05.2-18 THE RELATIONSHIP BETWEEN STRUCTURE, HYDROXYAPATITE CRYSTALLITE ORIENTATION AND ELASTIC PROPERTIES OF 12,000 YEARS OLD IRISH ELK HORN. By J.L. Katz, B. Roger*, P. Christel*, L. Sedel*, A. Meunier*, Biomedical Engineering Dept., Rensselaer Polytechnic Institute, Troy, NY

We have been involved in a joint research program with Drs. A.C. Kitchener, G.E. Bacon and J.F.V. Vincent (University of Reading) on the relationship between hydroxyapatite (HAp) crystallite orientation and the elastic properties of antler horn from the extinct Irish Elk. Our colleagues have measured the ratio of intensities of the 002 and 111 reflections in the neutron diffraction pattern of specimens from the dorsal, ventral, anterior and posterior quadrants of one of these 12,000 year old antlers. The 111 intensity is essentially a count of the total number of crystallites being measured within the specimen, while the 002 intensity is a measure of the number of crystallites whose "c" axes are parallel to a specific direction. For a randomly oriented powder of hydroxyapatite, the ratio of 002/111 intensities is very nearly unity. In the femur of a 20 year old human the 002 reflection is enhanced 3-fold over that found in the random powder, indicating a preferred orientation of crystallites whose "c" axes are aligned along the long axis of bone (G.E. Bacon, R.K. Griffiths, "Texture, stress and age in the human femur", J. Anat. (1951) 143, 97-101). Kitchener et al report that the degree of preferred orientation of HAp in the tension side of the antler has a higher degree of preferred orientation than that found in the compression side.
A section of the same horn, just adjacent to that from which the specimens were taken for the neutron diffraction experiments, was used to make ultrasonic wave propagation and scanning acoustic microscopic measurements of the elastic properties. Prior to such experiments, the mineral density distribution in the section was measured by computer tomography in a C.G.R. (France) system. The section was then cut into dorsal, ventral, anterior and posterior specimens for standard ultrasonic wave propagation measurements to obtain average elastic moduli values. In addition, a new laboratory built reflection scanning acoustic microscope (SAM) was used to obtain the variations in acoustic impedance properties across the specimen's area. In this case the acoustic impedance $Z = \rho v$ (ρ is the sample density, v is the longitudinal velocity) is obtained on a grid of 256 x 256 points across the specimen's surface. Using a spherically focused transducer at 20 MHz, a resolution of approximately 100 μm is obtained. While not providing the elastic modulus directly, the system does provide a mapping closely related to modulus. The mineral concentration across the middle of the whole section of horn in the ventral-dorsal direction as obtained from the CAT scan measurements, compares very well with the plot of the SAM acoustic impedance amplitude measured along an imaginary line through the mid-portion of the smaller individual dorsal and ventral specimens cut from the whole section. What is apparent is the difference in mineral distribution between the dorsal and ventral sections. It is clear also that the strong inhomogeneity in elastic properties correlates very well with the mineral distribution and crystallite orientation; the same degree of correlation is observed for the other aspects as well.

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05.2-19 CALCULATION OF ATOMIC STRUCTURE DEFORMATIONS IN A STRESSED CRYSTAL. By M. Catti, Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Italy.

Changes of the equilibrium crystal structure under an applied stress are the result of two partial processes, modifying either the lattice geometry or the atomic fractional coordinates only, respectively. The former one (lattice deformation) was accounted for previously (Catti, Acta Cryst., 1985, A41, 494-500). The latter (inner deformation) can be calculated by considering a second-order expansion of the static crystal energy $E(\underline{\eta}, \underline{u})$ with respect to lattice strain components, η_k, and to generalized atomic shifts, u_i (Born and Huang, Dynamical Theory of Crystal Lattices, 1954). For a given lattice strain $\underline{\eta}$, $E(\underline{u})$ is minimized so as to find the change of structural configuration $\underline{u}_o$ consistent with the least elastic strain energy, obtaining:

$$\underline{u}_o = -\underline{\underline{V}}_{uu}^{-1} \underline{\underline{V}}_{u\eta} \underline{\eta}, \quad (1)$$

where $\underline{\underline{V}}_{uu}$ and $\underline{\underline{V}}_{u\eta}$ are the matrices of energy derivatives $\partial^2E/\partial u_i \partial u_j$ and $\partial^2E/\partial u_i \partial \eta_k$. The contribution of the inner deformation to the elastic constants is $-\underline{\underline{V}}_{\eta u}\underline{\underline{V}}_{uu}^{-1}\underline{\underline{V}}_{u\eta}$.
Using an appropriately parametrized Born potential (electrostatic + dispersive + repulsive) to account for atom-atom interactions, explicit analytical formulas were derived for all the lattice sums involved in the energy derivatives, also in the case of a rigid-body model where the u_i quantities are molecular orientation angles and translations; a corresponding computer program was developed. The internal deformation of the structure caused by any elastic strain $\underline{\eta}$ can then be calculated by straightforward application of (1). Considering the stress-strain relation $\underline{\tau} = \underline{\underline{C}}\underline{\eta}$, where $\underline{\underline{C}}$ is the 6x6 matrix of elastic constants, the dependence of the inner deformation on applied stress is obtained:

$$\underline{u}_o = -\underline{\underline{V}}_{uu}^{-1} \underline{\underline{V}}_{u\eta} \underline{\underline{C}}^{-1} \underline{\tau}. \quad (2)$$

The parameters of the interatomic potential should be fitted to the crystal elastic constants. This method was applied both to partially ionic and to molecular crystals, such as forsterite (Mg_2SiO_4), benzene, naphthalene, treating molecular ions (SiO_4^{4-}) and molecules in the rigid-body scheme. The results allow to simulate the evolution of their structure configurations under a general anisotropic stress field. A prediction of this behaviour seems to be quite interesting, as very few experimental data of this kind are available; several applications can be found in the study of phase transitions induced by pressure, and in subjects such as geophysics, materials science and solid state chemistry.