

**PS08.00.35 CHEMICAL AND STRUCTURAL VARIATION IN SYNTHETIC LOVERINGITE,  $(Ca, Ti^{3+}, Ti^{4+}, Mn)_{22}O_{38}$ .** Peterson, Ronald C., Department of Geological Sciences, Queen's University, Kingston, Canada, K7L 3N6, Grey, Ian E., Cranswick, Lachlan, C.S.I.R.O. Division of Mineral Chemistry, P. O. Box 124, Port Melbourne, Australia

The relationships of loveringite to other phases in the system Ti-Mn-Ca-O, quenched from 1100°C and various  $f(O_2)$  have been studied. Structural variation as a function of composition has been determined by Rietveld refinement of powder X-ray data. The calculated  $Ti^{3+}$  content, based on 38 oxygen atoms, varies from 2.5 atoms per formula unit (apfu) when grown at an  $f(O_2)$  of  $10^{-15}$  to 5.5 apfu at  $10^{-18}$ . As an example, a loveringite grown at  $f(O_2)=10^{-16.7}$  has the composition  $Ca_{1.54}Mn_{2.18}Ti^{3+}_{4.55}Ti^{4+}_{13.73}O_{38}$ . The  $Ti^{4+}/Ti^{3+}$  ratio of a synthetic loveringite is also dependent on the other phases present which varies with the bulk composition of the charge. Other phases which coexist with loveringite at various compositions and  $f(O_2)$  are  $Ti_3O_5$ ,  $Ti_4O_7$ ,  $Ti_6O_{11}$ , pyrophanite, perovskite and rutile. Rutile coexists with loveringite at more oxidizing conditions while perovskite and/or  $Ti_3O_5$ , occur at more reducing conditions. Pyrophanite coexists with loveringite at more manganese-rich bulk compositions over a wide range of  $f(O_2)$ .

The unit cell of this closest-packed oxide structure varies most significantly with the calcium content. The substitution of  $Mn^{2+}+Ti^{4+}$  for 2  $Ti^{3+}$  maintains charge balance for different  $Ti^{4+}/Ti^{3+}$  ratios within loveringite. Ca in excess of 1 apfu and Mn are ordered into the largest octahedral site.

**PS08.00.36 THE IMPORTANCE OF INORGANIC SALT ADDITION IN DISORDERING THE STRUCTURE OF MECHANICALLY TREATED CHROMITE.** Razvorotneva L.I., Grigorieva T.N., Moroz T.N. United Institute of Geology, Geophysics and Mineralogy, Siberian Branch RAS, 630090 Novosibirsk, Russia

Mechanical explosion on solids causes their structure to be changed essentially. The changes are characterized by arising new inner interfaces as well as dislocations and various modes of point defects. The small concentrations of surfactants implanted in the layers near surface are favourable for enhancement of structure changes when disordering under mechanical explosion.

In the present work the introduction of the inorganic salts in the layers near surface of chromite as one of the most stable minerals to mechanical and chemical explosions was carried out.

The estimation of deformability degree of covalent bonds in inorganic addition - chromite system when forming the defects was defined by method of infrared spectroscopy. The appearance of additional vibrational frequencies indicating the formation of new complexes surface - addition was observed in the infrared spectra. The bands of the stretching internal modes of carbonate ions at 1375 and 1530  $cm^{-1}$  in the spectrum of the mechanically treated chromite with  $Na_2CO_3$  additions were recorded. These values differ from the free  $CO_3$ -ion mode value and 1460  $cm^{-1}$  band of  $Na_2CO_3$  inorganic salt.

The change of structure perfection of chromite was investigated by method of X-ray diffraction with using Fourier - analysis. When dissolving the mineral particles layer by layer the relationship between the sizes of coherent dispersion blocks as well as microdistortions and depth of layer near surface has been established. Size of coherent dispersion blocks depend on type of inorganic salt addition. When  $Na_2CO_3$  was added to chromite the last was destroyed till 500 Å blocks. Destruction was enhanced five-fold by using  $NH_4Cl$  as addition.

