

New Nano-Structured Microcrystalline Silica: Fire Agate

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1. Abstract

30 samples of fire agate (SiO_2) from Mexican new deposits (State of Aguascalientes, Calvillo and Jesus Maria municipalities) were documented using Raman Microprobe (RMP), Infrared reflection (IRS) Spectroscopy, Scanning Electron (SEM), and Atomic Force Microscopy (AFM). Fire agate, a non-transparent variety with multicolored fire, show a higher degree of organization of homogeneous nano-structure which is built from the ordered accumulation of a mixed nano-spheres of α -quartz and moganite which are characterized by appropriate size (mainly 250-320 nm diameter) for diffraction of visible light. This agate variety present the new natural nano-structure of two silica polymorphs which associated with common agate, that is, a irregular three-dimensional network of heterogeneous α -quartz and moganite spheres less 100 nm or more 320 nm in diameter. This work demonstrates that α -quartz and moganite nano-spheres are the elementary building blocks of this rare variety of agate.

3. Introduction

Scientists still have not adequately surveyed Mexico from a mineralogical or gemological point of view. But recent finds of amazonite, jadeite, topazolite, demantoid, and labradorite demonstrate the importance of systematic research of the Mexican subsoil, which may lead to the discovery of other gemstones and gem localities [1].

Recently the author has studied some new primary deposits of fire agate in the Aguascalientes State, Mexico. The recent investigation of *in situ* fire agate in Mexico has renewed interest in the geology and mineralogy of gem deposits in that country. More discoveries are anticipated with further exploration in the region.

The rarest gemological variety - fire agate - is a relatively recent newcomer among gemstones but a precise date of first discovery seems unrecorded [2]. Most gemmologists and geologists were puzzled the first time they saw fire agate about the origin of colour. It is known that the fire agate has achieved considerably popularity among amateur lapidaries and collectors, especially in the USA-Southwest, but it has not attained a similar status in the mainstream jewellery trade. The best fire agate gems with play-of-colour compare favorably to certain classes of precious opal. The best samples display vivid reflections of red, orange, yellow, green, and even blue, but these are rare. This play-of-colour agate variety always associated with common agate with no play-of-

colour.

Fire agate is commonly found in bright gold colours of fire, with more rare multicolored fire. The cause of the colour remains controversial, the most common explanation suggesting that the iridescence arises from a thin layer of minute iron oxide crystals (goethite) which give rise to interference of light, hence the colours [2]. More than 30 years ago [3], found no spheroidal structure in the translucent fire agate after etching and examination by SEM. Instead, found a platelet structure and thus is of the opinion that the colour arise from interference and not from diffraction.

The purpose of this study is to demonstrate with the aid of modern mineralogical methods that the nano-structure of fire agate from many Mexican deposits is close, and built by the higher degree organization of α -quartz and moganite nano-spheres, which are the elementary building blocks of this rare variety of agate.

4. Background Information

Mineralogists and gemmologists have known only two countries with deposits of this stone: in certain areas of northern Mexico (Aguascalientes and San Luis Potosí States) and the southwestern United States (Arizona, California and New Mexico). The major fire agate deposits were found in the Arizona state: Oat-

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man claims (Cuesta claims), Black Hills, Round Mountain, Deer Creek, Saddle Mountain, Slaughter Mountain, etc [2,4].

The main Mexican deposits of fire agate were discovered near Calvillo town in Aguascalientes state in 1973 (Figure 1 A, B). These deposits are located in two municipalities: Calvillo (mines: La Minita, El Chispaso, La Guadalupana, El Encino, Los Huenchos, Alicia, Las Amarillas, Mesa de los Indios, La Trinidad, etc.; 21°50'49"N 102°43'07"W) and Jesus Maria (mines: Guadalupe, Garabato, el Refugio). The most productive mine El Refugio (21°57'40"N 102°20'36"W) was discovered in the Terrero de la Labor community, in Mesa José Muñoz [5].

