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GROSSULAR/HYDROGROSSULAR IN RODINGITES FROM OTHRYS OPHIOLITE (CENTRAL GREECE): RAMAN SPECTROSCOPY AS A TOOL TO DISTINGUISH IT FROM VESUVIANITE

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Abstract: Raman Spectroscopy was employed to confirm the presence of hydrogrossular, rather than vesuvianite, in rodingites of the Othrys ophiolite suite, central Greece. The Raman spectra obtained from the fine-grained, weakly birefringent minerals, with anomalous bluish-grey interference colours documented the presence of hydrogrossular by its characteristic bands at ~360-362, 534-537, 817-819, 870-872 and 3600 cm^{-1}. No Raman spectra indicative of vesuvianite were obtained precluding the existence of this phase. The absence of vesuvianite implies that the metasomatising fluid phase was rather rich in CO_2, an observation which is also verified by the abundance of calcite and assists in further studying the evolution of these rocks.

Keywords: Raman Spectroscopy; Hydrogrossular; Vesuvianite; Rodingite; Othrys; Greece

1. Introduction

Rodingites are Ca-rich and silica undersaturated rocks, composed mainly of Ca-Al and/or Ca-Mg silicates. Though rare, they comprise a significant component of the ophiolite complexes.

They form during post-magmatic episodes and affect mainly mafic or ultramafic protoliths. They are genetically related either to serpentinisation (e.g. Coleman, 1977; Schandl et. al., 1989; O'Hanley et al., 1992; Hatzipanagiotou et al., 2003) or to the introduction of Ca-rich hydrothermal solutions (e.g. Hall & Ahmed, 1984; Hatzipanagiotou & Tsikouras, 2001). Their assemblages commonly include grossular/hydrogrossular, andradite, epidote, prehnite, vesuvianite and diopside depending mainly on temperature conditions and the composition of the implicated fluid phase.

The aim of this study was to ascertain the mineral assemblage which is present in the Othrys rodingites, employing the Raman technique in order to assist several interpretations concerning their petrogenetic evolution. Hydrogrossular and vesuvianite commonly show significant resemblance of their optical properties, their structure and their chemical composition (e.g. Fitzgerald et al., 1992), thus not easily discernible, even when microprobe or XRD are used.

Verification of the occurrence of vesuvianite is critical in a rodingite system since it forms only at very low activity of CO_2 of the fluid phase involved in the metasomatic process (Rice, 1983; Galuskin et al., 2003).

2. Geological Setting

Othrys is one of the most well-known ophiolite complexes within the Dinaric-Hellenic ophiolite belt of Western Greece. It has been termed the Mirna Group after Smith et al. (1975) which occurs in a nappe pile structure where the ophiolitic rocks are dismembered and emplaced in reverse stratigraphic order. From bottom to top, the Mirna Group ophiolite comprises the Sipetorrema Pillow Lava unit after Smith et al. (1975), the Kournovon Dolerite unit and isolated units of mantle rocks including the Agoriani Lherzolite, the Mega Isoma Lherzolite and the Kedron Harzburgite.

Rodingites are in association with serpentinised harzburgite of the uppermost tectonic units of the

Mirna Group. They occur as scarce fine-grained dykes of variable thickness (5-20 cm), in sharp contact with the peridotite (Fig. 1). They are generally white-coloured rocks with a rather homogeneous field aspect which could be subdivided into two groups, based distinctively on the occurrence or absence of significant amounts of well-formed calcite crystals. Locally, they are displaced or folded with b-axes striking NW-SE, parallel to the foliation.

Fig. 1. Outcrop of rodingitised dykes (white) in serpentinised harzburgite.

