REVISITING THE CUBIC BLUE CHALCEDONY FROM TRESTIA, MARAMUREȘ COUNTY, ROMANIA

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Abstract: The issue of the cubic morphology of chalcedony, in general, is still a matter of debate, although pseudomorphism after melanophlogite is gaining popularity. To address the origin of the cubic morphology of the Trestia chalcedony, the present study employed optical microscopy, XRD, FT-IR, micro-Raman, thermogravimetric and SEM methods which provided strong indication for a melanophlogite phase associated with the investigated chalcedony. The macro- and micro-features of the investigated samples, the clear XRD melanophlogite diffraction pattern, as well as the spectroscopic detection of CO_2 and SO_2 support this conclusion. Melanophlogite *per se* was not identified, as only structural and chemical fingerprints remain in the chalcedony which replaced it, and it is assumed that the hydrothermal and geochemical conditions required for its genesis are no longer met at Trestia. Furthermore, the study shows that the cubic crusts are independent of the morphology of the rock substrate and that they independently formed on a previously deposited silicate layer, thus precluding pseudomorphism after fluorite or magnetite as a cause for the cubic morphology. The blue color shows characteristics indicative of light scattering, but the identity of the scattering centers is poorly constrained. The loss of the blue color in the 150-500°C range coincides with the loss of the silanol groups, as shown by the thermogravimetric measurement, indicating that SiOH hosted by structural defects plays a part in the generation of the blue color. The results of the study are in close agreement with those reported by Ilinca (1989).

Keywords: chalcedony, melanophlogite, Rayleigh scattering, pseudomorphism.

1. INTRODUCTION

According to the nomenclature put forward by Flörke et al., (1991), chalcedony is the length-fast fibrous microcrystalline SiO_2. It is usually intergrown with the length-slow SiO_2 variety formerly known as quartzine, now referred to as lutecite or moganite (Hatipoğlu et al., 2010). In a comprehensive study on the growth of chalcedony, Heaney (1993) points out that while laboratory syntheses usually occur at temperatures in excess of 150°C (up to 400°C), some natural occurrences indicate less than 100°C (as low as 26°C). In a natural setting, high temperature chalcedony is associated with pulses of fractionated silica-rich solutions released by magma chambers, while in the case of the low temperature variety it is the meteoric water which has the dominant contribution. Deep-seated silica-rich fluids may become increasingly more viscous during their ascent, as a function of the drop in pressure and temperature, potentially to the point of becoming gel-like, which could in turn lead to the formation of quartz via the paths suggested by Ilinca (1989) (Figure 1). Heaney (1993) also points out that chalcedony does not precipitate directly from these fluids, which implies the existence of one, or more, intermediate phases.

Several causes for the blue color have been suggested: Fe, Ti, Ni, Mn and, to a lesser extent, S, Th, Tl, U and W impurities (Hatipoğlu et al., 2010), the scattering of light by micro-particles (Ilinca, 1989; Ilinca et al., 2009; Götze et al., 2020), microstructural features and water content (Svetova et al., 2021), and blue sylvite and fluorite microscopic inclusions, which in turn owe their color to "F" color centers (Moțiu & Ghiurcă, 1979).
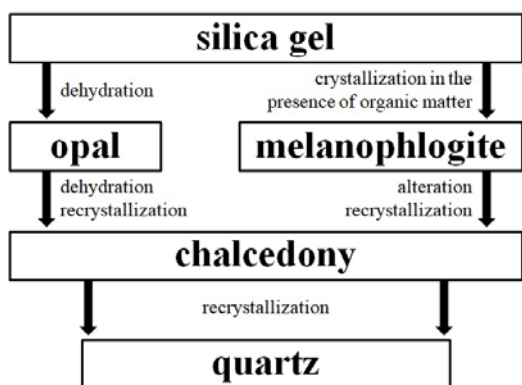
Figure 1. The silica gel – quartz transition scheme according to Ilinca (1989).

Svetova et al., (2021) likely refer to the scattering of light, because structural features such as sharp boundaries or density fluctuations can scatter light as well. This model becomes all the more plausible when considering that chalcedony fibers are, on average, 50-350 nm in size (Flörke et al., 1991), and thus compatible with Tyndall scattering, which requires scattering centers comparable in size to the wavelength of light, and also Rayleigh scattering if the fibers are less than 1/10 of the wavelength of blue light. However, it is also likely that the scattering centers are not inclusions at all, but rather the opposite. Voids and discontinuities, if small enough, can scatter light according to the Rayleigh model.

The Trestia chalcedony enjoys some measure of international recognition because of its blue color and cubic morphology. These two features have been the subject of a rather small number of dedicated studies, sometimes with contradictory results (Moțiu & Ghiurcă, 1979; Ilinca, 1989; Ghiurcă & Chira, 1998; Ilinca et al., 2009). The present study revisits the issue of the morphology and color of the Trestia occurrence based on new data gathered from thin cubic blue chalcedony crusts intimately related to the Mogoșa type andesites which outcrop in a quarry east of Trestia village. The aim of the present study is to settle the debate concerning the origin of the cubic morphology, a debate which is still present especially in the community of mineral collectors. This study also presents strong indication that melanophlogite was present at Trestia in association with the chalcedony. The actual identification of melanophlogite occurrences in Romania has not been achieved to date.

1.1. Previous research

Using X-ray spectrometry, Moțiu & Ghiurcă (1979) have determined the presence of K, Cl, Ca and S with X/Si ratios of 0.131, 0.119, 0.24, and 0.028, respectively. The similar K and Cl content was attributed to KCl (sylvite) inclusions, whereas Ca was assumed to have combined with F (which is not detectable by X-ray spectroscopy) to form CaF_2 (fluorite), as the S content is too low to account for the Ca, even if the presence of small quantities of CaS (oldhamite) is admitted. Rather loosely based on these findings, the blue color of the Trestia chalcedony was attributed to "F" color centers in sylvite and fluorite. The presence of melanophlogite was verified by Moțiu & Ghiurcă (1979) using X-ray diffraction (XRD), but none of the characteristic peaks were identified. Considering the scheme presented in Figure 1, it is likely that any initial melanophlogite has turned into chalcedony, leaving chemical fingerprints (such as SO_2, N_2, CO_2, CH_4, Xe and Kr) which are not suited for investigation by XRD. However, even if melanophlogite is still present in the chalcedony, the stress field produced by grinding during the preparation stage could potentially be enough to completely turn melanophlogite into quartz over a period of one hour (Skinner & Appleman, 1963).

