Research Article

Characterization of Natural Precious Opal Using Modern Spectroscopic Techniques in Ethiopia: The Case from Delanta, South Wollo

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The purpose of this study was to conduct characterization of the Delanta natural opals obtained from different mining sites. Characteristics of opals mined from different geological locality were examined. Six opal samples were collected from the main mining sites found in different localities from Delanta district and characterized using Fourier infrared spectroscopy, scanning electron microscopy, X-ray diffraction, and inductively coupled plasma optical emission spectroscopy characterization techniques. The scanning electron microscope micrographs showed that all the samples have relatively semi-ordered (semi-crystalline) structural surface morphologies composed of tiny spherical particles. The performed X-ray diffraction analysis showed that the samples have main peaks at 20.0 °, 21.72 °, 36.9 °, 44.0 °, and 56.85 ° with 2θ values between 10 ° and 60 °. The five diffraction peaks are characteristic peak positions of opal-CT. The Fourier infrared spectroscopy data indicated that the prominent absorption bands for cristobalite at 620 and 520 cm−1 were absent from the spectrum. Instead, three bands in the low frequency region centered at 470, 791, and 1100 cm−1 were observed because of the absorptions of the silicate framework (Si-O) vibrations. Moreover, spectra feature of molecular water and silanol (Si-OH) groups with broad absorption band centered around 3447 cm−1 and the O-H stretching vibration of water molecules and water bending vibration with an absorption band centered around 1634 cm−1 were observed. These values were consistently comparable with literature data. The inductively coupled plasma optical emission spectroscopy analysis showed that four main impurities (>500 parts per million) were Ca (~1,750–4,730 parts per million), Al (~1,990–4,319 parts per million), K (~1,670–3,895 parts per million), and Na (~595–3,723 parts per million). In general, this study revealed that all opal samples taken from six mining sites in Delanta district were found to be opal-CT as per the results of X-ray diffraction and Fourier infrared spectroscopy investigations.

1. Introduction

Opal gemstones are water-bearing non-crystalline materials, composed of microspheres of hydrated silica (SiO2.nH2O) with a high degree of structural disorder [1, 2]. Because of their optical properties, opals have been widely used for jewelry, for fabrication of highly efficient optoelectronic devices, and as ornamental elements in art works [3–5]. Due to high economic values and preciousness of opal resource, deep investigation and understanding of the physico-chemical properties of the mineral is an essential issue in gemstone industry.

The typical optical phenomenon of opal, called “play of color,” is as a result of the interaction of light with their pseudo-structure composed of regularly spaced layers consisting of sub-micron sized (approximately 250 nm in
diameter) silica spheres [6–8]. The presence or absence of the optical phenomenon (play of color) in opals used to classify them as: precious opals those exhibit flash of spectral colors and common opalsthe two do not exhibit flash of spectral colors. Even if common opals do not display play of colors, some common opals are attractive due to their opaque to translucent body color. While some rare opals are colorless, most opals present a body color: white, black, gray, brown, yellow to orange (as in fire opal), red, pink, blue, green, or violet, depending on mineral inclusions and on the existence of particular trace elements [9]. A number of these common opals have also significant commercial values. Opals vary in the crystallinity degree and in crystal-structure arrangement. Based on the mineralogical composition and atomic arrangements [10–12], opals can be classified into three types (opal-C, opal-CT, and opal-A) based on the main component revealed by X-ray diffraction (XRD), Fourier infrared spectroscopy (FTIR), Raman spectroscopy, and other techniques. Opal-C is a well-ordered form of silicate comprising mainly of α-cristobalite; opal-CT is semi-crystalline and made up of crystalline regions of α-cristobalite and α-tridymite; and opal-A is the most disordered type.

In the literature, there are handful reports on the study of Ethiopian opals. Even the existing few reports lacked detailed characteristic studies of the Ethiopian opals particularly the Delanta opal, mined from the different mining sites. On the other hand, there are many studies on the Australian “potch” opal, which have attracted more interest on customers in global market. On the contrary, it is possible to find extensive studies of common opals of geological significance. In most of these studies, the classical mineralogical classification and the Raman classification are used. The aim of this work was to characterize the Delanta natural opal dug out from different mining sites employing XRD, FTIR, SEM, and inductively coupled plasma optical emission spectroscopy (ICP-OES). As it is palpable, the characterization of the physicochemical properties of opals from a particular geographic area is important for several reasons. For instance, in the gem market, opals or other precious stones coming from specific place can be very valuable than others.

