## Determination of hydroxylapatite (HAP) crystallite orientation in fossil bones and teeth using Polarized Light Microscopy (PLM)

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Examination of modern and fossil bone and tooth thin sections by Polarized Light Microscopy (PLM) has been made difficult by literature citations that promote a profoundly confusing technique for thin section examination. Optical mineralogy may be easily used to determine the crystallographic orientation of crystalline components in mineralized tissues, but is seldom cited as more than a method of contrast enhancement (using a gypsum or mica accessory plate). An odd terminology has inadvertently crept into the biological literature that confuses birefringence contrast with the determination of optic orientation. It has become common for pathologists and histologists to refer to "positive" and "negative" birefringence when discussing the optical crystallographic orientation of a bone or tooth component, such as collagen and hydroxylapatite crystallites. The terms "positive" and "negative" birefringence have no meaningful counterparts in optical mineralogy or crystallography. This terminology is also used with no sense of the crystallographic orientation, and without adequately defining the optical properties of the components involved. Examination of the published descriptions of "positive" and "negative" birefringence show that what is really being described is a determination of the orientation of the crystallites in the "slow" or "fast" optical direction. In this paper I will attempt to make the techniques of PLM examination of fossil bone clear, suggest a uniform reporting method for literature citations and show how this simple technique can reveal information about the preserved microstructure of bone and tooth materials.

## A comparative study of the dissolution of hydroxyapatite and fluorapatite in the absence and presence of organic ligands

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Phosphorous is an essential nutrient for all living organisms and is involved in several important mechanisms including synthesis of DNA and RNA. Inorganic phosphate is its primary source and its bioavailability is dependent on biogeochemical processes such as the dissolution of fluorapatite (FAP) and hydroxyapatite (HAP). It is well known that microorganisms can modify dissolution rates of phosphate minerals via the release of organic acids or other complexing compounds. To understand the dissolution of FAP and HAP, it is therefore important to investigate how pH and organic ligands affect the surfaces of these minerals.

In this study, we used citrate, malonate and mellitate as model substances. Citrate is a tricarboxylic acid and malonate a dicarboxylic acid, both generally produced by bacteria. Mellitate is a synthetic hexacarboxylic acid included in the study to evaluate the effects of ligand charge on the release of phosphate. To distinguish the effects of pH from those of the organic ligands, the dissolution of FAP and HAP was also studied in the absence of the organic ligands.

We employed a multi-technique approach to achieve a more complete understanding of the dissolution of the two apatites. Potentiometry, atomic absorption spectroscopy (AAS), and UV spectroscopy have been used to collect quantitative adsorption and dissolution data. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy were used to follow the kinetics of coupled dissolution and surface complexation processes on a molecular level.

The results from the dissolution experiments show significant differences between FAP and HAP in pH dependent release of phosphate as well as in ligand induced release of phosphate. FAP and HAP also display differences with respect to ligand adsorption where HAP is seemingly more reactive. In general, however, the total ligand charge (i.e. the total number of carboxylate groups) appears to be the major factor controlling the extent of adsorption.