Based on the fact that the Trestia chalcedony was not identified in direct relation to the igneous rocks of the area, but only randomly scattered in the soil, Ilinca (1989) concluded that the chalcedony was formed from subaerial silica gels originating from hot springs. Popescu et al., (2013), however, recognize the association between the Trestia chalcedony and the andesitic pyroclastic rocks in the region. Ilinca (1989) attributed the color to the preferential scattering of blue light by unidentified nanometric inclusions which, on account of the loss of color upon heating, are likely fluid or organic in nature. On a related note, Götze et al., (2020) reported the partial loss of color after a 3 years exposure of blue chalcedony to room temperature conditions and natural light, and a partial return of color after storing the sample in water for 6 weeks. This experiment shows that water content can, at the very least, influence the blue color. The arguments for the scattering of light are the opalescent appearance of the chalcedony, considered characteristic for colloidal systems, and the color difference in reflected and transmitted light (blue and reddish, respectively). These observations are incompatible with the blue color related to "F" color centers. Furthermore, Ilinca (1989) points out that "F" color centers are merely accidental, and even if significant, the chromatic effect of some finely dispersed, partially blue colored inclusion in an otherwise colorless medium is negligible at best.

With respect to the cubic morphology, Ilinca (1989) makes the case for pseudomorphism after

melanophlogite, rather than fluorite. He argues that the microstructures observed in the cubic crystals from petrographic thin sections are similar to those caused by organic films in melanophlogite, and because quartz is found on both sides of the microstructures, the later are not caused by a refringence gradient. Kolesov & Geiger (2003) confirmed the interpretation of Ilinca (1989) stating that it is possible that not all of the organic compounds available in the environment are included in the clathrate structure of melanophlogite, and that the excess compounds form organic films on successive growth faces. Also, a 0.707% organic C content is reported, as well as IR bands (1435, 880, 715, 600 cm^{-1}) and XRD peaks (d/n: 5.960-6.004-6.077, 4.700, 3.870, 3.690-3.709-3.710, 3.579-3.588 Å) attributed to melanophlogite. Ilinca et al., (2009) cite the XRD results presented by Ilinca (1989) as the only direct evidence of melanophlogite at Trestia, and add that the perfect cleavage shown by the cubic chalcedony along (100) rules out pseudomorphism after fluorite, since fluorite only shows perfect cleavage along (111). It is unclear how the comparison between the crystallographic orientations of the cleavage planes of fluorite and melanophlogite works, considering that melanophlogite has no cleavage.

Ghiurcă & Chira (1998) reported that the Trestia chalcedony invariably occurs as 1 to 15 cm veinlets which replaced preexisting mineral associations, although the impressions of the substituted minerals are still visible. The Trestia chalcedony *always* shows shades of blue, and is *always* pseudomorphic. Moreover, instances of perimorphism (i.e. rather than filling the volume of a previous mineral as in the case of pseudomorphism, the chalcedony assumes the shape of other minerals by forming crusts around them) are also reported. In both pseudomorphism and perimorphism, fluorite is cited as the most frequent original mineral.

In summary, there are two different explanations for both the color and the morphology of the Trestia chalcedony. The first one, championed by Ghiurcă, attributes the blue color to finely scattered inclusions (likely sylvite and fluorite) which are partially blue because of "F" color centers, and the cubic morphology to pseudomorphism and perimorphism after fluorite. The second explanation, put forward by Ilinca, suggests that the blue color is the result of the Rayleigh scattering of light by unidentified nanometric inclusion, and that the cubic appearance is owed to pseudomorphism after melanophlogite. It is also worth mentioning that based on optical and XRD investigations, Dunning & Cooper (2002) and Dunning (2009) also concluded

that the cubic chalcedony occurrences from California are pseudomorphosed melanophlogite, adding weight to the model suggested by Ilinca (1989), and that the results which will be presented over the course of the present paper will further tip the balance in the same direction.

1.2. Melanophlogite

Because melanophlogite constitutes a significant part of the controversy surrounding the morphology of the Trestia chalcedony, some general aspects of its mineralogy must be presented. Melanophlogite is usually described as a rare (Tribaudino et al., 2008; Beard et al., 2013; Kanzaki, 2019), or very rare (Nakagawa et al., 2001), tetragonal SiO_2 polymorph with a clathrate structure and pseudocubic or globular habit. It is reported at just a dozen worldwide natural occurrences in Italy, Czech Republic, U.S.A. (California), Tanzania, Japan and Ukraine in association with sulphur deposits, Fe-rich rhodochrosite, volcanic rocks, serpentinite breccias, dolomite, marls and volcanoclastic rocks, hydrocarbon seep deposits, or natrocarbonatite lava (Beard et al., 2013; Miyajima et al., 2016). Lazzeri et al., (2017) suggests that the occurrence of melanophlogite is more extensive than previously thought. However, the mineral is difficult to determine and once formed, it is easily replaced by other SiO_2 polymorphs.

The ideal formula of melanophlogite is $46SiO_2 \cdot 6(N_2, CO2) \cdot 2(CH_4,N_2)$, and because of its clathrate structure, it can accommodate as much as 8 wt% (Nakagawa et al., 2001) H_2S, N_2, CO_2, CH_4, or OH molecules in the structural cages, and for this reason it shows some industrial (Kanzaki, 2019) and environmental potential as a trap for greenhouse gases and Rn (Navrotsky et al., 2003). Beard et al. (2017) points to a qualitative variation of the enclathrated molecules as a function of the environment in which the melanophlogite crystallized: a high S and low CO_2 and OH content is characteristic of sulphur deposits melanophlogite, in the case of melanophlogite hosted by carbonate-rich rocks, the enclathrated molecules are a mixture of CO_2 and OH, and the CH_4 molecule is predominant in undersea methane vent environments. According to Navrotsky et al., (2003), these molecules set the structural pattern of melanophlogite and facilitate its nucleation and growth.

The occurrence of melanophlogite appears to be restricted to veins and voids, where there is no shear stress which could have led to the loss of the gas molecules and collapse the mineral structure (Tribaudino et al., 2008). It can form at temperatures lower than 112°C (Skinner & Appleman, 1963), it

never grows directly on the host rock, and forms at the expense of preexisting opal (Skinner & Appleman, 1963; Tribaudino et al., 2008). According to Tribaudino et al., (2008), opal can be dissolved by subsequent CH_4-rich fluids, and the resulting mixture can lead to the crystallization of melanophlogite. This process would result in corroded opal grains surrounded by melanophlogite (Skinner & Appleman, 1963; Tribaudino et al., 2008), and is in some disagreement with the transition scheme proposed by Ilinca (1989) (Figure 1), unless it is considered that after dissolving the opal, the organic-rich fluid is sufficiently enriched in Si as to be considered a gel. The scheme can be easily adapted by placing opal between the silica gel and melanophlogite, in which case a plausible scenario for the Trestia chalcedony would be silica gel → dehydration → opal → partial dissolution by a fluid rich in organic molecules → pseudocubic melanophlogite → recrystallization → cubic chalcedony.