3. Petrography

The Othrys rodingites are subdivided into two groups characterized by different textures and assemblages. The group-1 rodingites (samples RD4, RD5) display a blasto-subophitic texture preserving local relics of primary subophitic texture; their assemblage includes diopside + chlorite + garnet + calcite + titanite + ilmenite. Garnet is a weakly birefringent hydrogrossular and forms either segregations of tiny, embryonic crystals or clear pseudomophic crystals after plagioclase, set between diopside (Figs. 2a, b). Due to its small crystal size and the resemblance to vesuvianite, hydrogrossular crystals are difficult to identify; hence its presence was verified employing the Raman technique. Chlorite has been developed after actinolite (an ocean-floor metamorphic product in the dolerite protolith) while diopside formed after chlorite or chlorite and calcite.

The group-2 rodingites (samples RD2, RD3) represent a more advanced stage of metasomatic alteration where igneous textures have been virtually obliterated by lepidoblastic, granoblastic and occasionally cataclastic textures. Their assemblage includes diopside + garnet + chlorite + titanite ± apatite. Garnet is represented by hydrogrossular, which disperses within the rodingite showing weakly birefringent crystals with anomalous bluish interference colours (Figs. 2c, d), thus could be misleaded with vesuvianite that also commonly occurs in rodingites. However, occurrence of vesuvianite is precluded while the presence of hydrogrossular has been again verified using Raman spectroscopy. In places, a younger generation of subhedral to euhedral diopside crystals form overgrowths on garnet.

4. Analytical methods

Raman spectra were obtained with a Renishaw Ramascope RM1000® Raman micro-spectrometer at the School of Mining and Metallurgical Engineering of the Technical University of Athens, Greece. Spectra were excited at room temperature with the 632.8 nm line of a red 19 mW He-Ne laser through an OLYMPUS® x100 objective. The numerical aperture of the objective is 0.9. The laser spot on the surface had a diameter of approximately 1 μm and a power of ~4 mW. Light was dispersed by a holographic grating with 1800 grooves/mm. The spectral resolution of about 0.4 cm^{-1} was determined by measuring the Rayleigh line of the He-Ne laser. The “scanning” mode was selected. 5 accumulations of 20 seconds each were made for each spectrum in a spectral range between 180 and 4000 cm^{-1}. In the cases of high luminescence laser power was reduced by 50% and 10 seconds per each accumulation were selected. Even though, in some cases no detectable Raman peaks appeared in the garnet spectra characterized of very high laser-induced sample fluorescence.

Electron microanalyses were carried out at the Laboratory of Electron Microscopy and Microanalysis, University of Patras. All elements were analyzed by electron-dispersive X-Rays (EDX) using EDS and WDS detectors attached to a JEOL JSM-6300 SEM. Operating conditions were accelerating voltage 15 kV and beam current 3.3 nA with 4 μm diameter beam. The acquired EDS and WDS spectra were corrected with the ZAF correction software. The total counting time was 60 sec and the dead-time 40 %. Synthetic oxides and natural minerals were utilized as standards for our analyses.

