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STUDIES OF CHRYSOPRASE AND MICROCRYSTALLINE SILICA VARIETIES FROM SERPENTINITES OF SZKLARY MASSIF (FORESUDETIC BLOCK, SW POLAND) BY RAMAN SPECTROSCOPIC TECHNIQUE – PRELIMINARY RESULTS

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Abstract: The mineralogical properties of green colored chalcedony varieties from weathering cover of slightly serpentinized peridotites (harzburgites) occurring near Szklary village on Foresudetic Block (SW Poland) are studied using Raman spectroscopy in the 200 – 1600^{-1} wavenumber region . The obtained results show, that in examined samples, the peaks like: 206, 265, 355, 394, 464, 696, 796, 808 cm^{-1}, characteristic for α-quartz were ascertained. In one sample, the characteristic moganite peak (502 cm^{-1}) was found. It implies that presence of other polymorphs of SiO_2 in crystalline structure, considered a proof for presence of moganite intergrowths with α-quartz. It indicate, that intensity of green color of measured samples of chrysoprase are not correlated with Raman spectroscopic data. It can be conclude, that examination of Raman spectra can be useful only to recognition of internal phase composition of green cryptocrystalline silica polymorphs occurring in weathering cover of serpentinized peridotites.

Keywords: Silica group, chrysoprase, Szklary, moganite, Raman spectra

1. INTRODUCTION

Raman spectroscopy is one of the most popular methods of mineralogical examination of inclusions in the internal parts of jewelry stones. As a nondestructive method of study, it is widely adopted in identification of structure of mineral phases as well as characterizing crystal mineral properties in heterogeneous, optically amorphic decorative stones such as volcanic glasses or silica-bearing decorative materials. De-

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spite the scattering intensities to slight differences in crystal structures and sensitivity of vibrational frequencies Raman spectroscopy is particularity useful in analyzing of degree of crystallinity of silica polymorphs, which are often found in massive chalcedony assemblages.

In 1976 Flörke with coauthors separated a new polymorph of silicate in chalcedones, which was named moganite (from Mogan site on Gran Canaria Island, Spain). It was accepted by IMA in 1999 (Grice and Ferraris, 2000). Kingma and Hemley (1994) identified 19 peaks characterizing this new mineral. The wavenumbers are (in cm^{-1}) 129, 141, 220, 265, 317, 370, 377, 398, 432, 449, 463, 501, 693, 792, 833, 1058, 1084, 1171, 1177, the strongest band is located around 501 cm^{-1}. Since then, owing to using Raman spectroscopy, this polymorph has been spotted more frequently, and its presence or absence can suggest fluid-rocks interaction, or the age of the rocks (Heaney, 1995). Aim of this article is presentation of preliminary data of Raman spectroscopy for chrysoprase occurring at Szklary locality in the SW Poland (Fig. 1). I tried to identify all possible existing polymorphic varieties of SiO_2 in differently colored specimens of chrysoprase from this site.

2. GEOLOGICAL SETTING AND MINERALOGY

Chrysoprase is low-temperature, microcrystalline variety of chalcedony often with heterogenic internal structure. Their name origins from Greek words such as: *chrysos* - gold and *prasithos* - meaning green (as color of garlic or onion leaves). This beautiful deeply green colored jewelry stone is known from Lower Silesia area from XVIII century. From 1775 year the name chrysoprase is tied to green chalcedony coming only from this region of Europe (Sachanbiński, 1980). Nowadays, only two sites of chrysoprase occurrence are known in SW Poland. One is localized at abandoned Ni-ore mine on Tomickie hills at vicinity of Szklary village (old German name: Glassendorf) near Ząbkowice Śl., 76 km south of Wrocław (Fig. 1). Other locality is abandoned, (closed from 1980 year) underground magnesite mine situated at vicinity of Wiry village near Sobótka town, 40 km south-west of Wrocław. In both cases, these thin chrysoprase veins transect upper, weathered parts of ultrabasic rocks. They are often converted into loose powdery brownish weathering products containing hydrated Fe-Ni oxides. In context of regional geology, pristine ultrabasic rocks are considered as lowest member of Lower Palaeozoic Ophiolite Suite, known also as the Sudetic Ophiolite (Majerowicz, 1979; Dubińska and Gunia, 1997; Majerowicz and Pin, 1989, 1994). Chrysoprases from Lower Silesia often occur as a steeply dipped single veins or veinlets in surrounding red-brownish weathering material after serpentinites. Their thickness varies from few millimeters to several centimeters and sometimes higher. Occasionally, they form small, irregular bodies like pockets or lenses, whose size ranges from few to several centimeters (Niśkiewicz, 1982). In old magnesite mine in Wiry, veins of chrysoprase form skeleton-like forms often intergrowed or included within magnesite veins.

