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Gem-quality rhodonite from Val Malenco (Central Alps, Italy)

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Abstract

Rhodonite from the Mn-deposit of Monte del Forno is one of the more attractive gemstones, together with andradite and nephrite jade, found in Val Malenco (Central Alps, Italy). A complete characterization of this mineral was provided using classical gemological methods and advanced techniques such as X-ray powder diffraction, EMPA-WDS chemical analyses, Raman and mid-infrared spectroscopy. Rhodonite ranges in color from pink, white-pink to green and pale brown, due to the occurrence of various accessory minerals including tephroite, spessartine, biotite, magnetite, calcite, quartz, and Mn-oxides and hydroxides. From a detailed microprobe study, performed both on thin section and rough samples, the resulted chemical composition scatters from the ideal formula $MnSiO_3$, due to the occurrence of other cations, such as Ca, Mg and Fe substituting for Mn. Consistent with results of X-ray powder diffraction and IR and Raman spectroscopy, the particularly low content of Ca in two points analysis suggests the hypothesis of the occurrence of pyroxmangite, probably as relict phase in a fine intergrowth with rhodonite. Data of rhodonite from the most famous classic deposits of the world (Russia, Japan, USA, Australia, Peru, Brazil and Sweden) are also used for comparison.

Key words: Val Malenco; Central Alps; Mn-ore deposit; rhodonite; pyroxmangite.

Introduction

A distinct feature of Val Malenco (or Malenco Valley, Central Alps, Italy) is the remarkable number of minerals which have attracted the interest of mineralogists and mineral collectors since the end of 19th century (e.g. Bedogné et al., 1993). Indeed, more than 250 species of minerals are present here, part of which can be seen in the “Historical, Ethnographic, Naturalistic and Mineralogical Museum of the Valmalenco” (Chiesa in Valmalenco, Sondrio). The valley is also renowned at international level for mining activity of minerals and rocks (e.g. talc, soapstone, serpentinite, gneiss) used for practical and decorative purposes.

Some of the mineral species occurring in Val Malenco are precious gemstones, such as the green variety of andradite known with the varietal name “demantoid”, which represents one of the best Italian gemstone (Adamo et al., 2009; Bocchio et al., 2010), or semiprecious materials (nephrite jade, rhodonite, “clinothulite”, serpentine minerals) carved for various ornamental objects or articles of fine jewelry. Recently, nephrite jade, which has been object of a study concerning its gemological and mineralogical properties (Adamo and Bocchio, 2013) and rhodonite, have gained a remarkable commercial value, being particularly appreciated in the gem market. As regards to rhodonite, first described by Jervis (1873), it occurs in the manganese mineralization within metamorphic rocks of Mesozoic age in two main localities: Monte del Forno and Val Scerscen (Ferrario and Montrasio, 1976; Peters et al., 1978; Bedogné et al., 1993). Both these deposits give samples of an agreeable aspect but the compact and fine-grained microstructure as well as the intense pink color of rhodonite from Monte del Forno make it more worthy of attention as gemological material (P. Nana, 2013, personal communication). In addition, the occurrence of quartz in close association with rhodonite makes easier the carving and polishing and improves significantly the color tones of this stone. The Monte del Forno rhodonite deposit is sited at 2761 m above sea level (Italian map F. 18, Tav. I NO, I.G.M., coord. 5658.3142) and, despite the logistic difficulties, might provide a notable quantity of material applying techniques that implicate the use of mines and pneumatic hammers (P. Nana, 2013, personal communication).

Notwithstanding rhodonite from Monte del Forno has indeed a significant gemological and economic interest, there are only few analytical data available in literature on this mineral and they go back to more than twenty years ago (Ferrario and Montrasio, 1976; Peters et al., 1978; Bedogné et al., 1993). In this light, we have undertaken this study, aimed to provide a complete gemological and mineralogical characterization of this gem material, also comparing the results with data from rhodonite worldwide. The samples, which belong to the private collection of P. Nana (Sondrio, Italy), were characterized by standard gemological methods, combined with X-ray powder diffraction, electron microprobe technique (EMPA-WDS), mid-infrared and Raman spectroscopy. In addition, this work provides a contribution to the study of the coexistence between rhodonite and its polymorph pyroxmangite, documenting the occurrence of this latter as intergrown with rhodonite.

Background Information

Rhodonite ($MnSiO_3$) is the Mn-rich member of the silicate mineral family commonly called *“pyroxenoid group”*. It is triclinic, and its structure is composed by endless silicate chains parallel to the *c* axis and made up of repeating five tetrahedral units (n = 5). The chains alternate with M octahedral sites, designed M1 through M5, where divalent cations reside (Deer et al., 1997 and references therein).

