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OPTICAL CRYSTALLOGRAPHY OF COESITE

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Abstract

Coesite prepared from hydrated silica gel between 50 and 80 kb and 700–900 C. in a Belt-type apparatus crystallized as hexagonal platelets flattened parallel to (010) and as lath-shaped crystals flattened parallel to (100) and elongated parallel to the *c* axis. Previous *x*-ray studies showed that coesite is pseudohexagonal and monoclinic; the biaxiality and orientation of its optical indicatrix also reveal its monoclinic character. The optical orientation is $X=b$ and $Z \wedge c = 4°\text{–}6°$ with $\beta=120°$. The optical constants are $\alpha=1.5940$, $\beta=1.5955$, $\gamma=1.5990$ (Na light; all ± 0.0005); $(+)2V=66.5°$ calculated from the indices of refraction, $(+)2V=64°$ measured with the universal stage; weak horizontal dispersion with $r<v$. Coesite is colorless, white when powdered, and has a subconchoidal fracture and a vitreous luster.

Simple contact twins of the normal type with (021) as composition plane are common. They range from anhedral grains to tabular heart-shaped crystals to tabular kite-shaped crystals with increasing morphological development and appear to be flattened normal to the a axis. Twinned crystals have a re-entrant angle of 90°; some have a second re-entrant angle of 62°.

The measured density of coesite is $2.915 \pm .005$. Using unit-cell dimensions of $a=c=7.14$ Å, and $b=12.37$ Å, based on an indexed powder pattern, $Z=16$, and the calculated density is 2.92. Refractive index-density relationships suggest that silicon is tetrahedrally coordinated in coesite in agreement with *x*-ray and infrared absorption results of other workers.

Introduction

Despite widespread interest in the stability (MacDonald 1956; Dachille and Roy, 1959a; Boyd and England, 1960a; Kennedy, 1960) occurrence (Chao *et al.*, 1960; Pecora, 1960; Shoemaker and Chao, 1960; Bunch and Cohen, 1961; Chao *et al.*, 1961; Cohen *et al.*, 1961; Littler *et al.*, 1961; Reid and Cohen, 1961, Shoemaker and Chao, 1961) and structural crystallography (Ramsdell, 1955; Dachille and Roy, 1959a; Zoltai and Buerger, 1959) of coesite, only fragmentary optical data for coesite have appeared in the literature (Coes, 1953; Khitarov *et al.*, 1957; Boyd and England, 1960a; Chao *et al.*, 1960). This paper presents a more complete optical crystallographic description of coesite which should be suitable for determinative purpose.

Synthesis

The coesite used in this study was prepared in a modified Hall Belt apparatus, an internally heated high-pressure device (Hall, 1960), from Davison Grade 923 silica gel. This material contains about 7 per cent of water, and spectrographic analysis showed 0.03 per cent Ca, 0.006 per cent Ti, 0.005 per cent Mg and 0.002 per cent Fe. The applied load for the

Belt apparatus was provided by a modified Hall multiple-piston ram (Hall, 1961) driven with a Sprague air-operated pump. The internal pressure in the Belt apparatus was determined by means of electrical resistance discontinuities of Bi, Tl and Ba, the fixed pressure points for which on the "new" mid-1960 absolute pressure scale are: Bi I–II at 25 kb, T1 II–III at 37.5 kb, Ba II–III at 59 kb, and Bi V–VI at 88 kb (Kennedy and La Mori, 1960, 1961). This apparatus is essentially a linear device to at least 100 kb. Temperatures were determined by means of a platinum/platinum-10 per cent rhodium thermocouple, the junction of which was spot welded to the platinum heater tube which contained the sample.

The optical constants of coesite were determined by immersion methods using sodium light on material prepared from the hydrated silica gel subjected to 75 kb and 775° C. for 115 hours. This run was composed solely of coarse single-crystal anhedral grains of coesite up to 0.9 mm in size. Relatively fine-grained anhedral coesite prepared anhydrously at 80 kb and 900° C. for 75 hours from silica gel which had been preheated at 1200° C. for 8 hours gave the same measured values for the α and γ indices of refraction.

