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## A REDETERMINATION OF EQUILIBRIUM RELATIONS BETWEEN KYANITE AND SILLIMANITE

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ABSTRACT. The equilibrium curve between kyanite and sillimanite has been established by quenching experiments at temperatures between  $1000^{\circ}$ C and  $1500^{\circ}$ C and pressures between 17 and 24 kilobars. The curve is given by the expression  $P = 4.1 + 13.2 \times 10^{-8} T$ , where the pressure, P, is in kilobars and the temperature, T, is in degrees Centigrade. There is some evidence that the phase boundary may depart from linearity at low temperatures, but no quantitative estimate of the amount of curvature can be obtained from present data.

If kyanite forms stably in nature, pressures of nearly 10 kilobars are required. This is equivalent to the weight of about 30 kilometers of overburden. Such great depths of burial are not required if pressure is contained by the strength as well as by the weight of the overlying rock. It is suggested that "tectonic overpressures" of a kilobar or more may exist in rocks which are undergoing deformation.

The inversion of kyanite to sillimanite is the simplest of the classical metamorphic isograds to characterize chemically. Both minerals are close to  $Al_2SiO_5$  in composition, with other elements usually present in very small amounts. Hence they may be regarded as pure phases of the same composition, and their equilibrium relations are therefore unaffected by complicating factors such as the bulk composition of the rock in which they occur or partial pressures of volatile components. The determination of their fields of stability in the laboratory carries direct implications about the conditions under which they were formed in rocks, subject only to the assumption that chemical equilibrium is closely approached in nature.

The chemical simplicity of these phases does not imply that reactions involving them are easy to produce in the laboratory. Both are extremely refractory and react with great reluctance at temperatures below 1000°C. In earlier work on this system (Clark, Robertson, and Birch, 1957), the temperatures required for reaction to take place in a reasonable time were uncomfortably close to the maximum attainable. The number of successful runs at high temperatures was limited by failure of the apparatus, and the reversibility of the reaction was perhaps not demonstrated as convincingly as one might desire. A phase boundary, based largely but not entirely on syntheses of kyanite or sillimanite, was established between 1000°C and 1300°C, despite these difficulties.

It is comparatively easy to maintain high temperatures and pressures for extended periods of time in apparatus in which pressure is transmitted by a plastic solid and the charge is heated by a tubular graphite heating element. Such apparatus has the disadvantage that the pressure must be calculated from the force applied to the piston which produces it, and corrections for friction and the finite strength of the pressure-transmitting medium must be made. In

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the previous work the pressure was measured directly and precisely by the change in resistance of a coil of manganin wire.

The present results, obtained with a solid pressure-transmitting medium, prove to be in good agreement with the previous experiments. Since the equipment used in the two studies is basically different, this agreement suggests strongly that both sets of data are essentially correct. It appears that the calculation of pressure in the present work is as accurate as could be expected, and it also appears that the phase boundary established previously is very close to the true equilibrium curve.

#### EXPERIMENTAL PROCEDURE AND RESULTS

The present work was done in apparatus that differs only in minor respects from that described by Boyd and England (1960). Calibration against the Bi I-Bi II transition, which takes place at 25.2 kilobars at  $25^{\circ}$ C, indicates that the pressure calculated from the load on the piston is greater than that experienced by the sample by about 13 percent at room temperature. This figure is reproducible to within a few tenths of one percent. Part of this loss of pressure is attributable to the strength of the talc sleeve which transmits the pressure. This will be lower at high temperatures, implying that a correction of less than 13 percent should be made. The pressures given below have been determined by reducing the value calculated from the load on the piston by 8 percent of the corrected pressure, in agreement with the practice of Boyd and England. The pressure calculated in this way is believed to be accurate to within 5 percent for the range of pressures through which the reaction could be followed in the present study.

Temperatures of the charges were measured with Pt-Pt 10 percent Rh thermocouples pressed against one end of the Pt capsule in which the charge was held. The thermal gradient in the furnace rarely exceeded 15°C in the length of the charge and never exceeded 20°C. No correction was made for the effect of pressure on the e.m.f. of the thermocouple.

