MICROSCOPICAL, RAMAN, AND XRD STUDY ON THE AGATES, CHALCEDONIES, OPALS, AND SILICIFIED WOODS FROM THE SOUTHERN APUSENI MOUNTAINS, ROMANIA

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Abstract. From a geological point of view, the southern slopes of the Apuseni Mountains are mainly composed of Jurassic and Cretaceous ofiolites and laramic volcanites, along with quaternary detritical deposits. Microcrystalline and amorphous silica gems were studied along with different varieties of common silica-bearing rocks, *i.e.*, agate, chalcedony, jasper, opal and silicified wood. The optical microscopy studies revealed grainy to fibrous textures in the case of chalcedony and agate and reticular textures in the case of silicified wood. The analyses showed that the red colour of the gemstones is due to the presence of iron oxides and sesquioxides. X-ray diffractometry pointed out a main peak at 26.64 degrees/2θ, characteristic to quartz, a main peak at 22 degrees/2θ, assigned to cristobalite, and another peak around 20 degrees/2θ, specific for moganite. In addition to α quartz, Raman analyses showed the presence of moganite, with a strong band located around 501 cm^{-1}, and also of graphite, with bands around 1360 cm^{-1} and 1576 cm^{-1} in the silicified woods. Moganite was identified during this study for the first time in Romania. Based on the transformation, at a microscopic scale, of moganite into microcrystalline quartz, we can establish the degree of diagenesis of the sediments, with direct indications regarding the age or maturity of agates from Romania. In spite of the common opinion that the silica gems only result from volcanic processes, an important role of diagenesis was inferred, based on the analysis of the bentonitization of the volcanic clasts.

Keywords: chalcedony, jasper, opal, silicified wood, moganite.

Rezumat. Studiu microscopic, analize Raman și XRD asupra agatelor, calcedoniilor, opalelor și lemnelor silicifiate din Munții Apuseni de Sud, România. Din punct de vedere geologic, versanții sudici ai Munților Apuseni sunt compuși în principal din ofiolite jurasice și cele cretacice și din vulcanite laramice, alături de depozite detritice cuaternare. Gemele din silice microcristalină și amorfă au fost studiate împreună cu diferite varietăți de roci silicatice comune - agat, calcedonie, jasp, opal și lemn silicificat. Studiile de microscopie optică au relevat texturi granuloase până la fibroase în cazul calcedoniei și texturilor de agat iar în cazul lemnului silicificat texturi reticulare. Analizele au arătat că culoarea roșie a pietrelor prețioase se datorează prezenței oxizilor de fier și a sesquioxizilor. Difractometria de raze X a arătat un peak principal la 26,64 grade/2θ, caracteristic cuarțului, un peak principal la 22 grade/2θ, atribuit cristobalitului și un alt peak în jur de 20 grade/2θ, specific moganitului. În plus față de cuarțul α, analizele Raman au arătat prezența moganitului, cu o bandă puternică situată în jurul a 501 cm^{-1}, precum și a grafitului, cu benzi în jurul 1360 cm^{-1} și 1576 cm^{-1} în pădurile silicifiate. Pe baza transformării, la scară microscopică, a moganitului în cuarț microcristalin, putem stabili gradul de diageneză a sedimentelor, cu indicații directe cu privire la vârsta sau maturitatea agatelor din România. În ciuda opiniei comune că gemele silicatice rezultă numai din procesele vulcanice, un rol important al diagenezei a fost dedus, pe baza analizei bentonitizării clastelor vulcanice.

Cuvinte cheie: chalcedonie, jasp, opal, lemn silicifiat, moganite.

INTRODUCTION

The Southern Apuseni Mts. (Western Carpathians) were known for hosting gem-quality SiO_2 varieties since the second half of the 19th century. Several occurrences in the region provide some of the most beautiful chalcedonies, even agates in Romania.