2. MATERIALS AND METHODS

The samples used in the present study have been collected from the Mogoșa andesites quarried east of the Trestia village, Maramureș County, Romania (47°34'37"N, 23°48'54"E).

On site, the investigated chalcedony is found as ca. 5 mm (rarely ca. 1 cm) thick crusts which clearly preserve both their base and top, thus providing a complete picture of the formation of the Trestia chalcedony at a glance.

Contrary to the claims of Ghiurcă & Chira (1998), who describe the Trestia chalcedony as exclusively cubic and bluish, the samples collected are sometimes botryoidal (Figure 2A), and rarely white (Figure 2B). Admittedly, they are usually bluish and show a very fine cubic morphology defined by 1-2 mm cubes (Figure 2C).

The samples show a variety of morphological features: some show cubic morphology in both the top and the base, with one side being coarser than the other, others have a cubic base and a botryoidal top, or a rather irregular, globular base and a botryoidal top. The chalcedony cubes frequently show twinning, similar to fluorite but closer in resemblance to melanophlogite. At times, a definite discontinuity between the cubic crusts and the underlying chalcedony is noticeable.

The base of the crusts often contains an irregularly shaped, cream colored opal, and/or a rusty phase which usually fills rhombic imprints in the body of the crust itself. Some samples also show varying degrees of alteration to opal, in the form of opaque milky white areas.
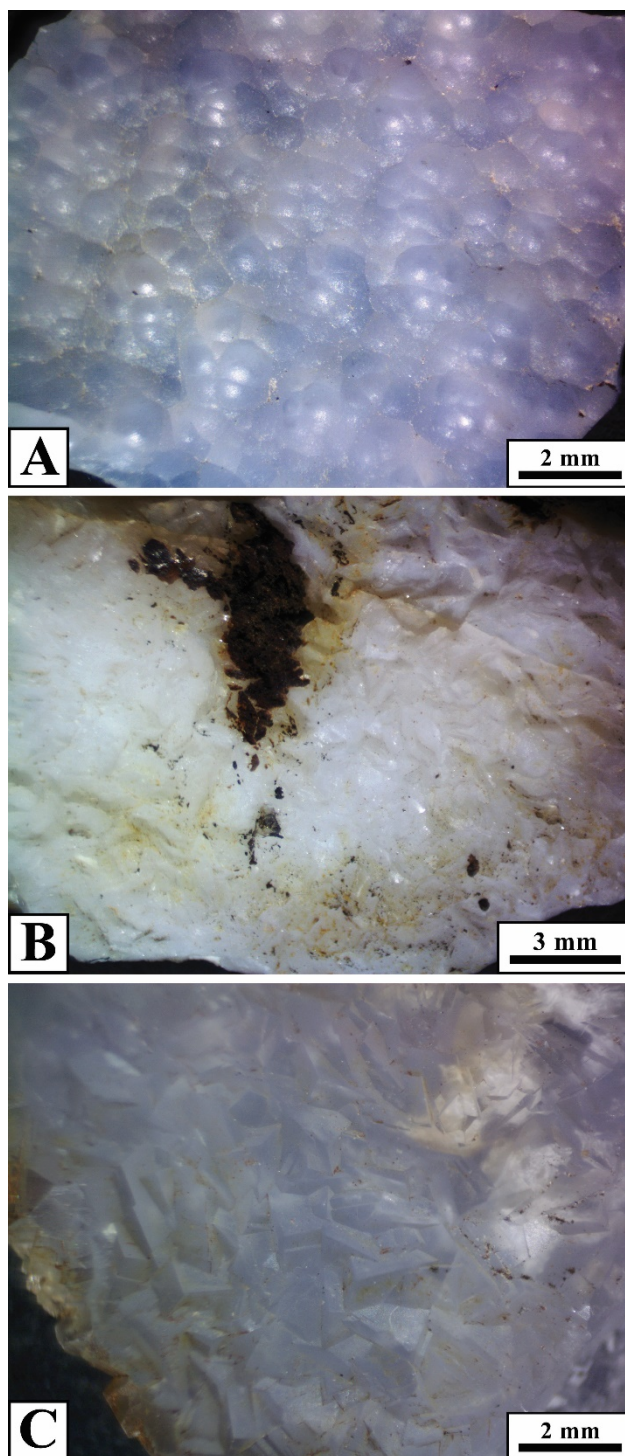

Figure 2. Stereo microscope pictures of the Trestia chalcedony showing: A – botryoidal habit; B – white color; C – typical appearance from the sampling area.

Some of the collected samples represent complete cross sections through small veinlets, and show small internal voids lined with cubic chalcedony.

Color wise, the samples range from white (rarely) to sky blue when viewed perpendicular to the plane of the crusts. When observed in cross section, the crusts show a banding which is usually largely

consistent with the morphology of the crusts. The bands can be milky-blue, milky-white, or colorless and transparent, with a luster ranging from greasy to glassy.

The methods employed were aimed at determining structural and compositional fingerprints which would provide clues regarding the causes of the cubic morphology and, perhaps, color. All investigations were carried out at the Geological Institute of Romania.

The optical observations were performed on raw and polished samples, transparent polished slices, and petrographic thin sections using binocular and petrographic microscopes.

The XRD investigations were carried out using a Bruker D8 Advance powder diffractometer over a 2Theta interval of 4-90°, with an increment of 0.03°/step and acquisition time of 1s/step, at 40 kV and 40 mA. The samples were crushed and the resulting grains were manually separated under the stereo microscope, from multiple samples from the same location, based on their appearance, into 4 categories: rusty, cubic, cream colored, and glassy colorless. For interpretation, the Diffrac$^+$Basic (Eva 13) software was used.

FT-IR (Fourier Transform – Infrared Spectroscopy) was performed in transmission using a Bruker Tensor 27 spectrometer over a 4000-400 cm^{-1} spectral domain and a spectral resolution of 4 cm^{-1}, 6 mm aperture, 10 kHz scanner velocity, and a sample scan time of 64 scans. The measurements were carried out on pellets with an average content of 2 mg sample powder and 148 mg KBr. The interpretation of the spectra was performed using the dedicated Opus 6.5 software.