Four materials were used as reactants in this study. Kyanite and sillimanite were synthesized from andalusite from Hill City, South Dakota and from metakaolinite prepared by firing Georgia kaolinite overnight at 600°C. The kaolinite, kindly supplied by G. C. Kennedy, contained as principal impurities 0.15 percent Na<sub>2</sub>O and 0.30 percent TiO<sub>2</sub> (analysis by C. G. Engel). No analysis of the andalusite is available. Kyanite from Burnsville, North Carolina and sillimanite from Brandywine Springs, Delaware were also used in the experiments. An analysis of the kyanite has been given by Todd (1950). The sillimanite is probably very pure, judging by its lack of color and the relatively small values of its lattice parameters (Skinner, Appleman, and Clark, 1961). Fine-grained samples of the aluminosilicates were prepared by elutriating in water for 6 minutes.

Experimental results are given in table 1 and are shown in figures 1 and 2. Products were identified by their X-ray diffraction patterns. The phase boundary in figure 2 is the same as that determined by the syntheses shown in figure 1. This boundary is reversible to within a kilobar, and the results of the experiments are insensitive to the particular reactant used. This conclusion was

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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	°C Temperature	Kilobars Pressure	Hours Duration	Reactants	Products
1500242AS1500242AS150024.52AK1500252½S + (K)K + (S)1400222½S + (K)K + (S)1400225¼K + (S) + H_2OK + C + G1400225¼K + (S) + H_2OK + C + G1400225¼K + (S)S + (K)140022.54AK + S + Q* + C*1400235S + (K) + H_2OC + G140023.15S + (K)K130020.54½K + (S)K + (S)130020.54½K + (S)K + (S)130020.52¼MKS + Q + C*1300212MKK + Q + C*120019.53MKK + Q + C*120019.53MKS + Q + C*1100184½MKS + Q + C*1100185½MKS + Q + C*1100185¼MKS + Q + C*100017.56¾MKS + Q + C*100017.518MK + (K) + (S)S + (K)90015.516¾MK + (K) + (S)S + (K)90015.515MK + (K) + (S)K + S9001715MK + (K) + (S)K + S	1500	23.6	3	K + (S)	S
1500242A $S + Q + C + C + K$ 150024.52AK1500252½S + (K)K + (S)1400222¼AS1400225K + (S) + H_sOK + C + G1400225¼K + (S) + H_sOK + C + G1400225K + (S) + H_sOK + C + C + G140022.54AK + S + Q + C + C + C + G1400235S + (K) + H_sOC + C + C + C + C + C + C + C + C + C +	1500	24	2	A	š
150024.52AK15002524.2S + (K)K + (S)14002224.4AS1400225K + (S)K + (S)14002254.4K + (S) + H_40K + C + G1400225K + (S)S + (K)1400235S + (K) + H_20C + G1400233AK + Q* + C*140023.15S + (K)K130020.544.2K + (S)S + (K)130020.544.2K + (S)K + (S)130020.524.4MKS + Q130021.52MKK + Q1300225S + (K)K120019.53MKS + Q + C*11001844.2MKS + Q + C*110018.55MKS + Q + C*11001854.4MKS + Q + C*100017.563.4MKS + Q + C*100017.518MK + (K) + (S)S + (K)90015.5163.4MK + (K) + (S)S + (K)90016.515MK + (K) + (S)K + S90016.515MK + (K) + (S)K + S	1500	24	2	A	$S + O^* + C^*$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1500	24.5	2	A	ĸ
