

Spectroscopic Studies on Natural Gem- Agate in Sedimentary and Volcanic Host Rocks from (Bellesa, Addis Zemen and Bure), in Amhara National Regional State (Ethiopia)

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Abstract: The representative samples of gem-agate were collected from bellesa, addis zemen and bure. The samples were identified and characterized by different physical property measuring devices and advanced spectroscopic techniques. In order to verify that the samples were indeed agate a refractometer, heavy liquid method and "MOHS HARDNESS PENCILS" were used. The performed physical analysis shows that the hardness value of addis zemen and bure agate are in the range of 6.5-7 and that of bellesa agate is 7 while the refractive index and specific gravity of both agate samples are similar and in the range of 1.53-1.54 and 2.4-2.7 respectively. The XRD and FTIR spectral data of agate samples from three zones of the Amhara National Regional state have a significant contribution in their identification and characterization. The content of different trace elements (Ca, Mg, Fe, Cu, Cd and Mn) was analyzed by FAAS technique. Generally the investigated agate samples by using FT-IR show a broad band around 4000-2500 cm⁻¹ for the O-H stretch of water molecule, around 3585cm⁻¹ structural defect of silanol group and around 1084cm⁻¹ for Si-O stretch and at low frequency 694cm⁻¹ indicates the O-H stretch of silanol group. An agate yielded P-XRD pattern is characterized by four broad reflections, the sharp and most intense diffraction peak is pointed at $2\theta = 26.65^\circ$, medium intense sharp peak at $2\theta = 20.00^\circ$, 24.00° and 50.14° , broad peak at 20.83° and 68.85° and there is also weaker reflection band occur around $2\theta = 55^\circ$ and 64.00° . The XRD pattern for the three samples from three localities (Bellesa, Addis zemen and Bure agate, Ethiopia) are almost similar and comparable with the results obtained from the previous studies of agate in other countries (Australia, Morocco, India and Turkey).

Keywords: Gemstone; Agate; FTIR; XRD; FAAS; Ethiopia.

1. INTRODUCTION

In a recent history, mineral resources have a high priority in the Socio-economic development of the world. Naturally, Ethiopia is elegant and blessed with rich mineral resources. Its diverse geology comprises a variety of precious and semi-precious gemstone as well as industrial minerals resources, which offers a great opportunity for mineral prospecting and development [1]. Quartz is the most abundant silica mineral in the earth crust, found all over the world. The mineral potential of Ethiopia lies mainly with the development of gold, potash, thermal energies, and industrial minerals. Some industrial minerals found in Ethiopia are marble, granite, gemstone, limestone, clay, gypsum, iron ore, diatomite, coal, copper, silica etc... [2].

A gemstone is the naturally occurring crystalline form of a mineral which is desirable for its beauty, valuable in its rarity, and durable enough to be enjoyed for generations [4]. Gemstone exploration has recent history in Ethiopia. Quite a few studies were conducted by foreign experts, while limited explorations have been done by the ministry of mines besides energy and geological survey of Ethiopia. Gemstone's have higher economic value for the people who deals with it, not only the miners, but also the traders and designers [5].

Agates are spectacular products of nature, which have a cryptocrystalline structure formed from microscopic particles, mainly fibrous and partially granular silica particles and they are found all over

the world including: Asia, Brazil, Germany, India, Italy, Mexico, Nepal, many part of African countries and the USA of different geological environments. They are found in many parts of Ethiopia like Tigray (Adwa, Mekele and Aksum), northern Showa (MehaleMeda, Ankober, Sela Dingay, Jehur, Debre libanose and Yita Mechael), Wollo Kutaber and diverse geological part of Amhara national regional state [6, 7].

