

MINERALOGICAL NOTES

those caused by absorption, overvoltage, characteristic fluorescence, background fluorescence. These results show that the Vlakfontein mackinawite is nickelian, justifying the name "nickelian

of this mineral as mackinawite has been determined by electron microscopy and comparison with the published data of the Outokumpu material. The cell parameters of this data.

Hardness, composition and cell-size data of Vlakfontein compared with data determined by the author together with published data from Outokumpu are given where possible. All of these data are given in

CONCLUSIONS

It is seen that the cell size of mackinawite increases with increasing nickel content and consequently hardness would be expected to decrease in cell size away from the iron-rich end. This is demonstrated though with respect to nickel, since it is not yet to be recorded. Variations in reflectivity and the birefringence (R_G-R_p at 589 nm wavelength) of the material is exceptionally high (22.2%). However, the orientations available for measurement may be limited for both reflectivity and microhardness. Variation in total metal content suggests a deficiency or may not be real. If real, the outstanding may be related to this. In spite of the discovery of mackinawite at Vlakfontein, mackinawite compositions are very restricted area of compositions, in which there may be a restriction imposed by structure or due to the metals.

ACKNOWLEDGEMENTS

This work was carried out at Imperial College, London, with the support of the Natural Environment Research Council. The permission of Dr. A. P. Millman to whom grateful thanks are due for advice regarding electron-probe microanalysis at Imperial College for preparation of the material.

REFERENCES

- C. MILTON (1963) Vallerite and mackinawite. *Abstracts of the Mineralogical Society* 73, p. 147.

MINERALOGICAL NOTES

1193

- EVANS, H. T., C. MILTON, E. C. T. CHAO, T. ADLER, C. MEAD, B. INGRAM, AND R. A. BERNER (1964) Vallerite and the new iron sulphide mackinawite. *U. S. Geol. Surv. Prof. Pap.* 475-D, 64-69.
- KUOVO, O., Y. VUORELAINE, AND J. V. P. LONG (1963) A tetragonal iron sulphide. *Amer. Mineral.* 48, 511-524.
- SINGH, D. S. (1965) Measurement of spectral reflectivity with the Reichert microphotometer. *Trans. Inst. Min. Metall. (London)* 74, (Part 14) 901-916.
- WAGNER, P. A. (1929) *Platinum Deposits and Mines of South Africa*. Oliver and Boyd, London.
- YOUNG, B. B. AND A. P. MILLMAN (1964) Microhardness and deformation characteristics of ore minerals. *Trans. Inst. Min. Metall. London* 73, (Part 7) 437-466.

THE AMERICAN MINERALOGIST, VOL. 54, JULY-AUGUST, 1969

ELASTIC PROPERTIES OF FLUORAPATITE

HYO SUB YOON AND R. E. NEWNHAM, *Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802.*

ABSTRACT

The elastic constants of Durango fluorapatite have been determined using the ultrasonic pulse superposition method. Room-temperature adiabatic stiffnesses are c_{11} 1.434, c_{33} 1.805, c_{44} 0.415, c_{12} 0.445, c_{13} 0.575, c_{66} 0.495 megabars. Comparison is made with measurements on bones and teeth.

Apatite occurs extensively in igneous rocks and is the most abundant phosphate mineral. It is also an important constituent of teeth and bones, so that its mechanical properties are of considerable medical interest. The elastic constants previously reported by Bhimasenachar (1945) have been questioned by Chung and Buessem (1967) who note a substantial deviation from the shear anisotropy curve obeyed by most hexagonal crystals. Because of their biological significance, we have re-measured the adiabatic stiffness coefficients of apatite by the ultrasonic pulse superposition technique.

Gem-quality yellow apatite from Durango, Mexico, was used in the ultrasonic experiments. Flawless, rectangular prisms about 1 cm³ in volume were cut from two large hexagonal crystals after orienting the specimens from back-reflection Laue photographs. Scraps from the two crystals were used for the chemical analyses given in Table 1. The two are nearly identical in composition, and compared to other fluorapatites (Deer, Howie and Zussman, 1962) show unusually large silica and rare earth concentrations, but very little MnO. Densities were determined by

the hydrostatic weighing method (Smakula and Sils, 1955) with distilled water as the immersion liquid. Both specimens were again identical within experimental error and a value of $3.2147 \pm .0004$ g/cc was used in computing elastic constants.