2. Experimental

2.1. Sample Details and Preparation. In order to conduct the detail characterization of the Delanta natural opals, 6 representative samples were collected from six main mining sites. The physical properties and photograph images of the samples are presented in Table 1 and in Figure 1, respectively.

After collection and leveling of the samples with different colors as shown in Figure 1, all the samples were powdered using crucible in chemistry department of Addis Ababa University and prepared for different characterizations as shown in Figure 2.

2.2. Testing. The surface morphologies of the samples were investigated by field emission scanning electron microscopy, FEI Inspect F50, with working accelerating voltage of 15 kV and beam current of 140 nA at Addis Ababa Science and Technology University. Because of the inorganic nature of opal, a carbon coating was made to mount fragments to provide conductivity to avoid charging effects of electrons on the surface of the samples.

Powder X-ray diffraction data were collected at Addis Ababa University with MiniFlex 600 X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å, 15 mA, 40 mV). The experiments were conducted in step-scan mode: 10–60° 2θ range and step size of 0.02°. FTIR spectra measurements were recorded using a Perkin-Elmer BX Spectrometer (400–4000 cm⁻¹ spectral range) in KBr to determine the functional group of the samples. The elemental analysis was investigated using ICP-OES of model ARCOFS HS12. The experiments were carried out employing a plasma power of 1400 W and pumping speed of 30 rpm and argon pressure of 6.75 bars. XRD and FTIR experiments were recorded at Addis Ababa University, and ICP-OES measurements were performed at Horticop Ethiopia (Debre-Zeit).

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM). From the SEM images of all opal samples, we tried to investigate the surface morphological behaviors. Figure 3 shows low magnification SEM images showing tiny spherical particles in opals; however, after 15–20 minutes of exposure of the samples to the electron rays and vacuum of the SEM, the water is lost and devitrification takes place. Consequently, microtexture with copious precipitation of tiny microspheres (Figure 3) agglomerated and constituted semi-crystalline heterogeneous sized stacked polyhedral microstructures. All the images showed relatively rough surfaces having different sizes of agglomerates with layer disposition.

Figures 3(a), 3(c), 3(e), and 3(f) show similar morphologies with comparatively bigger agglomerates. Particularly, Figures 3(c) and 3(e) show images with more phase separation between the particles. On the other hand, Figures 3(b) and 3(d) show smaller agglomerates and uniform particle size. In general, the SEM images show that all the samples have relatively certain semi-ordered structural surface morphologies composed of tiny spherical particles.

3.2. X-Ray Diffraction Analysis. It is well known that XRD is a powerful tool for structural characterization of materials in general and particularly very important for opal classification since the structural and spectroscopic properties of opals strongly depend on the crystallinity degree. The performed XRD analysis showed that all the samples have five diffraction peaks at 20°, 21.72°, 36.9°, 44°, and 56.8° with 2θ values between 10° and 60°. The five diffraction peaks are characteristic peaks for opal-CT minerals according to the Jones and Segnit [10] classification and other literature as shown in Figure 4.

3. From the XRDdiffraction spectra presented in Figure 4; the most intense peak occurs at about 21.7° with a very
weak shoulder at about 20°. There is also a weak reflection peak at about 35.9° resulting basically from $\alpha$-cristobalite with varying degrees of stacking disorder leading to the appearance of maxima which can be attributed to tridymite.

3.3. FTIR Spectral Analysis. Infrared absorption by mineral samples depends on the characteristics of the interatomic bonds in the mineral structure, the overall symmetry of the unit cell, and the local site symmetry of atoms within the unit cell. The technique is responsive to both long-range and short-range order in minerals. IR spectra can, therefore, be used to characterize and identify both crystalline and amorphous materials.