Coesite crystals in experimental products occurred in two habits: hexagonal platelets and euhedral to subhedral laths. The optical orientation of the former was determined on material synthesized from hydrated silica gel subjected to 80 kb and 850° C. for 1 hour. This product was composed solely of discrete euhedral crystals of coesite in the form of hexagonal flakes between 5 and 40 microns in diameter with an average diameter of about 10 microns (Fig. 1). The lath-shaped crystals range between 10 and 40 microns in length and constitute 10 to 20 per cent of runs made from (1) hydrous silica gel pressurized between 50 and 60 kb at temperatures between 700° and 900° C., and (2) dehydrated silica gel run at 80 kb and 900° C. The bulk of these products consisted of anhedral grains and irregular flakes of coesite. *X*-ray powder diffraction patterns of all samples used for optical study were in accord with published *x*-ray powder data for coesite (Coes, 1953; Khitarov *et al.*, 1957; Dachille and Roy, 1959a; Boyd and England, 1960a).

OPTICAL PROPERTIES

The measured optical constants for coesite are given in Table 1. Previously published optical data for coesite are also tabulated for comparison. Noteworthy is the low birefringence of coesite and the very low value for β-α. The optical orientation of the hexagonal platelets[1] and the lath-

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[1] A few 8-sided crystals were observed; the additional pair of faces appears to be $(\bar{1}02)$ and $(10\bar{2})$.

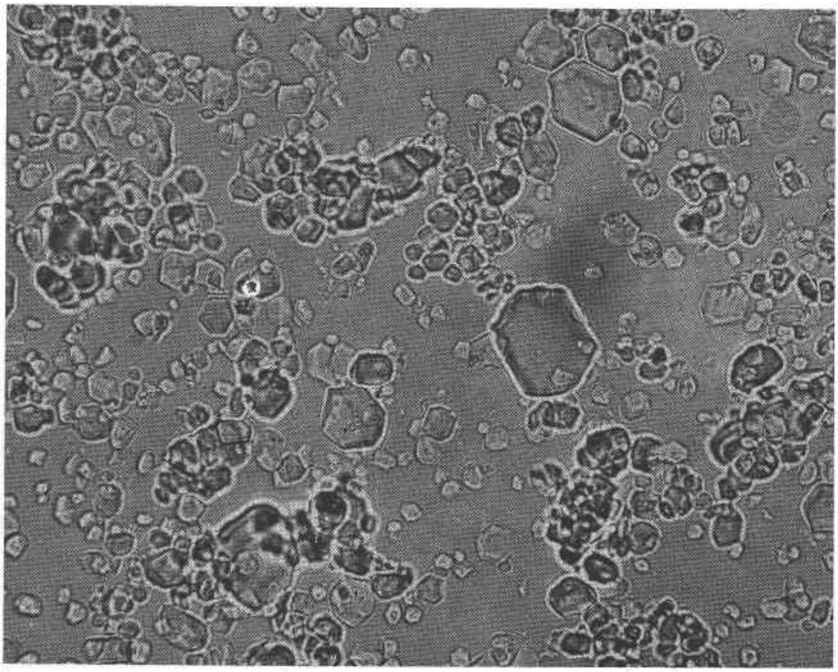

FIG. 1. Photomicrograph of pseudohexagonal platy crystals of coesite synthesized from hydrated silica gel at 80 kb and 850°C. 425×.

shaped crystals is shown in Fig. 2. Although Zoltai and Buerger (1959) chose the *c*-axis as the two-fold symmetry axis to emphasize the dimensional hexagonality of coesite, we have used the traditional monoclinic setting with the *b* axis as the axis of two-fold symmetry in conformity with conventional optical crystallographic practice. This setting was first selected by Ramsdell (1955) in his *x*-ray and morphological study of coesite and was later adopted by Dachille and Roy (1959a).