Rhodonite is named after the Greek word for rose (“*rhodon”*), in allusion to its color and is well known as attractive and decorative material used for ornamental objects. Its pink color is distinctive, although it can be confused with a few other pink gems, e.g. rhodocrosite ($MnCO_3$) and pyroxmangite ($MnSiO_3$). However, rhodochrosite is generally streaked with white minerals such as calcite and is reactive to warm dilute acids, whereas rhodonite is resistant to acids and is usually associated with manganese oxidation products. The distinction from pyroxmangite is instead more difficult and requires more advanced analytical techniques such as X-ray powder diffraction. This is due to the close similarity between the structures of these two minerals, both belonging to the pyroxenoid group, and differing only for the periodicity of the tetrahedral chains (n = 7 in pyroxmangite), as well as for the corresponding arrangement of the octahedrally coordinated cations. They are also considered polymorphs of $MnSiO_3$, with varying amounts of Ca^{2+}, Fe^{2+} and Mg^{2+} substituting for Mn^{2+}, but their temperature/pressure and compositional stability limits are still matter of debating (Ito, 1972; Peters et al., 1973; Ohashi et al., 1975; Maresch and Mottana, 1976; Brown et al., 1980; Akaogy and Navrotsky, 1985; Abrecht, 1988; Takahashi and Hariya, 1995; Zanazzi et al., 2008; and reference therein). Moreover, many data are reported in literature dealing with the coexistence of rhodonite and pyroxmangite, often present together as bladed intergrowth, in various types of ore deposits and Mn silicate-carbonate rocks (Ohashi et al., 1975; Jefferson et al., 1980; Pinckney and Burnham, 1988; Millsteed et al., 2005; Michailidis and Sofianska, 2010).

Rhodonite is generally recovered as massive materials, although single-crystals are rarely found and distributed on the mineral markets. Major gem-quality rhodonite sources include Sweden, Pajsberg (Lee, 1958), Russia, e.g. Malosedel’nikovskoe and Kurganovskoe deposits, Sverdlovskaya Oblast’, Middle Urals (Bukanov, 2006) and Magnitogorsk deposit, Čeljabinsk Oblast’, South Urals (Brusnitsyn, 2010), Australia, Broken Hill, New South Wales (Millsteed, 2005; 2006), U.S.A., Franklin, New Jersey (Nelson and Griffen, 2005), Canada, British Columbia (Simandl et al., 2001), Peru, Huánuco (Wilson, 1989), Brazil, Minas Gerais (Leverett et al., 2008; Quinn, 2004), and various localities in Japan (Ohashi et al., 1975). In Italy, rhodonite is present at Saint-Marcel, Val D’Aosta (Prabornaz mine, Mottana, 1986), Monte Civillina, Veneto (Schiavinato, 1953), Graveglia Valley, Liguria, Valgraveglia (ex-Gambatesa) and Molinello mines (Marchesini and Pagano, 2001), Alagna Valsesia, Piedmont (Feglierec mine, Peters et al., 1978), Strona Valley, Piedmont (Bertolani, 1967), Scortico, Apuan

Alps, Tuscany (Di Sabatino, 1967; Mancini, 1997), Campiglia Marittima, Tuscany (Capitani et al., 2003) and in Val Malenco (Sondrio), but only this last resort, together with Scortico, provides useful material for the purpose of gemology.

Geographic and Geologic Setting

Val Malenco is located at the boundary between Southeastern Switzerland and northern Italy, between the Pennidic and the Australpine domains of the Alps. Three majors structural complexes characterize this area; from east to west they are: 1) the Margna unit, composed of basement rocks with their Mesozoic sedimentary cover; 2) the Malenco unit that is one of the largest ultramafic masses of the Alps dominated by variably serpentinized ultramafic rocks; 3) the Monte del Forno ophiolite suite consisting of metabasaltic rocks (mainly composed of amphibolites, with locally preserved pillow structures), and a metasedimentary cover. The latter consists, at the bottom, of quarzitic rocks (known as “Basal Quartzites”), showing intercalations of Ca-silicate marbles and amphibole-pyroxene greenschists, while the upper level is composed of andalusite-garnet biotitic schists and diopside-plagioclase quartzoschists (Ferrario and Montrasio, 1976; Trommsdorff et al., 1993; Müntener et al., 2000; and references therein).

The Mn-ore deposit of Monte del Forno is associated with the amphibole-pyroxene greenschists occurring in the “Basal Quartzites”. The ore bodies (up to 20 m long and 1 m thick) have stratiform features and display a mineral association including rhodonite, spessartine garnet, tephroite, Mn-Ca carbonates, Mn-oxide/hydroxides, amphibole and quartz (Ferrario and Montrasio, 1976). Bedognè et al. (1993) report also the occurrence of other Mn-silicate such as pyroxmangite, braunite and bustamite. Rhodonite is usually massive and opaque but rare transparent crystals with a prismatic habit have been found (Bedognè et al., 1993).

Materials and Methods

A total of 10 samples, including both cut and rough specimens, of rhodonite from Monte del Forno, Val Malenco was investigated in the present study. The optical properties and the specific gravity were determined by standard gemological methods on cut samples. Refractive index was measured by the distant vision method using a Kruss refractometer using sodium light (589 nm) from a Leitz lamp, and methylene iodide satured with sulphur and C2I4 as a contact liquid (R.I. = 1.81), whereas a Mettler hydrostatic balance was used to determine the specific gravity.

