



Experiment title:

High-Pressure Powder-Diffraction Studies of Apatite
($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$)

Experiment
number:
HC439

Beamline:

ID9-BL3

Date of experiment:

from 22/3/96 to: 27/3/96

Date of report:

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Shifts:

5

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Report:

Members of the apatite family of minerals are not only common subsidiaries in almost all igneous rocks but are also found in sedimentary and metamorphic rocks. They are the most abundant of phosphorus-bearing minerals with a general formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$ where fluorine, chlorine and the hydroxyl ion can be mutually substituted to form pure end-members. Apart from being an extremely important accessory in a large number of mineral systems, apatite is a 'reservoir' of rare earth, or large lithophile, elements which are commonly used as metrological tracers. These tracers in themselves do not constitute any major mineralogical phase, or are accommodated in the major phases due to their low abundances and large ionic radii, but are of vital importance for determining the chemical constitution of the mantel source region and the evolution of the mantle through geochemical and tectonic processes.

Although apatite controls the Earth's budget of both phosphorus and light rare earth elements, and contains significant quantities of the volatile halide elements, relatively little is known about its compressional behaviour. To form accurate thermodynamic models of apatite in the Earth's deep interior, and hence establish a better understanding of the behaviour of the large lithophile tracer elements and phosphorus, it is crucial that the equation-of-state is

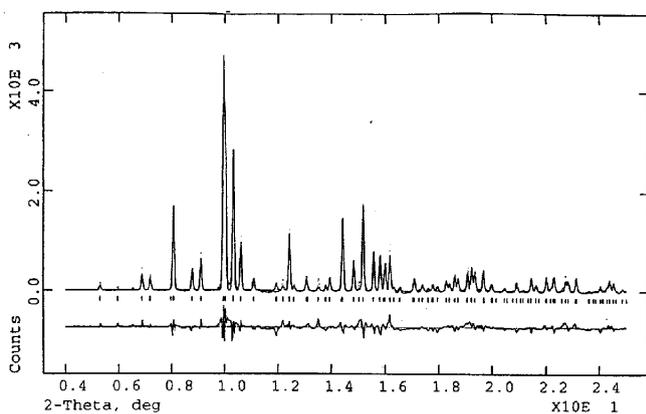


Figure 1

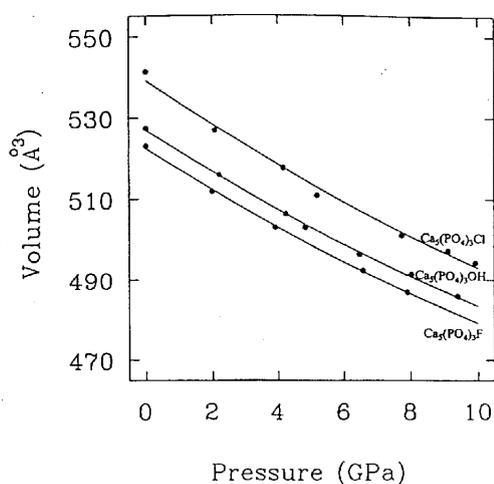


Figure 2

determined accurately. Towards this end we have performed high-pressure powder-diffraction experiments on the three end-member materials Ca~(POQ)gF, Ca~(PO&OH) and Ca~(POA)~Cl using angle-dispersive techniques and an image plate area detector on ID9 (BL3). A wavelength of 0.4735 Å was selected from the multipole wiggler radiation using both a mirror and a monochromator and the samples were pressurised in BGI¹ and DXR5² diamond anvil cells with a 4:1 methanol-ethanol mixture as a pressure transmitting medium. A typical example of the high quality of data obtained can be seen in Figure 1 which shows a full-structural Rietveld refinement of Ca₅(PO₄)₃OH powder data collected at 9.8 GPa.

The unit cell volumes for the three end members are plotted as a function of pressure to 10 GPa in Figure 2. The solid lines are Birch-Murnaghan fits to the data, with the constraint $K' = 4$ in all cases, which give $K_0 = 97.5(1.8)$ GPa, $97.9(1.9)$ GPa and $93(4)$ GPa for Ca₅(PO₄)₃F, Ca₅(PO₄)₃OH and Ca₅(PO₄)₃Cl respectively. Data were also collected to 20 GPa for Ca₅(PO₄)₃F and Ca₅(PO₄)₃OH and to 50 GPa for Ca₅(PO₄)₃Cl but, as the samples were no longer under hydrostatic conditions due to the well-known freezing of the methanol-ethanol pressure media, the data were not used for the equation-of-state determination. The data above 10 GPa did indicate, however, that there is no strong evidence for a structural phase transition in any of the materials and it can be expected that the apatite structure is stable, at least with respect to pressure, within the lithosphere.

¹ D. R. Allan, R. Miletich and R. J. Angel, Rev. Sci. Instrum. (1966) 67(3) 840-842

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