In the pulse superposition method (McSkimin and Andreatch, 1962, and McSkimin, 1965) a high-frequency quartz transducer is cemented to the specimen and an electrical signal is applied to the transducer, which in turn initiates an acoustic pulse in the sample. After traveling through the crystal, the acoustic pulse is reflected from the opposite face and returns to the transducer as an echo. There it excites an electric signal which is detected and displayed on an oscilloscope. Ultrasonic velocities are calculated from the delay time and specimen length with small corrections for the bonding material, salol (phenyl salicylate, m.p. 43°C). A short series of pulses spaced by the round-trip delay time are applied to enhance the echo by multiple reflection. X- and AC- cut quartz plates with resonant frequencies near 20 MHz are used to generate longitudinal and transverse pulses, respectively.

Apatite belongs to crystal class $6/m$ for which there are five independent stiffness coefficients relating stress to strain.

$$(c_{ij}) = \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix},$$

where $c_{66} = 1/2 (c_{11} - c_{12})$. Measurements are referred to right-handed orthogonal axes X_1, X_2, X_3 parallel to crystallographic directions [100], [120] and [001]. Hexagonal materials are transversely degenerate so that all directions in (00.1) are equivalent.

Pure mode directions for the hexagonal system have been derived by Brugger (1965). Three coefficients are determined from the density ρ , and the longitudinal and two transverse wave velocities along X_1 : $\rho v_L^2 = c_{11}$, $\rho v_T^2 = c_{66}$ and $\rho v_t^2 = c_{44}$. Measurements along X_3 give $\rho v_L^2 = c_{33}$ and $\rho v_T^2 = \rho v_t^2 = c_{44}$. A specimen cut at 45° to X_3 gives one pure mode $\rho v_T^2 = 1/2 (c_{44} + c_{66})$, and two mixed modes from which the remaining constant c_{13} is obtained.

$$c_{13} = [(c_{11} + c_{44} - 2\rho v^2)(c_{33} + c_{44} - 2\rho v^2)]^{1/2} - c_{44}.$$

Table 2 gives the experimental sound wave velocities from which the

SIC
Total ra
P.O
Ca
F
Cl
H
H

Analy
elastic
locity
only 0
differ
and g
sugges
ments
variab
It is

Table

Prop

method (Smakula and Sils, 1955) with distilled liquid. Both specimens were again identical and a value of $3.2147 \pm .0004$ g/cc was used in

n method (McSkimin and Andreatch, 1962, a-frequency quartz transducer is cemented to cal signal is applied to the transducer, which pulse in the sample. After traveling through lse is reflected from the opposite face and re- an echo. There it excites an electric signal ayed on an oscilloscope. Ultrasonic velocities ay time and specimen length with small cor- material, salol (phenyl salicylate, m.p. 43°C). ced by the round-trip delay time are applied to iple reflection. X- and AC- cut quartz plates ear 20 MHz are used to generate longitudinal ectively.

al class 6/*m* for which there are five indepen- elating stress to strain.

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix},$$

Measurements are referred to right-handed X_3 parallel to crystallographic directions [100]. nal materials are transversely degenerate so l) are equivalent.

or the hexagonal system have been derived by coefficients are determined from the density ρ . l two transverse wave velocities along X_1 : $\rho v_L^2 = c_{44}$. Measurements along X_3 give $\rho v_L^2 = c_{33}$ and cut at 45° to X_3 gives one pure mode $\rho v_T^2 = 1/2$ l modes from which the remaining constant c_{11}

$$c_{44} - 2\rho v_T^2)(c_{33} + c_{44} - 2\rho v_T^2)^{1/2} - c_{44}.$$

imental sound wave velocities from which the

TABLE 1. CHEMICAL ANALYSIS OF TWO CRYSTALS OF DURANGO APATITE

Wet Chemical Analysis			Spectrographic Analysis		
Wt%			Wt%		
SiO ₂	1.3	1.2	CeO ₂	0.70	0.70
Total rare earth	1.3	1.4	Y ₂ O ₃	0.076	0.079
P ₂ O ₅	41.0	41.4	La ₂ O ₃	0.49	0.49
CaO	52.8	52.3	ThO ₂	0.013	0.013
F ₂	3.2	3.4	SrO	0.068	0.064
Cl ₂	0.48	0.60	Fe ₂ O ₃	<0.05	<0.05
H ₂ O ⁺	0.17	0.10	BaO	<0.001	<0.001
H ₂ O ⁻	N.F.	N.F.	TiO ₂	<0.001	<0.001
			Al ₂ O ₃	<0.01	<0.01
			MnO	0.01	0.01
			MgO	<0.01	<0.01
			As, U, V	<0.01	<0.01
			Density (g/cc)		
				3.2147	3.2140

Analysts: Joseph B. Bodkin and N. H. Suhr.

elastic constants in Table 3 are computed. The eight independent velocity measurements provide cross-checks on c_{44} , c_{66} and c_{13} , differing by only 0.1, 0.4 and 3.0 percent, respectively. The re-determined constants differ significantly from the values reported by Bhimasenachar (1945) and give shear and compression anisotropies satisfying the relations suggested by Chung and Buessem (1967). Bhimasenachar's measurements were also on yellow Durango apatite ($\rho = 3.218$), but he used a variable-frequency resonance technique and much thinner specimens.

