

MS21 P01

Structural investigations of novel β -aminophosphonic acids Jakub Wojciechowski^{a*}, Henryk Krawczyk^b, Łukasz Albrecht^b, Wojciech M. Wolf^{ab} ^aInstitute of General and Ecological Chemistry, ^bInstitute of Organic Chemistry, Technical University of Łódź, Łódź, Poland.
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Investigated compounds represent a novel group of α -substituted- β -aminophosphonic acids which show similarity to phosphorus herbicides commonly used in agriculture. On the contrary to α -aminophosphonic acids, structural information on their β -analogs is limited to eight compounds only [1]. An X-ray analysis based on a low temperature data accompanied by the *ab initio* MP2 and B3LYP [2] calculations revealed that strong electron density delocalizations exist in all structures. In particular, the phosphorus – oxygen double bond has a strongly pronounced dipolar character. This situation prompts electron density back-donation from the oxygen lone-pairs towards the phosphorus atom bearing the large positive charge. Investigated compounds adopt *anti* conformation with the central P-C-C-N torsion angles close to 180°. This arrangement prompts mutual $\sigma(\text{C-N})-\sigma^*(\text{C-P})$ interactions. All oxygen and nitrogen atoms are involved in hydrogen bonding. In particular, the strongest symmetrical hydrogen bonds link oxygen atoms of the neighbouring phosphoryl groups. Additionally, several intra- and intermolecular interactions exist in the crystals. All those interactions are analysed using the Natural Bond Orbital [3] and Atoms in Molecules [4] approach at the *ab initio* level of theory. Wavefunctions are calculated either for the isolated molecules or within the periodic boundary conditions framework.

[1] Allen F. H., *Acta Cryst.* 2004, B58, 380.

[2] Frisch M. J., *et al.* 2003. *GAUSSIAN03*. Gaussian Inc., Pittsburgh, Pennsylvania, USA.

[3] Weinhold F., Landis C., *Valency and Bonding*. Cambridge University Press, Cambridge, 2005.

[4] Bader R. F. W., *Atoms in Molecules: A Quantum Theory*. Oxford University Press, Oxford, 1990.

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Surface Modification of Calcium-Nickel Hydroxyapatite by Grafting Organic Moieties Abdallah Aissa^a, Aggougui Hassen^a, Mongi Debbabi^a, Michel Gruselle^b, René Thouvenot^b ^aLaboratoire de Physico-Chimie des Matériaux, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia ^bLaboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR-CNRS 7071, FR-CNRS 2769, Université Pierre et Marie Curie, 4 place Jussieu, case courrier 42, 75252 Paris cedex 05, France. E-mail: hamad_2001ab@yahoo.fr

Solid solutions of mixed calcium-nickel hydroxyapatite $\text{Ca}_{(10-x)}\text{Ni}_x(\text{PO}_4)_6(\text{OH})_2$ were obtained by precipitation in aqueous medium. Apatitic surface has been modified by grafting phenyl phosphine or phenyl phosphonate in dichloromethane. All samples were analyzed and identified using: IR spectroscopy, DRX powder diffraction pattern, MAS-NMR ³¹P and thermographic analysis. X-ray powder analysis has shown that solid solutions are limited to $x=3$, and the crystallinity has been affected by the presence of organic moieties.

IR spectroscopy shows a new vibration modes appearing essentially at 2950 cm^{-1} , 1648 cm^{-1} , 1440 cm^{-1} , 720 cm^{-1} , 770 cm^{-1} and 696 cm^{-1} , related to phosphonate and phosphine groups.

An isotropic ³¹P NMR signal is observed for mixed calcium-nickel hydroxyapatite corresponding to the $(\text{PO}_4)^{3-}$ anion [1]. After reaction, the ³¹P spectrum for reacted apatite consists on two signals, one around + 2.8 ppm $(\text{PO}_4)^{3-}$ and – 6.3 ppm (phosphonate) respectively. The phenyl (C_6H_5) groups are removed by thermal treatment around 450°C. According to the results founded a mechanism was proposed for the formation of covalent P-O-P bonds as the result of a reaction between the organic reagent and $(\text{HPO}_4)^-$ ions of the apatite.

[1] W. P. Rothwell, J. S. Waugh, J. P. Yesinowski, *J. Am. Chem. Soc.* 1980, 102, 2637.

MS21 P03

Phosphate Mineral Equilibria At The Galiléia Pegmatite Fields, Minas Gerais, Brazil. Fernando Roberto Mendes Pires^a, Marco Antonio Fonseca^b, Maira da Costa de Oliveira Lima^a ^aDepartament of Geology, University Federal of Rio de Janeiro, Brazil, ^bDepartment of Geology, University Federal of Ouro Preto, Brazil.
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The numerous important phosphate-rich pegmatites from the Galiléia fields, studied under the chemographic viewpoint allowed us to show the relative similarity between the diagrams and the behavior of some phosphate minerals. Vivianite and laueite presence constitute a clear boundary in the increasing hydration conditions of the system, interrupting the developing of the less hydrated parageneses. Their absence will constrain the system to a restrict control in μH^+ , which determines changes in phase stability. Whiteite, on the other hand, constitute a limit in the μH^+ of the paragenesis, by blocking their development. Scorzalite may restrict the whiteite development, by forming barbosalite, hureaulite and it is allowed to predict that the association of scorzalite and frondelite constrains the appearance of the other phases, maintaining the system strongly μH^+ dependent. At least six distinct fields can be depicted in the $\mu\text{H}_2\text{O}-\mu\text{H}^+$ diagrams:

- 1) A less acid and moderately oxidized field dominated by cyrilovite, dufrénite, roscherite, faheyite, rockbridgeite, referred as basic iron phosphates and frondelite.
- 2) A less acid and less hydrated zone is dominated by the Be-Na rich assemblages, herderite, beryllonite and brazilianite, apatite and the more hydrated moraesite. These minerals were derived by partial acid leaching of beryl, and reaction with apatite.
- 3) Moderately acid and hydrated ($\mu\text{H}_2\text{O}-\mu\text{H}^+$) field corresponds to the lipscombite, beraunite, barbosalite, whitmoreite, rockbridgeite and bermanite. Leucophosphite, phosphosiderite, phosphoferrite and hureaulite and wicksite could be included in this intermediate or transitional group.
- 4) The field dominated by the supposedly primary phases consisting of apatite, triphylite, triplite, beusite, wyllicite, alluaudite, arrojadite, johnsomervilleite and amblygonite-montebrazite is stable under low $\mu\text{H}_2\text{O}$ conditions. Ferrisicklerite may also participate of this group.