X-ray powder diffraction (XRPD) measurements were carried out at room condition on 3 selected samples by means of a PANalytical X’Pert Pro diffractometer, equipped with an X’Celerator detector, using Cu*K*α radiation. A step scan of 0.02° 2θ was performed over the range 5 - 100° 2θ and NBS-Si(640c) was used as internal standard. The General Structure Analysis System (GSAS) software, implementing the Rietveld refinement method, was used to process XRPD data (Larson and Von Dreele, 1994; Toby, 2001).

Backscattered electron images and quantitative chemical analyses of major and minor elements were performed on rough samples and thin sections using a JEOL JXA-8200 electron microprobe in wavelength dispersion mode (EMPA-WDS) under the following conditions: 15 kV accelerating voltage, 5 nA beam current, and a counting time of 60 seconds on peak and 30 seconds on the background. Natural minerals (rhodonite for Si and Mn; olivine for Mg; omphacite for Na; ilmenite for Ti; K-feldspar for K; anorthite for Al and Ca; fayalite for Fe) and Cr metal for Cr, were used as standards. The raw data were corrected for matrix effects using a conventional ΦρZ routine in the JEOL software package.

A heating experiment was performed in a laboratory box furnace Tersid Elite mod. DRF 14/5 at 600 °C in air for 1 hour on a selected pink sample, ~ 4 x 2 cm in size.

Raman spectroscopic analyses were carried out on three samples using a Jobin Yvon HR800 LabRam μ-Raman spectrometer equipped with an Olympus BX41 microscope, an HeNe 20 mW laser working at 632.8 nm and a Charge Coupled Device (CCD) air cooled detector. The correct calibration of the instrument was obtained by checking, before every run, position and intensity of the Si band at 520.65 ± 0.05 cm^{-1}. In order to balance signal against noise, at least 50 cycles of 20 seconds were performed. The spectral region recorded ranged from 1200 cm^{-1} to 100 cm^{-1}, where lies the vibrational lattice modes of the different minerals. The obtained spectra were processed using ORIGIN vers. 6.0 software (originlab corporation, http://www.originlab.com). The identification of the mineral phases, giving rise to the different Raman bands observed, was performed on the basis of the Raman spectra in RRUFF database.

The mid-infrared spectrum of rhodonite was collected on a powdered sample in the 4000 - 400 cm^{-1} range, using a Perkin Elmer Frontier FTIR spectrometer, with a resolution of 4 cm^{-1} and averaging 200 scans.

Results

Gemological and physical properties

Rhodonite samples from Monte del Forno have a massive and opaque aspect, with a color ranging from pink, white-pink to green and pale brown (Figure 1), due to occurrence of various accessory minerals. Black veins and patches are also very common, as typical for this gemstone. The refractive index measured by the distant vision method, is 1.73 (st.dev. 0.01), whereas the specific gravity ranges from 3.43 to 3.65 g/cm^3. This variation is obviously influenced by the accessory minerals, although in the range of typical rhodonite (Deer et al., 1997). The samples contain, as resulted by optical observations, garnet, tephroite, biotite, magnetite, calcite, quartz, and Mn-oxides and hydroxides. The occurrence of all these minerals varies from sample to sample and affects the variation of color.

The X-ray powder diffraction pattern obtained from pink colored material showed that the main phase is rhodonite, with minor amounts of spessartine and quartz (an example is shown in

Figure 1. Polished specimens of rhodonite from Monte del Forno, Val Malenco.

Figure 2). Pyroxmangite, a polymorph of $MnSiO_3$ together with rhodonite, seems to be present but a sure and unambiguous identification only by means of XRPD is not possible, because of the strong overlap of the rhodonite and pyroxmangite peaks due to the close similarity in composition of the studied samples (Michailidis and Sofianska, 2010).

The refined cell parameters of rhodonite from Monte del Forno [a = 9.836(1) Å; b = 10.542(3) Å; c = 12.244(4) Å; α = 108.701(3)°; β = 103.297(2)°; γ = 82.212(1)°] are slightly larger