Micro Raman spectrometry was carried out using a Renishaw inVia system. Both polished samples and naturally occurring surfaces were analyzed over a 95.83-3196.7 cm^{-1} spectral interval, using a 532 nm laser at 0.5% power (to reduce fluorescence), 1800 l/mm grating, 10s exposure time, and 3-10 accumulations. The calibration was performed using a 520.5 cm^{-1} line of silicon.

Thermogravimetric and differential thermal analysis (TGA/DTA) were performed on the blue chalcedony from the top of the crusts and the cream colored opal from the bottom using a NETZSCH STA 449 C Jupiter simultaneous thermal analyzer, over a temperature interval of 30-1000°C, in an Ar atmosphere, with an increment of 10°C/min.

The heat treatment was carried out using a Nabertherm Controller P320 oven. The sample, a cubic banded chalcedony slice, was heated to 150, 300, and 500°C and maintained at said temperatures for 24 h. After each heating session, the sample was photographed under a stereo microscope, in both transmitted and reflected light.

SEM imaging was performed on cubic, Cr covered, chalcedony samples, using a Tabletop Hitachi TM 3030, operating at an accelerating voltage of 15 kV.

3. RESULTS AND DISCUSSION

3.1. Optical observations

The observations using the stereo microscope have shown a sharp, well defined, cubic morphology in the upper part of the chalcedony crusts, with no resemblance to the overall morphology of the base of the crust. Furthermore, where the cubic layer is chipped away, a rough botryoidal underlying layer is sometimes observed. This observation indicates a later deposition of the cubic layer on a botryoidal one, thus precluding any influence from the cubic morphology of an alleged pre-existing mineral assemblage. Similarly, the presence of voids lined with cubic chalcedony at the core of chalcedony veins leads to the same conclusion. These features are indicative of late deposition during the waning stages of the hydrothermal activity in the area.

The base of the crusts often shows cubic imprints which are generally larger than the cubes from the top side. These imprints are the result of perimorphism after the original, probably cubic, minerals on which the silica gel was deposited. Previous cubic chalcedony generations on which the collected samples were deposited are also a possibility. No morphological continuity or connection between the cubic imprints from the base and the cubic features from the top of the crusts is observed.

The cream colored opal previously mentioned gives off a green fluorescence when exposed to shortwave (254 nm) UV light. This behavior is caused by trace amounts of U in the form or uranyl (UO_2^{2+}) groups (Othmane et al., 2016).

Seldom, the chalcedony crusts show clear colorless cubic grains that contrast with the rest of the crust in terms of shape and color (Figure 3A & B) and which, based on their morphology, hint at melanophlogite. Also, a rounded, dew-like mineral phase (Figure 3C), reminiscent of some melanophlogite occurrences from Fortullino (Italy), is an intriguing and elusive presence in the base of the crusts. Hyalite, a variety of opal with clear glassy appearance and characteristic UV fluorescence caused by UO_2^{2+} groups, is also present.

With regard to color, both blue and white chalcedonies are milky in appearance. Areas which are not milky are invariably colorless. When thin, banded

chalcedony cross sections are observed in transmitted light, both the blue and white areas show reddish colors. This aspect may prove problematic in assessing the coloring mechanism. If, hypothetically, color centers were to spatially overlap with milky bands, then such areas would appear blue in reflected light and reddish in transmission, leading to the conclusion that Rayleigh scattering causes the blue color.
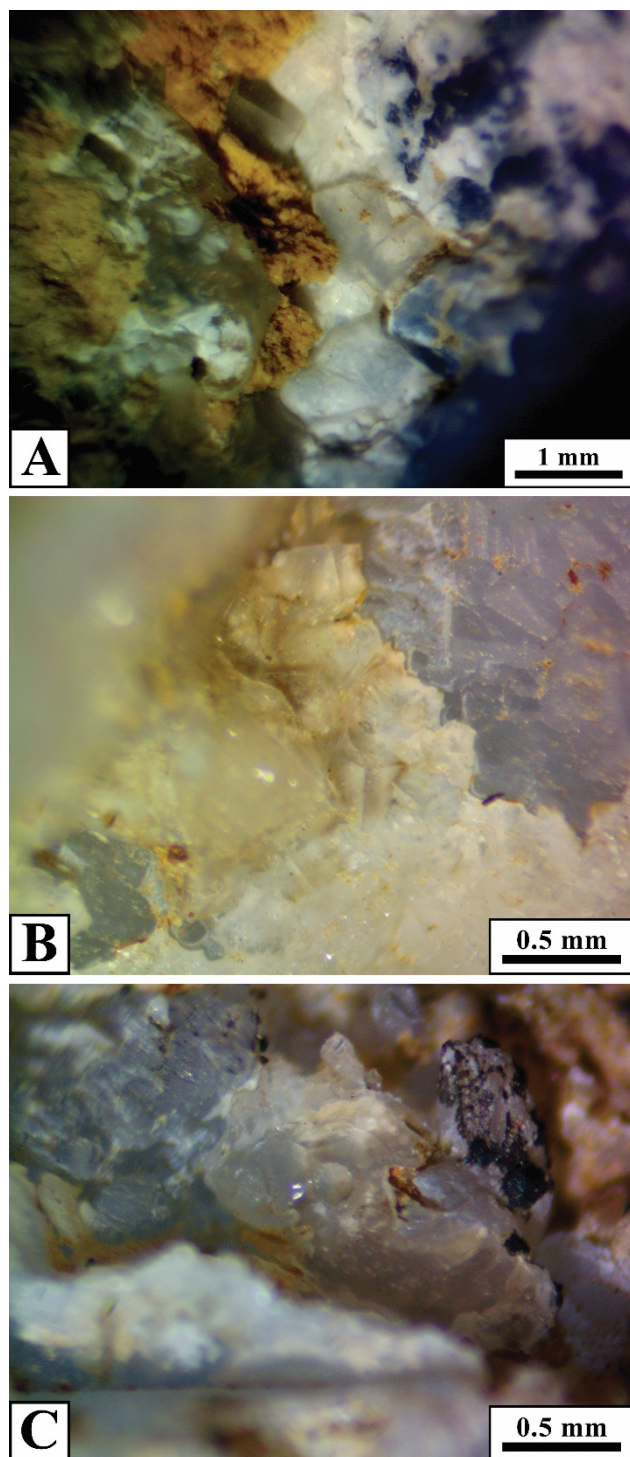

Figure 3. Stereo microscope pictures of features potentially related to melanophlogite: A – isolated cubic features on opal; B – cubic crust on a silica substrate; C – dew-like grain.