It is interesting to compare the elastic properties of fluorapatite with

TABLE 2. ULTRASONIC VELOCITIES FOR TRANSVERSE AND LONGITUDINAL WAVES IN FLUORAPATITE. DIRECTIONS REFER TO ORTHOGONAL AXES X_1 , X_2 , X_3

Propagation Direction	Displacement Direction	Velocity (km/sec)
X_1	X_1	$v_L = 6.680 \pm .005$
	X_2	$v_T = 3.922 \pm .003$
	X_3	$v_t = 3.590 \pm .003$
X_3	X_3	$v_L = 7.493 \pm .002$
	X_1	$v_T = 3.593 \pm .001$
45° to X_1 & X_3	$\sim 45^\circ$ to X_1 & X_3	$v = 6.867 \pm .004$
	X_2	$v_T = 3.765 \pm .002$
	$\sim 45^\circ$ to X_1 & $-X_3$	$v = 3.982 \pm .003$

TABLE 3. ROOM-TEMPERATURE ELASTIC CONSTANTS OF FLUORAPATITE. STIFFNESS COEFFICIENTS c_{ij} ARE GIVEN IN MEGABARS (10^{12} DYNES/CM²) AND ELASTIC COMPLIANCES s_{ij} IN RECIPROCAL MEGABARS

	Present Work	Bhimasenachar (1945)
c_{11}	1.434 (2)	1.667
c_{33}	1.805 (1)	1.396
c_{44}	0.415 (1)	.663
c_{12}	0.445 (3)	.131
c_{13}	0.575 (17)	.655
c_{66}	0.495 (2)	.76~
s_{11}	0.836 (5)	.748*
s_{33}	0.688 (10)	1.088
s_{44}	2.411 (3)	1.508
s_{12}	-0.175 (5)	.097*
s_{13}	-0.210 (10)	-.397
s_{66}	2.022 (8)	1.302

* Corrected for conversion errors pointed out by Hearmon (1956).

bone, which can be crudely approximated as a two-phase composite of hydroxyapatite and collagen. The apatite crystals in bone are small fibers about 40 Å across and 600 Å long (Engström, 1960), sometimes showing preferred orientation. Bones with a specific gravity of 1.8 contain about 30% hydroxyapatite by volume (Robinson, 1960). Measured values of Young's modulus (E) for similar bones range between 0.16 and 0.22 megabars (Smith and Keiper, 1965). Tooth cusp enamel is much less compliant, $E \sim 0.5$ megabars (Stanford; et al, 1958) and contains about 80% apatite.

Assuming equal strains, the law of mixtures applies to a two-phase composite, so that $E_b = E_a V_a + E_c V_c$, where E is Young's modulus, V the volume fraction, and subscripts a, b, c refer to apatite, bone, and collagen, respectively. Using the Voigt-Reuss-Hill averaging procedure (Hill, 1952) which is approximately correct for polycrystalline solids without voids, the new elastic constants in Table 3 give $E_a = 1.19$ megabars. Measurements of E_c have not been reported, but Young's moduli for similar materials are at least an order of magnitude smaller than apatite, so that $E_a \gg E_c$ and $E_b \cong E_a V_a$. This equation predicts values for E_b about twice the measured values for teeth and bones. There are several possible reasons for the discrepancy. The law of mixtures is probably inaccurate, since it is unlikely that apatite and collagen strain equally. Bone is much more complicated than the two-phase model assumes: the interspersed pore space, water and living tissue undoubtedly weaken it mechanically. Single crystal fluorapatite is probably stiffer

than the
phous
predic

The
work wa
Contract
tract No

BHIMASE
214.

BRUGGE
768.

CHUNG
1102

DEER, V
WH

ENGSTROM
E. I

HEARMON
349

HILL, R
A6.