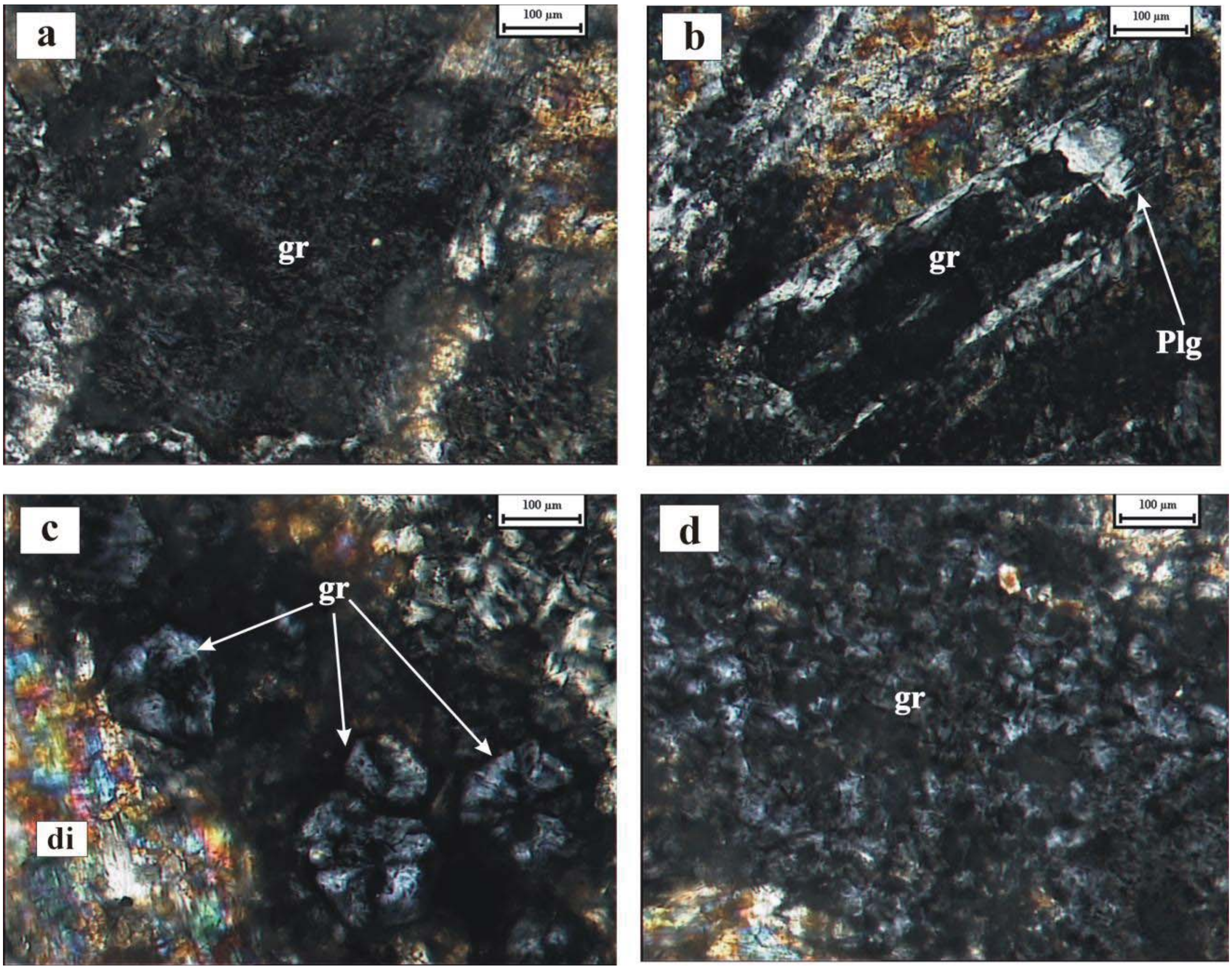

Fig. 2. Photomicrographs from the Othrys rodingites: a. group-1 rodingite (sample RD 4) with hydrogrossular (gr) in pseudomorphic development after igneous plagioclase; b. hydrogrossular overgrowing relic plagioclase (Plg), which towards the rim shows multiple twinning (sample RD 4); c-d. weakly birefringent hydrogrossular (gr) and diopside (di) in group-2 rodingite (sample RD 3).

5. Results

Raman spectra with bands at 360-362, 534-537, 817-821 and 870-872 cm^{-1} were obtained from the anisotropic minerals of the samples (Fig. 3). A minor peak at ~3600 cm^{-1} with variable intensity is also distinguishable (Figs. 3, 4). Broad laser-induced luminescence bands are observed in the spectral interval 1000-2500 cm^{-1}. The observed bands are most probably assigned to hydrogrossular. As revealed by the microanalyses (see Table 1) the grains analysed here comprise intermediate compositions between the grossular ($Ca_3Al_2(SiO_4)_3$) – hydrogrossular ($Ca_3Al_2(O_4H_4)_3$) end-members; therefore Raman band positions are expected to deviate from those of both pure hydrogarnet and pure silicate garnet (hydrogrossular and grossular, respectively). Moreover, in addition to Ca, the presence of Fe and Mg cations results in band position shifts compared to those of pure Ca-bearing garnet end members. Thus, the band at 360-362 cm^{-1} could most probably be mixed T/R(O_4H_4) and T/R(SiO_4) (Kolesov & Geiger 1998; 2005). The band at 534-537 cm^{-1} could be assigned to a T(OH) motion (Kolesov & Geiger, 2005). The bands between 600 and 900 cm^{-1} might correspond to a mixture of R(OH)/(Si-O) (Kolesov & Geiger 1998; 2005). The band at ~3600 cm^{-1} corresponds to the O-H mode. Its intensity varies as a result of varying OH^- content of the analysed