This situation would require a rather particular set of coincidences and while possible, it is unlikely. On the other hand, if the scattering of light is indeed the prevailing coloring mechanism, then the opalescent blue and white areas could be easily explained by variations in the size of the scattering centers. With increasing size, the light is no longer scattered according to the Rayleigh model, which requires dimensions in the range of 1/10 of the wavelength of light, but according to the Mie model, which allows for dimensions comparable to the wavelength of light. A visualization of the coexistence of these two scattering mechanisms is the partly cloudy daytime sky. As the Sun illuminates the atmosphere, the molecules in the air preferentially scatter the short wavelengths, while the larger ice crystals and water droplets from the clouds scatter the majority of the incident light.

This scenario is more plausible, but not yet confirmed. Scattered light is variably polarized at different angles from the direction of the incident light. In the case of Rayleigh scattering, when the sample is observed perpendicular to the direction of light using a polarizing filter, the rotation of the filter should cause an alternation of darker and brighter images. This phenomenon was not yet observed in the investigated samples, and more complex optical setups may be required.

It is worth mentioning that while the larger (>5 mm) cubes are intrinsically blue, the smaller ones are usually clear and colorless, and their perceived blue color is imparted by the milky-blue layer on which they rest. One possible reason is that the color itself is generated during the formation of chalcedony itself.

Figure 4 shows blue chalcedony nuclei forming in an otherwise clear and colorless host. This suggests that the blue color is not owed to the "F" color centers rich sylvite and fluorite inclusions postulated by Moțiu & Ghiurcă (1979), but rather to structural features, such as the thickness of the chalcedony fibers and/or structural discontinuities and voids, which are small enough to scatter light. A similar process is visible in some images of melanophlogite from Fortullino (Italy), except that the chalcedony nuclei are white and the globules in which they are forming are melanophlogite.

Petrographic microscopy has produced very similar results to those presented by Ilinca (1989), Skinner & Appleman (1963), and Chang & Nicolescu (2023). Most quartz domains contain square and chevron features (Figure 5) interpreted as remnants of the organic films from the initial melanophlogite.
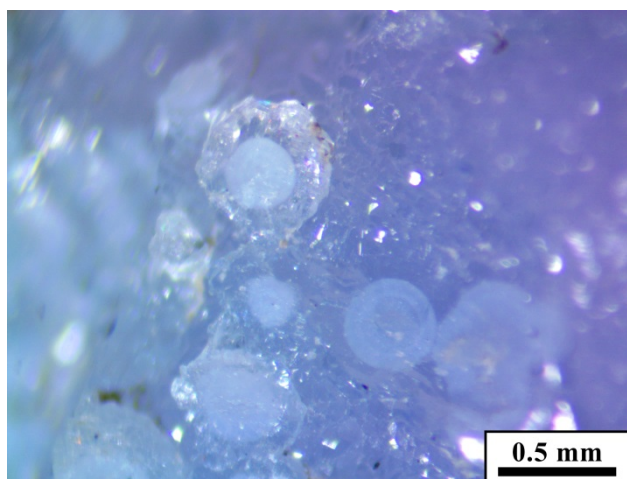
Figure 4. Stereo microscope pictures of rounded blue chalcedony nuclei in a colorless host (arguably a former melanophlogite phase).

The microscopic features from Figure 5B (as well as the general macroscopic features presented over the course of the paper) are similar to the point of identity with the macroscopic layered features from the images of cubic melanophlogite from the Giona mine (Sicily, Italy).

Figure 5C, in particular, which was taken on a thin section parallel through the plane of a cubic crust, shows that there is a consistent association between the individual chalcedony cubes and melanophlogite-like microscopic features. This is a strong argument in favor of melanophlogite as cause of the cubic morphology.

3.2. XRD

Quartz and moganite are present in all but the rusty samples, the latter showing a goethite – hematite composition. Considering that the rusty phase is usually associated with rhombic-square imprints in the base of the chalcedony crusts, it is interpreted as the result of the alteration of the magnetite over which the silica gel was locally deposited.

Melanophlogite diffraction peaks, corresponding to the characteristic d values of 5.99570, 5.46143, 3.86323, 3.70910, 3.57651, 3.34469, 3.24876, and 2.11756 Å, were clearly identified in the rather unassuming cream colored phase from the base of the chalcedony crusts, (Figure 6).

Interestingly, the cubic chalcedony itself did not show any XRD indication of melanophlogite. This could be the result of either the complete transformation into chalcedony, or of the presence in smaller quantities than the detection limit of the instrument used.
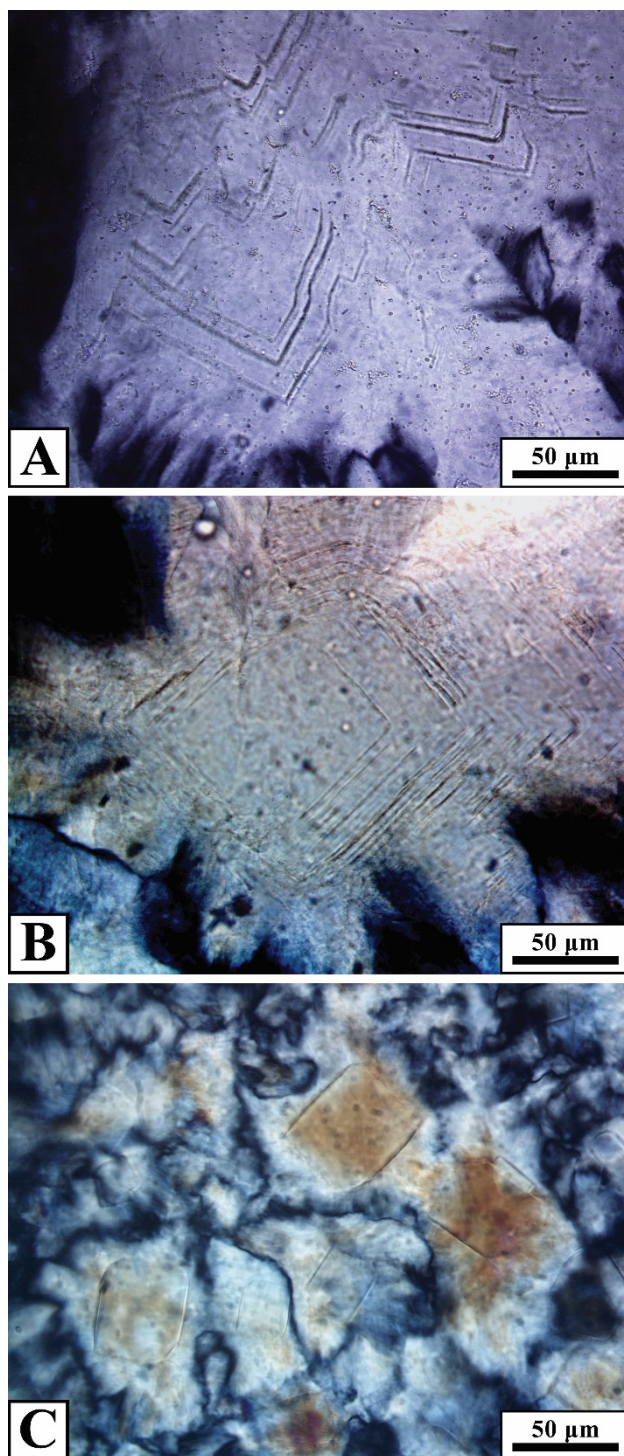