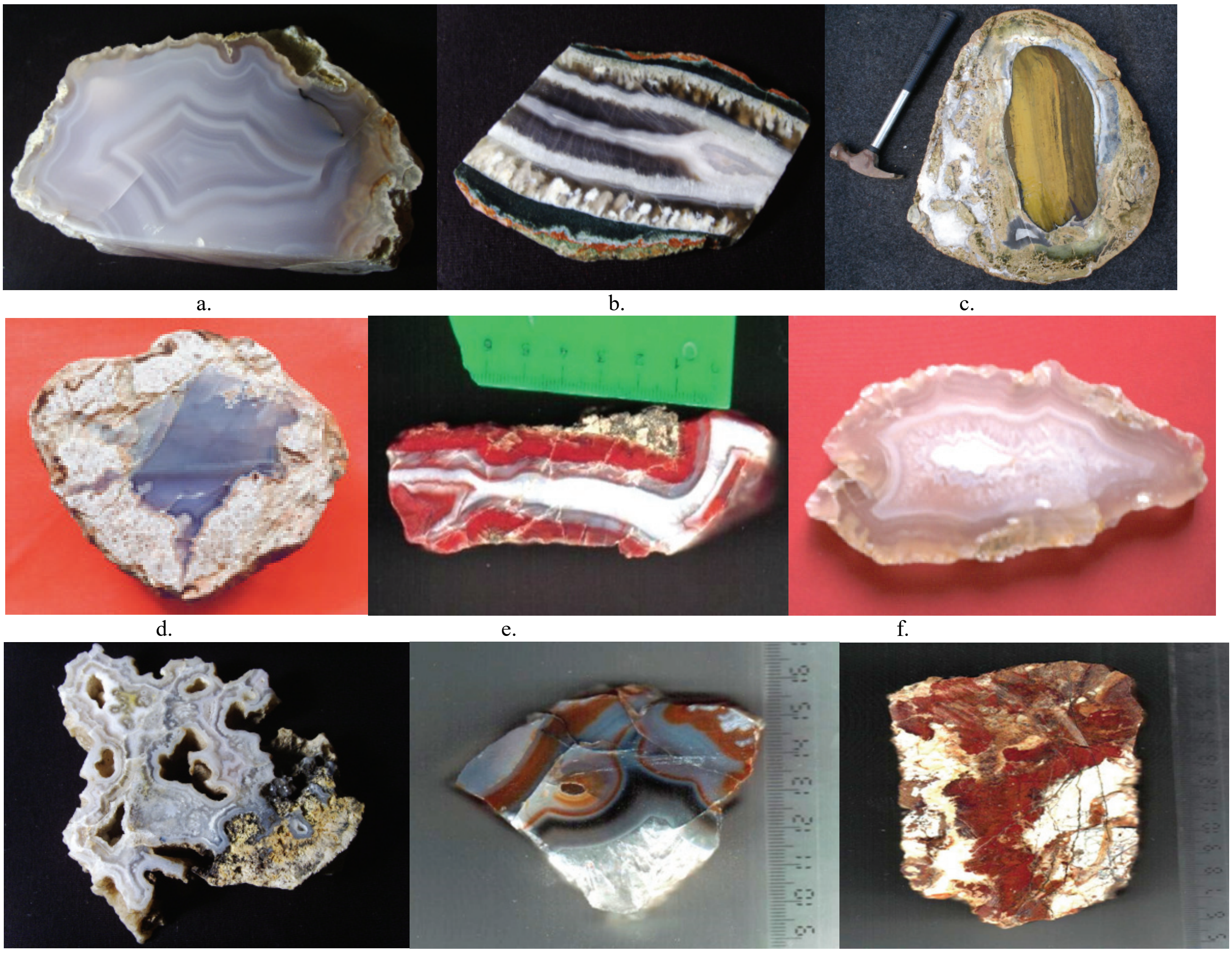
The best-studied occurrence was Gurasada, due to the remarkable diversity of SiO_2 varieties found in the Paleocene pyroclastic and tuffs: chalcedony (including agate), jasper, opal, silicified wood. Most of the samples show macroscopic and/or microscopic variations in colour (grey-red-blue-white), transparency or texture (from massive to banded). Other chalcedonies from the Southern Apuseni Mts. originate from Rachiş (from Cretaceous „ophiolitic" pyroclastics) and Techereu (from Paleocene rhyolites). Famous sites from the Baia Mare area: Trestia - chalcedony and Oraşu Nou – opal (related to the Neogene volcanism), were included for comparison. In the previous studies (e.g. CONSTANTINA & MOXON, 2010) the geological frame and the analytical procedures are methodically presented. Fig. 1 presents the types of gems identified in the studied areas.

According to UDUBAŞA et al., 2002, moganite has been previously mentioned in a metamorphosed manganese ore deposit at Tolovanu, East Carpathians, by HÂRTOPANU (in NEDELCU et al., 1997); no analytical data are given for this mineral at that time (HÂRTOPANU, 2004). A first mention for Romania of the moganite is in UDUBAȘA et al. 2006. The current study refers to its presence in the agate.

MATERIAL AND METHODS

After a preliminary macroscopic evaluation (Mineralogical Laboratory – Geological Institute of Romania), the samples (prepared as thin sections) were thoroughly examined under the polarized light microscope for mineral identification, the grade or type of crystallisation, and the relations between different minerals or phases. Other applied analytical investigations were Raman spectroscopy (Institut für Physikalische Chemie, Würzburg, Germany), XRD (Department of Earth Sciences, Cambridge University, UK and Atomic Structures and Defects in Advanced Materials

Laboratory – National Institute of Materials Physics - Romania), and thermogravimetry (Department of Earth Sciences, Cambridge University, UK) (Fig. 1).



a. b. c.

d. e. f.

g. h. i.

Figure 1. a, f, h. agates (Gurasada), b. onix (Gurasada), c. siliceous concretion with jasper core (Gurasada), d. chalcedony (Techereu), e. agate (Rachiș), g. chalcedony (Gurasada), i. silicified wood (Gurasada).

RESULTS

Microscopical Study

Usually, agates and chalcedonies are lightly coloured, with the central part most frequently represented by white-milky crystalline quartz that grades into microcrystalline and fibrous silica of grey and red colours. Microscopically, the quartz microcrystals have been classified according to their structure; the granular one prevails, and in addition, fibrous and lamellar varieties have been identified.

The microscopic structures evidenced in our samples were represented by: granular structures, structures based on long fibres, fan-like structures, rosette-like structures, hematite interlayers (Fig. 2).

As regards the jasper, the colour is mainly given by iron oxides (hematite) and hydroxides.

The microscopic study of silicified wood highlights the vegetal (cellular) structure of the wood fully replaced by silica (CONSTANTINA, 2008).

Raman Study

Raman spectroscopy is used as a powerful tool for mineral phase identification in geological samples, and for characterizing the crystal chemistry of heterogeneous materials. A special case is represented by mineral polymorphs, such as the SiO_2 phases. The main mineral component of microcrystalline silica, SiO_2 is low-, or α-quartz. Based on X-ray diffraction, FLÖRKE et al. (1976) have evidenced a new silica polymorph, “moganite” that often forms an intimate intergrowth with α-quartz in many microcrystalline SiO_2 varieties. Moganite was recognized as a new species by IMA in 1999 (IMA1999-035).

Micro-Raman spectroscopy (short-range order) proved to be the perfect tool for detecting its presence and for evaluating the moganite-to-quartz ratio (Figs. 3, 4). In order to have sufficient comparative data for the micro-Raman measurements, we have investigated a wide and diverse range of microcrystalline and amorphous gem minerals in the SiO_2 group, from several Romanian occurrences (POP et al., 2004).