Here, we report FTIR powder spectra, collected in the range of 400–4000 cm$^{-1}$, in Figures 5 and 6. The results are totally well matched with those already available in the literature for related samples. Like most of the reported FTIR studies of opal-CT [10, 13, 14], this study showed that prominent absorption bands for cristobalite at 620 and 520 cm$^{-1}$.
were absent from the spectrum [15] (Figure 5). All the samples taken from the different mining sites of Delanta district showed bands attributable to tridymite at 1100, 791, and 470 cm$^{-1}$, which is generated by inter-tetrahedral Si-O vibrations (Figure 5) is predominantly critical information in determining the type of opals we are studying [17] as presented in Figure 6. Furthermore, as we can see from Figure 5, the bands at 2921 cm$^{-1}$ and 2852 cm$^{-1}$ are symmetrical and asymmetrical stretching vibrations of the methylene group C-H [18] bond in the material since our samples are natural opals. Likewise, all the samples exhibit absorption bands at approximately 3447 and 1634 cm$^{-1}$ both attributed to O-H vibrations of water.

3.4. Elemental Analysis. The ICP-OES data for the six samples analyzed are listed in Table 2. Trace element analysis is important for understanding some physical properties of gem opals, like color and luminescence [4]. The ICP-OES data of the six samples from six different mining sites of Delanta district are presented in Table 2.

Figure 3: SEM images of opal samples: (a) Ds-1, (b) Ds-2, (c) Ds-3, (d) Ds-4, (e) Ds-5, and (f) Ds-6.

As presented in Table 2, the four main impurities (>500 ppm) were Ca (~1,750–4,730 ppm), Al (~1,990–4,319 ppm), K (~1,670–3,895 ppm), and Na (~595–3,723 ppm). Other elements present in lesser amounts were (in order of decreasing concentration) Fe (~70–254 ppm), Mn (~3.0–7.6 ppm, except sample Ds-2 with 1,157.8 ppm), Zn (~0.4–2.0 ppm), and Cu (~0.04–0.95 ppm). The other impurity element tested from all the six samples was Mg. The result showed that three samples (Ds-1, Ds-3, and Ds-6) have Mg concentrations < 0.002 ppm. On the other hand, the other three samples (Ds-4, Ds-5, and Ds-2) have Mg concentration of ~47, 82, and 172 ppm, respectively.

The chemical composition of opals is commonly related to that of host rocks influences opal properties such as color and luminescence [4, 9]. The body color is typically associated with inclusion of colored minerals, whereas the abundance of some elements decides the color of the opal [4, 9]. Even if there are few reports [4, 19, 20] on the chemical composition and other spectroscopic analysis of the Delanta opal, the present study gives a detailed analysis focusing on specific mining sites in the district. When we see the concentration of elements in this study in comparison with a previous study reported by Gaillou et al. [4], even if the researchers did not mentioned the specific mining sites, the differences in concentration of some elements (Na, K, Fe) is significant. The concentration of Na samples: Ds-1, Ds-2, and Ds-3, Ds-4 is much greater than the concentration Na reported by Gaillou et al. [4]. When we compare the concentration of K, even if the K concentration of samples Ds-3 and Ds-5 is comparable with concentration values of the reported values, samples Ds-2 and Ds-4 of this study have much greater concentration values. But when we compare the concentrations of Ca, Mg, Mn, Cu, and Zn, the concentrations we get are comparable with the concentrations reported by Gaillou et al. [4] even if Mg was not detected from three samples of this study. The detection of Mn in all of the samples is probably due to the presence of dendrites of todorokite.

Sample Ds-2 from Alehuat is identified and differs from other samples by the highest concentration of Mn, Fe, Mg, and average value of Zn (1,157.83, 254.39, 172.38, and 1.58), respectively.

Generally, in this study, we observed that elements Zn, Mn, and Cu have low concentrations in all the six investigated samples and their presence does not look related to the color of the opals. When we observe the concentration of Fe, it is reasonable to associate with the color of the samples: the brownish dominated color of sample Ds-2 is due to the highest concentration of Fe, whereas the lower Fe concentrations in
**Figure 4:** XRD diffraction patterns of opal samples mined from different geological localities of Delanta.

**Figure 5:** FTIR representative spectra profile of opal samples from Delanta district taken from mining site Workwasha.
opal samples Ds-1 and Ds-6 determine the yellow tint color. This relationship between Fe concentrations with the colors of opal samples was also reported by different authors including Gaillou et al. [4]. The existence of the impurity Fe in opals of the study area perhaps occurs as inclusion of Fe oxyhydroxides that determine the yellow or orange colors [4]. When we see the variations of elemental concentrations in the samples, the variation of Ca and K is highly significant relative to the variation of concentrations of other elements with the lithological origins of the samples and can then be valuable to determine the provenance.