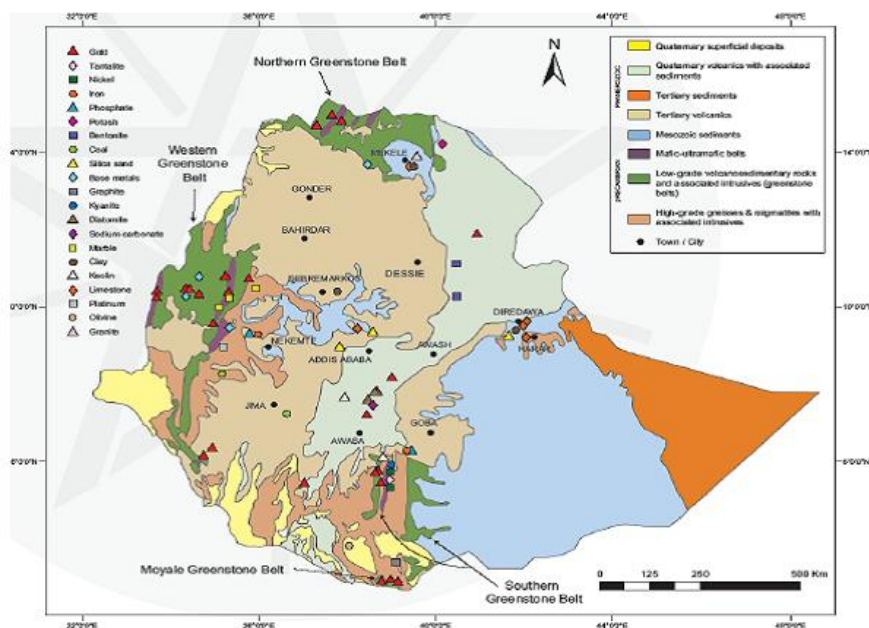
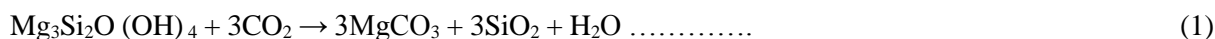


Figure1. key mining operations and mineral deposit in Ethiopia [3]

Agates are known a unique natural wonder for their amazing colors and different formation patterns, being widely used for jewelry and craft making, which is banded form of finely-grained, microcrystalline quartz. Despite their beauty and popularity, they are mainly composed by silica (a small molecule formed by only few atoms of silicon (Si) and oxygen (O)) with some sort of impurities [8].

Agate is a microcrystalline form of silica (SiO₂). It presents a chemical composition of around 97% of silica and less than 1% of non-volatile impurities. The concentration of impurity from H₂O and Si-OH is up to 2%. Silica in agates is composed by two of its polymorphs: α-quartz and up to 20% of moganite. In 1999, Zoetze *et al.*, presents the structure of agate can probably be interpreted as alternating formation of fine-grained, highly defective chalcedony inter grown with moganite, and coarse-grained low-defect quartz [10].

To explain about how do agates form, several theories are settle down, but basically all of them state that agates form by the systemic deposition of silica in cavity walls generally resulting in banded patterns. The geochemical study demonstrated that the formation of agate can be a complex, multi-steps process. A very simple description of this process is that high temperature, pressure or ionized surface and magmatic waters are capable of dissolving the silica from the rocks where they pass through. When these water flow or evaporate, there is the formation of silica deposition [11].



These agates have banded crystal architecture with successive parallel layers to the side of cavities. These are the feature of cooling magma fluids in the form of bubbles of steam and other gases which overtake the process of solidification and are frozen in cavities. Later the fluid carrying alkali silicate percolates in to these bubbles and triggers coagulation and to become silica jell. Designers often take advantage of the intriguing patterns these stones have to offer to create unique and fascinating pieces [10].

Many agates form in areas of volcanic activity where, water rich in dissolved silica (SiO₂) flow through fractures and cavities in igneous rocks. When the solution is highly concentrated with dissolved silica, a silica gel can form on the walls of these cavities. That gel will slowly crystallize to form microcrystalline quartz. And also agates typically form in igneous rocks such as basalt, rhyolite, and andesite, they can also form in sedimentary rocks such as limestone [12].

The spectroscopic techniques like Fourier Transform Infrared (FTIR), X-ray diffraction (XRD) and Flame Atomic Absorption Spectroscopy (FAAS) techniques were found to be useful scientific tools in identifying the natural gemstones. All of these techniques can perform the characterization or qualitative screening through elemental quantification of natural gem agate. It can be used to quantify the elements found in gem-agate as well as other materials that serve as evidence of certain treatment processes [30].