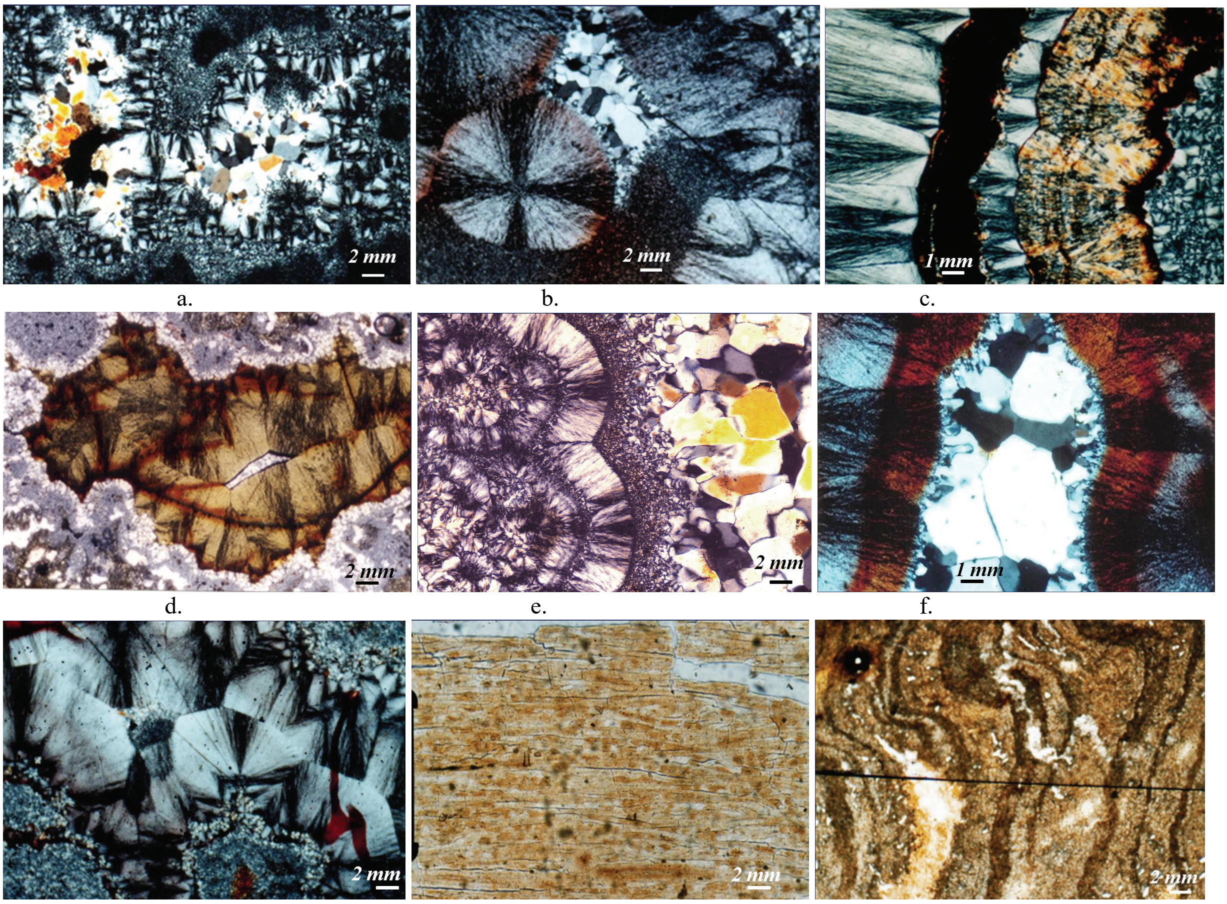


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Figure 2. a. Crypto- and microcrystalline quartz with an agate-type texture (N+) from Gurasada; b. Rosettes of fibrous quartz (carnelian) associated to/with microcrystalline quartz (N+) from Gurasada; c. Banded fibrous quartz. Iron oxyhydroxide-rich bands are visible (N+) from Gurasada; d. Jasper, Fe oxyhydroxides within the fibrous silica (N+) from Gurasada; e. Chalcedony consisting of fibrous silica (rosettes) and microgranular and fibrous (rosette fan type) silica (N+) from Techereu; f. Microcrystalline quartz and hematite in fibrous silica (N+) from Rachiş; g. Fibrous silica and Fe-oxyhydroxides (N+) from Rachiş; h. Silicified wood: the specific structure is preserved (longitudinal section) (1N) from Gurasada; i. Silicified wood: the specific structure is preserved (transversal section) (1N) from Gurasada.

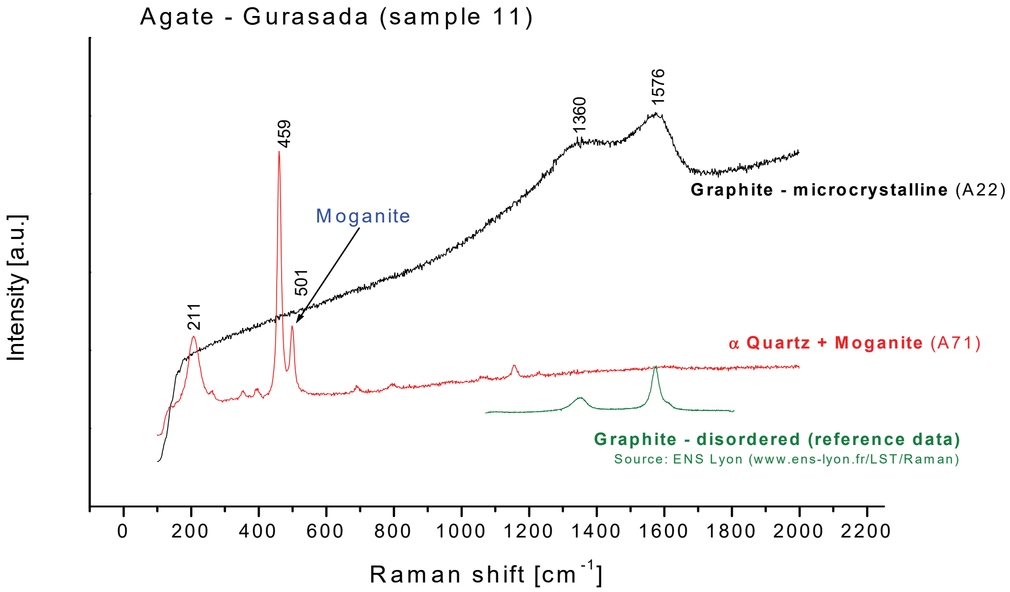

Figure 3. Raman spectra of the agate from Gurasada (POP et al., 2004, with completions).

