δ-aminolevulinic acid follows the common pathway into the pyrolle rings which are common to the structure of porphyrin and bilirubin. However, the two compounds differ in that glycine is a good heme precursor in vivo whereas δ-aminolevulinic acid is not (*6*). The second component is seen only in those individuals who are given glycine.

Previously we reported that, in dogs given 700 r of total body radiation with resultant marrow aplasia and depressed heme synthesis, labeled bilirubin appeared in the bile with peak activity at 4 hours after administration of glycine-2-C^{14} (*4*). The peak is analogous to the first peak for human plasma. Therefore the first component is present when red cell production is depressed and does not appear to be dependent on erythropoietic heme synthesis. Its appearance at times before the appearance of labeled heme indicates that the heme of hemoglobin is not an obligatory precursor. Its rapid appearance in the plasma in man within 30 to 90 minutes after administration of C^{14}-labeled δ-aminolevulinic acid also suggests that it may represent an anabolic bilirubin formed by a direct pathway from heme precursors.

The second peak seen in human plasma after administration of C^{14}-labeled glycine is analogous to a secondary plateau noted in "bile fistula" dogs with active erythropoiesis. In those dogs with active heme formation following venesection, labeled bilirubin appeared rapidly in the bile with an initial peak at 24 hours; then it fell to a plateau at 48 hours, with plateau activity remaining to the 5th day (*4*). The second component in human plasma and the plateau in the bile of dogs are absent under those circumstances in which heme synthesis from the labeled precursor is minimal or absent, as in man given C^{14}-labeled δ-aminolevulinic acid and in the radiated dog. This suggests that this second component is dependent on the synthesis of labeled heme, and its abolition in the marrow-depleted irradiated dog indicates that it originates in the bone marrow. Its presence on the 3rd or 4th day suggests that it may arise from newly-formed erythrocytes or late normoblasts that took up the pulse of radioactivity as early precursors of red cells (*7*).

L. G. ISRAELS, T. YAMAMOTO
J. SKANDERBEG, A. ZIPURSKY
Medical College, University of Manitoba, Winnipeg, Canada

References and Notes

1. I. M. London, R. West, D. Shemin, D. Rittenberg, *J. Biol. Chem.* **184**, 351 (1950).
2. C. H. Gray, A. Neuberger, P. H. A. Sneath, *Biochem. J.* **47**, 87 (1950).
3. I. M. London and R. West, *J. Biol. Chem.* **184**, 359 (1959); ——, D. Shemin, D. Rittenberg, *ibid.*, p. 365; M. Grinstein, R. M. Bannerman, J. D. Vavra, C. V. Moore, *Am. J. Med.* **29**, 18 (1960); G. W. James and D. Abbot, *J. Clin. Invest.* **40**, 1051 (1961); C. H. Gray and J. J. Scott, *Biochem. J.* **71**, 38 (1959); L. G. Israels and A. Zipursky, *Nature* **193**, 73 (1962).
4. L. G. Israels *et al.*, *Brit. J. Haematol.*, in press.
5. P. G. Cole and G. H. Lathe, *J. Clin. Pathol.* **6**, 99 (1953).
6. J. J. Scott, *Ciba Foundation Symposium on Porphyrin Biosynthesis and Metabolism* (Churchill, London, 1955), pp. 43–59.
7. Supported by a grant from the National Cancer Institute of Canada.

29 November 1962

Aluminum Silicate System: Experimental Determination of the Triple Point

Abstract. *The kyanite-sillimanite-andalusite triple point exists in the pressure-temperature plane at 8 ± 0.5 kb and 300 ± 50°C. Reactions are accomplished experimentally with a Bridgman opposed-anvil press (with an external furnace), modified to provide shearing of the sample charges. All three equilibrium boundaries are proved by reversed reactions.*

Problems of the existence and location of the kyanite-sillimanite-andalusite triple point on the pressure-temperature plane have been of considerable interest to petrologists and geophysicists (*1, 2*). Unfortunately, thermochemical data in this system are not easily obtained, and experimental reactions are difficult.

Kennedy (*3*) reviewed experimental results in the high pressure-temperature range in the system Al_2O_3-SiO_2-H_2O. Clark (*4*) redetermined the equilibrium boundary for kyanite-sillimanite with reversed reactions in the range 900°C, 16 kb to 1500°C, 24 kb with a solid medium press. The other two boundaries, kyanite-andalusite, and andalusite-sillimanite, have not been previously determined because of the difficulties of synthesizing andalusite. Nevertheless, phases closely resembling andalusite have been found in the products of hydrothermal runs (*5*).

The apparatus used in the present study is a Bridgman opposed-anvil press (with external furnace), modified to provide alternating shear action to the specimen. The press was designed by F. Birch and is similar to the one described by Dachille and Roy (*6*). Heat-treated tool steel anvils of ¼-inch working diameter and 1⅛-inch outside diameter were used. The pressure on the specimen was calculated from the ratio of areas and the pressure measured on the large piston with a bourdon gauge; the temperature was measured with a chromel-alumel thermocouple located axially at the base of the lower anvil.