Figure 5. Crossed polars images of the Trestia cubic chalcedony showing relict melanophlogite features. A – chevron features; B – square features; C – section through the plane of a cubic chalcedony crust.

However, the XRD investigations reported by Ilinca (1989), presumably performed on the chalcedony cubes, point to the presence of melanophlogite. Different samples may preserve various percentages of the initial melanophlogite.
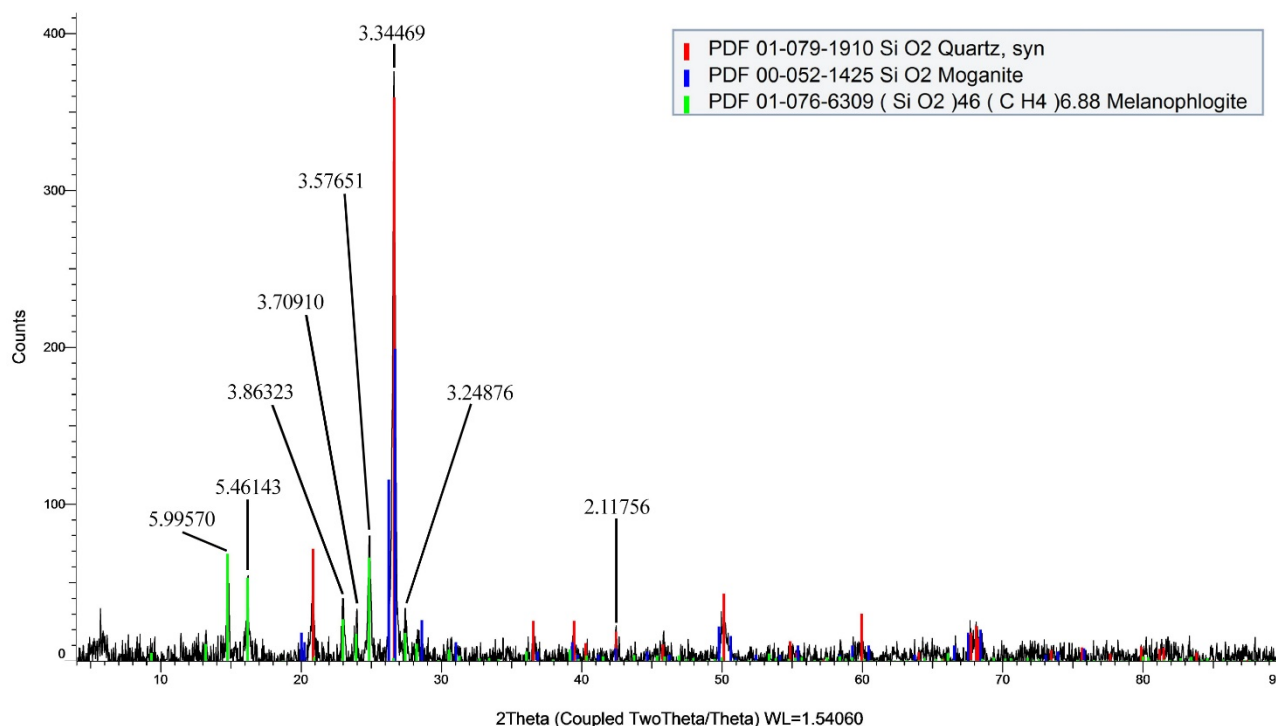
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Figure 6. The interpreted XRD spectrum of the cream colored phase from the base of a chalcedony crust, showing clear diffraction peaks (d values marked on the figure) associated with melanophlogite.

3.3. FT-IR

The FT-IR spectra of the cream colored opal (Figure 7), which based on the XRD results hosts melanophlogite, shows OH stretching at 3446 (associated with molecular water and SiOH) and 695 cm^{-1}, OH bending at 1636 cm^{-1}, Si–O vibrations at 2926, 1879 and 796 cm^{-1}, asymmetric Si–O–Si stretching at 1094 cm^{-1}, and Si–O asymmetrical bending at 465 cm^{-1}. The samples gave particularly strong CO_2, and SO_2 signals, as indicated by the 2349-2335 cm^{-1} and 1383 cm^{-1} centered transmittance peaks, respectively. Samples of cubic chalcedony and chalky opal also show faint SO_2 peaks, but negligible CO_2 signals.

3.4. Micro Raman

The CO_2 Fermi diad is often present in the cream colored opal and the clear cubic crusts at 1280 and 1382 cm^{-1} (Figure 8 A & B, respectively) and dominates the spectra in terms of peak intensity. This result is in agreement with the FT-IR spectra for the same phases. CO_2 alone can be the predominant templating guest molecule, as is the case of the Fortullino occurrence (Italy) (D'Alessio et al. 2019), but more data is required for the positive identification of melanophlogite. There is no clear indication of the other gas molecules usually associated with melanophlogite, or its characteristic peaks, as reported by Tribaudino et al. (2008), and at

this point the Raman evidence is inconclusive.

3.5. TGA/DTA

The thermogravimetric investigations have shown a rather continuous (with an obvious increase at ca. 700°C) 1 wt% loss in the case of the cubic blue chalcedony and up to 5 wt% loss for the cream colored phase, over a 30-1000°C interval. Molecular water is lost at ca. 150°C, the water from the silanol groups is lost at temperatures of up to 600°C, and the subsequent loss of mass is attributed to the degassing of OH⁻ from structural sites (Graetsch et al., 1985).

The transition of melanophlogite into cristobalite at 900-1000°C reported by Skinner & Appleman (1963) was not observed under the experimental parameters defined by the present study.