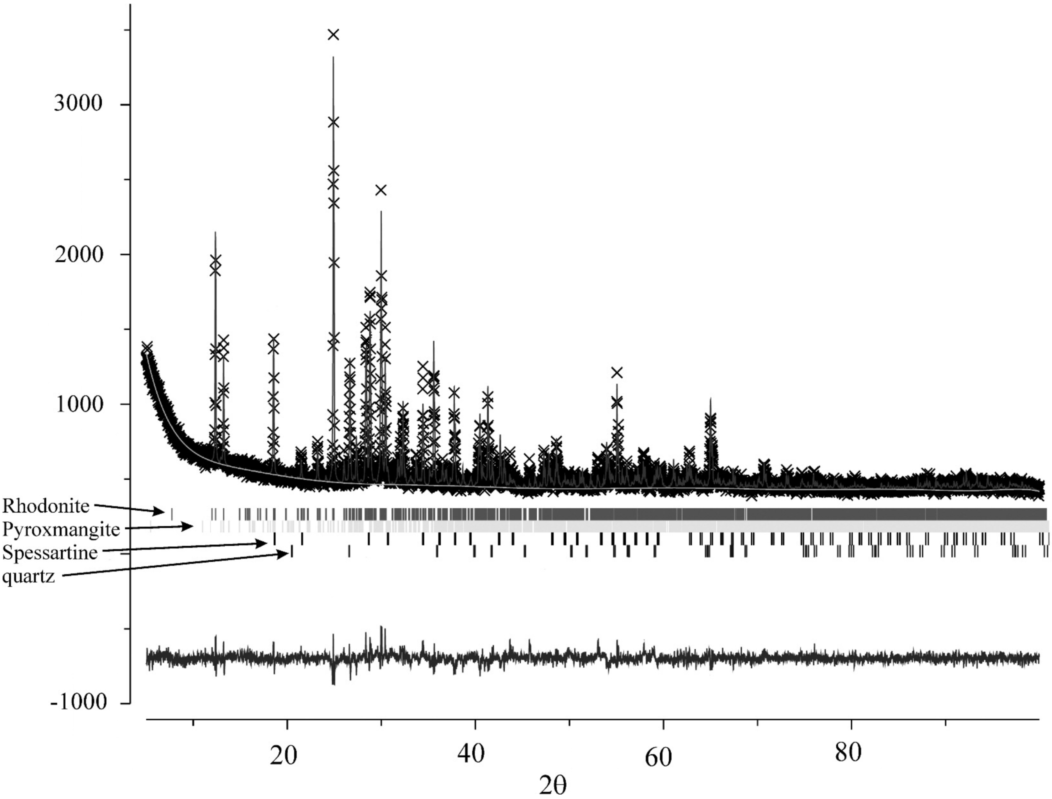

Figure 2. Rietveld refinement of the X-ray powder diffraction pattern of rhodonite from Monte del Forno, Val Malenco. The lower pattern represents the residual between the calculated and experimental curves.

than those listed by Deer et al. (1997) but are consistent with those reported by Nelson and Griffen (2005) for rhodonite from various localities containing a high calcium content. According to the data reported in literature, the increasing of *a* dimension with Ca is in line with the general trend of the pyroxenoid minerals (cfr. references quoted by Deer et al., 1997).

The heat treatment, which is often used to improve the color of gemological material, was carried out on a pink sample that showed a change of color, turning from brown to dark brown, at 600 °C. The change of color by heating was already observed by Ito (1972) and it has been more recently attributed to the oxidation of Mn^{2+} to Mn^{4+} (Paião and Watanabe, 2008).

Raman spectroscopy

The Raman spectrum of rhodonite from Monte del Forno is presented in Figure 3. The 1089 cm^{-1} and the 720 cm^{-1} bands are related to carbonate impurity, whereas the most of other bands can be assigned to different Raman modes of rhodonite (Makreski et al., 2006). In particular, the strong band at 1001 cm^{-1} is assigned to ν_1 symmetric stretching mode of the SiO_4 units, whereas the two bands at 978 and 943 cm^{-1} are two components of the ν_3 symmetric stretching, and the strong and sharp peak at 671 cm^{-1} is assigned to the Si-O-Si ν_4 bending mode (Mills et al., 2005; Makreski et al., 2006). The band at 1048 cm^{-1} could arise from OH deformation of the surface adsorbed water, as well as the 883 cm^{-1}

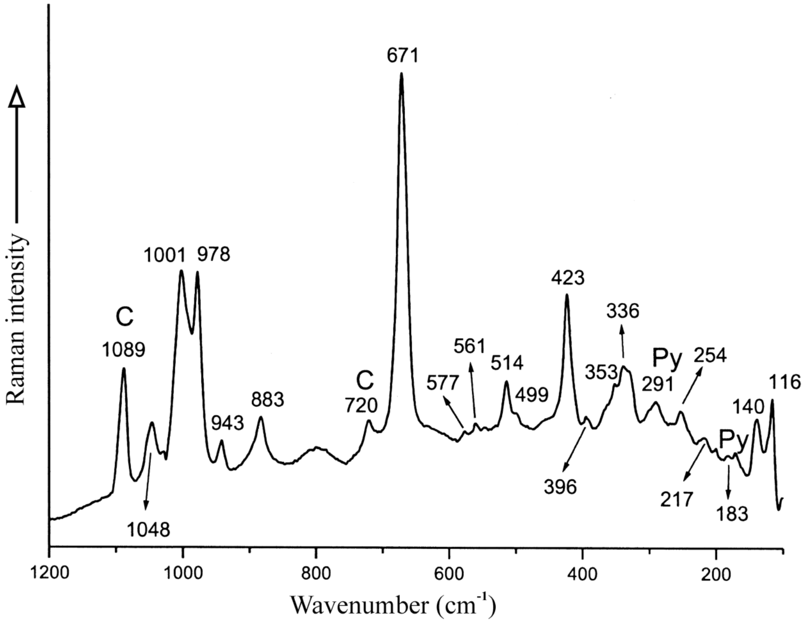

Figure 3. The Raman spectrum in the 1200 - 100 cm^{-1} range of the rhodonite here investigated (C = carbonate and Py = pyroxmangite).

