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ELASTIC PROPERTIES OF FLUORAPATITE

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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

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	~45° to X_1 & X_3	$v = 6.867 \pm .004$
	X_2	$v_T = 3.765 \pm .002$
	~45° 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 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.

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