Figures 3, 4, 5 show the Raman spectra for heterogenous agates, chalcedonies, and jasper. In figure 3 a sample of agate from Gurasada is analysed and the result consists of bands with distinctive mineralogical composition: (α-quartz + moganite) vs. "pure" microcrystalline graphite (disordered carbon). Graphite shows broad D (~ 1360 cm^{-1}) and possibly G+D' (~1576 cm^{-1}) bands indicating strong structural disorder.

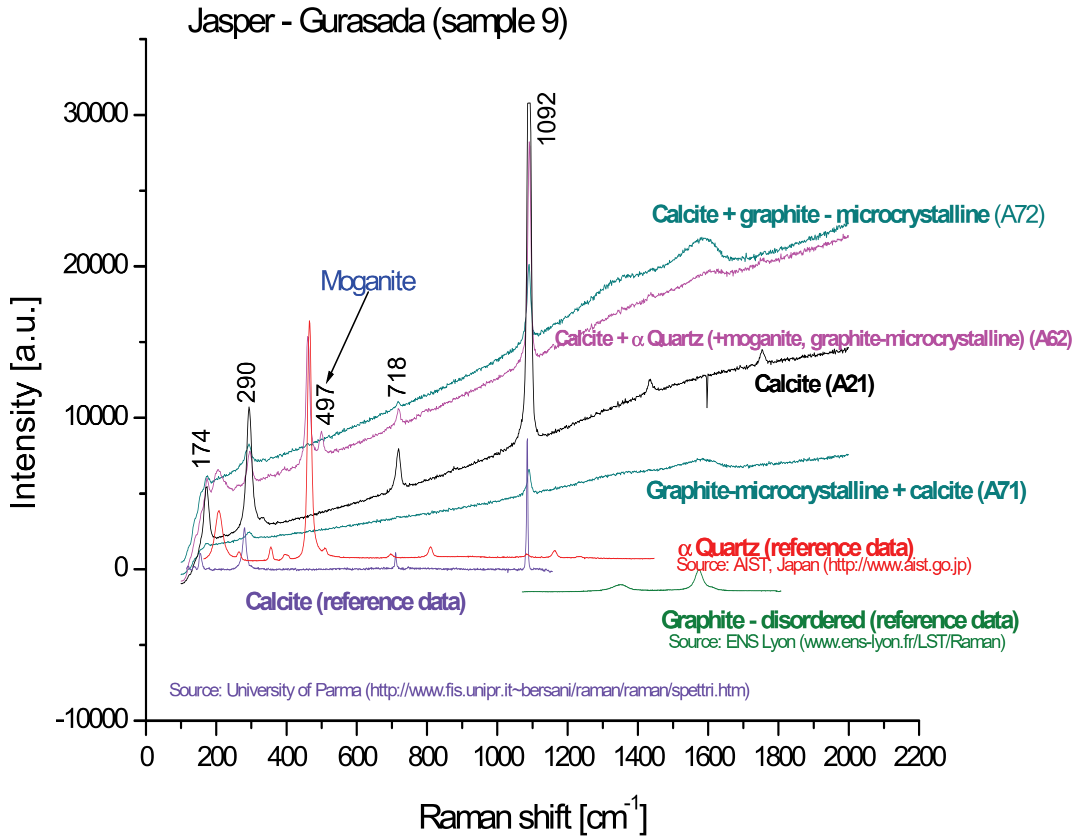

Figure 4. Raman spectra of the jasper from Gurasada (POP et al., 2004, with completions).

Figure 4 presents the spectra of the jasper from Gurasada, characterized by the presence of calcite, as a distinctive phase, or in mixtures with microcrystalline graphite, or α-quartz (+ moganite).

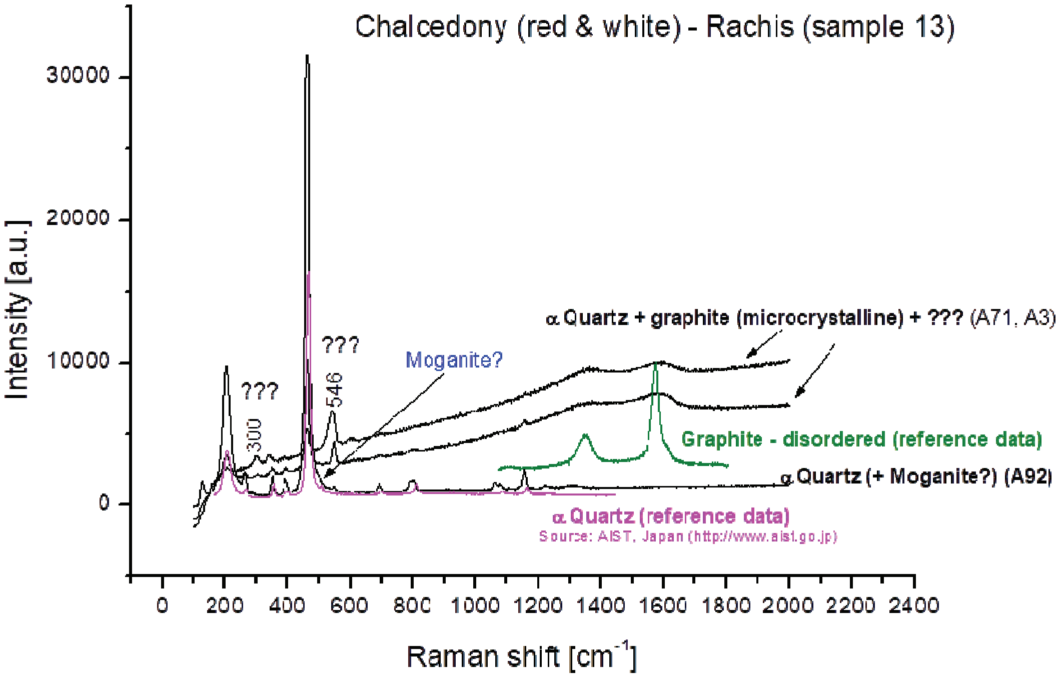

Figure 5. Raman spectra of the red & white chalcedony from (POP et al., 2004, with completions).