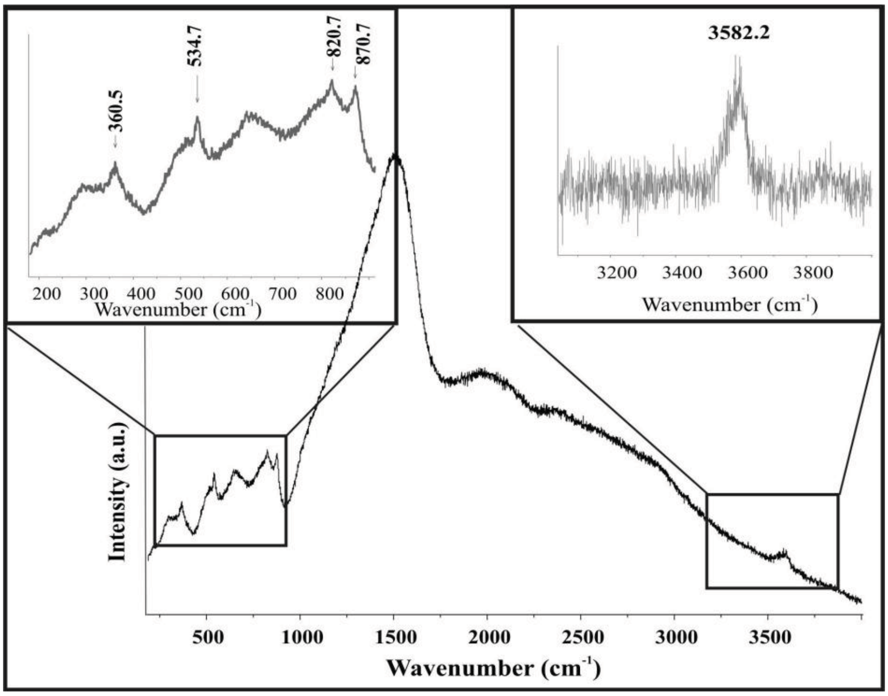

Fig. 3. A representative Raman spectrum of hydrogrossular from a rodingite of Othrys (sample RD 2); 632.8nm, He-Ne laser.

hydrogrossulars (see Fig. 4), an observation also verified by SEM/EDX analyses (Table 1). However, Raman spectra are not suitable for quantitative determination of OH in garnets (Arredondo & Rossman, 2002). Moreover, the laser wavelength used (632.8 nm) is not very sensitive to the OH$^-$

