

[s10.m1.p1] Cation distribution of solid solutions of calcium and cadmium hydroxyapatite. A. Nounah¹, J.L. Lacout², J.M. Savariault³. 1: *Laboratoire de Chimie Physique, Département de Chimie, Faculté des Sciences, B.P. 28/S, Agadir, Maroc.* 2: *CIRIMAT - Physico-Chimie des Phosphates, UMR CNRS, ENSCT-INPT, 38 rue des 36 ponts, 31400 Toulouse, France* 3: *Centre d'Elaboration de matériaux et d'Etudes structurales, CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France*
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The apatites form a large family of phosphate compounds whose hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is the well-known representative term. They generally crystallize in the hexagonal system (space group $\text{P6}_3/\text{m}$). The almost compact assembly of orthophosphate ions PO_4 defines two channels in which the cations are localized. The apatitic structure can accommodate a great variety of substituents both in anionic and cationic sites.

Hydroxyapatite presents a good model of biological apatite; it constitutes the inorganic phase of teeth and bones. Cadmium is one of the ions which can be found in biological apatite. It is a toxic element which follows the food chain and can induce serious bone troubles, e.g. itai-itai illness and osteoporosis. So the knowledges of interactions of cadmium with calcium phosphate, the location of cadmium in the apatitic structure are of interest in order to investigate the relation with bone apatite. The substitution of Ca^{2+} with Cd^{2+} in hydroxyapatite is of extreme biological significance since it explains the mechanisms of incorporation of cadmium into the skeletal system.

Solid solutions of cadmium and calcium hydroxyapatite, $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2$ with $0 \leq x \leq 10$, were synthesized by a wet process in basic medium. All the samples were characterized by X-ray diffraction, IR-spectrometry and chemical analysis. The a and c axis lattice constants of cadmium-calcium apatites vary linearly with composition according to Vegard law. The slight shift to lower wavenumbers of the PO_4 and OH infrared bands is due to the contraction of the unit cell and to the cation-oxygen interactions.

The distribution of the calcium and cadmium ions between two non-equivalent crystallographic sites, I and II, were determined by the Rietveld method (program DBW 3.2S). The sites are differing in symmetry and coordination. The results of the powder-fitting structure refinements show that whatever its amount in the apatites, cadmium is located simultaneously in both cation sites with a slight preference for site II. The bond valences are in agreement with the site occupancy-factors of cations in the two sites. The interatomic distances and the bond angles calculated using the ORFFEC program were studied.

[s10.m1.p2] Synchrotron powder diffraction study of the structural phase transition of Friedel salt $\text{Ca}_2\text{Al}(\text{OH})_6^+ \text{Cl}^- \cdot 2\text{H}_2\text{O}$. J.-P. Rapin^a, G. Renaudin^b, E. Elkaïm^c and M. François.^a *Laboratoire de Chimie du Solide Minéral UMR 7555 BP 239 F54056 Vandoeuvre-les-Nancy Cedex.*^b *Laboratoire de Cristallographie - Université de Genève, 24 quai Ernest-Ansermet CH-1211 Genève 4.*^c *Erik Elkaïm Laboratoire LURE, Bat 209D, Centre universitaire Paris Sud, B.P. 34 - 91898 Orsay Cedex*
 Keywords: advanced methods, structure determination, powder data.

The title compound, calcium oxide-dialuminium trioxide-calcium chloride hydrate, also called Friedel's salt and formulated $\text{Ca}_2\text{Al}(\text{OH})_6^+ \text{Cl}^- \cdot 2\text{H}_2\text{O}$, belongs to the AFm family of phases, which are hydrated products encountered in cement paste. It also belongs to the more general category of compounds called Lamellar Double Hydroxides (LDH). Because of structural data [1] not in agreement with our own results, structural properties of Friedel's salt have been revisited, especially by using synchrotron radiation.

This compound presents a structural change at 35°C, first detected by Differential Scanning Calorimetry and polarized light microscopy. The transition undergoes from a low temperature and monoclinic (space group $\text{C2}/\text{c}$) to a high temperature and rhombohedral (space group $\text{R}\bar{3}$) modification.

Synchrotron powder diffraction data at low temperature ($T < 35^\circ\text{C}$) have been recorded and the structure resolved by the direct methods. Finally, the high and low temperature diffractograms are fitted by Rietveld method and the results are compared with those based on single crystal data [2].

Photographs recorded during observations with polarized light microscopy at various temperatures and showing the variation of the optical properties of the compound (from transparent monodomain to birefringent polydomains) are also presented.

[1] Terzis A., Fillipakis S., Kuzel H.J., Burzlaff H., *Zeit. Krist.* 181 (1987) 29-33

[2] Renaudin G., Kubel K., Rivera J-P., François M. *Cem. Concr. Res.* 29 (1999) 1937-1942.