This paper presents the result of the application of some advanced analytical technique such as X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy for discrimination between natural gem agate hosted in Amhara national regional state (north Gondar, south Gondar and west Gojam) with the other natural gem agate studied by different researchers in different countries as well as various trace elements (Ca, Mg, Fe, Cu, Cd, Zn and Mn) in the sample is analyzed by flame atomic absorption spectrometry (FAAS). It would provide more information concerning the real structure of agate and characterize all genetic aspects of natural gem agate hosted in Amhara national regional state (Bellea, Addis zemen and Bure).

The objective of this study is to identify and characterize natural gem-agate hosted in Amhara National Regional State of (Bellea, Addis zemen and Bure agate), Ethiopia using spectroscopic techniques.

2. MATERIALS AND METHODS

2.1. Instrumentation and Apparatus

A refractometer of United Kingdom manufacture was used to measure the refractive index of agate with an optical contact liquid of 1.79 ± 0.05 at 25 °C. The specific gravity was measured using heavy liquid test (Lithium salt with specific gravity value 2.57 (UK)). Mohs Hardness Pencils (UK) was used to measure the hardness value of agate sample. A diamond pacific machine (UK Manufacture) was used to cut agate sample and a diamond paste machine (UK) was used to polish (clean) the agate sample. The ball mill grinder was used for grinding the agate sample. A sieve with 0.1 mm size was used to sieve powdered agate samples. An electronic digital balance (Denver instrument company USA) was used to weigh the powdered agate sample. Spectrum 65 FT-IR spectrometer (PerkinElmer instrument company U.S.A) was adjusted in transmittance mode and equipped with a 4x beam condenser with resolution 4 cm^{-1} and scanning speed auto (16 mm/sec) in the wave length range of 400 cm^{-1} up to 4000 cm^{-1} , was used for recording infrared transmission spectra of agate sample using KBr pellet method.

Miniflux 600 powder diffractometer (Rigaco instrument company, USA) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a scan speed of $1^\circ/\text{min}$ and in the range between $10\text{-}70^\circ 2\theta$ was used to collect X-ray powder diffraction data for quantities and semi quantitative analyses of the mineral phase in the agate sample and host rocks.

Borosilicate Erlenmeyer flask and hot plate were used to digest the agate sample. Filter paper was used to distill the digested agate sample. The pipettes (1mL, 2mL, 5mL), 100mL, 50mL volumetric flask, 50mL of Erlenmeyer flask and beakers were used to dilute the standards and samples' solution. An atomic absorption spectroscopy (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A.) equipped with air/acetylene flame, with a hallow cathode lamp for the determination of Manganese, Cadmium, iron, calcium, zinc, copper and magnesium were used.

2.2. Chemicals and Standard Solutions

Chemicals that were used in the analysis are analytical grades. Deionized and distilled water was used for cleaning of glassware and for dilution of samples. Ethanol was used for washing the crystal sample after cutting. KBr(obtained in the PerkinElmer (U.S.A) accessories and consumable kit). 48% of HF (Anala R, PARK: Hydrofluoric acid Solution Northampton scientific Laboratory supplies, U.K), 69-72% (Analytical R, IMO: Nitric acid solution BDH Laboratory supplies, England) of HNO_3 , 35.38% of HCl (Blulux, Laboratory reagent, Blulux Laboratories (p) LTD-121001), and 30% of w/v H_2O_2 (MS Laboratory Reagent, Medical PVT.LTD, New Delhi) were used to digest the agate samples. Stock standard solution of the metals Ca (1000 mg/L), Fe (1000 mg/L), Mn (1000 mg/L), Mg (1000mg/L), Zn (1000mg/L), Cd (1000mg/L) and Cu (1000mg/L) prepared for an atomic absorption spectrophotometer (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A.) were used for the preparation of calibration curves for the determination of metals in the samples.