Some optical and structural properties (color, preciousness, and atomic arrangement) of opal samples mined from different mining sites of Delata distinct are compared with the same properties of opals from other countries (Australia, USA, Slovakia, Madagascar, and Mexico) from the literature [21] as presented in Table 3. Compared with the listed countries, opals taken from different locations of Delata district are all precious with different colors (Figure 1). But many opal samples taken from different locations of the aforementioned countries are common with almost one type of color. Some precious opals are seen in few locations of Australia, USA, and Slovakia. When we consider the classification of opal samples based on atomic arrangements, all the samples taken from Delata district are opal-CT. But in addition to opal-CT, opal-A is found in Australia and Slovakia, and opal-C is mainly found in Mexico.

**Table 2: Concentration (in ppm) for trace elements within each opal sample by ICP-OES (Ds-1: Workwasha, Ds-2: Alehuat, Ds-3: Necho, Ds-4: Abbetach, Ds-5: Chegen, and Ds-6: Gelbate).**

| Element | Ds-1   | Ds-2   | Ds-3   | Ds-4   | Ds-5   | Ds-6   |
|---------|--------|--------|--------|--------|--------|--------|
| Ca      | 2,258.46| 4,338.71| 1,756.16| 4,737.35| 2,402.43| 2,782.30|
| Al      | 2,634  | 3,152  | 4,287.51| 2,934  | 4,319  | 1,990.78|
| Mg      | <0.002 | 172.38 | <0.002 | 47.04  | 81.92  | <0.002 |
| Na      | 3,723.24| 1,130.13| 1,995.66| 2,019.39| 595.18 | 3,376.62|
| K       | 2,466.55| 3,416.98| 1,670.00| 3,894.75| 1,840.77| 2,461.04|
| P       | 478.91 | 364.58 | 415.69 | 438.16 | 353.58 | 251.51 |
| Fe      | 70.31  | 254.39 | 185.95 | 226.41 | 183.93 | 86.50  |
| Mn      | 4.91   | 1,157.83| 7.11   | 7.65   | 2.99   | 4.90   |
| Cu      | 0.95   | 0.65   | 0.41   | 0.32   | 0.04   | 0.19   |
| Zn      | 1.82   | 1.58   | 1.88   | 1.87   | 1.29   | 0.44   |
4. Conclusion

The main purpose of this study was to conduct characterization of natural opal samples (all precious and collected from different mining sites) from Delanta district, South Wollo, Ethiopia. The study provides a classification of samples based on the characterization results. So as to draw a clear picture of what has been done, the main conclusions are summarized as follows.

Six colored raw opals (all play of color) were collected from different lithological representative mining sites of Delanta district. To make the samples ready for characterization, we removed the soil from the body of all the samples and the samples were crushed using crucible. In this study, SEM, XRD, FTIR spectra, and ICP-OES methods were employed to study the morphological, structural, and chemical properties of the samples. The SEM micrographs showed that all the samples have relatively semi-ordered structural surface morphologies composed of tiny spherical particles. However, samples taken from Alehuat and Abobetach showed relatively smaller agglomerates and uniform particle sizes. As it is palpable, XRD is one of the appropriate analytical methods to classify opals as opal-A, opal-CT, and opal-C. The performed XRD analysis showed that all samples are polycrystalline and have five diffraction peaks at 20°, 21.72°, 36.9°, 44°, and 56.8° which are characteristic XRD diffraction patterns of opal-CT indicating the play-of-color nature of samples since play-of-color opals belong to either the opal-A group or opal-CT group. Likewise, the FTIR spectra characterization showed five main peaks known for opal-CT in the literature (1100, 791, 470, 2923, and 2852 cm⁻¹). Generally, both XRD and Raman spectra measurements showed with good agreement that the samples collected from all sites are opal-CT. The ICP-OES analysis showed that four main impurities (>500 ppm) were Ca (~1,750–4,730 ppm), Al (~1,990–4,319 ppm, K (~1,670–3,895 ppm), and Na (~595–3,723 ppm). Other elements present in lesser amounts were (in order of decreasing concentration) Fe (~70–254 ppm), Mn (~3.0–7.6 ppm, except sample Ds-2 with 1,157.8 ppm), Zn (~0.4–2.0 ppm), and Cu (~0.04–0.95 ppm).

Data Availability

The data used to support the findings of this study are included in this paper. If additional data is needed, the authors can provide.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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