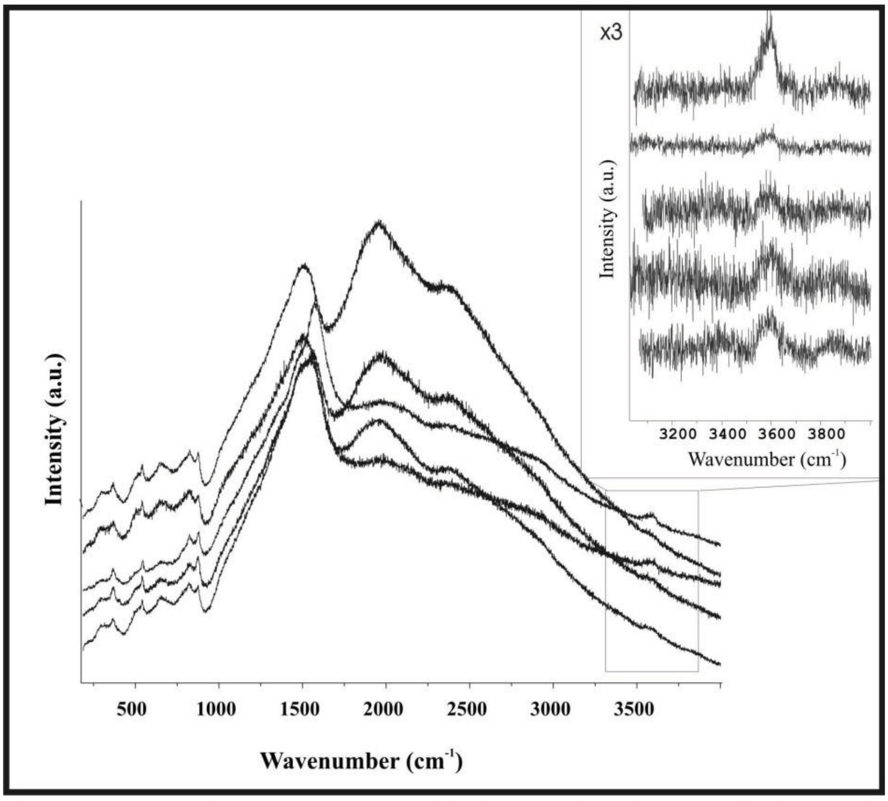

Fig. 4. Representative Raman spectra of hydrogrossulars from a rodingite sample (sample RD3) with varying OH-mode intensities; 632.8nm, He-Ne laser.

modes in hydrous mineral phases and thus the bands corresponding to these modes are not so well-expressed.

Table 1. Representative microanalyses of garnets from the rodingites of Othrys.

	Hydrogrossular					
Sample	RD 2	RD 2	RD 3	RD 3	RD 4	RD 5
Anal.	gr2.1	gr2.7.5	gr3.2.1	gr3.1b.8	gr 2	gr 4
SiO_2	36,13	33,27	33,89	33,88	33,96	33,85
TiO_2	2,18	1,12	1,81	1,71	0,49	1,49
Al_2O_3	17,92	20,34	19,84	20,51	18,47	16,33
$Fe_2O_3{}^t$	2,43	1,69	2,48	2,14	9,01	8,18
MnO	0,05	-	0,01	0,04	-	-
MgO	-	-	-	0,02	3,37	1,32
CaO	36,67	36,11	36,64	36,77	30,71	34,51
Na_2O	0,21	0,03	0,31	0,16	-	-
Cr_2O_3	-	-	-	-	-	-
Total	95,59	92,56	94,98	95,23	96,01	95,68
Structural formulae on the basis of 12 O						
Si	2,878	2,714	2,702	2,692	2,696	2,727
Al^{IV}	0,122	0,286	0,298	0,308	0,304	0,273
	3,000	3,000	3,000	3,000	3,000	3,000
Al^{VI}	1,559	1,667	1,564	1,610	1,422	1,276
Ti	0,131	0,069	0,109	0,102	0,029	0,090
Fe^{3+}	0,146	0,104	0,149	0,128	0,538	0,496
Cr	-	-	-	-	-	-
Fe^{2+}	-	-	-	-	-	-
Mn	0,003	-	0,001	0,003	-	-
Mg	-	-	-	0,002	0,399	0,159
Ca	3,129	3,156	3,130	3,130	2,612	2,979
Na	0,032	0,005	0,048	0,025	-	-
	5,000	5,001	5,001	5,000	5,000	5,000
Alm	-	-	-	-	-	-
Andr	7,97	5,73	8,26	7,13	29,95	27,28
Gross	91,91	94,27	91,71	92,68	55,26	66,91
Pyrope	-	-	-	0,09	14,79	5,81
Spess	0,12	-	0,03	0,10	-	-
Uvar	-	-	-	-	-	-