Despite the hexagonal dimensional symmetry of coesite ($a=c$, $\beta=120°$) revealed by *x*-ray studies (Ramsdell, 1955; Dachille and Roy, 1959a; Zoltai and Buerger, 1959) and the regular 120° angles in the [010] zone (Figures 1 and 2; Zoltai and Buerger, 1959, Figure 2), the distribution of *x*-ray intensities shows that coesite is monoclinic (Ramsdell, 1955; Zoltai and Buerger, 1959). This conclusion is confirmed independently by the distribution of crystal faces in the [010] zone (Ramsdell, 1955, Fig. 2; Zoltai and Buerger, 1959, Fig. 2), the biaxial character of coesite, and the orientation of the optical indicatrix (Fig. 2). The latter shows that extinction in the plane of the pseudohexagonal platelets is not exactly symmetrical, and that Z makes an angle of 4° to 6 with *c*

Table 1. Optical Properties of Coesite

		Present Study	Coes (1953)	Khitarov *et al.* (1957)	Boyd and England (1960a)	Chao *et. al.* (1960)
Indices of Refraction	α	1.5940 ±0.0005 measured in Na light at 28° C. corrected to 25 ° C.	1.599	1.594 ±0.001	1.593 ±0.002	—
	β	1.5955[1]	—	—	—	1.595
	γ	1.5990	1.604	1.597	1.597	—
	$\gamma-\alpha$	0.005±0.001	0.005	0.003±0.001	0.004	Very low
Optic sign:		(+)	(+)	(−)	(+)	—
Optic angle:		66°34′ (calculated from indices of refraction) 64° (measured with universal stage)	54°	61°	64°	—
Dispersion:		Horizontal with $r<v$ (weak)	—	—	—	—
Optic orientation:		$X=b$ $Z\wedge c=4°-6°$ $\beta=120°$	—	—	—	—
Twinning:		Simple contact twins with twin and composition plane (021)	—	Simple contact twinning on (021) and (100)	—	—
Habit:		Hexagonal platelets and euhedral to subhedral laths with (+) elongation and ‖ extinction (synthetic)	Hexagonal plates with "unsymmetrical extinction" (synthetic)	Euhedral laths with (+) elongation and ‖ extinction (synthetic)	Hexagonal plates and laths (synthetic)	Irregular grains (natural)
Color:		Colorless				
Luster:		Vitreous				
Cleavage:		None, subconchoidal fracture				

[1] The calculated value of β using $2V=64°$ is 1.5954.

in the *ac* plane. Because $\beta = 120°$ it is not possible to make a distinction between (001) and $(\bar{1}01)$ morphologically, so that there are two equally valid choices for the *a* axis (Figure 2A). Some hexagonal platelets show elongation parallel to *c*.

The lath-shaped crystals are flattened parallel to (100) and elongated parallel to *c*. As a result, they show parallel extinction and positive elongation in agreement with coesite laths described by Khitarov *et al.* (1957). The terminal angle formed by the intersection of the trace of a terminal face with the *c* axis ranges from about 30° to 60°, and these angles may be different at opposing ends of a euhedral lath in agreement with the morphological characteristics of the [010] zone of coesite (Ramsdell, 1955, Fig. 2; Zoltai and Buerger, 1959, Fig. 2; Khitarov *et al.*, 1957, Fig. 3, 5, 6). Some euhedral laths do not show equal development of all the faces of a terminal form so that they do not appear symmetrical with respect to the *ac* plane (Khitarov *et al.*, 1957, Fig. 5).

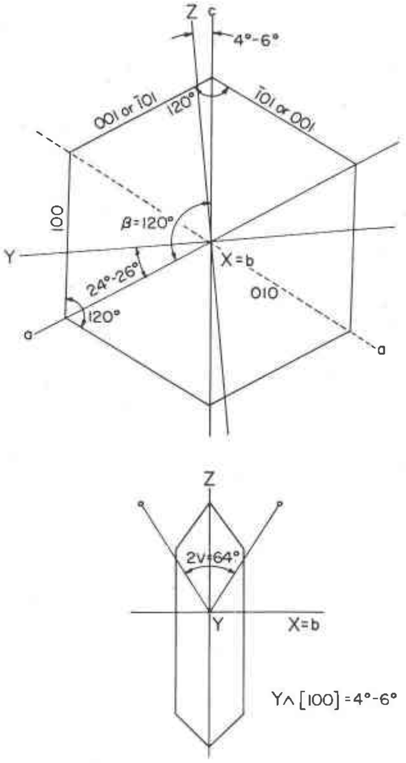

FIG. 2. Optical orientation of coesite. A. (top) Pseudohexagonal platelet of coesite. B. (bottom) Lath-shaped crystal of coesite.

