

NOTES AND NEWS

THE FORMATION OF COESITE AND KYANITE FROM PYROPHYLLITE  
AT VERY HIGH PRESSURES AND HIGH TEMPERATURES

A. A. GIARDINI, J. A. KOHN, D. W. ECKART, AND J. E. TYDINGS  
*U. S. Army Signal Research and Development Laboratory, Fort  
Monmouth, New Jersey*

In the course of studies carried out during the past two years on various chemical systems at elevated pressures and temperatures, the alteration of pyrophyllite specimen capsules was investigated. The pyrophyllite was found to decompose to coesite and kyanite, the present note being a preliminary report on this finding. Additional, more detailed studies will be presented as a portion of a more comprehensive paper at a future date.

A few words are in order concerning pyrophyllite-like materials as components in high-pressure equipment. The use of catlinite as a compressible, solid, pressure transmitting material was first recognized by Bridgman (1938). More recently, massive pyrophyllite (commercially, Tennessee Grade A Lava Stone or Wonderstone) has received wide acceptance both as a solid, pressure-transmitting medium, and as an electrical and thermal insulator in equipment capable of generating sustained very high pressures and high temperatures (Birch and Robertson, 1957; Hall, 1958; Giardini, Tydings and Levin, 1960). Both materials are very fine-grained, relatively homogeneous, hydrous aluminum silicates that are readily machinable. Compositionally, pyrophyllite is relatively pure and can be described by the chemical formula  $H_2Al_2(SiO_3)_4$ , whereas catlinite may contain up to 8 or 9%  $Fe_2O_3$  and occasional traces of quartz. In practice, catlinite generally performs in a manner superior to pyrophyllite because of the high coefficient of static surface friction imparted by the presence of  $Fe_2O_3$ , which tends to restrict flowage under pressure. With respect to availability, however, catlinite is difficult to obtain, whereas pyrophyllite can be purchased in commercial quantities of relatively uniform quality. Consequently, the latter is in general use today in static high-pressure high-temperature devices.

Figure 1 shows a sectioned specimen capsule (graphite charge) before being subjected to elevated pressures and temperatures. A detailed description of the entire pressure apparatus has already been given (Giardini, Tydings and Levin, 1960).

Figure 2 depicts a polished section of a specimen capsule that was stressed at 85 kilobars (1,250,000 psi) and heated to approximately 1600° C. in the vicinity of the charge. The latter in this case was graphite (A, Figure 2), placed between two solid nickel cylinders (B). Note the

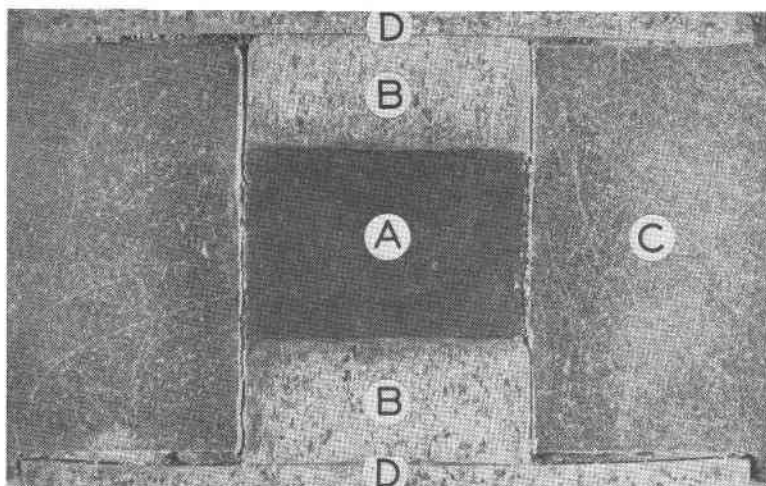


FIG. 1. Axial section of an assembled specimen chamber before stressing: A, graphite charge; B, solid nickel cylinders; C, pyrophyllite ring; D, nickel contact caps. 7.3 $\times$ .

zone of alteration (C) surrounding the charge. Similarly altered zones have been observed when the charge consisted of other materials, *e.g.*, barium titanate, contained within platinum or tantalum electrical resistance heating tubes. In area D, beyond the alteration zone, pyrophyllite was found to be unchanged. It is interesting to note the forma-