band (water libration mode, Mills et al., 2005), although this latter can be also a result of Si-O stretchings (Makreski et al., 2006). The Raman spectrum below 600 cm^{-1} is rather complex, due to the mixed character of the vibrational modes and the assignment of the various bands is more difficult. However, the 423 cm^{-1} band is one component of the O-Si-O ν_2 bending mode of rhodonite and the 340 cm^{-1} could be ascribed to the stretching vibrations of the MnO_6 and CaO_6 octahedra in rhodonite (Makreski et al., 2006). The Raman spectrum of pyroxmangite, probably present in minor amounts in our samples, in agreement with XRPD, is reported in the RRUFF database, and, to our knowledge, there are no detailed studies in literature. According to the RRUFF database (no. R060999, showing the more significant bands at 997, 974, 877, 700, 668, 522, 452, 422, 363, 336, 297, 268, 183, 161 cm^{-1}), we observed that the Raman features of pyroxmangite mostly overlap with those of rhodonite. However, the occurrence in our spectra of the band at 291 cm^{-1}, as well as the very weak band at 183 cm^{-1} (Figure 3), both attributed to pyroxmangite, may confirm the presence of this mineral.

Infrared spectroscopy

The infrared spectrum of rhodonite is rather complex, being characterized in the 1100 - 400 cm^{-1} range by many absorption bands (Figure 4), due to different fundamental vibrational modes of this pyroxenoid (Makreski et al., 2006). The high-wavenumber region (1100 - 750 cm^{-1})

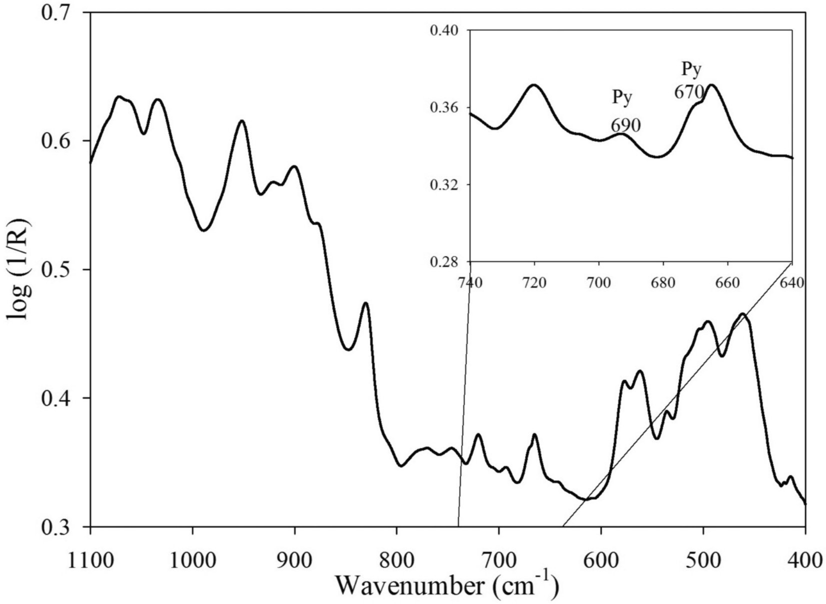

Figure 4. The infrared spectrum in the 1100 - 400 cm^{-1} range of the rhodonite here investigated investigated (Py = pyroxmangite).

consists of two strong and broad absorption bands containing seven intense maxima at 1071, 1058, 1030, 950, 920, 900 and 875 cm^{-1}, all attributed to Si-O stretching vibrations of the SiO_4 tetrahedra of rhodonite (Ryall and Threadgold, 1966; Makreski et al., 2006). The region between 750 and 550 cm^{-1} is even more complex, with various absorption features. The number of bands in this range is directly related to the number of SiO_4 tetrahedra in the repeat unit of the chain and can provide indication of the type of pyroxene or pyroxenoid (Ryall and Threadgold, 1966; Makreski et al., 2006). We observed more than the five peaks expected for rhodonite (with five tetrahedra in its repeating unit) and it is probably related to the occurrence of other phases. The five peaks at 718, 664, 638, 574 and 561 cm^{-1} are associated with the deformation of the Si-O linkages in rhodonite (Ryall and Threadgold, 1966; Makreski et al., 2006). We observed two other additional bands at 690 and 670 cm^{-1}, also found by Makreski et al. (2006) and attributed to quartz impurities, although Ryall and Threadgold (1966) considered the 690 cm^{-1} feature still related to rhodonite. However, we also suggest the possible contribution of pyroxmangite, which indeed has two additional peaks with respect to rhodonite (for a total of seven absorption bands in the 550 - 750 cm^{-1} range, according to its tetrahedral repeating unit), located at 695 and 673 cm^{-1} (Ryall and Threadgold, 1966). The absorption bands found below 550 cm^{-1} (i.e. 534, 513, 502, 492, 458, and 412 cm^{-1}) are the result of the vibrations from the YO_6 octahedra of rhodonite and they do not allow to discriminate between the different pyroxenoids (Ryall and Threadgold, 1966; Makreski et al., 2006).

