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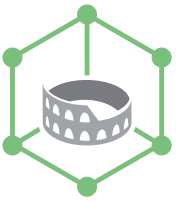

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Characterization of plagioclase solid solution by Raman spectroscopy: a procedure for the determination of the chemical composition

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Plagioclases are framework silicates occurring in planetary crusts: on Earth they are the most common rock-forming minerals of igneous, metamorphic and sedimentary rocks, the most abundant minerals on the Moon and widespread in basaltic rocks on Mars and in asteroids like Vesta. Plagioclases are involved in several key reactions of petrologic interest, as igneous and metamorphic reactions. Plagioclases can be described as a solid solution ranging from the Na-endmember, albite ($NaAlSi_3O_8$), to the Ca-endmember, anorthite ($CaAl_2Si_2O_8$), in which the Si:Al ratio varies.

The investigation of their chemical composition is a key-point to understand the petrologic evolution of the parent rocks. EDS or WDS chemical analyses or laser ablation are common techniques used to get information about plagioclase composition. They require the preparation of the sample and are time-consuming and expensive.

In this work, we propose Raman spectroscopy as a procedure to gain chemical information from plagioclases. A similar approach has already been applied to different classes of minerals as garnets, amphiboles and serpentine group. Unlike the aforementioned minerals, the major problem in plagioclases is their mixing behaviour which is complicated by the various compositional-driven phase transitions and by the Al,Si ordering. Over most of the compositional range, plagioclases have the collapsed $C\bar{1}$ structure with no Al,Si order (*i.e.* the high albite structure), whereas on the anorthite-rich side the solid solution has the $I\bar{1}$ structure due to the increasing tendency to Al,Si ordering. The complete order with strictly alternating Al,Si is achieved only in pure anorthite.

The most comprehensive Raman investigation on feldspars (Freeman et al., 2008) led to a classification of the major structural types without a detailed study of the changes of the Raman features within the plagioclase composition. We performed Raman investigation on a series of well characterized plagioclases, previously analysed by powder-XRD, TEM, IR spectroscopy and calorimetry (Carpenter et al., 1985; Tribaudino et al., 2010; Atkinson et al., 1999;

Benisek et al., 2013). The samples consist of 20 homogeneous purified natural, low structural state plagioclases, showing the highest degree of Al,Si order possible for each composition. The chemical composition ranges from An_0 to An_{100}.

The difference in Raman wavenumber between the two major peaks (I_a and I_b) of the plagioclases is here proposed to be indicative of their composition in terms of An composition. From Fig. 1 (*left side*), where I_a and I_b differences are plotted *vs*. the An content, it is possible to directly read the composition for the An-rich terms (An > 60%). In order to obtain compositional information for Ab-rich plagioclases too, we need to plot I_a and I_b differences *vs*. the linewidth of the most intense Raman mode w(I_a), as shown in Fig. 1 (*right side*). We point out that the dependence of the composition from the linewidth can be obtained only for ordered plagioclases. For that reason, the composition of disordered Ab-rich plagioclases cannot be correctly obtained with this method. Both methods have been tested on three different mineralogical case studies: plagioclase crystals found in Juvinas eucrite meteorite, anorthite crystals into a CAI inclusion within the Renazzo carbonaceous chondrite meteorite, and plagioclase crystals with heterogeneous chemical composition from the Marsili volcano. The "Raman chemical compositions" suggested by our methods are in good agreement with the chemical analyses for plagioclase samples with An content > 60 mol%. The methods fail for disordered albite-rich samples where the contribution to the linewidth by the disorder is unknown.

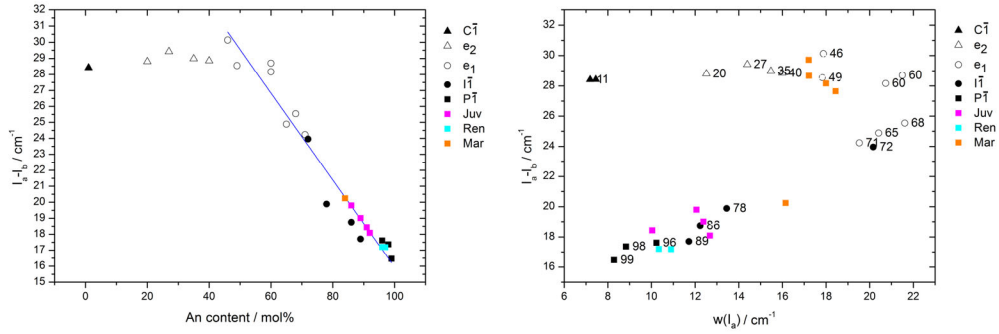

Fig. 1: Wavenumber differences I_a-I_b versus the An content (*left side*) and versus the linewidth of the most intense Raman mode w(I_a) (*right side*). Coloured squares refer to the case studies.