The host rocks are rhyolitic breccias close to volcanic domes. The breccias are part of an Oligocene-Miocene volcanic package. The mineralization is in cavities and fractures of the volcanic breccia, which was deposited as a rhyolitic flow. The deposit shape is very irregular. The potential depends on the volcanic breccia outcrops.

The mine el Refugio has been a major producer of fire agate with nodules up to 6 cm in diameter and the samples with multicolored fire (Figure 1 C, D). During peak production periods, the mines of this area have produced over 10000 pieces of rough fire agate per week [5] reported the deposit of fire agate from Mexico in the state of San Luis Potosí, from which much material was mined. Our more recent fieldwork has not confirmed the presence of fire agate deposits in these geological settings and the present author have not found a description of this Mexican fire agate in geological, mineralogical and gemological literature.



Figure 1 (A, and B). Fire agate deposit el Refugio (Aguascalientes state, Jesus Maria municipality, Mexico) in the host rhyolitic breccias rocks close to domic sources and some typical samples (C, D) of this mineral with multicolored fire.

There was much interest and demand for fire agate in Mexico and USA. This was not to be for long at the Mexican mines there was severe mining problems. The mines became ponds for much of the year and there were mud slides and collapsing in of the mines. Some of the Mexican mines were up to 100 feet deep. It must be understood that the mines in Mexico were in very isolated mountainous areas often just a trail into the mountains. It was a problem, and often impossible to get in heavy earth moving equipment to remove the top soil or over burden to expose the agate bearing very specific volcanic rock. It is also not easy to extract the fire agate from pockets and seams in these rocks [5].

Currently, local inhabitants, in a very small scale, carry out the exploitation in all mines intermittently. According with conversations of the local people, the extracted and selected mineral is polished with manual methods, - in an artisanal way. The pieces are sold during the work trips of the peasants to the United States of America.

5. Experimental Details and Materials

The present work is based on Raman Microprobe (RMP), and Infrared Reflection Spectroscopy (IRS), Scanning Electron (SEM), and Atomic Force Microscopy (AFM).

RMP and IRS have been by researchers methods of mineral “fingerprinting” and a combined use of these techniques permits to identify practically all mineralogical, gemological and archaeological objects [6, 7]. These methods present many comparative advantages in comparison to the majority of well-known traditional mineralogical techniques.

In this study, the natural samples of the fire agates from Calvillo and Jesus Maria mines were examined in the beginning with RMP. Their Raman spectra were recorded with multi-channel micro-Raman LabRam 300 spectrometer (Horiba Jobin-Yvon). In order to obtain more information about these natural materials, the mineralogical composition of all studied samples was examined using single point micro-Raman spectroscopy.

In contrast to RMP, the IRS technique is not very known method in advanced mineralogy, gemology, archaeometry and geoarchaeology [6]. The IRS is a non-destructive method that can be used in the study of minerals, gemological and archaeological materials with natural surfaces, i.e., crystallographic faces, planes of cleavage, non-uniform surfaces, and cut and mounted stone materials. We have used some modern IRS technique (for example, HYPERION spectrometer).

The SEM work was performed using a field-emission Jeol JSM 7600F microscope at magnifications up to 100000-400000x. All samples were observed with the SEM, first on a fresh break, then after a 30 s attack with hydrofluoric acid (HF) diluted to 10% vol-

ume in water. A film, about 5 nm thick of copper alloy was used to coat them.

AFM was used to obtain images of the topography at the nanometer scale. The experiments were performed in air with a commercial AFM JSPM 5200 Scanning Probe Microscope operating in non-contact mode.

Most of the preliminary work was done on several dozen fire agates from various deposits in Mexico, from the State of Aguascalientes (for example, Calvillo municipality: Mine Las Amarillas, near Calvillo town; and Jesus Maria municipality: Mine El Refugio).

6. Results and Discussion

The index of refraction and specific gravity of all our samples are within a narrow range ($n_e=1.539-1.544$ and $2.57-2.64$, respectively), indicating that fire agates constitute a homogeneous group of materials from the point of view of their average bulk properties.