Additional peaks at 829, 768, and 743 cm^{-1} can be attributed to the occurrence of manganese oxides and/or hydroxides closely associated with rhodonite (Van Der Marel and Beutelspacher, 1976).

Mineral chemistry

Backscattered electron images (e.g. Figure 5) show the association of rhodonite with manganoan calcite, Ca-Mn carbonates, manganoan hydroxides and the two main accessory silicates, garnet (averaged composition on 10 analyses: $Sps_{91.6}Alm_{1.0}Grs_{7.2}Prp_{0.2}$) and tephroite (averaged composition on 10 analyses: $Tep_{97.8}Fo_{1.5}Fa_{0.7}$).

Selected chemical analyses of the Monte del Forno rhodonite sample are presented in Table 1, while the entire set of analyses (380 points) is plotted graphically in Figures 6 and 7. The set includes also the analyses of the heated sample that resulted unchanged before and after the

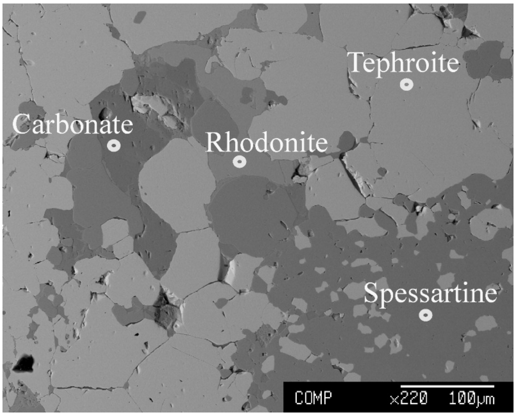

Figure 5. Backscattered electron image of rhodonite and some associated minerals.

heating treatment. All the samples are composed by rounded microcrystals (up to 100 - 200 µm) that are essentially unzoned (X-ray maps performed on the thin section confirmed this assessment) but the chemical composition across both rough samples and thin sections changes

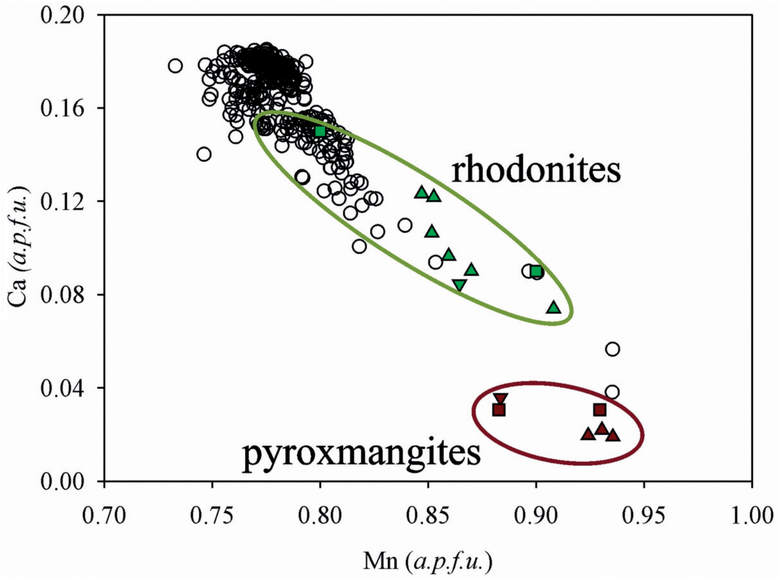

Figure 6. Compositional variation of Ca versus Mn of coexisting rhodonite-pyroxmangite from Val Malenco (empty circles) and from other Italian localities (Peters et al., 1978; Mottana, 1986). Triangle down, triangle up and square: samples from Saint-Marcel, Val Scerscen and Alagna, respectively. Rhodonite in green and pyroxmangite in red. The ellipses refer to the samples from literature.