140022244AS14002254K + (S)K + (S)14002254K + (S) + H_4OK + C + G1400225K + (S)S + (K)140022.54AK + S + Q* + C*1400235S + (K) + H_4OC + G1400235S + (K) + H_4OC + G140023.15S + (K)K1350215K + (S)S + (K)1300204½K + (S)K + (S)130020.54½K + (S)K + (S)130021.52MKK + Q130021.52MKK + Q130022.55 S + (K)K120019.53MKK + Q + C*120020.52%MKK + Q + C*120020.52%MKK + Q + C*1100184½MKS + Q + C*1100184½MKS + Q + C*1100185MKS + Q + C*100017.56%MKS + Q + C*100017.56%MKK + Q + C*90015.516%MK + (K) + (S)S + (K)90015.515MK + (K) + (S)K + S90016.515MK + (K) + (S)K + (S)	1500	25	21/2	S + (K)	K + (S)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1400	22	21/4	A	S
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1400	22	5	K + (S)	K + (S)
1400225K + (S)K + (S)S + (K)140022.54AK + S + Q* + C*1400235S + (K) + H_2OC + G1400233AK + Q* + C*140023.15S + (K)K1350215S + (K)K1300204½K + (S)S + (K)130020.54½K + (S)K + (S)130020.52¼MKS + Q1300212MKS + Q130021.52MKK + Q1300225S + (K)K120020.52¼MKK + Q + C*120020.52¼MKK + Q + C*120020.52¼MKK + Q + C*1100184½MKK + Q + C*1100184½MKS + Q + C*1100176½MKS + Q + C*100017.56¾MKK + Q + C*100017.56¾MKK + Q + C*90015.516¾MK + (K) + (S)S + (K)90016.515MK + (K) + (S)K + S90016.515MK + (K) + (S)K + (S)	1400	22	51/4	$K + (S) + H_{*}O$	$\mathbf{K} + \mathbf{C} + \mathbf{G}$
140022.54AK $K + C^*$ 1400235 $S + (K) + H_2O$ $C + G$ 1400233A $K + Q^* + C^*$ 140023.15 $S + (K)$ $K$ 1350215 $K + (S)$ $S + (K)$ 130020 $4\frac{1}{2}$ $K + (S)$ $K + (S)$ 130020.5 $4\frac{1}{2}$ $K + (S)$ $K + (S)$ 130020.5 $2\frac{1}{4}$ $K K$ $S + Q$ 130021.52 $MK$ $S + K + Q$ 130021.52 $MK$ $K + S + Q + C^*$ 120019.53 $MK$ $S + Q + C^*$ 120020.5 $2\frac{3}{4}$ $MK$ $K + Q + C^*$ 110018 $4\frac{1}{2}$ $MK$ $S + Q + C^*$ 110018 $4\frac{1}{2}$ $MK$ $S + Q + C^*$ 110017.5 $6\frac{3}{4}$ $MK$ $S + Q + C^*$ 100017.5 $6\frac{3}{4}$ $MK$ $K + Q + C^*$ 100018 $5\frac{1}{4}$ $MK + (K) + (S)$ $S + (K)$ 90015.516\frac{3}{4} $MK + (K) + (S)$ $S + K$ 90016.515 $MK + (K) + (S)$ $K + S$ 90016.515 $MK + (K) + (S)$ $K + (S)$	1400	22	5	$\tilde{K} + (\tilde{S})$	S + (K)
1400235 $S + (K) + H_2O$ $C + G$ $C + C + C + C + C + C + C + C + C + C +$	1400	22.5	4	A	$K + S + O^* + C^*$
1400233A $K + Q^* + C^*$ 140023.15 $S + (K)$ $K$ 1350215 $K + (S)$ $S + (K)$ 130020 $4\frac{1}{2}$ $K + (S)$ $K + (S)$ 130020.5 $4\frac{1}{2}$ $K + (S)$ $K + (S)$ 130020.5 $2\frac{1}{4}$ $K + (S)$ $K + (S)$ 130021.52 $MK$ $S + K + Q$ 130021.52 $MK$ $K + Q$ 130022.5 $S + (K)$ $K$ 120019.53 $MK$ $S + Q + C^*$ 120020 $2\frac{3}{4}$ $MK$ $K + Q$ 110018 $4\frac{1}{2}$ $MK$ $S + Q + C^*$ 110018 $4\frac{1}{2}$ $MK$ $S + Q + C^*$ 110017 $6\frac{1}{2}$ $MK$ $S + Q + C^*$ 100017.5 $6\frac{3}{4}$ $MK$ $K + Q + C^*$ 100017.5 $6\frac{3}{4}$ $MK + (K) + (S)$ $S + (K)$ 90015.516\frac{3}{4} $MK + (K) + (S)$ $S + K$ 90016.515 $MK + (K) + (S)$ $K + S$ 9001715 $MK + (K) + (S)$ $K + (S)$	1400	23	5	$S + (K) + H_{0}O$	C + G