Synthetic gels of composition $Al_2SiO_5 \cdot xH_2O$ fired at 600°C for 6 hours were used to define the stability fields, and all three polymorphs were synthesized. Three naturally occurring materials were used in seeded runs to reverse reactions near the equilibrium boundaries. They are andalusite from Laws, Calif., and Mount Washington, N.H., sillimanite from Monroe, N.Y., and kyanite from Minas Gerais, Brazil. Phases were identified with a Norelco x-ray diffractometer. X-ray patterns of the products were compared with those of the seeded reactants in order to determine whether the seed had grown at the expense of the starting phase. Unless distinct growth of the seed material could be observed, the results were judged inconclusive.

Experimental results are presented in Table 1 and shown diagramatically in Fig. 1. Good agreement is found with the extrapolated extension of Clark's (*4*) kyanite-sillimanite curve. The kyanite-andalusite and andalusite-sillimanite boundaries are located in zones where the experimental results are inconclusive. Reactions are sluggish in these

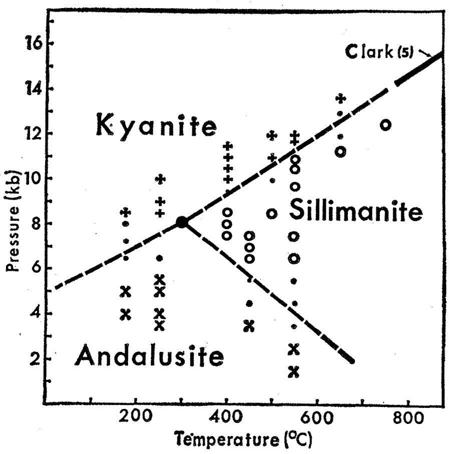

Fig. 1. Syntheses of kyanite, sillimanite, and andalusite. Pluses stand for runs in which kyanite was produced, circles for runs in which sillimanite was produced, and crosses for runs in which andalusite was produced. Dots stand for runs in which the results were inconclusive. The solid line (upper right) is Clark's (*4*) curve.

regions probably because of the extreme refractory nature of the phases themselves. In addition, pressure gradients are known to exist in the specimen at these low pressures (Montgomery *et al.*, 7), but reversed reactions indicate that the boundaries exist. It is important to note that all of the reversed reactions listed in Table 1 were run without the addition of gels or water. This excludes possibilities of hydrous phases predicted by Thompson (*1*), and also of the possibility that $(OH)^-$ ion enters nonhydrous phases.

Table 1. Experimental results in the system Al_2SiO_3. K, kyanite; S, sillimanite; A, andalusite; G, Al_2SiO_5 gel; Q, quartz; C, corundum. Parentheses denote a phase present in relatively minor amounts; in the case of reactants, the minor amounts are seeds introduced in the natural materials.

Temperature (C°)	Pressure (kb)	Time (hr)	Reactants	Products
750	12.5	½	G	S
650	11.3	½	G	S
650	12	½	G	K+S
650	13	½	G	K+S
650	13.7	½	G	K
550	9.7	½	G	S
550	10.5	½	K+(S)	S
550	10.9	½	K+(S)	S
550	11.3	½	S+(K)	S+(K)
550	11.3	½	K+(S)	K+(S)
550	11.7	½	S+(A)	K+(S)
550	12	½	S+(K)	K+(S)
500	8.5	½	G	S
500	10	½	G	K+S
500	11	½	G	K+(S)
500	12	½	G	K
400	7.5	6	G	S
400	8.0	6	K+(S)	S
400	8.5	7	K+(S)	S+(K)
400	8.7	6	G	K+S
400	9.5	12	K+(S)	K+(S)
400	9.5	12	S+(K)	S+(K)
400	10	7	S+(K)	K+(S)
400	10.5	6	S+(K)	K+(S)
400	11	6	G	K
400	11.5	6	G	K+Q+C
550	1.5	½	S+(A)	A+(S)
550	2.5	½	S+(A)	A+(S)
550	3.5	½	S+(A)	S+(A)
550	4.5	½	G	A+S
550	5.5	½	A+(S)	A+(S)
550	6.5	½	A+(S)	S+(A)
550	7.5	½	A+(S)	S+(A)
450	3.5	2	S+(A)	A
450	4.5	3	S+(A)	S+(A)
450	5.5	2	A+(S)	A+(S)
450	6.5	3	G	S
450	7	2	A+(S)	S+(A)
450	7.5	2	A+(S)	S+(A)
250	3.5	8	K+(A)	A+(K)
250	4	7	G	A
250	5	6	G	A
250	5.5	8	K+(A)	K+(A)
250	6.5	12	K+(A)	A+(K)
250	6.5	12	A+(K)	K+(A)
250	7.5	12	K+(A)	A+(K)
250	7.5	8	A+(K)	A+(K)
250	8.4	8	A+(K)	K+(A)
250	9	6	G	K
250	10	7	G	K
175	4	12	G	A
175	5	6	G	A
175	6.5	6	K+(A)	K+(A)
175	6.5	6	A+(K)	A+(K)
175	7.3	6	G	A+K
175	8	6	G	A+K
175	8.5	6	G	K
175	8.5	6	A+(K)	A+(K)

The resulting triple point is located at 8 ± 0.5 kb and 300 ± 50°C. This is in fair agreement with the qualitative diagram of Miyashiro; the curves in Fig. 1 have been drawn on the basis of the values of slopes determined by Skinner *et al.* (*8; 9*).

