Low-temperature heat capacity of bone

The development of models for biomechanical behaviour has been handicapped by the insufficient thermodynamic data on bone. Hopkins *et al.* [1] measured the heat capacity of flourapatite, $Ca_5(PO_4)_3F$. Chu [2] used these data to correlate the phonon mean free-path in bone with the dimensions of the hydroxyapatite crystallites in bone. He found that the specific heat of $Ca_5(PO_4)_3F$ is lower, by a factor of 8, than the estimated values derived from sound velocity assuming a Debye model. Thus, a Debye model is presumably also insufficient to provide specific heat values for hydroxyapatite (HAP). The heat capacity of synthetic HAP has been reported as early as 1951. This paper reports the heat capacity of bone between 30 and 240 K, and the thermodynamic functions in terms of entropy and enthalpy have been derived from these data.

The sample was taken from the right femur of an 18-month cow; a section from the mid-diaphysis was cut with the length in approximately the same direction as the bone axis. A low-speed saw with a diamond blade (4″ in diameter and 0.012″ in thickness) was used with distilled water as the lubricant and coolant during the cutting. After the periosteum was removed, the sample was dried for 24 h at 100° C under vacuum, during which the mass was reduced from 27.56 to 25.05 g.

An Evanohm resistance heater (1000 ohm) was wound non-inductively around the sample with a minute amount of GE 7031 varnish for thermal anchoring. For temperature determinations, a Lake–Shore platinum thermometer was greased and inserted into a tight-fitting hole drilled along the length of the sample.

Heat capacity, C, measurements were made between 30 and 240 K in a conventional adiabatic calorimeter, using pulsed Joule heating to induce small temperature increments of the sample. The experimental data are shown in Fig. 1.

The values of heat capacity are matched to the equation

$$C = a_0T + a_1T^2 + a_2T^3 + a_3T^4 + a_4T^5,$$

using a least-square fit program, from which the entropy, S, and enthalpy, H, values were also derived and are shown in Fig. 2. Fig. 3. shows the present heat capacity results compared with those

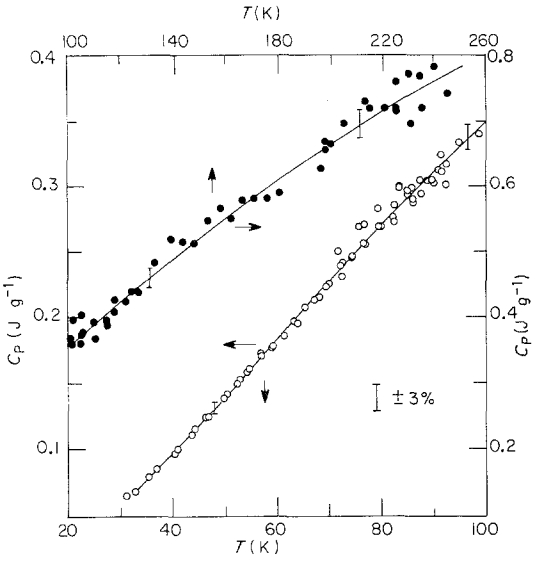

Figure 1 Experimental values of heat capacity of bone plotted against temperature.

of hydroxyapatite and flourapatite from the previous work by Egan *et al.* [3] and Hopkins *et al.* [1], respectively. The higher values for the bone sample are probably due to the relatively large contribution of its organic components. For the same reason, it is expected that the heat-

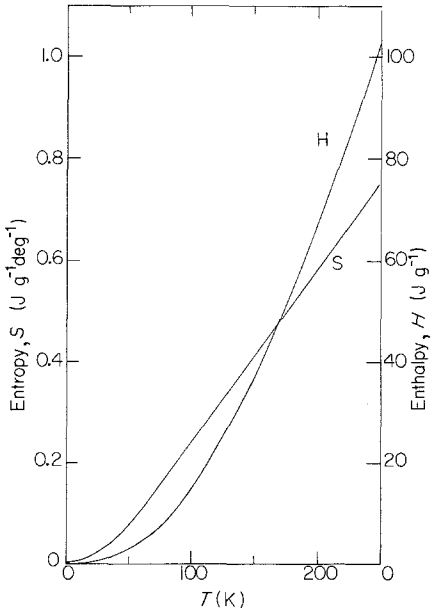

Figure 2 Estimated values of entropy and enthalpy of bone plotted against temperature.

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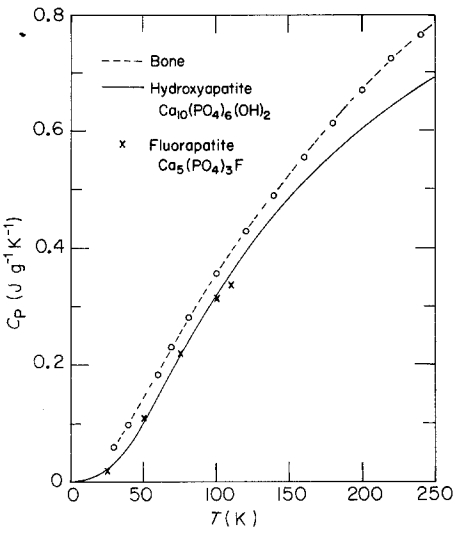

Figure 3 Heat capacity of bone (- - - -), hydroxyapatite (———) and fluorapatite (x) plotted against temperature.

capacity data cannot be fitted to any simple model such as a Debye Function, even though they do increase monotonically with temperature, much in the same way as do the data for the apatite crystals. Using the measured values for HAP of Egan *et al.* it is seen that $(C_{bone} - C_{apatite})/C_{bone}$ varies from 12 to 21% between 40 and 240 K. Thus, between 80 and 90% of the contribution to the total specific heat may be attributed to apatite in bone. This is almost in proportion to the weight of apatite in bone. The bulk thermal expansion coefficient of collagen is about 20 times the longitudinal expansion coefficient of collagen fibres [4]. As a result, there is an anisotropy in the thermal expansion coefficient in bone which, however, disappears when bone is de-organified [4]. Thus, a Debye model would be inappropriate as a framework to analyse the specific heat of bone unless its vibrational spectra are characterized by several Debye temperatures.

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References

1. R. H. HOPKINS, D. H. DAMON, M. S. PIOTROWSKI, J. H. WALKER and J. UTHOFF, *J. Appl. Phys.* **42** (1971) 272.
2. T. K. CHU, *J. Appl. Phys.* **43** (1972) 3207.
3. E. P. EGAN, Jr, Z. T. WAKERFIELD and K. L. ELMORE, *J. Amer. Chem. Soc.* **72** (1950) 2418.
4. A. R. LIBOFF and M. H. SHAMOS, in "Biological Mineralization" edited by I. Zipkin (John Wiley, New York, 1973) p. 335.

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