According to degree of their crystallinity, the Szklary chrysoprases were divided into three groups (Sachanbiński, 1980). First, opal-rich group, is built mostly of opal shows presence of water (up to 5.48% vol.). This opal have a conchoidal fracture, semi-glassy to waxy shine and refractive index in the range of 1.445-1.447. Second, chalcedony group, consists of micro- to fine-crystalline structure, uneven fracture and glassy shine. The third, recognized group of Szklary silica-bearing samples represents of coarse crystalline chalcedony occasionally converted to crystalline quartz. As it was described by Sachanbiński (1980) chrysoprase from Wiry mine has sugar-like appearance and it contains mainly of chalcedony groundmass (about 95% vol.). Sometimes, the small inclusions of chrome spinel and magnetite are also observed there (Sachanbiński, 1980). Polish chrysoprases are considered one of the most valuable worldwide gemstones used i.e. in jewellery.

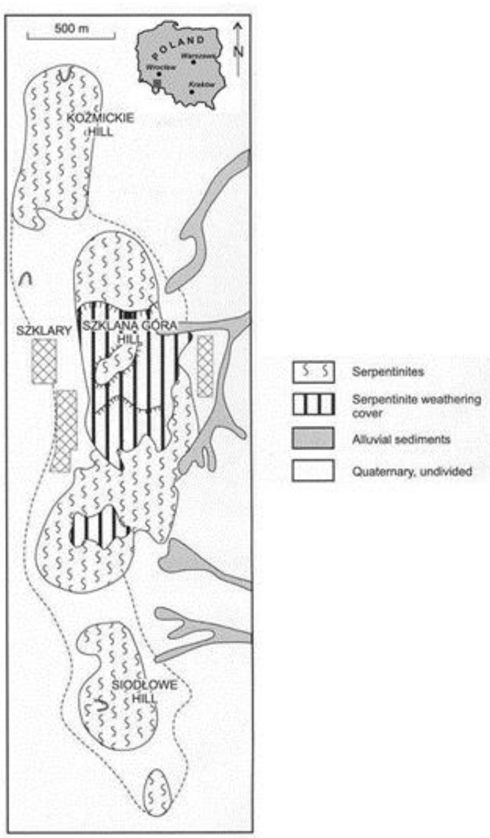

Fig. 1 Geological sketch of the Szklary massif (simplified) based on Badura and Dziemiańczuk geological map (1981) vide: Gunia (2000)

3. METHODS AND MATERIAL

Three samples of chrysoprase from Szklary site have been analyzed using gemological B&W Tek Inc BTC 162 785H-SYS Micro-Raman spectrometer (Fig. 2). Samples were excited by 785 nm wavelenght red light laser source with time ranged from 10 to 20 ns. The obtained peaks were recorded in 200 – 1600 cm^{-1} range. The studies were carried out during (one month long) testing time of MicroRaman B&W Tek spectrometer in Gemmological Laboratory of Antique Seller, “Pod Gryfami” in Wrocław.

All of investigated chrysoprase samples are specimens from the collection of Mineralogical Museum, University of Wrocław. They represented different kinds of jewelry stones.

Sample marked as No. 0 (see Fig. 2) is oval shaped chrysoprase cabochon, 10 mm in diameter, translucent, with glassy shine and light green color. Refractive index measured by distance vision method is about 1.550.

Sample No. 1 (see Fig. 2) is a circle shaped cabochon sized 10x8mm, translucent, with glassy shine with deep green color. Measured value of R.I. is about 1.546.

Sample No. 9 (see Fig. 2) is a small slab of microcrystalline silica sized 40x35 mm and 4 mm in thickness. Among regional collectors this kind of chrysoprase is known as a “plasma”. It is dark apple green in colour, opaque with characteristic sugar-like internal structure and patchy appearance with areas with different tints of green. Despite the poor polish of outer surface of specimen, precisely determination of R.I. value is impossible.