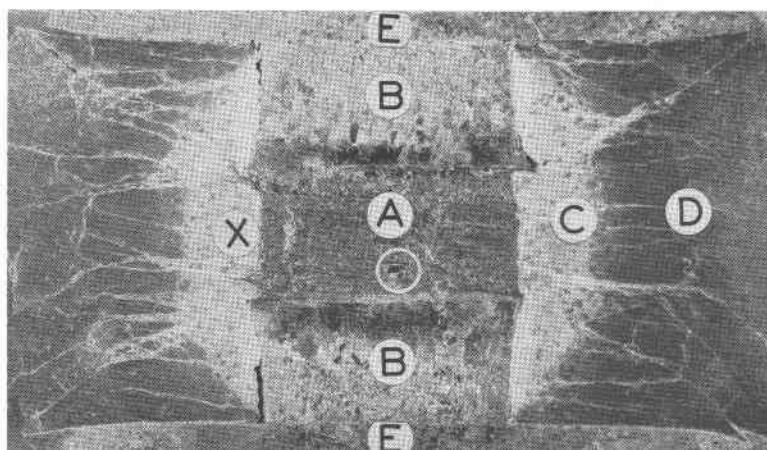


FIG. 2. Axial section of a specimen chamber stressed at 85 kilobars and heated to approximately 1600° C.: A, graphite charge (note circled diamond crystal); B, solid nickel cylinders (note recrystallization); C, altered pyrophyllite; D, unaltered pyrophyllite; E, nickel contact caps. 7.3 $\times$ .

tion of small amounts of  $\text{NiAl}_2\text{O}_4$  (spinel-type) at the interface between the nickel plug and the graphite charge. The aluminate was more abundant at higher temperatures. The graphite charge often showed intrusion by thin coesite veins (Fig. 3), demonstrating a surprising mobility for the silica phase at these pressures.

Polished sections and thin sections (both of these along capsule axis) were examined with a petrographic microscope; a few samples were further studied by electron microscopy. Positive identification of phases

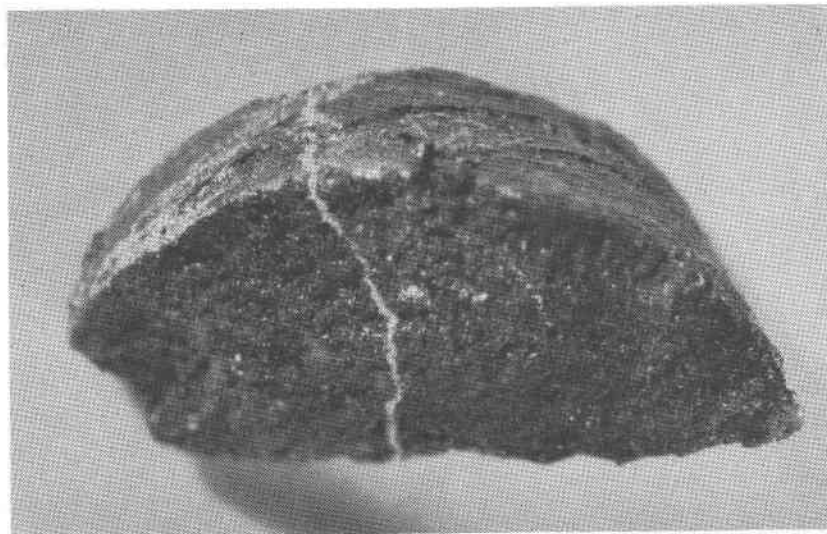


FIG. 3. Graphite charge showing intrusion by thin vein of coesite (30 $\times$ ).

was made by powder  $x$ -ray diffraction of small specimens removed from polished sections. Coesite reference standards were prepared by subjecting quartz, mixtures of quartz and sodium silicate, and sodium silicate alone, all sealed within platinum capsules, to 51 kilobars at 1500 $^\circ$  C.