Figure 5 presents the red & white chalcedony from the Rachiş spectra consisting of α-quartz (+ minor moganite?); locally α-quartz is intergrown with microcrystalline graphite and an unidentified phase(s?), possibly responsible for the red colour of the gem material.

Heterogenous chalcedonies and jasper from the Gurasada analyse is presented in figure 6. They consist of an intergrowth of α-quartz and moganite. No correlation was found between the colour of the gem material and the mineralogical composition.

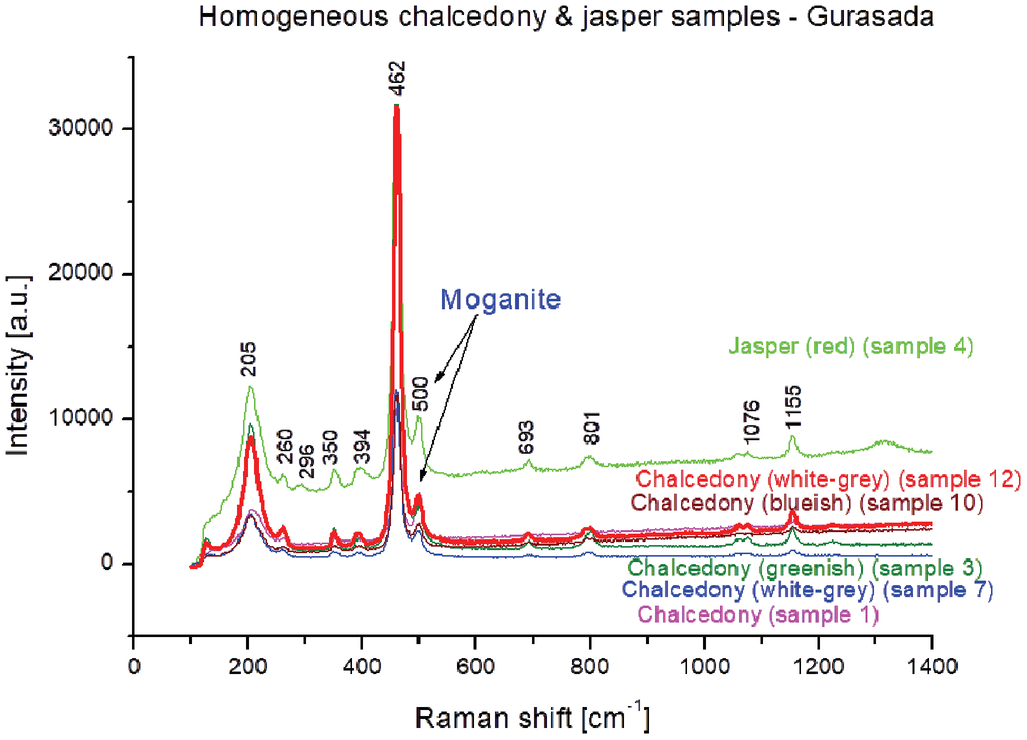

Figure 6. Raman spectra of jasper samples from Gurasada (POP et al., 2004, with completions).

Heterogenous amorphous or quasi-amorphous silica varieties (Figs. 7, 8): based on the comparison with reference spectra of various types of opals (A, C, and CT), the main amorphous phase in opal from Gurasada is defined as opal CT. A full range of transitions from opal CT to α-quartz is evidenced by the set of selected spectra. Moganite occurs in the more crystallized areas of the sample, intergrown with α-quartz.

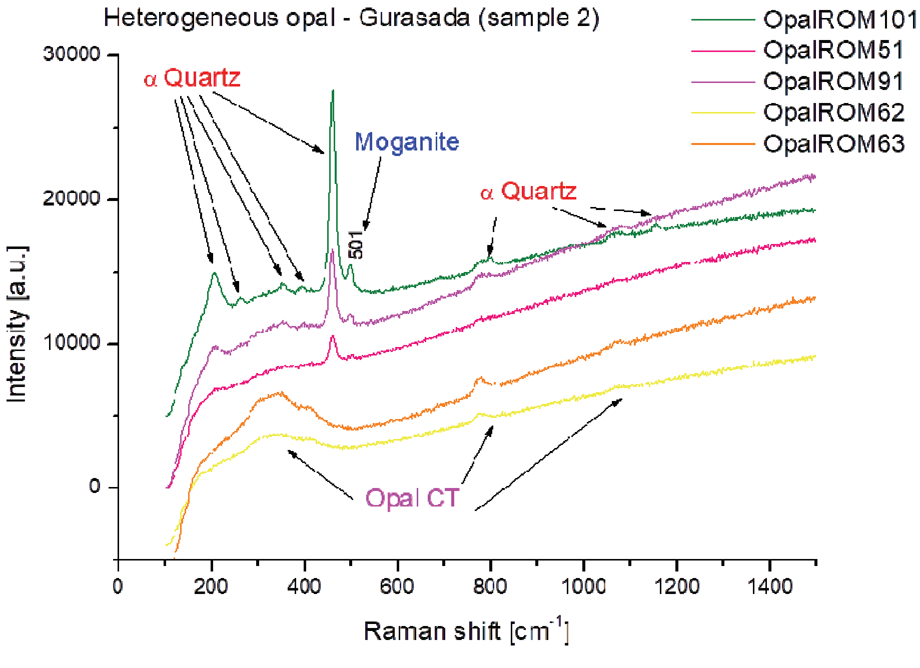

Figure 7. Raman spectra of the opal from Gurasada (POP et al., 2004, with completions).

The silicified wood from Gurasada shows a very complex and heterogeneous mineralogical composition (Fig. 8): zones of opal (CT? – see the comparison with reference spectrum) with minor amounts of α-quartz (+ moganite? and an unidentified phase) alternate with zones consisting of (αq + microcrystalline graphite), and respectively "pure" microcrystalline graphite.

The following two figures (9 and 10) present the Raman - based evaluation of the moganite-to-quartz ratio.

