz. The relative amount of gain of one Al_2SiO_5 polymorph over the other was determined by regrinding the quenched charges until the quartz peaks were reduced to their intensities in a "standard mix" of known amounts of the minerals. In the present run, about 40 percent of quartz which had been treated by prolonged grinding in an agate mortar was added to the degraded kyanite-sillimanite mix and homogenized carefully. A uniform mechanically packed strip of the mix, 0.5 cm X 2 cm, was placed in the beam of a Norelco copper X-ray tube, and the integrated intensity of the (100) reflection of the quartz was measured with fixed scaling and scanning-time constants. A reproducibility of about ± 10 percent was the best that could be obtained by this method. The quartz-bearing mix was sealed with 30 wt percent of water into a platinum capsule and was run at 750°C and 10.5 kb for 47 hours. The quenched charge was mounted, and the X-ray peak intensities measured in a manner as nearly identical to the procedure for the starting material as possible. All of the phases, especially the quartz, showed appreciable recrystallization with apparent increases in all integrated intensities. The charge was then ground in an agate mortar with frequent X-ray scanning interludes until the peak intensities of the quartz were very nearly equal to those of the starting material. The total regrinding time was about 15 min. Although the diffractogram of the unground charge indicated a small growth of kyanite relative to sillimanite, the diffractogram of the reground charge had grossly weakened kyanite peaks. The overall interpretation based on the regrinding procedure would be that the kyanite had decreased relative to sillimanite by at least 50 percent. Some of the exact procedures of Althaus, such as automatic grinding, a rotating X-ray mount, and ultra-high intensity X-ray source could not be reproduced here. Moreover, the grinding time used by Althaus to prepare his "standard mix" for amount determinations, a mix, apparently different from his actual starting mix, was not given by him, and it was not stated by him if the minerals were separately ground or ground together. If his assumptions are true, however, the degree of grinding of his quenched charge and of his standard mix should be immaterial. The grinding times necessary to reduce the intensities of the quartz diffraction peaks in the charges to the values characteristic of the

standard mix were given by Althaus as ½ to 1½ hours. The strong indication of run 11, table 1, is that the regrinding treatment can bias considerably the relative growth signal in favor of sillimanite because of the preferential degradation of kyanite in grinding. The procedure of Althaus was criticized by Richardson, Bell, and Gilbert (1968) from this standpoint.

A simple surface-energy analysis indicates why severe grinding of the kyanite-sillimanite starting mix would bias the equilibrium in the direction of raising the apparent pressure of sillimanite stability. Peak widths at half-height for the (120) reflection of sillimanite and the (200) reflection of kyanite were measured for the highly ground starting mix. The values were 0.21° and 0.39° 2θ respectively. The values for the lightly ground materials were 0.16° and 0.19° respectively. The considerable broadening is due to a combination of very small average grain size and internal strains induced in grinding. The former cause is probably the major contributor because of the low plasticity of these minerals. Under high magnification the ground powder was an unresolvable turgid mass with only an occasional speck of observable birefringence under crossed polarizers. A formula of Klug and Alexander (1954, p. 512) was used to estimate average grain size of the kyanite perpendicular to (200):

$$d_{200} \sim \frac{\beta_{1/2} \cos \theta}{0.9\lambda},$$

where λ is the X-ray wavelength, $\beta_{1/2}$ is the peak width at half-height, and θ is the Bragg angle. The calculated average d(200) for kyanite is 210 A°. Assuming somewhat prismatic microcrystals, with one direction twice as long as this and the third direction equal, the calculated surface energy for kyanite in the starting mix is 1.05×10^8 cm²/mole. A similar calculation gives about one-fifth this value for the sillimanite.

Proceeding further on the assumption that the preponderance of line broadening is due to high surface area, a value of specific surface energy is needed to estimate the free energy contribution due to grinding. Data for the specific surface energies of solids are not abundant. Gilman (1960) measured accurate values for cleavage faces of some ionic crystals. His values range from 230 ergs/cm² for the $(10\bar{1}0)$ cleavage face of calcite to 1200 ergs/cm² for the (100) cleavage face of MgO. Chave and Schmalz (1966) found from pH measurements that the specific surface energy of calcite goes up rapidly with decreasing grain size below about 500 A°. Interfacial energies in many metals vary from 5 ergs/cm² to 800 ergs/cm² depending on the degree of crystallographic mismatch of adjacent grains (McLean, 1965). Values of 15 ergs/cm² to 375 ergs/cm² for the surface tensions of liquids against liquids and liquids against air are given by Young and Harkins (1963). Fyfe, Turner, and Verhoogen (1958) use an average value of $\sigma = 100$ ergs/cm² for silicate minerals and 1000 ergs/cm² for quartz. In view of the foregoing data a value of $\sigma = 100$ ergs/cm² seems conservative for aluminum silicates. Using this

value and the calculated surface areas of the minerals, an excess Δ G of 200 cal/mole for the reaction sillimanite $\rightarrow$ kyanite may be calculated. The value so derived is based entirely on the preferential comminution of kyanite in grinding and does not consider the probable circumstance that kyanite has the higher specific energy of the two minerals (Fyfe, Turner, and Verhoogen, p. 73), which would tend to raise the Δ G value. An energetic bias of this amount would raise the pressure requirements for stability of the starting mix kyanite relative to the starting mix sillimanite by 1400 bars. This is probably a conservative figure and is quite in keeping with runs 5 to 10 of table 1.

In summary, it has been shown that hydrothermal runs of a few days duration at 750°C on severely ground starting mixes of kyanite and sillimanite fail to produce clear evidence of kyanite growth at pressures at least 2 kb above the stability limit of sillimanite for unstrained materials. Course-grained, unstrained kyanite is the stablest phase above about 8.5 kb at 750°C, but such kyanite is slow to nucleate and grow under such conditions. At 10.5 kb and above, kyanite commences to grow in runs of a few days duration, but so does the sillimanite, and a regrinding of the quenched charge can obliterate any resulting signal of kyanite growth.

The danger of bias should be suspected in experiments on severely ground sillimanite and andalusite mixes because of the small Δ H and Δ V of the sillimanite-andalusite reaction.

If the idea of energetic bias in reactions among high-surface phases is carried to the limit of proto-crystalline nucleii forming from amorphous or extremely unstable materials, it might well explain the coincidence in apparent location of the kyanite-sillimanite inversion found by the extrapolation of Clark (1961), based on the used of fired kaolin starting material, and that of Bell (1963) using a shearing squeezer high-pressure device, in which initial drastic crushing of the mineral charge might have reduced it to nearly amorphous character. Under this interpretation a higher specific surface energy of kyanite would play a leading role in influencing the relations.

It might be that experiments on ultra-ground phases have a direct application to some natural occurences. Metastability in some instances of alumino-silicate petrogenesis is beginning to loom as a distinct possibility (Hollister, 1968). Experiments similar to those of Althaus might be more meaningful, therefore, than those of Richardson, Bell and Gilbert in certain applications. Nevertheless, the need to specify exactly the state of aggregation of starting materials and products in preparing an equilibrium pressure-temperature diagram is exemplified by the Al_2SiO_5 system.

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