CRYSTAL HABIT

Data at present are too incomplete to draw any generalizations relating the crystal habit of coesite to the p-t conditions of growth. Coes (1953) prepared discrete 0.6 mm pseudohexagonal platy crystals in his internally heated pressure device (Roy and Tuttle, 1956) by reacting dry sodium metasilicate with diammonium phosphate at 700°C. and 40 kb for 16 hours. Boyd and England (1960a, Figure 2) synthesized coesite as 0.4–0.8 mm hexagonal flakes and euhedral laths by pressurizing silicic acid in an anvil apparatus at 24 kb and 700° C. for 2 hours. In the Belt apparatus hydrated silica gel yields euhedral to subhedral laths of coesite between 50 and 60 kb and 700° and 900° C. in 1 hour, and pseudohexagonal plates at 80 kb and 850° C. in 1 hour; dehydrated silica gel yields some laths at 80 kb and 900° C. in 75 hours. The morphological development of coesite appears to be influenced by the type of high-pressure device employed (possibly reflecting internal pressure gradients and shear effects) and the kind of reactant used as much as by the over-all p-t conditions of growth.

TWINNING

Simple contact twins of coesite are fairly common in all experimental products, but most of them are anhedral grains. Those that show some morphological development are tabular flattened approximately normal to the composition plane and the *a* axis, and have heart-shaped to kite-shaped outlines depending on the perfection of the crystal forms. Measurements with the universal stage show that these are normal twins with (021) as the composition and twin plane (Fig. 3) in agreement with *x*-ray studies by Ramsdell (1955). As noted by Ramsdell, the re-entrant angle between (010) and $(\underline{010})$ is 90° with the common edge parallel to the *a* axis. A sketch of a tabular kite-shaped simple contact twin of coesite flattened normal to the *a* axis is shown in Fig. 4. Indices assigned to the crystal faces are based on comparison of microscopically measured angles with interfacial angles calculated from the unit cell dimensions (Table 2). Some of the twins show two re-entrant angles as shown in Fig. 4; others show only the 90° re-entrant angle formed by the intersection of $(0\bar{1}0)$ and $(\underline{010})$, and (010) and $(\underline{0\bar{1}0})$ intersect (021). Ramsdell has reported 100 twinning in coesite by *x*-ray methods, but also points out the absence of morphological evidence for such twinning inasmuch as (001), (011), and $(0\bar{1}1)$ are symmetrically disposed with respect to $(\bar{1}01)$, $(\bar{1}11)$, and $(\bar{1}\bar{1}1)$ so that all faces of a 100 twin can be indexed as if it were a single crystal (Ramsdell, 1955, p. 978). Twinning on (100) was not definitely established in this optical study. The orientation of the optical indicatrix, however, shows that the maximum symmetrical extinction angles against the trace of (100) in the zone normal to (100) would be