The Raman spectra of all 30 samples were collected in different zones (with and without play-of-colour) and show evidence a mixed phase fire agate that is the intergrowth of two silica polymorphs: α -quartz and moganite (Figure 2A, Table 1). The Raman spectra always show the typical Raman spectrum of α -quartz, with a very strong maximum at about 464 cm^{-1} and very little variation [6]. The most intense peaks of moganite are centered at 502 , 220 , and 129 cm^{-1} , whereas groups of less intense bands are found in the ranges $250-480$, $650-850$, and $1040-1210\text{ cm}^{-1}$ [8].

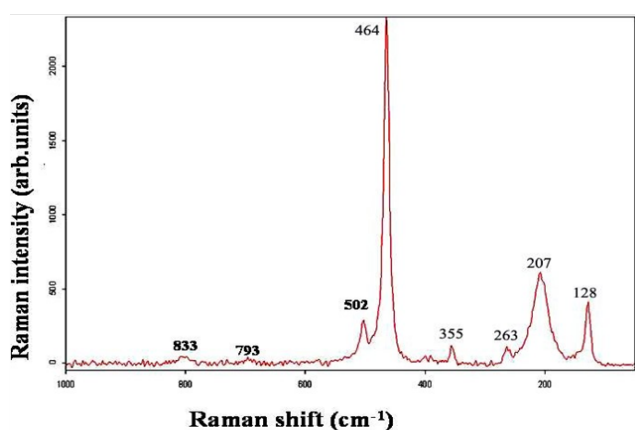


Figure 2A

Table 1: Raman peaks (cm^{-1}) for α -quartz, fire agate and C-T opal between 100 and 1300 cm^{-1}

α -Quartz (Scott and Porto, 1967)	Moganite and Kingma [16,17]	Fire agate	C-T Opal (Ostrooumov [1])	Mode symmetry and assignments [7,15]
128 s	129 m	128 s	133 w	E (LO+TO): lattice modes
207 s,bd	220 m	207 s	233 w	A ₁ : lattice modes
264 m	265 w	263 m	272 w	E (LO+TO): lattice modes
356 m	-	355 m	325vs	A ₁ : lattice modes
395 m (sh)	398 w	396 m	-	E (TO): lattice modes
401 w	-	402 w	412 w	E (LO): lattice modes
464 vs	463 w	464 vs	460 w	A ₁ : Si-O-Si sym stretch
-	502 vs	-	-	T-O-T: Si-O-Si sym stretch
511 w	-	510 w	-	E (LO): Si-O stretch
696 w	693 m	697 w	633 w	E (LO+TO): Si-O-Si sym stretch
795 w,sh	792 w	796 w	786 w	E (TO): Si-O-Si stretch
808 w	833 w	807 w	961 w	E (LO): Si-O-Si bending
1069 w, sh	-	1067 w	1076 w	E (TO): Si-O-Si asym stretch
1085 w	1084 w	1083 w	-	A ₁ : Si-O-Si asym stretch
1162 w	1171 w	1161 w	-	E (LO+TO): Si-O-Si asym stretch
1230 w	-	1232 w	1222 w	E (LO): Si-O-Si asym stretch

N.B.: Relative intensities are denoted by: s=strong, m=medium, w=weak, v=very, sh = shoulder; assignments: str =stretch, def=deformation, sym = symmetric, asym=asymmetric.

The detailed identification of the vibrational modes of different forms of silica has been made in previous publications by several authors who assigned all of the observed bands [9,10]. In accordance these data, the strongest band in the spectrum of quartz at 464 cm^{-1} is due to a symmetrical stretch vibration (tetrahedron breathing). It is also known from the infrared spectra of various silicate materials that the asymmetric Si-O stretch is in the $1200-900\text{ cm}^{-1}$ region while the symmetric stretch has been assigned to the $800-600\text{ cm}^{-1}$ region.

