

COMPOSITIONAL ANALYSES OF F, Cl AND OH BY RAMAN SPECTROSCOPY IN APATITE FROM MAFIC-ULTRAMAFIC PIPES OF THE IVREA VERBANO ZONE (NW ITALY). P. Kollegger¹, F. Zaccarini¹, R. J. Bakker¹, G. Garuti¹ and O.A.R. Thalhammer¹, ¹Department of Applied Geosciences and Geophysics, University of Leoben, Peter Tunner Str.5, Leoben, Austria (peter.kollegger@unileoben.ac.at).

In this contribution we present the Raman spectra obtained from selected apatites occurring in mafic-ultramafic pipes of the Ivrea Verbano zone (WN Italy). These pipes, hosting Ni–Cu–Platinum group elements (PGE) sulphide deposits, have an alkaline signature and are enriched in volatiles and fluids that encouraged the formation of hydromagmatic phases like apatite, phlogopite and amphibole [2]. Based on accurate electron microprobe analyses, the apatites of our study are characterized by a wide spectrum of substitution of F, Cl and OH and therefore all the three end-members (fluor-, hydroxyl- and chlorapatite) have to be taken in consideration for the Raman study.

Electron microprobe quantitative analysis is one of the most used techniques to analyse apatites and to discriminate the three endmembers. However, the analysis of light elements ($Z < 9$) such as O and F, by electron microprobe, presents numerous problems and H cannot be detected. As a consequence, OH can be only calculated and reliable analyses of F can be obtained only with very modern electron microprobe, equipped with appropriate diffracting crystals. Furthermore, apatite is generally unstable under the high-voltage electron beam that produces relatively large craters on the crystals. Therefore, the size of apatite should be at least bigger than 50 microns. Thus, to analyse precisely apatite using electron microprobe is not always an easy target.

In the last 20 years, Raman spectroscopy was successfully applied to determine the compositional variation in apatite, involving great application areas such as biological research (dental and bone investigation), palaeontology (fossilized teeth) and medicine (cancer research) ([1],[4],[3]). These previous studies indicate that Raman spectroscopy can provide, in principle, relatively simple and fast semi-quantitative analyses of the anion composition also on very small apatite crystals.

The structure of apatite, (Ideal: $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$), is influenced by the different size and structural position of the monovalent anions (F, Cl and OH), shifting the cell parameters. A free phosphate group (PO_4^{3-}) possesses four Raman-active modes ν_1 (980 cm^{-1}), ν_2 (363 cm^{-1}), ν_3 (1082 cm^{-1}) and ν_4 (514 cm^{-1}). In our samples we could observe that each of the modes is shifted to lower levels and that the FWHM of the single peaks are widened by the incorporation of other species than F. Because our samples do not possess apatites with an end-member composi-

tion we included other studies ([1],[5],[4],[6]) for correlation with our data.

The results of this study demonstrated, for the first time, that there is a linear correlation between the Raman shift and the FWHM of the peaks, with the composition of the apatites not only between two end-members, but between the end-member fluorapatite on the one hand and the end-members hydroxyapatite plus chlorapatite on the other hand (Fig.1). We showed that the influence of Cl and OH on the Raman active modes of the apatite's phosphate group is nearly the same. Therefore Raman investigations provide an instrument for the quantification of F contents in comparison with the sum of Cl plus OH.

Knowledge of the presence of F, Cl or OH in apatite provides information about fluid phase properties at formation conditions in geological environments.

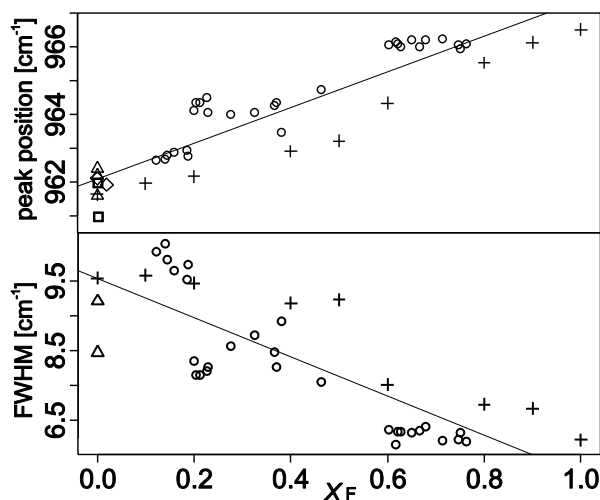


Fig. 1: a) peak position, and b) FWHM of the ν_1 PO_4^{3-} band in correlation to $X_F = \text{F}/(\text{F}+\text{Cl}+\text{OH})$ [apfu.]. Open circles: this study; Crosses: F-Cl apatites; Triangles: OH apatites; Rectangle: $(\text{OH})_{0.29}\text{Cl}_{0.69}\text{F}_{0.02}$ apatite. [1],[4],[5],[6]

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