Table I lists the phases found in zone C (point X) of Fig. 2 at various combinations of temperature and pressure; the charge in this series was barium titanate within a platinum heating tube. Pressures were determined by extrapolation from the first two pressure-induced bismuth electrical resistance discontinuities; the accuracy is approximately  $\pm 5\%$ . Temperatures were obtained by linear extrapolation of input power versus platinum melting point at the particular pressure employed; the accuracy is approximately  $\pm 50^\circ$  at 500 $^\circ$  C. and  $\pm 100^\circ$  at 2000 $^\circ$  C. Coesite and kyanite were invariably the major decomposition products at the more extreme P-T conditions. The tabulated data show the kyanite-

TABLE I. PYROPHYLLITE REACTION PRODUCTS

Pressure (kilobars)	Temperature (° C.)	Reaction Products		
		(principle)	(secondary)	(trace)
10 <sup>-3</sup>	500	pyrophyllite		
10 <sup>-3</sup>	1000	modified pyrophyllite		
10 <sup>-3</sup>	1500	mullite	SiO <sub>2</sub> glass	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
13.5	500	pyrophyllite		
13.5	1000	pyrophyllite		
13.5	1770	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	quartz	
27.0	25	pyrophyllite		
27.0	500	pyrophyllite		
27.0	1000	pyrophyllite		
27.0	1500	kyanite	coesite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
27.0	1900	kyanite	coesite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
40.5	1500	coesite	kyanite	
40.5	2070	coesite	kyanite	
47.25	2100	coesite	kyanite	
54.0	25	pyrophyllite		
54.0	500	pyrophyllite		
54.0	1000	pyrophyllite		
54.0	1500	coesite	kyanite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
54.0	1950	coesite	kyanite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
54.0	2000	coesite	kyanite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
67.5	25	pyrophyllite		
67.5	500	pyrophyllite		
67.5	1000	pyrophyllite		
67.5	1500	coesite	kyanite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
67.5	2000	coesite	kyanite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
81.0	25	pyrophyllite		
81.0	1000	pyrophyllite		
81.0	2000	coesite	kyanite	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>

coesite onset at a temperature between 1000° and 1500° C. and a pressure between 13.5 and 27 kilobars. Kyanite is slightly more predominant than coesite up to a pressure between 27 and 40.5 kilobars, above which coesite is the principal phase. The "modified pyrophyllite" obtained at standard pressure and 1000° C. is essentially a dehydrated phase, the x-ray diffraction pattern of which is only slightly changed from that of the original pyrophyllite. This is probably the same phase as that noted by Carte (1955).

Petrographic examination of the alteration zone material obtained at 67.5 kilobars and 2000° C. showed essentially two phases (Fig. 4): a very fine-grained, markedly birefringent, rod-like material (kyanite), and a somewhat more coarsely grained, flaky phase of lower birefringence

(coesite). The kyanite appeared more uniform in crystallite size, averaging approximately  $1 \times 5 \mu$ . Coesite, on the other hand, showed fragments as small as  $1 \mu$  and large flakes up to  $40 \times 85 \mu$ .

Since the original synthesis of coesite (Coes, 1953), interest in this material has grown steadily, the pace having been quickened by its recent discovery at Meteor Crater, Arizona (Chao, Shoemaker and Madsen, 1960). This positive identification of a natural occurrence firmly estab-

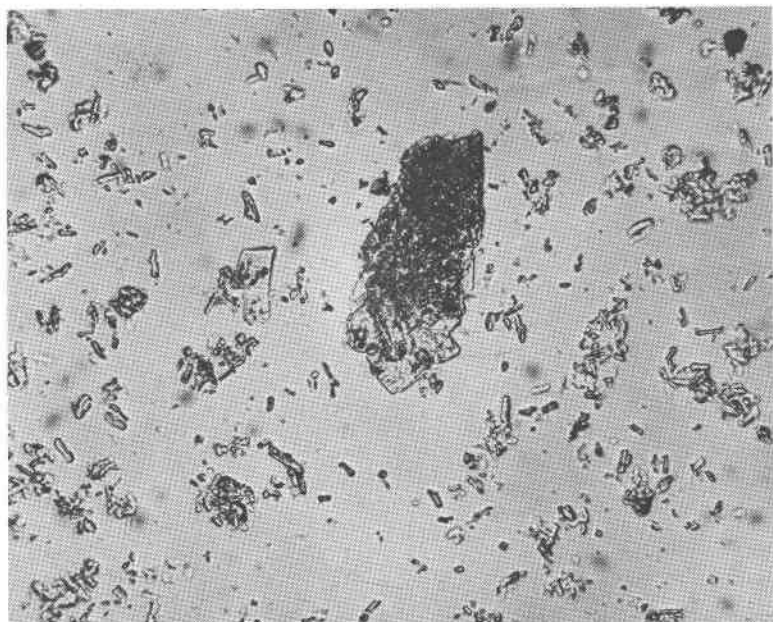


FIG. 4. Photomicrograph showing kyanite (fine-grained, rod-like) and coesite (large flakes) from alteration zone material obtained at 67.5 kilobars and  $2000^{\circ}$  C.; transmitted light, 1.54 immersion oil ( $390\times$ ).