The most intense peak of the 502 cm^{-1} in the moganite spectrum is correlated to Si-O stretching mode, whereas peak below about 400 cm^{-1} originate from torsional vibrations and O-Si-O bending modes [8]. The strongest bands in the moganite spectra, which occur in the range of $400-530\text{ cm}^{-1}$, involve motions of O in Si-O-Si symmetric stretching-bending modes. The Raman frequencies of these modes are found to correlate with the number of tetrahedral that form rings within framework silicate structure [10]. The position of the 502 cm^{-1} mode in the moganite spectrum, in agreement with this proposed model, has confirmed that the structure of moganite consists of four-membered rings of corner-sharing SiO_4 tetrahedra.

Therefore, in answer to [10,11], these Raman results have shown first of all, that fire agates are not opals. According to [6], the vol-

canic opals from Mexico have similar Raman spectra characterized by a very strong general band (apparent maximum toward 325 cm^{-1}) that shows a complex structure with lines of weak to medium intensity (**Table 1**).

The IRS spectra obtained from all areas of the studied fire agates show that these samples are highly homogeneous, containing only one variety a mineral such as α -quartz (**Figure 2B**; **Table 2**). This mineral was identified on the basis of its intense IRS bands at 1174 and 1110 cm^{-1} (Si-O-Si stretching modes). Furthermore, the reflectance spectrum of quartz displays a well defined lobe of prominent reflection doubling at 800 and 780 cm^{-1} (Si-O stretching modes) that is typical for (10-10) orientation [1]. We have not observed any bands of moganite in the IRS spectra.

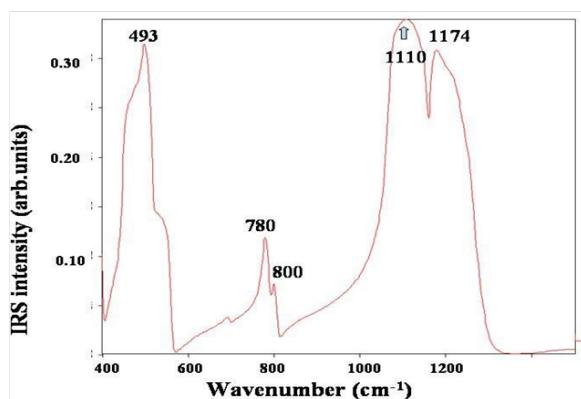


Figure 2. A) Raman spectra and B) Infrared reflection spectra of fire agate sample from el Refugio deposits.

Table 2: Infrared reflection spectra (wavenumber, cm^{-1}) of α -quartz, fire agate and C-T opal See table 1 for relative intensities identification.

α -Quartz (Ostrooumov)	Fire agate	C-T Opal (Ostrooumov)	Assignments (Williams)
1174 vvs	1174 vvs	-	Si-O asym str
1110 vvs	1110 vvs	1106 vvs	Si-O asym str
800 m	800 m	800 m	Si-O-Si bends
780 m	780 m	789 m	Si-O-Si bends
695 w	695 w	-	Si-O-Si bends
540 m	540 m	-	Si-O def
490 s	493 s	473 m	O-Si-O def

Figure 3 shows a SEM picture of common (a), (b) and fire agate (c), (d) originating from El Refugio mines. No organized structure can be seen with the SEM on a fresh break (**Figure 3 a & c**), even at the highest magnification: 100000). This nanostructure is revealed only by attack with diluted hydrofluoric acid (10% vol. HF for 30 seconds). Then one sees a network of quartz and moganite spheres. It appears as a random conglomerate of spheres of several hundred of nanometers, which we call “nano-spheres”.

In the areas without play-of-colour (**Figure 3b**), SEM investigations have shown the heterogeneous nano-structure which are characterized by different diameters of the α -quartz and moganite spheres: less ($<150\text{ nm}$) or more ($>330\text{ nm}$) or agglomera-

tions of small spheres which do not produce the diffraction of white light. Mexican play-of-colour agates show a higher degree of organization of homogeneous nano-structure (**Figure 3d**), in which the nanoparticles form the α -quartz and moganite spheres of appropriate size (mainly $250\text{--}320\text{ nm}$ diameter) for diffraction of visible light. There is a continuum of nano-structures between fire agate and common agate without play-of-colour. The more organized the structure and the more round and homogeneous the α -quartz and moganite spheres are, the more noticeable the diffraction colours appear. The nano-structure of common agate is built by the random accumulation of heterogeneous α -quartz and moganite spheres less 100 nm or more 320 nm in diameter.