PETER M. BELL

Dunbar Laboratory, Harvard University, Cambridge, Massachusetts

References and Notes

1. J. B. Thompson, *Am. J. Sci.* **253**, 65 (1955).
2. S. P. Clark, E. Robertson, F. Birch, *ibid.* **255**, 628 (1957).
3. G. Kennedy, in *Advances in Geophysics*, H. E. Landsberg and J. Van Mieghem, Eds. (Academic Press, New York, 1961), p. 320.
4. S. P. Clark, *Am. J. Sci.* **259**, 628 (1961).
5. H. S. Yoder, *Am. J. Sci.* (Bowen vol.), 569 (1952); D. M. Roy, *Am. Mineralogist* **39**, 140 (1954); D. M. Roy and R. Roy, *ibid.* **40**, 147 (1955); H. G. F. Winkler, *Geochim. Cosmochim. Acta* **13**, 42 (1957); J. J. Hemley, *J. Phys. Chem.* **63**, 320 (1959); C. M. Warshaw, *Proc. Natl. Conf. Clays Clay Minerals* **7**, 303 (1960); R. Carr and W. Fyfe, *Geochim. Cosmochim. Acta* **21**, 99 (1960).
6. F. Dachille and R. Roy, in *Modern Very High Pressure Techniques*, R. H. Wentorf, Ed. (Butterworth, Washington, 1962), pp. 163–180.
7. P. W. Montgomery, H. Stromberg, G. H. Jura, G. Jura, *Am. Soc. Mech. Eng. Paper 62-WA-308* (1962), p. 1.
8. B. J. Skinner, S. P. Clark, D. Appleman, *Am. J. Sci.* **259**, 651 (1961); A. Miyashiro, *Geol. Soc. Japan J.* **55**, 218 (1949).
9. Supported by Air Force contract AF19(604)-7319 in conjunction with the Crystal Growth Section of the Air Force Cambridge Research Laboratory, and the Committee on Experimental Geology and Geophysics of Harvard, which supplied the apparatus. The advice and comments of Professors F. Birch, G. Simmons, C. S. Hurlbut, and J. B. Thompson are appreciated.

11 February 1963

Rare-Earth Elements in Tektites

Abstract. *The rare-earth element content of three tektites has been determined by neutron activation analysis. The relative abundance patterns are all nearly alike and are identical to the pattern characteristic of well-differentiated terrestrial sediments. Possible consequences of finding this pattern in truly extraterrestrial matter are considered.*

The problem of the origin of tektites continues to defy solution. Certain of the properties of tektites bespeak a purely terrestrial origin for these glassy objects while other properties seem unexplainable unless tektites arrived on earth from outer space. A résumé of the various postulates of their origin with an extensive bibliography is given in Mason's recent book (*1*).

We have examined the rare-earth element distribution in three tektites. The rare-earth elements are nearly identical in chemical properties, and they act as a coherent group geochemically (*2*). In nature, partial separation of any of the lanthanides from the rest of the group requires a specific process such as fractional crystallization or, perhaps for europium or cerium, may involve a change in oxidation state.

The processes leading to the formation of the several classes of chondritic and some achondritic meteorites have yielded only one distribution pattern for rare earths relative to each other (*3*), a pattern different from any terrestrial material yet studied. This pattern is believed to be that of the presumed homogeneous solar nebula from which solid bodies in the solar system derived.

The only other widespread rare-earth distribution reported is that found in well-differentiated terrestrial sediments (limestones, sandstones, and shales) from North America, Europe, Asia, and Antarctica (*4, 5*). Essentially this same pattern occurs in deep-seated basic and ultrabasic terrestrial rocks (*3, 6*) and is apparently representative of the earth's crust and upper mantle. It is identical with that found in chondrites for the elements europium through lutetium but is increasingly enriched in the lighter elements, so that relative to the heavier lanthanides, lanthanum is about 6 times more abundant in the earth's crust than it is in meteorites. The absolute concentrations of the rare-earth group are 10 to 100 times greater in terrestrial materials than in chondrites. It is plausible to assume that the crustal and upper-mantle distribution resulted from the slow differentiation of a chondritic proto-earth into our present zoned planet, with enrichment of lithophile elements in its outer portions. Each acid igneous rock thus far examined has its own distinct pattern (*7, 8*), usually highly fractionated with respect to the pattern of chondrites or that of sediments. Therefore, the constancy of this distribution in sediments arises solely because their components are extremely well mixed and derived from sufficiently extensive provenances to average out the idiosyncrasies of the various igneous precursors.

Approximately 15-g portions each of an australite, bediasite, and philippinite tektite (*9*) were pulverized and mixed separately for neutron-activation analysis. Some 2-g portions of each were