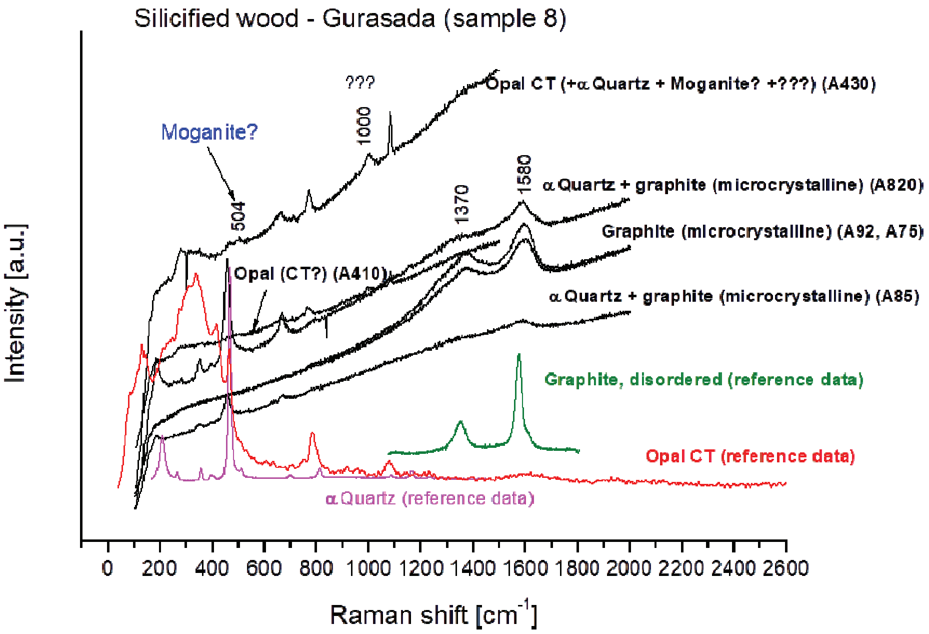

Figure 8. Raman spectra of the silicified wood from Gurasada (POP et al., 2004, with completions).

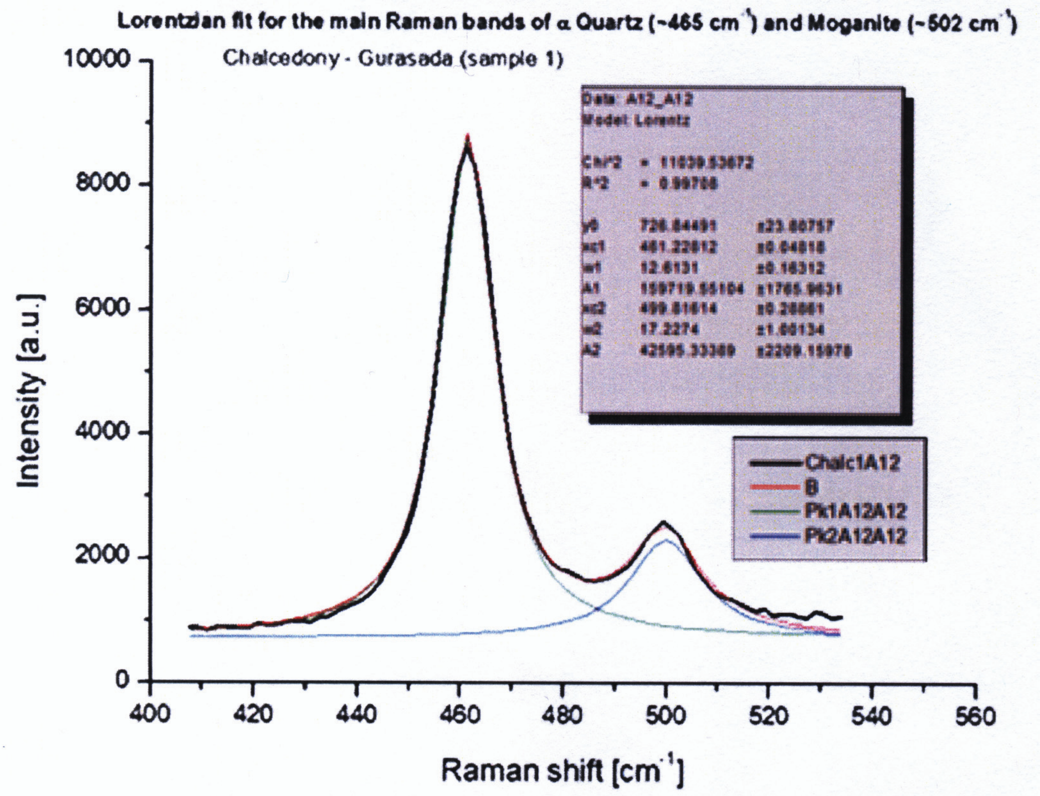

Figure 9. Raman spectra of α-quartz (~465 cm^{-1}) and moganite (~502 cm^{-1}) in chalcedony from Gurasada.

Variations in the moganite-to-quartz ratio (Fig. 9) are revealed by varying intensity ratios of the main symmetric stretching-bending vibrations of α-quartz (~465 cm^{-1}) and moganite (~502 cm^{-1}), respectively (Figs. 9 and

10). Band integrals were calculated according to the procedure indicated by GÖTZE et al. (1998) from (the band heights) x (the half-widths) x 100 [%], assuming Lorentzian-shaped Raman bands.

In order to quantify the moganite content in the samples (or areas of the samples) showing an exclusive (α-quartz + moganite) composition, the calibration curve proposed by GÖTZE et al. (1998) was used (Fig. 10). Values were calculated for the Raman bands integral ratios, I(502)/I(465) and the estimated moganite content [%] (undetected in silicified woods → > 20% in Gurasada agates).