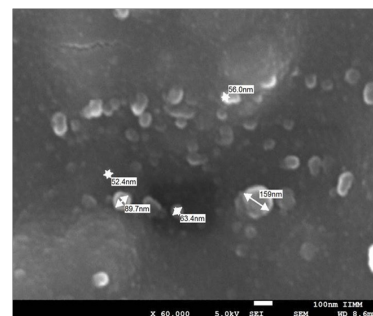


Figure 3A

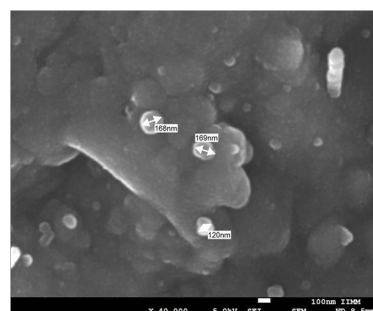


Figure 3B

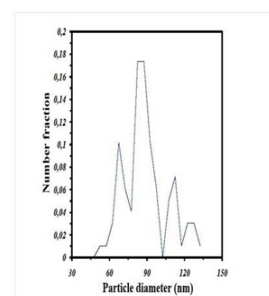
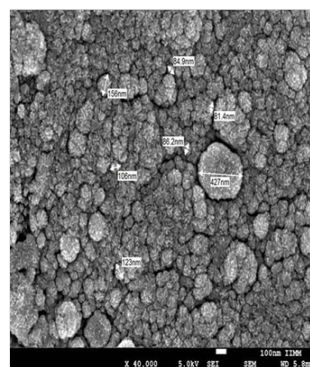


Figure 3C

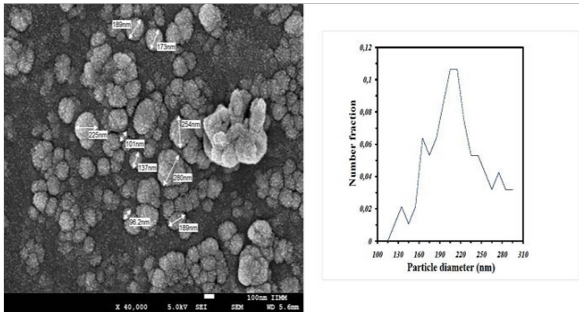


Figure 3. Representative SEM micrographs of common and fire agates from El Refugio deposits. No organized structure is seen with the SEM of fresh breaks of common (a) and fire (b) agates. After HF attack, common (c) and fire (d) agates show (micrographs on the left) a heterogeneous and homogeneous nano-structure which are characterized by different diameters of the α -quartz and moganite spheres: fire agates with play-of color show a higher degree of organization with ordered α -quartz and moganite nano-spheres that are characterized by appropriate size for diffraction of visible light. Distribution of particle sphere diameters in the nanostructure of the newly discovered fire agate (graphs on the right): in common agate most of the spheres are 90-140 nm (c), a size too small to diffract light, whereas the fire agates are built from a random aggregation of more big, near-spherical grains, averaging 160 to 270 nm in size (d). The software we used was ImageJ, an open-source image processing program designed to generate scientific multidimensional images.

The EDS chemical mapping was performed not only on the fire agate but also on their environs where common agate was observed. These maps indicate the existence of Si and some Fe in the studied samples and their same homogeneous distribution in these different agates with or without play-of-colour. Therefore, our results have not confirmed the most common explanation [2] suggesting that the iridescence arises from a thin layer of minute iron oxide crystals which give rise to interference of light, hence the colour of fire agate.