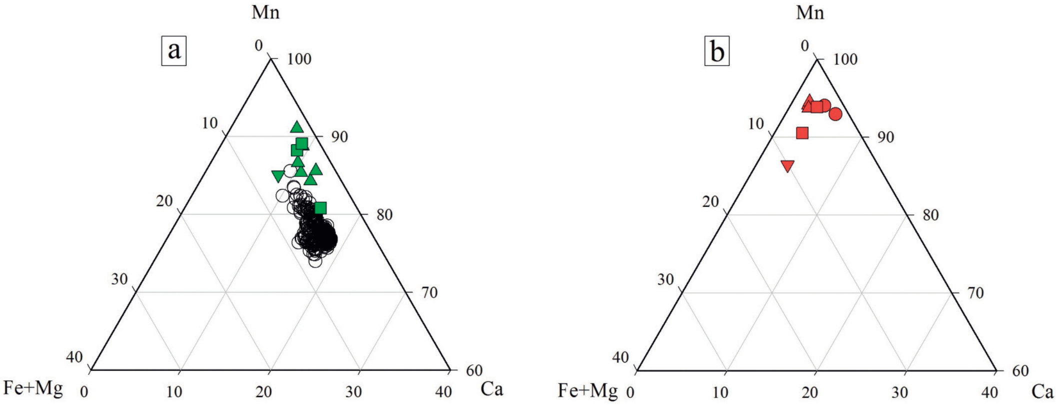

Figure 7. Ternary diagram of Mn, Ca and Fe+Mg: a) rhodonite and b) pyroxmangite. Symbols as in Figure 6.

significantly. In fact, while the content of Si is almost stoichiometric (Si = 4.94 - 5.10 apfu), that of Mn scatters from the idealized formula ($Mn_5Si_5O_{15}$) due to the occurrence of other cations in M-sites (Ca, Fe, Mg, Ti). In some crystals also minor amounts (0.02 - 0.05 wt%) of Ni, Sr, Ba and Zn oxides were detected. According to Mottana (1986), the absolute amounts of ions substituting for Mn vary from one locality to the others, probably reflecting the type of carbonate present, the bulk composition of the mother-rock as well as the availability of the elements. The inspection of Figure 6 suggests that:

i) there is a negative correlation between the manganese and calcium content both in our samples and in rhodonite from some others Italian localities in the Alps reported in literature (Val Scersen and Alagna: Peters et al., 1978; Saint-Marcel: Mottana, 1986);

ii) most of the analyses plot in a very restricted area of the diagram but enlarge the field of variation of rhodonite from the Alps up to 0.93 apfu of Ca vs 3.67 apfu of Mn;

iii) two analyses (Table 1: n. 11 and 12) differ significantly from all the other ones both in Mn and Ca content and plot very close to the area defined by pyroxmangite coexisting with rhodonite from Val Scersen, Alagna and Saint-Marcel (see reference above). This result could confirm the occurrence, suggested on the basis of X-ray diffraction data, infrared and Raman

Table 1. Representative electron microprobe analyses of the Monte del Forno samples (wt%).

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	47.00	46.76	46.40	47.08	46.94	47.23	47.11	46.96	46.94	46.63	46.40	46.79
TiO_2	-	-	0.07	-	-	-	-	0.02	0.03	0.02	-	0.03
Al_2O_3	0.02	0.02	-	0.01	-	-	0.02	0.01	0.01	-	-	0.02
FeO	3.26	3.27	3.20	2.51	2.04	1.26	1.36	1.33	1.78	0.13	0.16	0.18
MnO	41.53	41.80	41.68	43.36	44.21	44.80	45.48	44.65	45.25	49.43	51.42	51.56
MgO	0.68	0.66	0.65	0.64	0.54	0.93	0.90	0.99	1.33	0.39	0.36	0.56
CaO	7.26	6.41	6.79	6.30	6.18	6.21	5.51	6.11	4.40	3.92	2.46	1.66
Total	99.75	98.92	98.79	99.91	99.91	100.43	100.38	100.07	99.74	100.63	100.81	100.84
Number of ions on the basis of 3 oxygens												
Si	1.002	1.006	1.001	1.004	1.003	1.002	1.001	1.000	1.003	0.996	0.997	1.001
Ti	-	-	0.001	-	-	-	-	-	-	-	-	-
Al	0.001	-	-	-	-	-	0.001	-	-	-	-	-
Fe	0.058	0.059	0.058	0.045	0.036	0.022	0.024	0.024	0.032	0.002	0.003	0.003
Mn	0.750	0.761	0.761	0.783	0.800	0.805	0.819	0.805	0.819	0.894	0.935	0.934
Mg	0.022	0.021	0.021	0.020	0.017	0.029	0.028	0.032	0.042	0.012	0.012	0.018
Ca	0.166	0.148	0.157	0.144	0.141	0.141	0.125	0.139	0.101	0.090	0.057	0.038
Sum	1.998	1.995	1.999	1.996	1.998	1.999	1.999	2.000	1.997	1.995	2.003	1.995

spectra, of some rare crystals of pyroxmangite in the rhodonite sample from Monte del Forno, probably intergrown with the more ubiquitous rhodonite and undetectable by optical observations.

The ternary Mn-Ca-(Mg+Fe) diagrams (Figure 7) emphasize the chemical difference between rhodonite and pyroxmangite which, except for the sample from Saint-Marcel, plot closer to the Mn vertex. All pyroxmangite samples contain an amount of Ca lower than that of coexisting rhodonite.