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1400	23	3	A	$K + O^* + C^*$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1400	23.1	5	S + (K)	K
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1350	21	5	$\mathbf{K} + (\mathbf{S})$	S + (K)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1300	20	41/2	$\mathbf{K} + (\mathbf{S})$	K + (S)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1300	20.5	41/2	$\mathbf{K} + (\mathbf{S})$	$\mathbf{K} + (\mathbf{S})$
1300       21       2       MK $S + K + Q$ 1300       21.5       2       MK $K + Q$ 1300       22       5 $S + (K)$ $K$ 1200       19.5       3       MK $S + Q + C^*$ 1200       20       234       MK $K + S + Q + C^*$ 1200       20.5       234       MK $K + Q$ 1100       18       4½       MK $K + Q$ 1100       18.5       5       MK $S + Q + C^*$ 1100       18.5       5       MK $S + Q + C^*$ 1100       18.5       5       MK $K + Q$ 1000       17       6½       MK $K + Q$ 1000       17.5       6%       MK $K + Q + C^*$ 1000       18       5¼       MK + (K) + (S) $S + (K)$ 900       15.5       16%       MK + (K) + (S) $S + K$ 900       16.5       15       MK + (K) + (S) $K + S$ 900       16.5       15       MK + (K) + (S) $K + (S)$ 900       17       15       <	1300	20.5	21/4	MK	S + Q
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1300	21	2	MK	S + K + Q
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1300	21.5	2	MK	K + O
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1300	22	5	S + (K)	K
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1200	19.5	3	MK	$S + O + C^*$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1200	20	23/4	MK	$K + S + O + C^*$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1200	20.5	23/4	MK	K + Q
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1100	18	41/2	MK	$S + Q + C^*$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1100	18.5	5	MK	$S + (K) + O + C^*$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1100	19	4	MK	K + Q
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1000	17	$6\frac{1}{2}$	MK	$S + O + C^*$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1000	17.5	63/4	MK	$S + O + C^*$
9001518MK + (K) + (S) $S + (K)$ 90015.516%MK + (K) + (S) $S + K$ 90016.515MK + (K) + (S) $K + S$ 9001715MK + (K) + (S) $K + (S)$	1000	18	51/4	MK	$\mathbf{K} + \mathbf{O} + \mathbf{C}^*$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	900	15	18	MK + (K) + (S)	S + (K)
900 16.5 15 $MK + (K) + (S) K + S$ 900 17 15 $MK + (K) + (S) K + (S)$	900	15.5	163/4	MK + (K) + (S)	S + K
900 17 15 $MK + (K) + (S) K + (S)$	900	16.5	15	MK + (K) + (S)	K + S
	900	17	15	MK + (K) + (S)	K + (S)