AFM images were acquired to be certain that the structure observed was not an artifact. Figure 4 presents the results obtained for common (**Figure 4a**) and fire (**Figure 4b**) agates from Mexico. AFM images of fresh breaks of common agates show the random accumulation of small nanograins about 40-140 nm for very largest. From those images, it is clear that fire agate is built from a random aggregation of small near-spherical grains, about 200 nm in size on average. The apparent diameter of these grains actually ranges from about 250-320 nm for the very largest. The lower limit is dictated by the size of the tip and is therefore not significant. However, the range of sizes observed with AFM is consistent with that observed with SEM. Therefore, this range can be considered as representative of the real internal structure of fire agate. This nano-structure is found in all of our samples of fire agate from Mexico. Moreover, there is in our experience no significant difference among samples from a same deposit or among samples from different deposits.

Until now, the nano-structure of fire agate had never been resolved. RMP, IRS, SEM, and AFM investigations have demonstrated that this agate variety present the new natural nano-structure of structurally ordered mineral which associated with common agate, that is, a no regular three-dimensional network

of α -quartz and moganite spheres less 100 nm or more 330 nm in diameter.

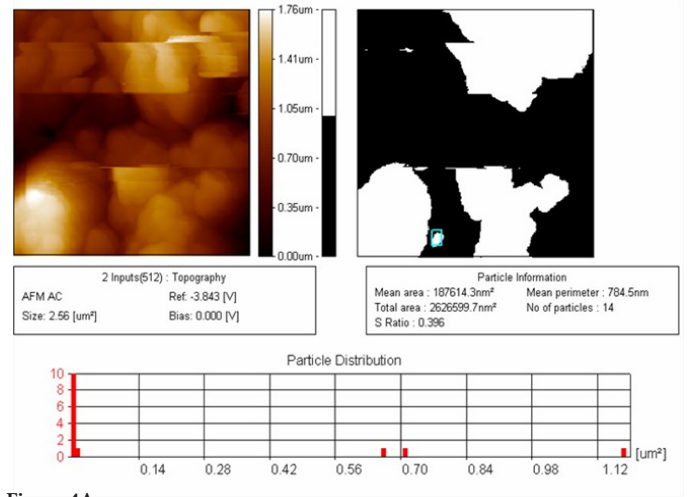


Figure 4A

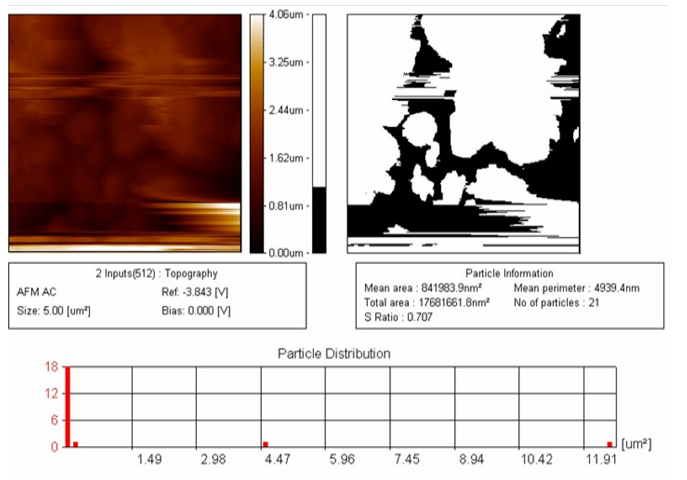


Figure 4B

Mexican opals - natural gem materials - offer a similar image, with a much wider variety of nano-to microstructure [12-14]. These opals, with or without play-of-colour are opal CT (for Cristobalite-Tridymite) - that is the XRD shows diffraction peaks for highly disordered Cristobalite, with abundant Tridymite stacking. SEM investigations proved that in general the building blocks of these CT opals are roughly spherical silica particles about 10-40 nm in diameter, and are best seen in AFM. The elementary building block of fire opal is a silica nanograin of about 20 nm in diameter. It is an order of magnitude smaller than the objects assembled in the classically described play-of-colour opal. The structure of all other varieties of opal, CT or A, could actually be described as various arrangements of nanograins [12]. Hence, these nanograins may constitute the true elementary building blocks of opal. The silica nanograins coalesce to give micron-sized spheroidal digenetic bodies (lepispheres). Volcanic play-of-colour opals show a higher degree of organization, in which the nanoparticles form pseudo spheres or aggregates of appropriate size (~200 nm diameter) for diffraction light. That is why we could suggest very close mechanism for the nanostructure formation of the fire opal and fire agate: there is a continuum of nano-