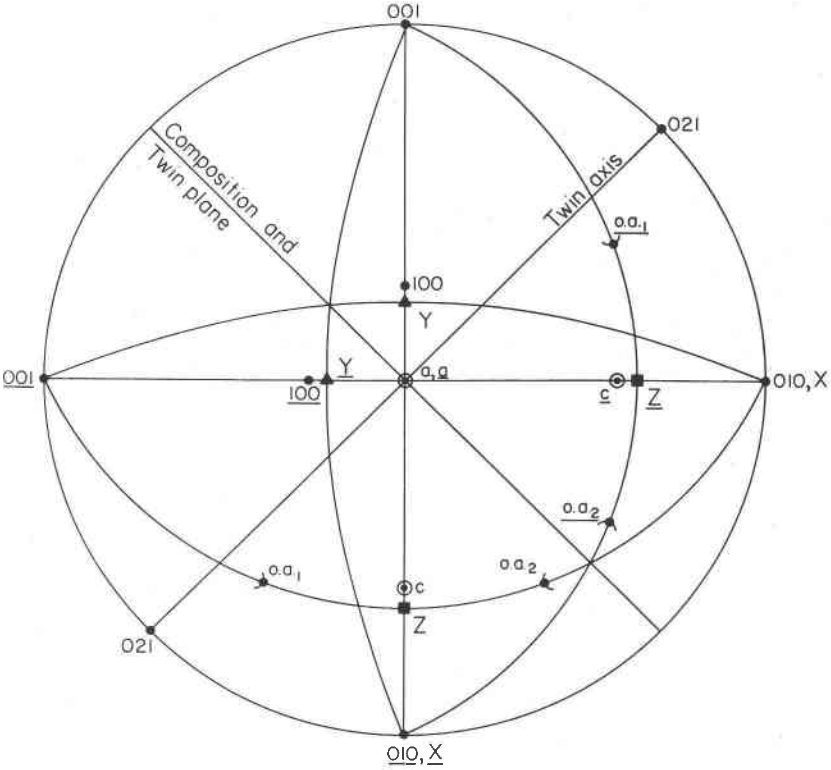

FIG. 3. Stereographic projection of simple contact twin of coesite.

about 5°, and, in view of the low birefringence of coesite in general (0.005) and of sections in the [100] zone in particular (*ca.* 0.0015 to 0.0035), such twins might easily go undetected by optical observation.

DENSITY, UNIT CELL CONTENTS AND UNIT CELL DIMENSIONS

Ramsdell (1955) pointed out that a value of 17 for the unit cell contents (Z) of coesite is obtained from the unit cell dimensions he determined (Table 2) and the density of 3.01 reported by Coes (1953) and checked by himself, whereas the space groups he determined for coesite require that Z be 16. Similarly, Zoltai and Buerger (1959) found that coesite contains 16.6 formula weights of SiO_2 per cell using the cell dimensions they determined (Table 2) and an assumed density of 3.01. To resolve these anamolous values of Z. Dachille and Roy (1959a) redetermined the unit-cell parameters from an indexed powder pattern and measured the density by sink-float as 2.93±0.02. They concluded that that Z=16 and that the theoretical density of coesite is 2.90. The odd

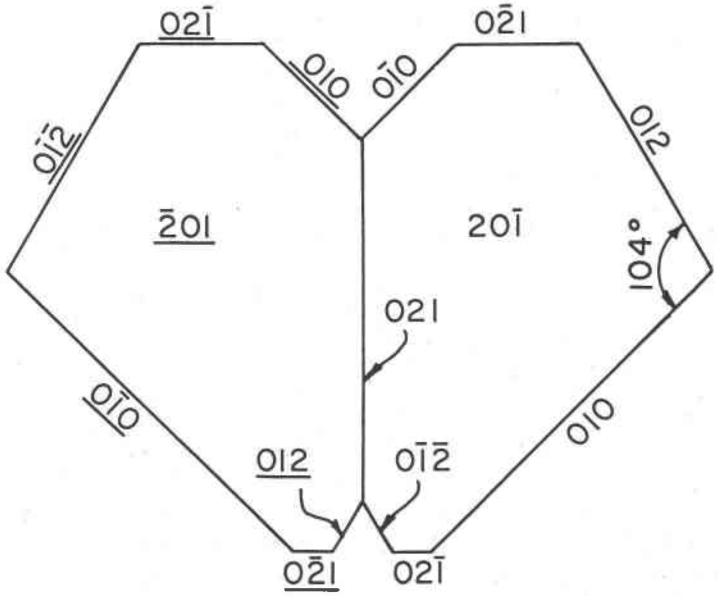

FIG. 4. Sketch of tabular kite-shaped simple contact twin of coesite flattened normal to the a axis. Composition plane: (021); twin axis: [021]; re-entrant angles: $(0\bar{1}0)\wedge(\underline{010})=90°$, $(0\bar{1}\bar{2})\wedge(\underline{012})=62°$