2.3. Location and Accessibility of the Sample

The samples were collected from Amhara national regional state particularly (Bellesa, Addis zemen and Bure). The research sites are situated at different latitudes, longitudes and elevations. Bellesa has a latitude and longitude of 13° 12' 35"N 38° 8' 25"E, respectively and an elevation of 2133 meter above sea level), Addis Zemen (has a latitude and longitude of 12°07'N 37°47'E, respectively and an elevation of 1975 meters above sea level) and Bure (has latitude and longitude 10° 41' 59.99" N 37° 03' 60.00"E, respectively and elevation of 2091 meter above sea level).



Figure2. Sample site location in the amhara national regional state, Ethiopia

2.4. Collection of Agate Samples

The agate samples were collected from the Polly technique colleges (Gondar, Debretabor and Bihar Dar) in cooperation with Administrative Zone Technical Vocational Enterprise Development Departments of South Gondar Zone, Debretabor; North Gondar Zone, Gondar and West Gojam Zone, Bahir Dar, and these three samples of natural gem agates were obtained from mining.

2.5. Determination of Gemological Properties

The physical properties of the samples were measured in order to verify that the samples are indeed agate or not. These gemological (non-destructive) characterization techniques were performed on representative samples. The physical measurements were performed at Gondar poly-technique College gemological testing laboratory, Gondar in Maraki branch. For these purpose a refractometer UK manufacture was used to measure refractive index (RI) with an optical contact liquid of 1.78 ± 0.05 RI at room temperature and the specific gravity was measured by heavy liquid method (Lithium salt). "The instruments of MOHS HARDNESS PENCILS" were used to determine the hardness values of agate samples

2.6. Sample Preparation

By following the procedure in below, the natural gem agate samples were washed with distilled water in order to remove surface contamination and dried in sunlight. The samples were cut with a diamond pacific machine and polished by a diamond paste. After that the samples were washed by distilled water, ethanol and dried in air and then grounded in to a fine powder by using ball mill grinder and sieved with a 0.1 sieve.

2.6.1. Sample Preparation for FT-IR

The FTIR analysis was carried out by taking powdered gem-agate samples exactly 2mg for each (measured using electronic digital balance) and mixed with 200mg KBr in order to prepare circular pellet.

2.6.2. Sample Preparation for XRD

The XRD patterns analysis was carried out by taking powdered natural gem-agate samples and transferred it into sample holder of the instrument

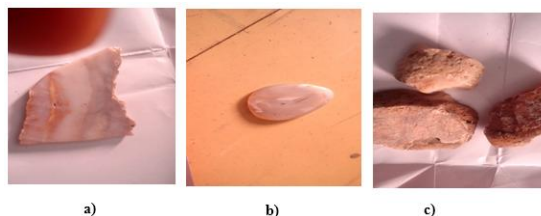


Figure3. The natural gem agate samples from (a) North Gondar, (b) South Gondar and (c) West Gojam.

2.6.3. Sample Preparation for FAAS

For FAAS analysis, from three powdered agate samples (0.5 g each) was weighed and put in to three replicate 50mL borosilicate glass of Erlenmeyer flask and 5ml conc. 69-72% HNO₃, 2ml 35.5% HCl, 1ml 30% w/v H₂O₂ and 2mL of 48% HF were added. Then after the Erlenmeyer flasks were heated on hot plate and the solution evaporated near dryness. After that 2 mL 48% HF was added and heated for a few times until precipitation of SiO₂ is eliminated as SiF₄ vapors. Cooling down to the room temperature, 2mL conc. HCl and 5 mL of distilled water were added. Finally the solution was transferred in to 250 mL volumetric flasks and filled up with redistilled water up to the mark [34].

2.7. Physical Measurements

2.7.1. Characterization Using FTIR

Before the samples were run in the spectrum 65 FT/IR spectrometer PerkinElmer (U.S.A), the instrument's total inspection was done by measuring absorbance of the standard polystyrene film and empty sample compartment turn by turn. A background (KBr) measurement was done. Powdered FT-IR spectra was collected at Addis Ababa University on 65 FT-IR PerkinElmer (U.S.A) spectrometer equipped with KBr beam splitter. Approximately 2mg of the sample was weighed using electronic balance and mixed with KBr powder (200mg for each sample).The mixtures were further powdered to mix well and then put in the instrument sample holder for solid sample analysis. Then each sample was examined by spectrum 65 FT/IR spectrometer PerkinElmer (U.S.A) operated at transmittance mode and resolution 4 cm⁻¹ and scanning speed auto (4 mm/sec) in the wavelength range of 400 cm⁻¹ to 4000 cm⁻¹.