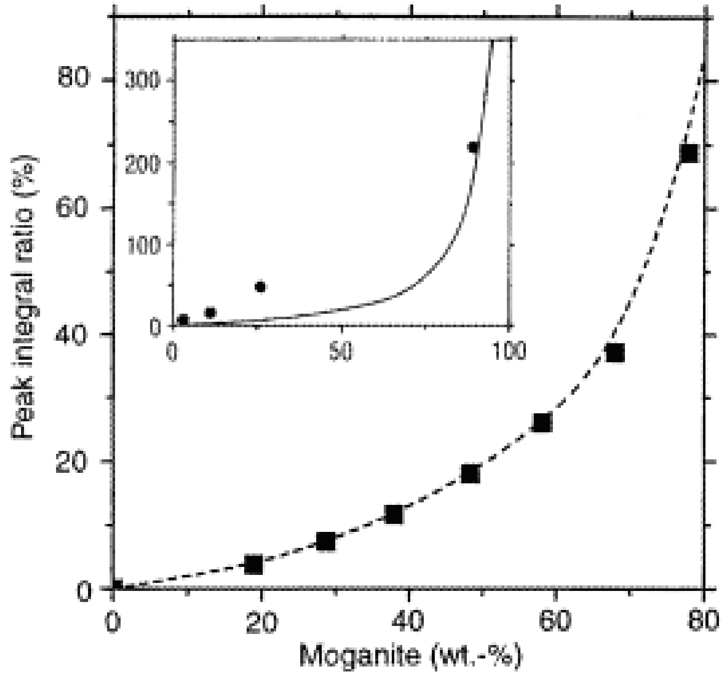

Figure 10. Application of the calibration curve proposed by GÖTZE et al. (1998)
for the calculated values of the Raman bands integral ratios, I(502)/I(465) and the estimated moganite content [%].

XRD and Thermogravimetric Study.

A suite of agates from the Southern Apuseni Mountains of Romania has been characterised using powder X-ray diffraction, thermogravimetry, and density determinations. A comparison of the data on these agates with other worldwide regions reveals discrepancies (Fig. 11). The crystallite size, density, defect-site water, and moganite content demonstrate that these agates can be characteristically divided into two groups, especially the Gurasada agates. One group reveals properties that are consistent with a contemporaneous formation around the age of the ~75Ma old host. Host rock bentonitization is a likely silica source for the second group of agates that have apparently formed ~ 55 Ma later. Additionally, a number of the Gurasada agates contain cristobalite that exists as a white rind and within the agate structure (CONSTANTINA & MOXON, 2010).

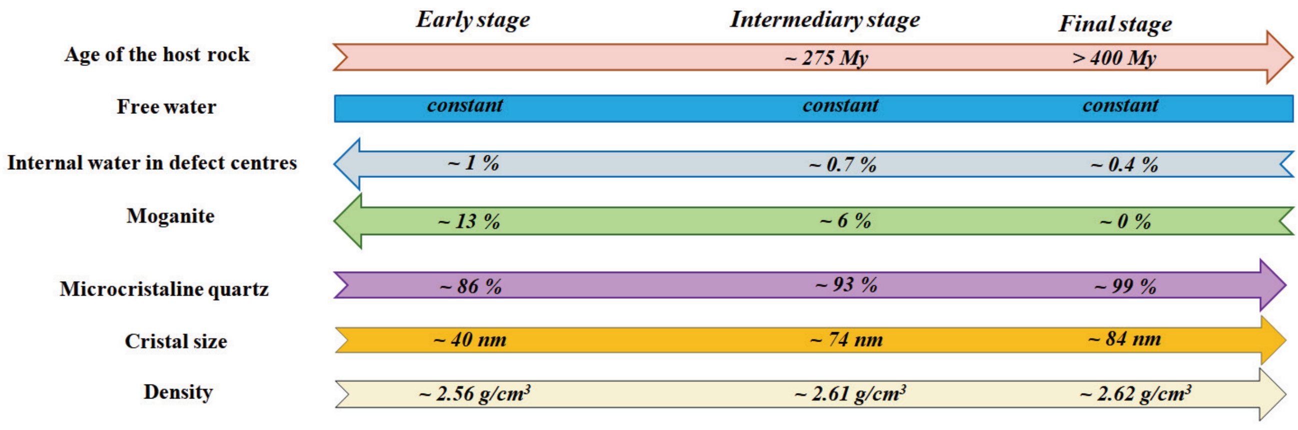

Figure 11. Scheme for the quantitative evaluation of the agates age based on the content of internal water,
microcrystalline quartz, moganite, crystal size, and density.

The study performed on the Gurasada chalcedony indicates its formation by bentonitization of the pyroclastic breccia (Figs. 12 and 13).

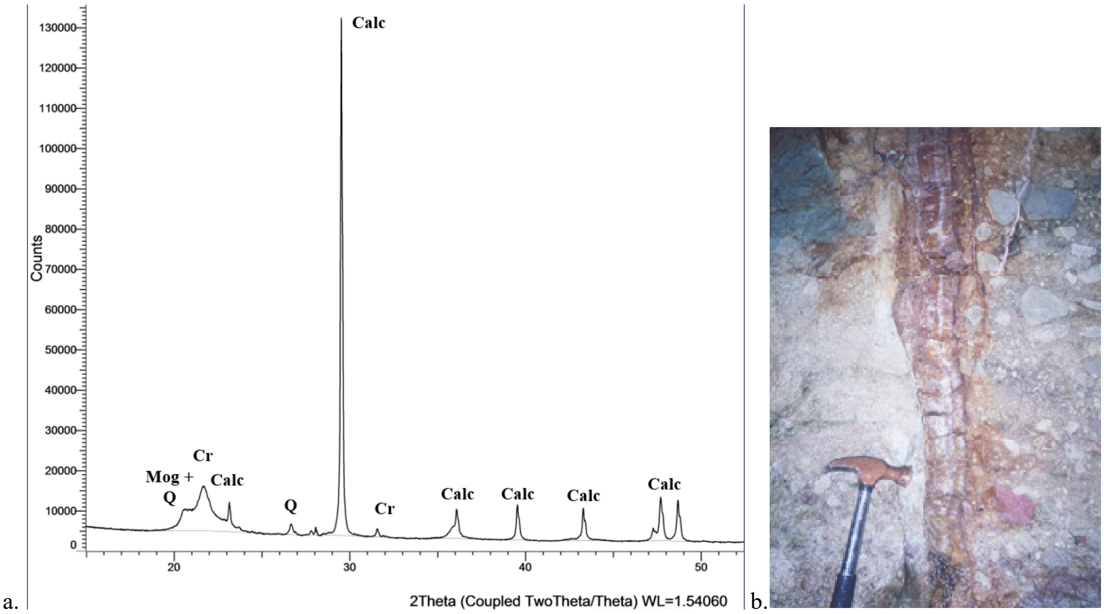

Figure 12. a. Diffractogram of the Gurasada chalcedony consisting of α-quartz (Q), moganite (Mog), calcite (Calc), and cristobalite (Cr). b. Chalcedony vein in altered pyroclastic breccia (Gurasada) (CONSTANTINA & MOXON, 2010).