and microstructures between opals with and without play-of colour. In this continuum there is the same phenomenon in the nanostructure of these two silica mineral assemblages that we have underlined previously: the more organized the structure and more round the spheres are, the more noticeable the diffraction colour appear. This work demonstrates that fire opal, and possibly many other opal varieties, is actually a natural nano-material, built from blocks of nanometric scale, and not from an aggregate of silica particles of sub-micron size.

The same conclusions we could propose for the fire agates. The broad range of the diffraction colours displayed by natural Mexican fire agates is due to the diameter of α -quartz and moganite spheres that form their three-dimensional periodic structural grid. The SEM investigations proved that in general, the building blocks of such volcanic agates are roughly spherical α -quartz and moganite particles about 250-320 nm. According to Sanders (1964), the formula used to calculate the monochromatic diffraction colours possible from play-of- colour opals from sedimentary Australian deposits was: $\lambda_{\text{maximum}}=2.37D$, where D is the diameter of the silica spheres forming the precious opals. At first, we used this formula for the characterization of diffraction colour of Mexican opals [1,15] and then for fire agate. In accordance with the α -quartz and moganite particles size, the majority of the fire agate samples display vivid reflections of red, orange, and yellow colour.

In addition, the maximum wavelength minimum that can be diffracted by the fire agate structure is determined by the relationship:

$$\lambda_{\text{minimum}}=\lambda_{\text{maximum}}\sqrt{1-1/\mu^2}=0.72\lambda_{\text{maximum}}$$

It has been established that spheres of homogeneous silica that have the diameter from 250 to 300 nm compose precious fire agates. This diameter determines diffraction colour or the diversity of its diffracted colours. By using Sanders formula (1964) one can predict that small α -quartz and moganite spheres of 250 nm will yield yellow colours. Green diffracted colours are typical of the fire agates that have α -quartz and moganite spheres of 210-230 nm diameters. The largest spheres, with diameters of 250-320 nm diameter yield orange and red colours. Those fire agate that are formed of α -quartz and moganite spheres greater than 330- 350 nm or less than 150 nm do not yield diffracted colours [16-20].

Hence, the wavelength of the light diffracted by precious fire agate depends directly of the diameter of the spheres of α -quartz and moganite. This is why the fire agates with small spheres of these two silica polymorphs have in general a green-yellow play-of-colour, while the fire agates with large spheres of α -quartz and moganite are characterized by an orange-red play-of-colour. Therefore by analysis of diffraction colour of fire agates it is possible to determine the diameter of α -quartz and moganite

spheres.

7. Conclusions

The structure of fire agate could actually be described as various arrangements of α - quartz and moganite nano-spheres. Hence, these nano-spheres may constitute the true elementary building blocks of this rare variety of agate [20-23]. This research demonstrates that fire agate is actually a new natural nano-structured gem mineral, built from homogeneous spheres of nanometric scale. Mexican common agates without play-of colour which associated with fire agate show a lower degree of organization with fully disordered α -quartz and moganite nanospheres that are characterized by no appropriate size for diffraction of visible light. The nanostructure of this common agate explains the absence of play-of-color. In this case, we can consider the following general explanations for the lack of play-of-color:

1. The spheres do not have the same size (heterogeneous structure),
2. The spheres are not perfectly spherical,
3. The spheres are the same size but not well organized,
4. The spheres are too small (<150 nm) or too large (>300 nm) to diffract light.

In some cases two or more of these conditions occur in the same sample of the common agates.

The processes controlling the geological formation of play-of-color versus common agates are not completely understood, nor are the processes that control precipitation versus crystallization of this rarest mineralogical and gemological variety form of silica.

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