McSKIN
804

ROBINSON
104

SMITH
804

STANFORD
104

TERME
104

ELASTIC CONSTANTS OF FLUORAPATITE. STIFFNESS
IN MEGABARS (10^{12} DYNES/CM²) AND ELASTIC
CONSTANTS s_{ij} IN RECIPROCAL MEGABARS

Present Work	Bhimasenachar (1945)
1.434 (2)	1.667
1.805 (1)	1.396
0.415 (1)	.663
0.445 (3)	.131
0.575 (17)	.655
0.495 (2)	.76
0.836 (5)	.748*
0.688 (10)	1.088
2.411 (3)	1.508
-0.175 (5)	.097*
-0.210 (10)	-.397
2.022 (8)	1.302

Values pointed out by Hearmon (1956).

may be approximated as a two-phase composite of apatite and collagen. The apatite crystals in bone are small, about 600 Å long (Engström, 1960), sometimes 1000 Å long. Bones with a specific gravity of 1.8 contain about 60% apatite by volume (Robinson, 1960). Measured values of E for similar bones range between 0.16 and 0.20 (Keiper, 1965). Tooth cusp enamel is much less porous (Stanford; et al, 1958) and contains about 95% apatite.

If the law of mixtures applies to a two-phase composite, $E = E_a V_a + E_b V_b$, where E is Young's modulus, V the volume fraction, and the subscripts a, b, c refer to apatite, bone, and collagen. The Voigt-Reuss-Hill averaging procedure is approximately correct for polycrystalline solids. The elastic constants in Table 3 give $E_a = 1.19$ megabars. Values of E_b have not been reported, but Young's modulus for bone is at least an order of magnitude smaller than that for apatite and $E_b \cong E_a V_a$. This equation predicts values of E for teeth and bones. There are large discrepancies for the discrepancy. The law of mixtures is probably not applicable. It is unlikely that apatite and collagen strain independently. The problem is more complicated than the two-phase model as bone contains water and living tissue undoubtedly. Single crystal fluorapatite is probably stiffer

than the hydroxyapatite found in bones, much of which appears amorphous (Termine and Posner, 1966). All these factors tend to lower the predictions for E_b , bringing them closer to experiment.

ACKNOWLEDGMENTS

The authors wish to thank Drs. Z. P. Chang and J. H. Gieske for their assistance. This work was sponsored in part by the Army Materials and Mechanics Research Center, Contract No. DA 19-066-AMC-325 (X), and in part by the Office of Naval Research, Contract No. N(ONR)-656(27).

REFERENCES

- BHIMASENACHAR, J. (1945) Elastic constants of apatite. *Proc. Indian Acad. Sci.* **A22**, 209-214.
- BRUGGER, K. (1965) Pure modes for elastic waves in crystals. *J. Appl. Phys.* **36**, [3], 759-768.
- CHUNG, D. H., AND W. R. BUESSEM (1967) The elastic anisotropy of crystals. In *International Symposium on Anisotropy in Single Crystal Refractory Compounds*, sponsored by Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock-Forming Minerals*, Vol. 5. John Wiley and Sons, New York, p. 325.
- ENGSTRÖM, A. (1960) Ultrastructure of bone material. In K. Rodahl, J. T. Nicholson and E. M. Brown, Jr. (eds.), *Bone as a Tissue*. McGraw-Hill, New York, 251-261.
- HEARMON, R. F. S. (1956) The elastic constants of anisotropic materials-II. *Adv. Phys.* **5**, 346.
- HILL, R. (1952) The elastic behaviour of a crystalline aggregate. *Proc. Phys. Soc. (London)* **A65**, 349-354.
- McSKIMIN, H. J. (1965) Variations of the ultrasonic pulse-superposition method for increasing the sensitivity of delay-time measurements. *J. Acoust. Soc. Amer.* **37**, [5], 864-871.
- , AND P. ANDREATCH (1962) Analysis of the pulse superposition method for measuring ultrasonic wave velocities as a function of temperature and pressure. *J. Acoust. Soc. Am.* **34**, [5], 609-615.
- ROBINSON, R. A. (1960) Chemical analysis and electron microscopy of bone. In K. Rodahl, J. T. Nicholson and E. M. Brown, Jr. (eds.), *Bone as a Tissue*, McGraw-Hill, New York, 186-250.
- SMAKULA, A., AND V. SILS (1955) Precision density determination of large single crystals by hydrostatic weighing. *Phys. Rev.* **99**, 1744-1746.
- SMITH, R. W., JR. AND D. A. KEIPER (1965) Dynamic measurement of viscoelastic properties of bone. *Amer. J. Med. Electron.* **4**, [4], 156-160.
- STANFORD, J. W., G. C. PAFFENBARGER, J. W. KUMPULA, AND W. T. SWEENEY (1958) Determination of some compressive properties of human enamel and dentin. *J. Amer. Dent. Assoc.* **57**, [Oct.], 487-495.
- TERMINE, J. D., AND A. S. POSNER (1966) Infrared analysis of rat bone: age dependency of amorphous and crystalline mineral fractions. *Science* **153**, 1523-1525.