# Experimental Results

MK, metakaolinite; A, andalusite; K, kyanite; S, sillimanite; G, glass; Q, quartz; C, corundum.

Parentheses indicate phase present in minor amounts. \*Metastable phase.

arrived at previously (Clark, Robertson, and Birch, 1957), but the present evidence is much less equivocal.

Kyanite and sillimanite were synthesized together in several runs close to the equilibrium curve. This is probably due to small gradients of pressure and temperature. The persistence of both phases can be attributed, in part at least, to the extreme sluggishness with which reaction between kyanite and sillimanite takes place close to the equilibrium curve.

Attempts were made to locate the equilibrium curve at temperatures below 1000°C, using as a reactant metakaolinite seeded with about 10 percent each of kyanite and sillimanite. In runs 1 kilobar or more away from the extrapolated phase boundary at 900°C, the polymorph stable under the conditions of the experiment was decidedly the more plentiful product of the run. The results of runs closer to the equilibrium curve were not sufficiently clearcut

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Fig. 1. Syntheses of kyanite and sillimanite. Circles stand for runs in which andalusite was the reactant, squares represent metakaolinite, and crosses and pluses represent metakaolinite seeded with kyanite and sillimanite. Solid symbols mean kyanite was produced, open symbols mean sillimanite, and open symbols with a diagonal line mean both. Crosses represent the growth of sillimanite and pluses the growth of kyanite.

to permit them to be assigned definitely to either field of stability. Both kyanite and sillimanite grew in about equal amounts.

Several experiments in which the reactant was either kaolinite or an aluminosilicate to which a small amount of water had been added were carried out at temperatures above 1000°C. These runs produced corundum plus glass, in agreement with the results of Yoder and Schreyer (1959) at lower pressures. The water content of these charges is not really known, as it was not possible to demonstrate the absence of leak during the run. These observations of melting are of only qualitative value as a result. The appearance of corundum in these experiments is of interest because it suggests a possible explanation of the metastable formation of quartz plus corundum that plagued the previous study (Clark, Robertson, and Birch, 1957). In those runs, kaolinite or andalusite which contained pyrophyllite as an impurity were heated in unsealed capsules. It is possible that partial fusion and the nucleation of corundum took place before all the water escaped. Once formed, corundum will persist practically indefinitely. The appearance of this metastable assemblage was not troublesome in the present work.

#### COMPARISONS WITH OTHER WORK

The present results are compared with those of the previous study (Clark, Robertson, and Birch, 1957) in figure 3. Within the common range of experiment (1000°C to 1300°C) the two sets of data agree to within 1 kilobar. The discrepancy could be reduced by applying a smaller correction for friction and the strength of the pressure medium to the present results, but the difference is probably within experimental error as it stands. It may also be a measure of the width of the zone of indifference between kyanite and sillimanite.

#### Equilibrium Relations between Kyanite and Sillimanite



Fig. 2. Conditions under which the reaction was reversed. Solid squares represent sillimanite formed from kyanite, solid circles represent kyanite formed from sillimanite, and open squares represent unaffected kyanite.

The curves in figure 3 have been extrapolated to low temperatures without regard for other reactions that complicate the stable phase diagram. Natural occurrences suggest the existence of a triple point between andalusite, kyanite, and sillimanite at moderate temperatures and pressures. It has also been suggested, although not demonstrated, that quartz plus corundum have a field of stability (Aramaki and Roy, 1958). This suggestion does not agree well with natural evidence; in the rare cases in which they both occur in the same rock, quartz and corundum are usually separated from each other by an aluminous silicate. One of the commonest occurrences of margarite is as a coating surrounding corundum crystals in quartzose rocks (Pratt and Lewis, 1905).

The slope of the phase boundary determined in the present study is 13.2 bars/degree. This is slightly larger than the value found previously (about 10 bars/degree), but it is decidedly smaller than the slope calculated from room-temperature thermochemical data. Todd (1950) found that the change in entropy of the reaction at room temperature was  $123\pm6$  decijoules/mol°C, and an extensive study of the lattice parameters of kyanite and sillimanite (Skinner, Clark, and Appleman, 1961) shows that the change in volume is  $5.80\pm0.03$  cm<sup>3</sup>/mol. According to these figures, the slope of the phase boundary is  $21.2\pm1.1$  bars/degree.

High-temperature X-ray studies at atmospheric pressure (Skinner, Clark, and Appleman, 1961) show that kyanite has a larger thermal expansion than sillimanite at moderate temperatures.  $(\partial \Delta V / \partial T)_{P=0}$  is about  $0.4 \times 10^{-3}$ cm<sup>3</sup>/mole °C at 200°C and decreases at higher temperatures. The net decrease in  $\Delta V$  between 0° and 1000°C is about  $3\frac{1}{2}$  percent. It is unlikely that this result will be greatly altered at the pressures of the equilibrium curve. The effect of pressure on  $\Delta V$  is likely to be no larger than the effect of temperature

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according to the argument given previously (Clark, Robertson, and Birch, 1957).