TABLE 2. DENSITY, UNIT CELL DIMENSIONS AND UNIT CELL CONTENTS OF COESITE

	Ramsdell (1955)	Zoltai and Buerger (1959)	Dachille and Roy (1959a)	Present Study
Density	3.01 (measured)	3.01[3]	2.93±0.02 (measured); 2.90 (x-ray)	2.915±0.005 (measured); 2.919 (calculated)
a, Å	7.23	7.17	7.16±0.01 from indexed	7.14±0.01 from indexed
b, Å	12.52	7.17	12.39 powder	12.37±0.01 powder
c, Å	7.23	12.38	7.16±0.01 pattern	7.14±0.01 pattern[4]
β	120°	90°	—	120° (morph.)
γ	90°	120°	—	90° (morph.)
Volume, Å^3	536[1]	550	550	546
Z (calc.)	17[2]	16.6	16	16
Space Group	$C\frac{2}{c}$ or Cc	$B\frac{2}{b}$	—	—

[1] Probably a misprint; the calculated cell volume is 567 Å^3 which when used with a density of 3.01 gives $Z=17.1$.

[2] Ramsdell points out that the space groups require a value of 16.

[3] Taken from measured value of Coes (1953) and Ramsdell (1955).

[4] Pattern obtained with a 114.6 mm camera and Mn-filtered FeKα_1 radiation, $\lambda=1.93597$, from hexagonal flakes produced from silica gel at 80 kb and 850 C3.

TABLE 3. RELATION OF REFRACTIVE INDEX TO DENSITY

	Specific refractivity, $\frac{n-1}{d}$	Specific refraction, $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	Molar refraction (Specific refraction ×mol. wt.)	Specific refractive capacity $\left(\frac{\alpha\beta\gamma}{d}\right)_{\text{coesite}}$ $\left(\frac{\omega^2\epsilon}{d}\right)_{\text{quartz}}$
Coesite	0.204	0.117	7.02	1.393
Low Quartz (1)	0.206	0.119	7.14	1.400
Low Quartz (2)	0.205	0.119	7.14	1.39

$n_{(\text{coesite})} = \sqrt[3]{\alpha\beta\gamma}$.
$n_{(\text{quartz})} = \sqrt[3]{\omega^2\epsilon}$.
(1) Data calculated from $\epsilon=1.553$, $\omega=1.544$, and $d=2.647$ (Swanson *et al.*, 1954).
(2) Data from Allen (1956) based on same values for ϵ and ω and $d=2.664$.

condition of a measured density greater than the *x*-ray density prompted us to redetermine the density of coesite. This was done by a combination of sink-float and pycnometric methods[2] using several 0.5 mm to 0.9 mm single-crystal fragments of coesite from the hydrous 75 kb run which yielded the material on which the optical constants were determined. The density was found to be 2.915±.005. This was confirmed on 0.01 to 0.2 mm particles of coesite prepared anhydrously at 80 kb and 900 C. Coesite, therefore, is 10 per cent denser than quartz.

Based on an indexed powder pattern of the hexagonal flakes of coesite obtained at 80 kb, the cell volume is 546 Å^3 and the value of Z is certainly 16 as stated by Dachille and Roy (Table 2). The calculated density is 2.92. The cell volume of 546 Å^3 is slightly smaller than that previously reported, but the coesite crystals studied by Ramsdell (1955) and Zoltai and Buerger (1959) were produced by chemical reaction at about 40 kb and the coesite examined by Dachille and Roy (1959a) was apparently produced from some form of silica at a pressure less than 40 kb.

The relationship between index of refraction and density may be expressed numerically in several ways (Table 3). As shown by *x*-ray analysis (Zoltai and Buerger, 1959) and supported by infra-red absorption spectra (Dachille and Roy, 1959b), silicon in coesite is tetrahedrally coordinated. Consequently, the numbers calculated for coesite from the refractive index-density equations should be approximately equivalent to those of quartz (Jaffe, 1956; Dachille and Roy, 1959b), and, in fact, the calculated data for coesite (Table 3) are in excellent agreement with those for quartz given by Allen (1956).

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[2] Methylene iodide-benzene and acetylene tetrabromide-carbon tetrachloride solutions whose density was determined by calibrated floats and a pycnometer.

References

Allen, R. D. (1956) A new equation relating index of refraction and specific gravity. *Am. Mineral.*, **41,** 245–257.

Boyd, F. R. and England, J. L. (1960a) The quartz-coesite transition. *Jour. Geophys. Res.* **65,** 749–756.