2.7.2. Characterization Using XRD

To analyze, three gem-agate samples by using the modern analytical technique of (miniflux 600 powder X-ray diffractometer) Rigaku instrument company U.S.A with rotating copper target of voltage 220v and current 15 A, the fixed mass of powdered agate samples were weighed and transferred into the sample holder of the instrument.

The instrument was adjusted with Cu tube and a graphic monochromator with CuK α radiation ($\lambda=1.5418\text{\AA}$) and a scan speed of 1 $^\circ$ /min in the range between $2\theta = 10-70^\circ$. The Powdered X-ray diffraction (XRD) experiment was performed at Addis Ababa University in Ethiopia.

2.7.3. Trace Metal Determination Using FAAS

To analyze the agate samples using the FAAS, the instrument were adjusted in appropriate manner such as, wave length selector; hallow cathode lamp, slit width, fuel valve and etc. The absorbance of the analytic line is a function of several parameters, burner head position (vertical, horizontal) and flow rate of used gases. Optimal values of these parameters are those, which yield maximum absorbance value. The optimization procedure was carried out by studying the effect of one parameter while keeping the others constants at appropriate values. To carry out this study the acetylene and airflow rate were kept constant. Before the samples were run in BUCK SCIENTIFIC MODEL 210 VGP, FAA spectrometer, the presence of precipitate in the sample as well as standard solution were refined and total inspection was done by measuring the absorbance of distilled water.

For the determination of metals in (Bellese, Addis zemen and Bure agates, five series of standard metal solutions (Table-2) were prepared by diluting the standard solutions of the metal with distilled water. A blank (distilled water) and standards were run in flame atomic absorption spectrophotometer to establish five points of calibration curve. Each Sample solutions were aspirated into the FAAS instrument and direct readings of the metal absorbance were recorded. Three replicate determinations were carried out on each sample. The operating conditions of FAAS employed for each analyte are given below (Table 3).

Table2. Series of working standards for determination of metals in North Gondar, South Gondar and West Gojam agate varieties using flame atomic absorption spectrometer

No	Element	Concentration of Standards (µg/ml)	Correlation coefficient (R)
1.	Ca	0.1, 1, 1.5, 2, 2.5	0.808
2.	Zn	0.1, 0.5, 1, 1.5, 2	0.946
3.	Mg	0.5, 1, 1.5, 2, 2.5	0.958
4.	Mn	0.1, 0.5, 1, 1.5, 2	0.919
5.	Fe	1, 3, 5, 7, 9	0.960
6.	Cu	0.1, 0.5, 1, 1.5, 2.5	0.991
7.	Cd	0.1, 0.5, 1, 1.5, 2	0.997

Table3. Instrumental operating conditions for determination of metals using (FAAS)

Element	Wavelength (nm)	Energy (J)	Slit Width (nm)	Current (mA)	Detection limit (mg/L) from the instrument's operator mnnual
Mn	283.2	3.783	0.7	2	0.03
Zn	213.9	3.3	0.7	2	0.005
Mg	285.2	4.529	0.7	1	0.005
Ca	422.9	4.086	0.7	2	0.05
Fe	248.3	3.84	0.2	7	0.05
Cu	324.7	3.839	0.7	7	0.01
Cd	228.8	3.24	0.7	2	0.03