In Figure 8 we report representative analyses of rhodonite from literature: Sweden, USA, Peru, Australia (Nelson and Griffen, 2005), Brazil (Leverett et al., 2008), Russia (Brusnitsyn, 2010) and Japan (Ohashi et al., 1975). The samples from USA include the rhodonite variety called "fowlerite" from Franklin, differing from the typical rhodonite for the high amount of ZnO (up to 10 wt%). As a whole, the chemistry of Italian rhodonites compare well with that of the other world localities. However, samples from Brazil, Australia and Japan shift away from Ca-Mn line, owing to the extent of cationic substitution of Mg and Fe for the major cations Mn and Ca, while "fowlerite" moves toward the Ca vertex.

Discussion and Concluding Remarks

Despite the occurrence of rhodonite in the Mn-ore deposit of Monte del Forno has been described since 1873 (Jervis, 1873), only in the last decade this mineral entered the market as gem material.

This study, performed both on cut and rough samples, aimed to provide new insight into the characterization of this material. As regards to the gemological properties, they are comparable with those of rhodonite worldwide. The heating treatment affects the changing from an agreeable

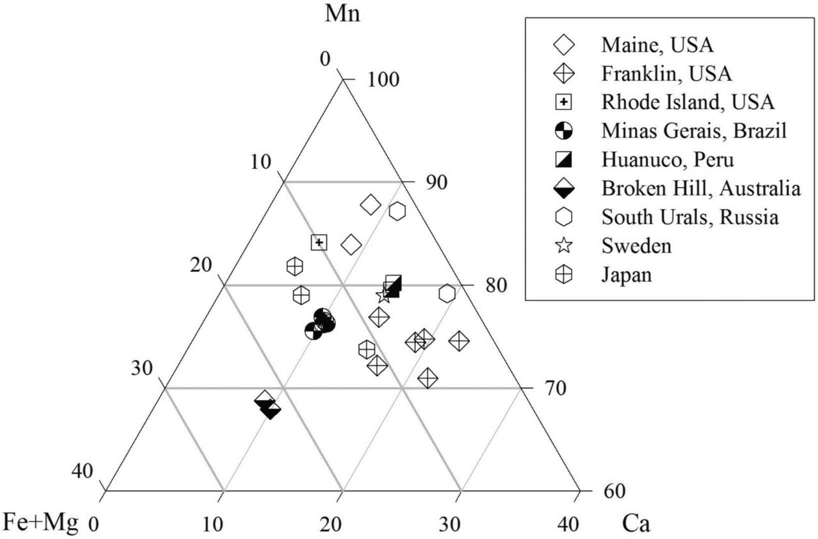

Figure 8. Ternary diagram of Mn, Ca and Fe+Mg of selected samples of rhodonite from literature.

pink to an unattractive dark brown color. The carved material is mainly composed by rhodonite, with minor amounts of other phases, such as spessartine, tephroite, quartz, Ca-Mn carbonates, Mn-oxides and -hydroxides which affect the final color of the gemstone. Rare crystals of pyroxmangite also occur, although distinction between this mineral and rhodonite is rather difficult and require multiple analytical techniques. The use of Raman and IR spectroscopy together with X-ray diffractometry permitted to reveal the presence of the two phases. Moreover, the two minerals could also be distinguished on the basis of their chemistry, as well as by their good match with data from literature. The composition of these two pyroxenoids is indeed quite similar but rhodonite contains an amount of calcium higher than pyroxmangite which is, on the contrary, enriched in manganese.

Experimental data suggest that the relative stability of rhodonite and pyroxmangite is a function not only of temperature and total pressure but also of the chemistry, especially of the Ca/(Ca+Mn) atomic ratio and the CO_2 content of the fluid phase (Abrecht and Peters, 1975; Maresch and Mottana, 1978). According to Bedognè et al. (1993) the Monte del Forno ore deposit underwent metamorphic conditions higher than that of the Mn-mineralizations of Val Scerscen (estimated at 420 ± 30 °C and 3 ± 2 Kb by Peters et al., 1978) because the rocks, enclosed in the contact aureole of the Val Masino-Bregaglia pluton, yielded a strong heating up to 600 °C and were permeated by magmatic fluid. The higher temperature as well as changing f_{CO2} conditions, could have favoured mineral reactions between Mn-silicates and the Ca-silicate bearing marbles, intercalated in the “Basal Quartzite”. Thus, the activity of Ca-rich solutions could have stabilized rhodonite structure with respect to pyroxmagite that remained only as relict phase (Abrecht and Peters, 1975; Mottana, 1986; Abrecht, 1988; Michailidis and Sofianska, 2010).

Although additional mining activities could be limited by access difficulties, the geological features of Monte del Forno deposit suggest that there is a significant potential for further production of rhodonite, whose attractive pink color and relatively high price continue to create interest in jewelry.

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