3.6. Thermal treatment

Heating the sample to 150°C did not cause any significant change to the color. At 300°C, the discoloration became obvious, and at 500°C a total loss of color was observed, and the sample became opaque white in appearance. When observed in transmitted light, the sample became progressively more opaque and yellowish-brown (Figure 9).

The loss of the blue color is explained by the destruction of the scattering centers which can be brought about through expulsion from the chalcedony even at the relatively low temperature of 300°C
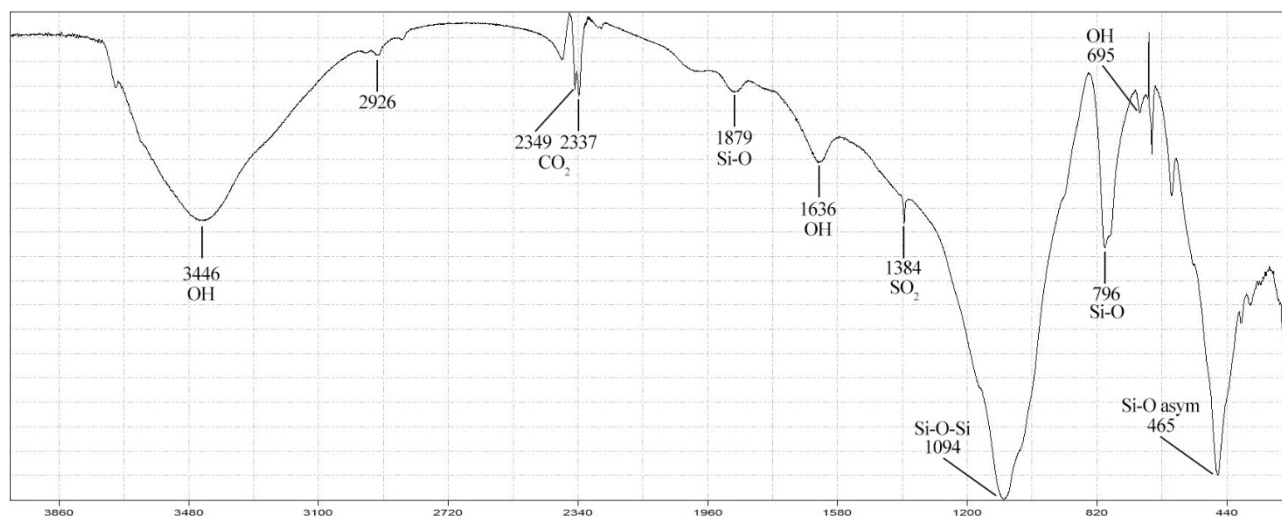
Figure 7. The FT-IR transmittance spectrum of the cream colored phase from the base of a chalcedony crust with melanophlogite XRD signals showing molecular vibrations associated with the presence of melanophlogite.
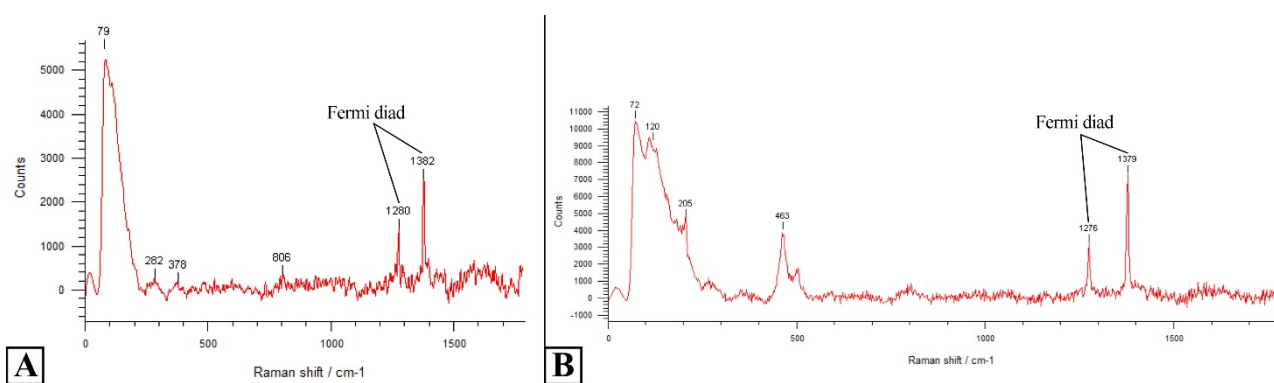

Figure 8. Representative micro Raman spectra showing strong peaks at 1280 and 1382 cm^{-1} associated with the CO_2 Fermi diad in cream colored opal and the clear cubic crusts.
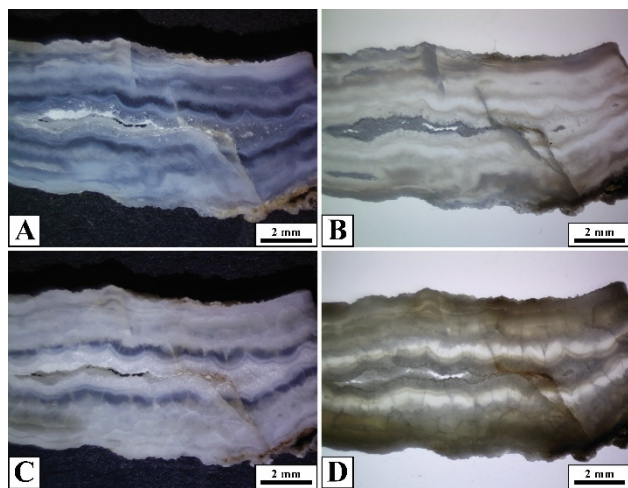

Figure 9. Stereo microscope pictures of a thin slice from the Trestia chalcedony in reflected light (A) and transmitted light (B) prior to the thermal treatment, and in reflected light (C) and transmitted light (D) at the end of the thermal treatment.

(water, for example), or by an increase in size resulted from thermal stress (as in the case of light scattering nanometric discontinuities and voids). In any case,

the fact that the samples do not become colorless and clear after heating indicates that the heated chalcedony contains new, larger, temperature induced scattering centers which scatter according to the Mie model.

After the thermal treatment, a thin slice of chalcedony was submerged in water, in the dark, at room temperature, for 60 days, to verify if hydration will cause some of the blue color to reappear, as in the case of the experiment described by Götze et al. (2020). The result was that the blue color did not reappear. The different outcome is explained by the fact that the investigated samples are not the same in terms of color stability, and different causes for the blue color are likely involved. Unlike the sample used by Götze et al. (2020), the Trestia chalcedony is not known to bleach as the result of exposure to sunlight. According to Graetsch et al., (1985), the loss of the water from the SiOH groups is irreversible, unlike the loss of molecular water.