lishes the mineralogical name coesite, as opposed, for example, to the term "silica-C" (Sosman, 1954). The general crystallography of coesite (Ramsdell, 1955) and its crystal structure (Zoltai and Buerger, 1959) have been described, along with further accounts of its synthesis and characteristics (Khitarev, Slutskiy and Arsen'yeva, 1957). In addition, several studies have been made of quartz-coesite relationships (MacDonald 1956; Dacheille and Roy, 1959; Boyd and England, 1960).

As of 1954, the synthesis of kyanite had not yet been achieved, the difficulty having been ascribed to the required octahedral coordination for  $Al^{3+}$  (Roy and Osborn, 1954). More recent investigations, however,

have resulted in successful laboratory preparations of kyanite (e.g., Kennedy, 1955; Clark, Robertson and Birch, 1959).

The Meteor Crater occurrence of coesite has suggested "that the presence of coesite may afford a criterion for the recognition of other impact craters on the earth and perhaps ultimately on the moon and other planets" (Chao, Shoemaker and Madsen, 1960). This possibility has been further discussed in light of a second natural occurrence of coesite at Rieskessel caldera in Bavaria, Germany (Pecora, 1960).

The synthesis of coesite from a complex silicate under laboratory conditions of relatively static pressures and temperatures, as described in this communication, implies that the occurrence of coesite in nature need not be restricted to environments of impact stress upon quartz-rich materials. Relatively long-duration stresses (shear, compressive, or combinations thereof) also will induce coesite formation from silica or from simple or complex silicates, providing that sufficiently high temperatures occur sometime during the period of elevated pressure. Consequently, coesite might be expected to occur in silicate compositions, not only at depths sufficient to provide necessary compressive stress, but also at near-surface localities that have undergone severe metamorphism.

The occurrence of kyanite in nature is almost invariably associated with relatively intense metamorphic activity. The present co-synthesis of kyanite and coesite shows that conditions of stable formation for the two are compatible, at least within the limits covered here. It might be inferred, then, that coesite and kyanite are potentially co-existent natural phases. Should this prove to be the case, once the overall chemistry of a locality is established, the relative abundance of coesite and kyanite could be used to provide information on the pressure-temperature environment. Thus coesite—originally a laboratory curiosity—may prove to be a significant index mineral not only to pinpoint specific natural phenomena, e.g., impact craters, but also to establish the severity of a local geophysical environment.

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Note added in proof: A third natural occurrence of coesite has been found. Chao, Fahey and Littler (1961), Coesite from Wabar Crater, near Al Hadida, Arabia: *Science* **133**, 882-3.

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#### LATTICE CONSTANTS OF SYNTHETIC LAWSONITE

CARL W. F. T. PISTORIUS, *National Physical Research Laboratory,  
Council for Scientific and Industrial Research, Pretoria, Union  
of South Africa*

Natural lawsonite,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , is orthorhombic, space group  $C22_1$  (Pabst 1959), with lattice constants ranging between  $a_0 = 8.82\text{-}8.90$  kX,  $b_0 = 5.76\text{-}5.87$  kX,  $c_0 = 13.19\text{-}13.33$  kX (Gossner and Mussgnug 1931, Wickman 1947, Rumanova and Skipetrova 1959). The remarkable fact that the molar volume of lawsonite, despite its two molecules of water, approximates that of anorthite,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , is an indication that lawsonite might only be stable at high water vapor pressures. The stability of lawsonite should be scarcely affected by load pressure though very strongly influenced by water pressure. Fyfe and Turner (1958) pointed out that this makes lawsonite an excellent indicator of high water pressures.

Pure synthetic lawsonite has, in fact, up to the present moment only been synthesized under conditions of very high water pressure (Coes 1955; Pistorius, Kennedy and Sourirajan, in press). The latter authors