——— (1960b) Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750 C. *Jour. Geophys. Res.* **65,** 741–748.

Bunch, T. E. and A. J. Cohen (1961) Precambrian coesite (abs.) Paper presented at First Western Nat'l Meeting, Amer. Geophys. Union, Los Angeles, December, 1961.

Chao, E. C. T., J. J. Fahey and J. Littler (1961) Coesite from Wabar Crater, near Al Hadida, Arabia. Science, **133,** 882–883.

——— E. M. Shoemaker and B. M. Madsen (1960) First natural occurrence of coesite. *Science,* **132,** 220–222.

Coes, L. (1953) A new dense crystalline silica. *Science,* **118,** 131–132.

Cohen, A. J., T. E. Bunch and A. M. Reid (1961) Coesite discoveries establish cryptovolcanics as fossil meteorite craters. *Science,* **134,** 1624–1625.

Dachille, F. and R. Roy (1959a) High-pressure region of the silica isotypes. *Zeit. Krist.* **111,** 451–461.

——————— (1959b) The use of infra-red absorption and molar refractivities to check coordination. *Zeit. Krist.,* **111,** 462–470.

Hall, H. T. (1960) Ultra-high-pressure high-temperature apparatus: the "Belt." *Rev. Sci. Inst.,* **31,** 125–131.

——— (1961) High-pressure apparatus, *in Progress In Very High Pressure Research,* 1–8, John Wiley & Sons, New York.

Jaffe, H. W. (1956) Application of the rule of Gladstone and Dale to minerals. *Am. Mineral.* **41,** 757–777.

Kennedy, G. C. (1960) Phase relations of some rocks and minerals at high temperatures and high pressures, *in Advances in Geophysics,* **6,** 303–322, Academic Press.

——— and P. N. LaMori (1960) Fixed pressure points for calibration of high pressures (abs.), *Bull. Geol. Soc. Am.* **71,** 1903.

——————— (1961) Some fixed points on the high pressure scale; *in Progress in Very High Pressure Research,* 304–311, John Wiley & Sons, New York.

Khitarov, N. I., A. B. Slutsky and R. V. Arsenieva (1957) Synthesis and characteristics of coesite—the stable modification of silica at high pressures. *Geokhimiya,* **8,** 666–672 (in Russian).

Littler, J., J. J. Fahey, R. S. Dietz and E. C. T. Chao (1961) Coesite from the Lake Bosumtwi Crater, Ashanti, Ghana (abs.). Paper presented at Annual Meeting of Geol. Soc. Amer., Cincinnati, November, 1961.

MacDonald, G. J. F. (1956) Quartz-coesite stability relations at high temperatures and pressures. *Am. Jour. Sci.,* **254,** 713–721.

Pecora, W. T. (1960) Coesite craters and space geology. *Geotimes,* **5,** 16–19, 32.

Ramsdell, L. S. (1955) The crystallography of "coesite." *Am. Mineral.* **40,** 975–982.

Reid, A. M. and A. J. Cohen (1961) Discovery of coesite in Darwin glass (abs.) Paper presented at First Western Natl. Meeting, Amer. Geophys. Union, Los Angeles, December, 1961.

Roy, R. and O. F. Tuttle (1956) Investigations under hydrothermal conditions, *in Physics and Chemistry of the Earth,* Vol. 1, 138–180, (Fig. 5), Pergamon Press.

Shoemaker, E. M. and E. C. T. Chao (1960) Origin of the Ries Basin, Bavaria, Germany, (abs.) *Bull. Geol. Soc. Am.* **71,** 2111–2112.

——— (1961) New evidence for the impact origin of the Ries Basin, Bavaria, Germany. *Jour. Geophys. Res.*, **66,** 3371–3378.

SWANSON, H. E., R. K. FUYAT AND G. M. UGRINIC (1954) Standard X-Ray Diffraction Powder Patterns, Vol. III, *Nat. Bur. Stand., Circ.* **539,** 25.

ZOLTAI, T. AND M. J. BUERGER (1959) The crystal structure of coesite, the dense high-pressure form of silica. *Zeit. Krist.* **111,** 129–141.

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