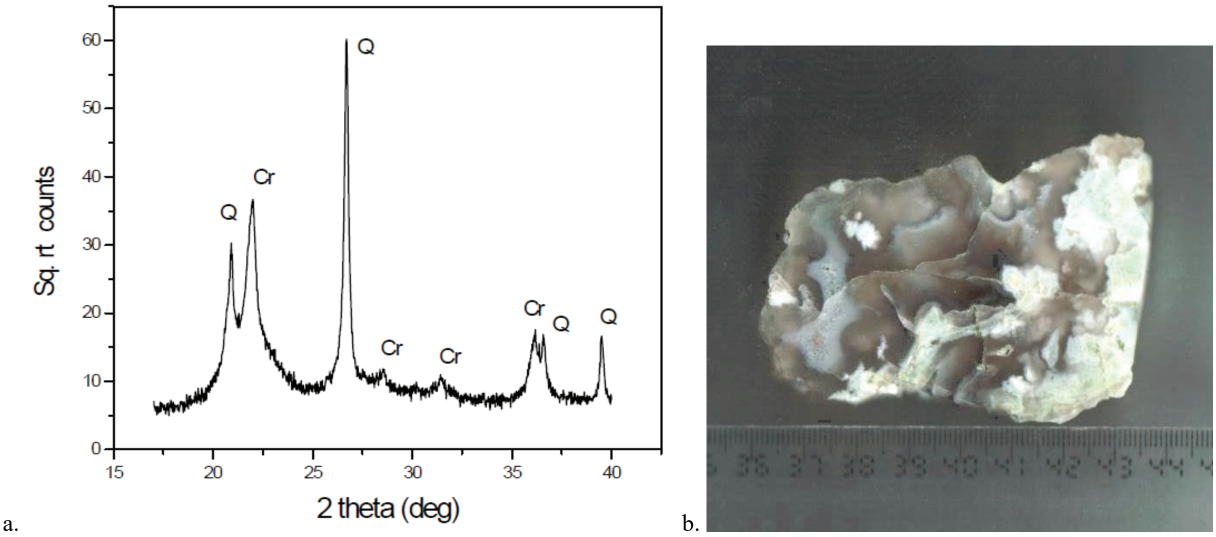

Figure 13. a. XRD signals from the white material surrounding the agate: the diffractogram shows good reflections from quartz (Q) and cristobalite (Cr) (CONSTANTINA & MOXON, 2010); b. White - grey agate sample (Gurasada).

CONCLUSIONS

The Southern Apuseni Mts. are an area characterized by a large variety and high amounts of gem-quality SiO_2 varieties, hosted by a wide range of rock complexes.

Microscopically, the quartz microcrystals have been classified according to their structure, the granular one being dominant; along with fibrous and lamellar varieties have also been identified. The microscopic structures evidenced in our samples were represented by: granular structures, structures based on long fibres, fan-like structures, rosette-like structures, hematite interlayers.

Raman study. The homogeneous microcrystalline samples (chalcedony, jasper) consist of a mixture of quartz and moganite; the homogeneous amorphous ones (opal) consist of opal-CT with traces of moganite. No correlation between the colour & texture of the mineralogically homogeneous samples and their composition could be traced by micro-Raman measurements.

Crystallite size and moganite content. XRD scans of the agates & chalcedonies showed that 13 samples contained moganite and α-quartz only; the remaining five samples contained either additional calcite or cristobalite. The overall mean crystallite size for the samples is ~ 45 nm. Sample diffraction data fit to estimate the moganite content 7-17 % with an overall mean of 11%.

Thermogravimetric Analysis. The high temperature heating of samples containing either calcite or cristobalite was not investigated, as these would produce an increased non-quantifiable mass loss. The value of the defect-site water from the remaining samples is between 0.43 – 1.55% with a 1.03% mean. The mean defect-site water as a function of the host rock age does produce a statistically significant linear relationship for host ≤ 60. The free water plays an important role in dissolving the more soluble moganite that later recrystallises as α-quartz. As the mean free water is independent of age, then any freshly generated free water must eventually leave the agate.

Density measurements results were between 2.58 – 2.65 g/cm^3 with a mean of 2.6 g/cm^3. Water mobility over the geological time-scale converts the more soluble and lower density moganite (2.55 g/cm^3) into higher density chalcedony (2. 57→2.62 g/cm^3).

One factor that is different with the Romanian agates compared to agates from other regions is the identification of strong opal-C signals (the low-temperature silica polymorph of cristobalite). The recognition of hidden cristobalite in agate reveals a possible important indicator for agate genesis as one route for agate formation could be along an amorphous silica pathway: opal-A (amorphous silica) → opal-CT → opal-C → quartz.

The high crystallite size group of Gurasada agates have demonstrated properties that are in agreement with the radiometrically determined age of the 75 Ma host rock; it is most likely that their formation was linked with the host rock volcanism. The genesis of the low crystallite size group of agates would appear to have had a different silica source, however. For these samples, the determined crystallite size and defect-site water indicate an origin around 20 Ma ago. The moganite content and density determinations are less precise but still suggest an origin < 30 Ma ago (MOXON, 2002; MOXON & REED, 2006; CONSTANTINA & MOXON 2010). The lack of volcanism in the area and the observed host rock alteration would suggest that the silica source for these later formed agates would be the bentonitization of the pyroclastic breccia.

The present paper adds new data regarding the mineralogical composition analyse of the SiO_2 potential gems from the Southern Apuseni Mts., in order to establish their genesis, unfortunately without exhausting all the possibilities but creating a database useful for further comparisons.

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