The effect of pressure on  $\Delta S$ , the entropy change of the reaction, is given by the Maxwell relation  $(\partial \Delta S/\partial P)_T = -(\partial \Delta V/\partial T)_P$ . At high temperatures the pressure effect is small because  $(\partial \Delta V/\partial T)_P$  is small, and at low temperatures it is small because the pressures of the equilibrium curve are low. The increase in  $\Delta S$  is unlikely to exceed 3 percent under any conditions. The effect of allowing for the derivatives of volume and entropy discussed so far is to increase the slope of the phase boundary, in conflict with the experimental results. But the predicted increase is much less than the reduction in slope of about 50 percent that is required to secure agreement between the high-temperature, high-pressure experimental results and the room-temperature thermochemical data.

Measurements of heat capacity at high temperatures (Kelley, 1949) indicate that a change in  $\Delta S$  with temperature may alter the slope of the phase boundary by roughly the amount required to bring the two sets of data into agreement. The change in slope may be uncertain by as much as 50 percent, however, and no account was taken of the correction in drawing the phase boundary in figure 3 for this reason. Because heat capacities of solids usually depart most widely from their classical values at low temperatures, most of the curvature probably takes place below 500°C. Hence the position of the phase boundary will not be greatly affected by this correction.

#### GEOLOGICAL IMPLICATIONS

The high pressures required to form kyanite stably, which were an unexpected result of the previous work (Clark, Robertson, and Birch, 1957), are substantiated by the present study. Temperatures of a few hundred degrees seem to be required to produce regional metamorphism, which means that a pressure of 7 to 10 kilobars is roughly the minimum compatible with stable formation of kyanite in nature.

Depths of burial are commonly related to pressure by  $P = \rho gh$ , where  $\rho$  is the mean density between the surface and depth h, and g is the gravitational acceleration. The scale at the top of figure 3 has been calculated for  $\rho$  equal to 2.67 gm/cm<sup>3</sup> in the crust and 3.33 gm/cm<sup>3</sup> in the mantle. A depth of more than 35 km is required to reach a pressure of 10 kilobars; this implies that kyanite schists formed at depths equivalent to those towards the base of the "normal" sea-level crust, on this model. This conclusion does not follow if the phase boundary has appreciable curvature at high temperatures, but such behavior, although not impossible, is certainly improbable.

If kyanite-bearing rocks are to be formed at depths in excess of 20 km, large vertical movements must have taken place in the past. Such large amplitudes of motion might accompany the formation of a major mountain root, but they seem unlikely to result from less extreme orogenic episodes. The depth required for the stable formation of kyanite in a mountain root may be greater than that required elsewhere because of the high temperatures that may exist in a thickened crust (Birch, 1950; Clark and Niblett, 1956). This could lead to the formation of zones of kyanite-bearing rocks near the margins of the root, with sillimanite in the central, hot portion. This is the spatial distribution of the aluminosilicates found in New Hampshire, for example (Billings, 1956).

These great depths of burial can be escaped, or at least lessened, if pressures in the crust are sustained by the strength as well as the weight of the overlying rock. The mere existence of deformation in metamorphic terrains implies that stress differences exceeded the strength of the rocks, and the nature of the deformation suggests that the stresses causing it were compressive relative to  $\bar{\rho}$  gh rather than tensile. This implies that the mean of the principal stresses at times exceeds  $\bar{\rho}$  gh. The magnitude of this "tectonic overpressure" is set by the strength of the rocks that support it.

A rough notion of how large the overpressure may become may be obtained from a simple model. Consider a small spherical cavity in the Earth inside which the pressure is P, and suppose that the stress due to the weight of the overlying rock is simply a hydrostatic pressure. In this case the stress difference in the rock surrounding the cavity is zero when  $P = \bar{\rho} gh$ . We now calculate the largest value of  $P_E = P - \bar{\rho} gh$  allowed by the strength of the wall rock.  $P_E$  can be identified with the maximum tectonic overpressure in that it is the maximum mean stress that can be contained. No account of the origin of this pressure is given. It is assumed that tectonic forces do in fact build up the maximum tolerable pressures, and that they are relieved by yielding of the rocks, probably mainly in the vertical direction.