Low-temperature (ordered) vesuvianite typical of rodingites would have been expected to give its diagnostic peaks at ~635 and 695 cm^{-1} (Paluszkiewicz & Zabinski, 2004; Galuskin et. al., 2007). For comparison, vesuvianite crystals from a museum sample were analysed. Dominant peaks at ~370, 638 and 694 cm^{-1} were observed (Fig. 5). However, no peaks at these positions were obtained from the rodingites studied thus precluding the possibility for the existence of this phase.

The occurrence of clinopyroxene (of diopside composition) and chlorite was also testified using Raman spectroscopy. Raman spectra typical of clinopyroxene were obtained from matrix pyroxenes, as well as from pyroxene microinclusions in garnets. The low-wavenumber region is dominated by three bands between 300 and 400 cm^{-1} (~322, 353, 388 cm^{-1}) corresponding to lattice modes (Sharma et al., 1983; Mernagh & Hoatson, 1997). The high-wavenumber region is characterized by two dominant bands at ~666 and 1013 cm^{-1} corresponding to Si-O_b-Si and Si-O_{nb} symmetric stretching vibrations, respectively (O_{nb}: non-bridging oxygens, O_b: bridging oxygens, (Sharma et al., 1983; Mernagh & Hoatson, 1997)). Chlorite was identified as a matrix phase by its typical peaks at ~202, 549, 674-677 and 3580-3666 cm^{-1} (Kleppe et al., 2003).

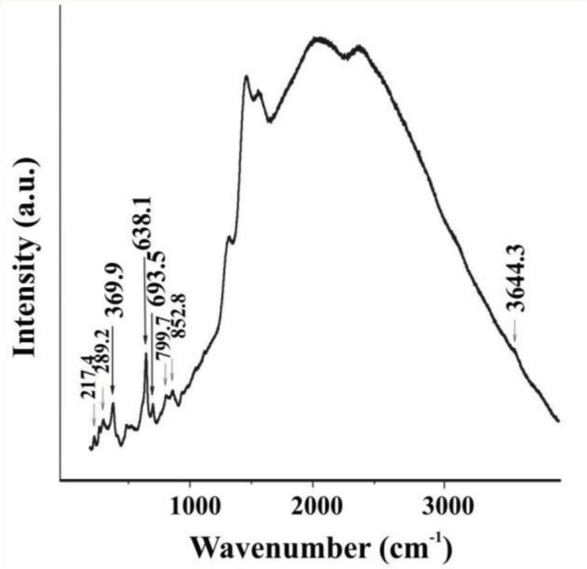

Fig.5. A Raman spectrum of vesuvianite from a museum sample; 632.8nm, He-Ne laser

6. Conclusions

Raman spectroscopy has been proven to be a useful tool for locating hydrogrossular in the samples and exclude the presence of vesuvianite in rodingites from the Othrys ophiolite, Greece. In the case that both minerals were present, this technique would be able to easily distinguish them, as the comparison with the museum sample is showing. Hydrogrossular forms small and weakly birefringent crystals, hence hard to be distinguished from vesuvianite. Neither polarizing and scanning electron microscopy nor XRD were diagnostic for discriminating these two phases. The presence of hydrogrossular was testified in all the samples studied. Although, thoroughly checked for vesuvianite, it was not found in any of the samples, implying that the metasomatising fluid phase was rather rich in CO_2. This was further supported by the presence of calcite and the observed behaviour of REEs assisting in constraining a T-X_{CO2} evolutionary path for the formation of the rodingites (Tsikouras et al., 2009).

A future multiwavelength Raman study of hydrogarnets might provide more information on their Raman spectrum dependence on the laser wavelength and composition (e.g. luminescence source, quantitative determination of the OH content based on the band intensity e.t.c).

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