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High pressure Raman spectroscopy on Ca-clinopyroxenes

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Ca-rich clinopyroxenes are considered as major constituents of the Earth mantle. For this reason, they are the subject of several experiments aimed to describe their thermal and compressional behaviors in order to model the elastic properties of the mantle. However, little is known about the pressure-induced changes in the Raman spectra of Ca-rich clinopyroxenes. Ca-clinopyroxenes have monoclinic symmetry (space group *C*2/*c*). The general formula of pyroxenes is $M2M1T_2O_6$, where M2, M1, and T are cations hosted respectively in a distorted eight-fold-coordinated polyhedron (M2), in a regular octahedron (M1), and in a tetrahedron (T); the anion is invariably oxygen.

The samples of this study have formula $Ca^{2+}M1T_2O_6$, where M1 is populated by Mg^{2+} or Co^{2+}, and the T site by Ge^{4+} or Si^{4+}. They are all synthetic (Mantovani et al., 2015), except for Si diopside (Prencipe et al., 2000). An ETH-type diamond anvil cell (DAC) was used for the high-pressure experiments. The crystalline samples (100 x 60 x 50 μm) were placed in the gasket hole along with some ruby chips for pressure measurements by the ruby-fluorescence method (precision ±0.05 GPa). Methanol:ethanol = 4:1 mixture was used as hydrostatic pressure-transmitting medium (Angel et al., 2007). Room and high-pressure Raman spectra were collected in compression up to 7.6 GPa for silicates and to 8.27 GPa for germanates, respectively, using an Olympus BX40 microscope attached to a Jobin-Yvon Horiba LabRam confocal Raman spectrometer. The samples were excited with the 473.1 nm blue light of a doubled Nd:YAG laser. The spectra were collected in backscattering geometry in the spectral range 100-1000 cm^{-1}. Every measurement of the ruby fluorescence was calibrated using the emission lines of a spectroscopic zinc-vapour lamp. The positions of the fluorescence and Raman bands were obtained from a Gauss-Lorentzian deconvolution procedure with the LabSpec v. 5 software, with an uncertainty of about 1 cm^{-1}.

The high-pressure Raman experiments showed no phase transition within the *P*-ranges investigated, as all the peak positions vary linearly as a function of pressure. Our data confirm the previous experimental findings on Si-diopside (Chopelas et al., 2000). In all the investigated

samples, all the Raman peaks shift upon compression, but the major changes in wavenumber are attributed to the bending and stretching modes of the tetrahedral chains (*i.e.*, the building units of the pyroxene structure) (Figure 1). Upon compression, the kinking angle between tetrahedra decreases and the wavenumber of the bending mode increases (Lambruschi et al., 2015). Among the samples, Ge-pyroxenes show the higher *P*-induced peak-position shifts, being more compressible than corresponding silicates.

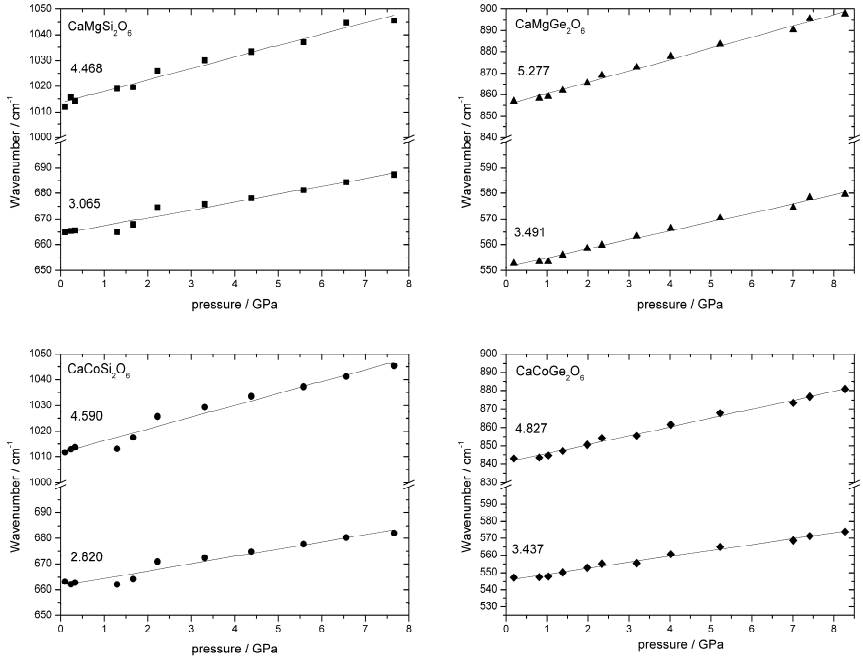

FIGURE 1: Raman shifts for selected bands vs. pressure for $CaMgSi_2O_6$, $CaMgGe_2O_6$, $CaCoSi_2O_6$, $CaCoGe_2O_6$. Lines are the fits through the data-points: their slopes $\Delta\nu/\Delta P$ are given.

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