Considering that the loss of color coincides with the loss of the SiOH groups, in the 150-600°C range, and that the expected addition of molecular

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water during rehydration does not impart a blue color, it can be concluded that silanol defects are the determining coloring factor in the case of the Trestia chalcedony.

3.7. SEM

SEM imaging has shown striking morphological similarities between the cubic features of the Trestia chalcedony and cubic chalcedony from California (Figure 10). The morphology of the chalcedony in Figure 10D is explicitly associated with melanophlogite by Dunning (2009).

Structures reminiscent of what Skinner & Appleman (1963) and Tribaudino et al., (2008) described in relation to melanophlogite growing on corroded opal crystals have also been observed. Figures 10 A&B clearly show thin cubic crusts developed on rounded silicate domes. While it is possible that perimorphism can play a role in the augmentation of the overall cubic appearance of the Trestia chalcedony samples, it is clear that a preexisting cubic mineral phase is not required to explain this peculiar feature.

4. CONCLUSIONS

The present study has shown that there is no relevant relationship between the morphology of the substrate and the cubic morphology of the Trestia chalcedony. The cubic crusts developed as a separate phase during the last stages of the evolution of the hydrothermal system, on previously formed, non-cubic, silicate crusts.

The cubic morphologies observed using optical and SEM methods are consistent, to the point of identity, with those described for melanophlogite. This qualitative comparison with melanophlogite rather compelling point in favor of melanophlogite as a precursor for the cubic chalcedony of today. Furthermore, since the cubic crusts appear as distinct from the corroded silica underlying layer, they must have formed at the expense of the latter, and not directly from the silica gel.

However, melanophlogite crystals have not been identified, and it is doubtful that such an occurrence exists at Trestia because the melanophlogite transformed into other silica polymorphs over the course of millions of years, and only its structural and chemical fingerprints remain.

The optical microscopy, XRD, FT-IR, and micro-Raman results point to trace melanophlogite structural and chemical features and therefore, it is the conclusion of the present study that the late hydrothermal cubic phase previously mentioned is
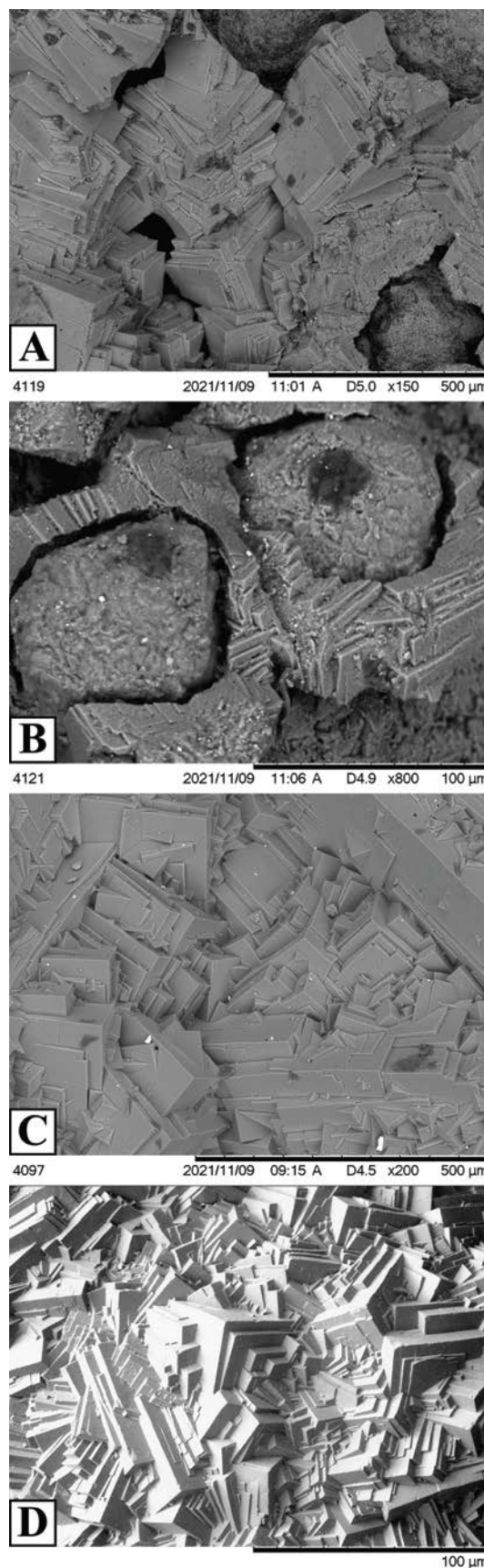

Figure 10. SEM images showing: A & B – cubic crusts on a rounded substrate; similarities between the cubic chalcedony from C – Trestia (present study); D – Vaughn Mine, California (Dunning, 2009).

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melanophlogite. This does not mean, however, that the cubic structures observed today are melanophlogite, and the conclusion merely states that there is indication of a melanophlogite precursor to the Trestia chalcedony. In essence, under the circumstances of the present study, this is the furthest that the research on the cubic morphology of the chalcedony can go, unless a relatively fresh occurrence is identified in the area, which could provide a direct link between melanophlogite and opal-chalcedony.

The aspects listed above point to the following sequence of events: deposition of a silica gel, opalization, partial dissolution caused by a fluid rich in organic molecules, precipitation of melanophlogite and, eventually, recrystallization and the formation of chalcedony. This sequence is in strong agreement with the one proposed by Ilinca (1989), and satisfies the requirement of Heaney (1993) for an intermediate phase between fluid and melanophlogite. Furthermore, the occurrence of voids lined with cubic chalcedony in some of the chalcedony veins precludes pseudomorphism.

The chromatic properties are consistent with the scattering of light, as indicated by the color differences in reflected and transmitted light and the association between the blue color and the opalescent appearance. On the other hand, the polarized character of the scattered light, which is expected in the case of scattering, was not observed. The scattering centers have not been identified, but the clear loss of color in the 300-500°C temperature range suggests that a fluid phase (likely silanol groups) associated with nanometric structural defects and discontinuities plays an important role. As observed in the investigated samples (Figure 4), the color is likely formed at the same time as the chalcedony itself, thus adding weight to the existence of structurally facilitated light scattering centers, and rendering pre-existing blue mineral inclusions unlikely.

The questions concerning the cubic morphology and color of the Trestia chalcedony have been addressed in a rather general sense, and while the general research direction has been set, the finer details of the topic will require additional chemical and structural means of investigation in order to fully describe the geochemical fingerprints and optical features of the chalcedony.

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