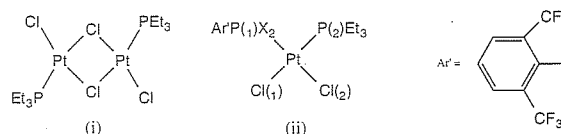
**PS08.00.37 SYNTHESIS AND X-RAY IDENTIFICATION OF TITANIUM PHOSPHATE COMPOUNDS.** M.L. Castro Reis<sup>1</sup>, C. Castro Ribeiro<sup>2</sup>, M.A. Barbosa<sup>2</sup>, IIGM - Instituto Geológico e Mineiro, Rua da Amieira, 4465 S. Mamede de Infesta, Portugal, INEB - Instituto de Engenharia Biomedica, Pra. ca Coronel Pacheco, 1, 4000 Porto, Portugal, and <sup>2</sup>FEUP - Faculdade de Engenharia da Universidade do Porto, Rua dos Bragas, 4099 Porto Codex, Portugal.

In order to investigate the influence of Ti ions in the molecular structure of hydroxyapatite (HAp) dissolution studies were carried out using 0.9% sodium chloride solution to which different concentrations of Ti ions were added, ranging from 1 to 2000 ppm. The crystallinity of solids was studied by XRD techniques. For Ti concentrations in solution smaller than 350 ppm, hydroxyapatite undergoes an isomorphous substitution ( $Ca \rightarrow Ti$ ) and the X-ray pattern revealed HAp single phase. By EDS it was possible to establish that this HAp is Ca-deficient (Ca/P, lower than 1.67) and it is transformed into an amorphous or a poorly crystallised phase for solutions containing Ti ions in concentrations of about 400 ppm. The "amorphous" phase can be a precursor of the formation of a titanium hydrogen phosphate compound, to which reference is made below. The lifetime of this precursor phase is sensitive to experimental conditions: with increasing time and temperature its crystallinity increases. When the concentration of Ti ions is higher than 400 ppm a crystalline phase is detected in early stages and its X-ray diffraction data seem to correspond to a mixture of the  $\alpha$ -titanium hydrogen phosphate hydrate [ $\alpha$ - $Ti(HPO_4)_2 \cdot 2H_2O$ ] and  $\gamma$ -titanium hydrogen phosphate hydrate [ $\gamma$ - $Ti(HPO_4)_2 \cdot 2H_2O$ ]. The X-ray diffraction data of the crystalline phase obtained were compared with data from the literature\* for  $\alpha$  form and  $\gamma$  form. However, some reflections in positions non predicted,  $d=9.05, 6.4, 4.8 \text{ \AA}$ , may correspond to a new phase or a mixed layered compound of the  $\alpha$  and  $\gamma$ -form. Usually, the layers are stacked along the  $c$  axis and the stacking matrix is formed by epitaxial overgrowth. In this case  $a$  and  $b$  axis are exchangeable. The preliminary results of the mixed layered compound formed from both polytypes ( $\alpha$  and  $\gamma$ ) point towards a stacking matrix (1:1), with a layer spacing of approximately 19.2 Å, which can be responsible for the reflections observed. On the other hand, the diffuse nature of the scattering pattern suggests that this material possesses a low level of crystallinity and/or a very small crystallite size.

\*A. N. Christensen et al, Acta Chemica Scandinavica 44 (1990) 865-872.

**PS08.00.38 CRYSTALLOGRAPHIC STUDIES OF PHOSPHORUS CIS-PLATIN ANALOGUES WITH POSSIBLE LINKS TO ANTI-CANCER ACTIVITY.** Mark D. Roden, Dr Keith B. Dillon, Judith A. K. Howard, University of Durham, England

A series of phosphorus (III) compounds,  $RPX_3$ , ( $X=H, F, Cl, Br, I$ ) and some low co-ordinate phosphorus (III) compounds have been reacted with a platinum complex (i) to form cis-platin analogues (ii). These compounds have been shown to exhibit anti-cancer activity. The rate at which compounds hydrolyse in an aqueous media is very important when considering them to be practical *in vivo* anti-tumour agents. The relationship between the rate of hydrolysis of the Pt-Cl bond and its bond length will be described.



Crystallographic studies of these compounds have revealed that the Pt-Cl(2) bond trans to P(1) is significantly shorter than the cis Pt-Cl(1) bond. We believe that this variation can be correlated with the strength of the Pt-P(1) bond, which is in turn governed by the electronegativity of the substituents X, attached to P(1). Therefore by synthesising analogues with varying X substituents we hope to engineer a compound with Pt-Cl bond lengths with the optimum strength for *in vivo* pharmaceutical action.