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If the wall rock behaves as a perfectly plastic material obeying the Tresca yield criterion (which in this case states that the maximum stress difference cannot exceed Y, the yield point in simple tension), the maximum permissible value of  $P_B$  is (Hill, 1950, p. 104):

#### $P_E = 2/3 \ Y \ln (E/3(1-\sigma) Y).$

If Poisson's ratio,  $\sigma$ , is set equal to 1/3, and Young's modulus, E, is taken to be 500 kilobars (Birch, Schairer, and Spicer, 1942),  $P_E$  is found to be 3.7 kilobars if Y = 1 kilobar and 0.52 kilobars if Y = 0.1 kilobar. If plastic flow is not allowed in the wall rock,  $P_E = 2/3 Y$ , a result which is identical to that obtained by Birch (1955) from a different argument.

Griggs, Turner, and Heard (1960) have observed tensile strengths greater than 1 kilobar in several rocks at 5 kilobars confining pressure and  $800^{\circ}$ C. As these authors are careful to point out, however, the experimental results refer to rates of strain that may exceed those occurring in nature by a factor as large as  $10^{12}$ . This implies that the strengths of rocks may be substantially smaller under natural conditions than under the conditions of these laboratory tests. This problem is complicated by recrystallization. The strength of a rock under natural conditions may be determined by the relative rates of deformation and recrystallization.

An overpressure persisting for only a few thousand years, a time that is short geologically speaking, could significantly affect the mineralogy of the rock. A value of Y of a few hundred bars might persist for short times during active deformation; this leads to overpressures of 1 kilobar or more. Since 1 kilobar corresponds to the weight of nearly 4 km of overburden in the crust, the reduction in the depth of burial required may be considerable.

Evidence of the existence of tectonic overpressures in rocks, other than the fact that deformation takes place, is usually indefinite. No clearcut distinction between tectonic pressure and deep burial can be made in most regionally metamorphosed terrains, because no way of determining depth independently of pressure has been found. Estimates based on thickness of strata are vitiated by tectonic thickenings and thinnings of unknown magnitude. Although distorted crystals of kyanite are common, they only show that deformation followed growth. It may also have accompanied it, but there is no proof of this. An unusual local occurrence of kyanite is in the contact aureoles of granitic bodies in SW Ankole. Combe (1932) noted that kyanite occurs in the schists only where they have been strongly deformed by the forceful emplacement of the granites.

The hypothesis of tectonic overpressures represents a return to the stress mineral concept of Harker but in modified form. Harker supposed that the fields of stability of minerals were influenced by shear. This idea has fallen into disrepute in recent years, both on theoretical grounds (Verhoogen, 1951; Macdonald, 1957) and because of the occurrence of stress minerals in rocks that show little or no evidence of deformation (Miyashiro, 1949, 1951). Tectonic overpressures provide a different reason for "stress minerals" (most of which are in reality high-pressure minerals) to be associated with shear. In the present view, shearing stresses make possible an increased mean principal

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stress and bring high-pressure minerals into their fields of stability at depths where they would normally be unstable at the prevailing temperature.

The real basis of the stress mineral concept is petrographic observation, although Harker (1939) also cited the experimental evidence then available in its support. The concept is not the result of any single observation, but rather the result of accumulated experience that certain minerals, one of which is kyanite, characteristically occur in strongly deformed rocks. Although Harker's explanation of it is probably wrong, the association of kyanite with deformation nonetheless exists. An attractive feature of the hypothesis of tectonic overpressures is that it provides a natural explanation of some of the observations that formed the basis of the stress mineral concept.

It cannot, of course, be inferred that all kyanite is produced in regions of tectonic overpressure. Considerable depths of burial are undoubtedly necessary as well. It is highly desirable that the rough calculations used here to arrive at an upper limit to the tectonic overpressure be refined and improved as experimental data on the strength of rocks accumulated. A better understanding of the stresses and movements that have affected the Earth's crust can emerge from such work, and this is almost certain to advance our knowledge of orogenic and metamorphic processes.

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