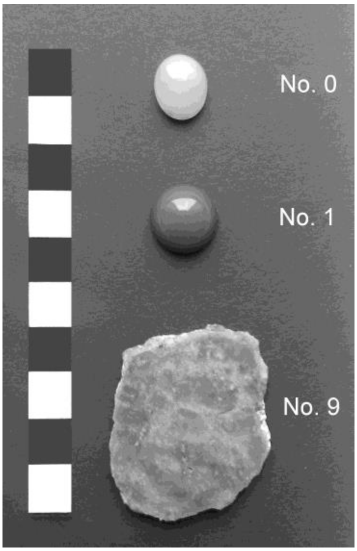

Fig. 2. Three analyzed samples

4. RESULTS AND DISCUSSION

The obtained results of measurements of Raman spectra for Szklary chrysoprase are listed in table 1 together with results measured by Gillet and Le Cléach (1990), and showed on figure No. 3. Chalcedonies show a bulk composition represented mainly by α-quartz. The most intense peaks are located in ranges: 206, 265, 354, 464 cm^{-1}.

In examined samples, aside from peaks characteristic for α-quartz like 206, 265, 355, 394, 464, 696, 796, 808 cm^{-1}, trace peaks were found that may suggest presence of other polymorphs of SiO_2 in crystalline structure. Characteristic for moganite peak (502 cm^{-1}) was found only in sample No. 9, which - appearing around value of 500 cm^{-1} according to Kingma and Hemley (1994) is considered a proof for presence of moganite intergrown with α-quartz. No correlation has been found between intensity of color and mineral composition.

Tab. 1. Raman wavelength results of Szklary chrysoprase compared with α – quartz results by Gillet and Le Cléach (1990)

Raman Shift (cm^{-1})			Gillet and Le Cléach (1990)
No. 0	No. 1	No. 9	α - quartz
206	206	208	128
264	262	264	206
356	308	316	265
394	352	354	355
464	392	394	394
532	464	464	401
570	544	502	450
614	640	698	464
638	688	806	511
706	744	966	696
806	796	1060	796
850	880	1160	808
942	918	1224	1069
1038	954		1085
1066	1222		1162
1160			1230
1212			

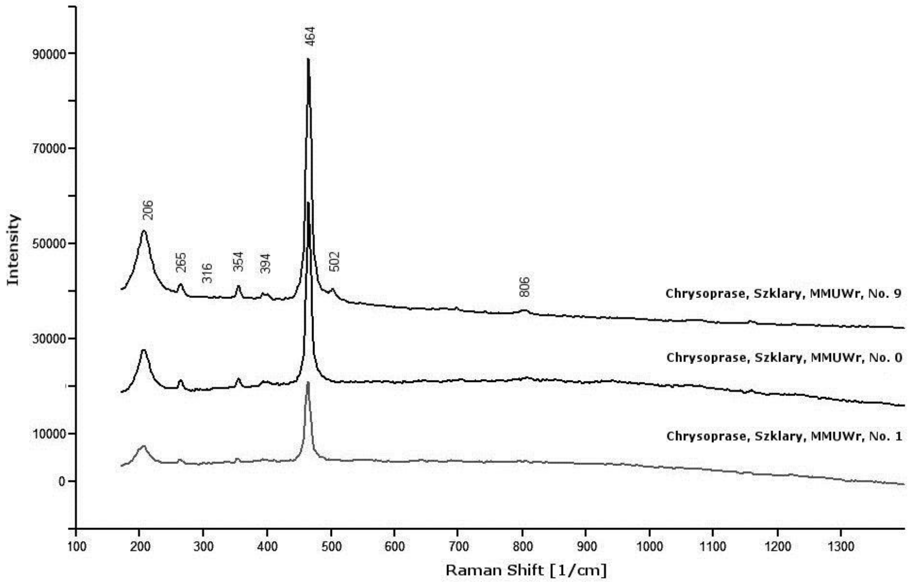

Fig. 3. Raman spectra of chrysoprase samples from Szklary (SW Poland)

5. CONCLUSIONS

- All examined chrysoprase specimens show microcrystalline structure typical of chalcedony.
- Correlation between the intensity of color and Raman spectra was not observed in examined samples.
- Most of measured peaks overlap peaks characteristic to α-quartz.
- One of the samples shows peak at 502 cm^{-1} suggesting presence of moganite.
- Trace Raman spectra not tied to quartz presence need more detailed examination to rule out measure errors and background influences.

Due to limited number and variety of samples (gem quality chrysoprases, cabochone cut, silica slab) obtained results characterize just the selected Raman spectra of studied Szklary green chalcedonies only in very general scope. Further studies of these samples using other spectroscopy methods are in progress.

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