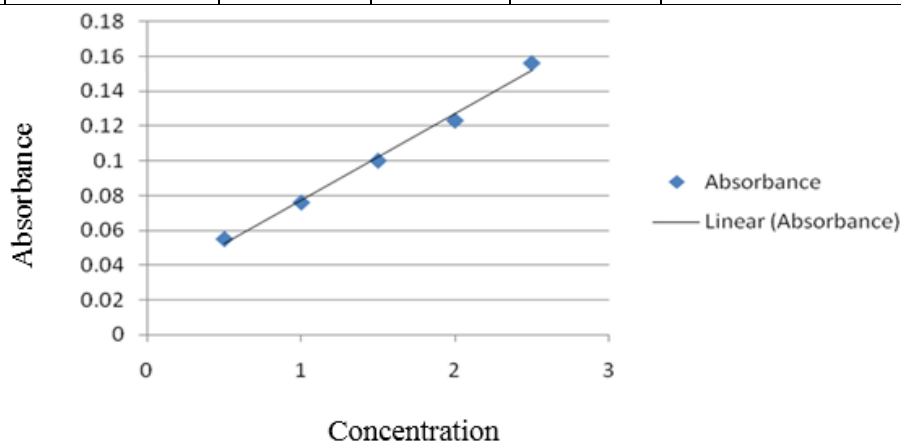


Figure4. Calibration graph for calcium standard solution

$$Y = 0.049x + 0.027; R^2 = 0.992$$

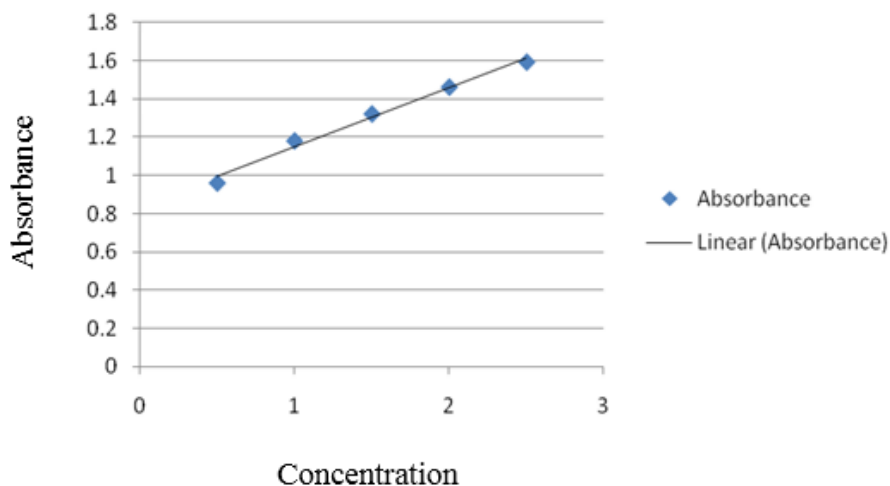


Figure5. Calibration graph for magnesium standard solution

$$Y = 0.308x + 0.84; R^2 = 0.987$$

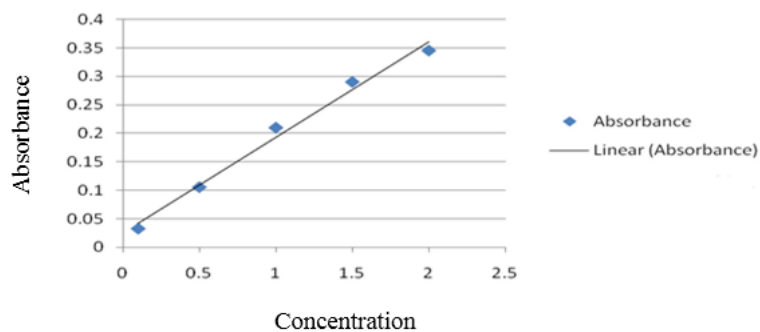


Figure6. Calibration graph for manganese standard solution

$$Y = 0.168x + 0.025; R^2 = 0.987$$

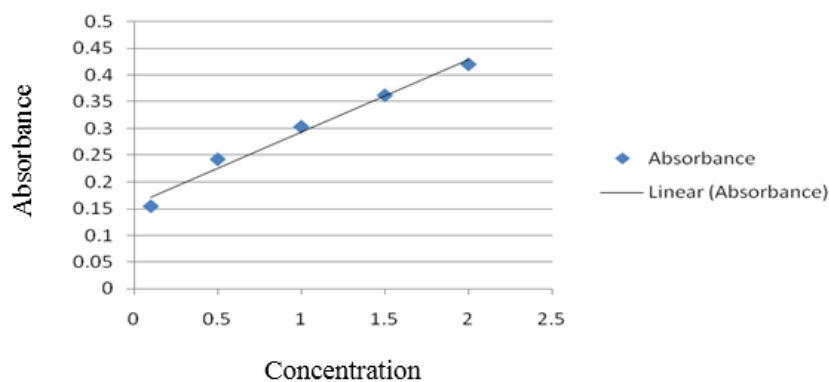


Figure7. Calibration graph for copper standard solution

$$Y = 0.135x + 0.158; R^2 = 0.982$$

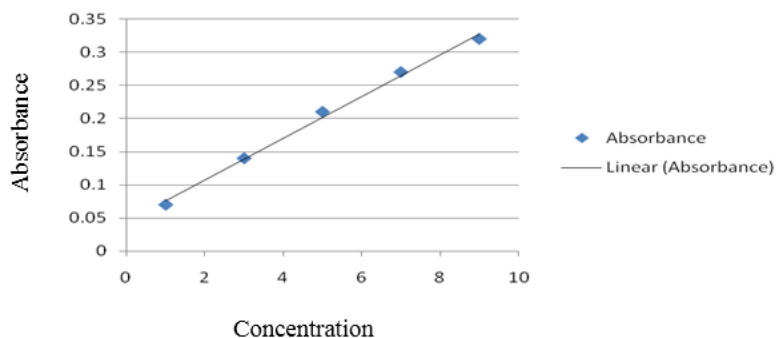


Figure7. Calibration graph for copper standard solution

$$Y = 0.135x + 0.158; R^2 = 0.982$$

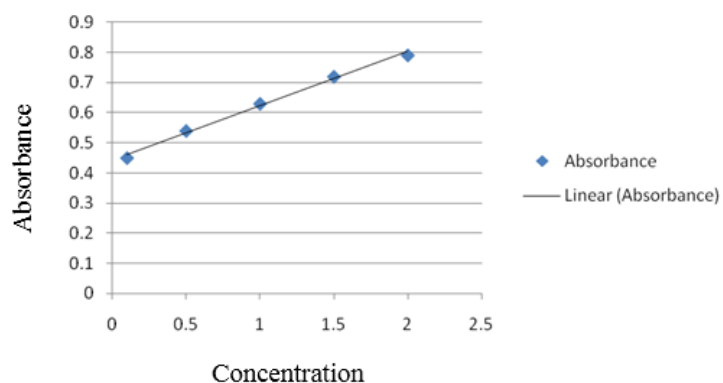


Figure9. Calibration graph for zinc standard solution

$$Y = 0.179x + 0.443; R^2 = 0.994$$

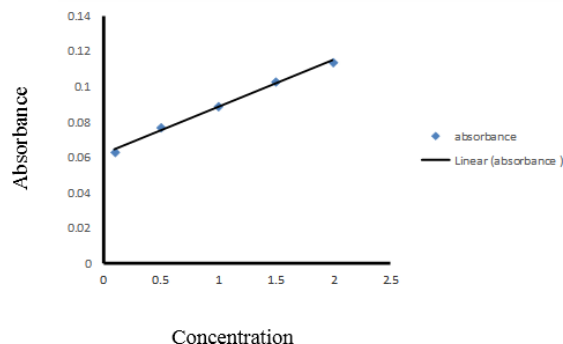


Figure10. Calibration graph for cadmium standard solution

$$Y = 0.0266x + 0.0621; R^2 = 0.995$$

3. RESULTS AND DISCUSSION

3.1. Gemological Properties

To verify the investigated natural gem agate samples were indeed agate, non-destructive gemological characterization techniques were performed on representative samples. First, average specific gravity value of representative samples were measured by heavy liquid method using (Lithium salt). The results were within the range of 2.4-2.7. A similar result was observed in [24]. Because of optical character and optical sign, refractive index values of representative samples were determined by using standard refractometer device with an optical contact liquid of 1.79 RI. The refractive index values of the investigated samples were within the range of 1.53-1.54. Similar results were observed in [26].

"The "Mohs hardness pencils" were used to determine the hardness of gem-agate samples. This physical analysis shows that the hardness value of the addis zemen and bure agates are similar and they were within the range of 6.5-7 and that of bellea is 7. Thomas Arter reported that the hardness values of agates are within the range of 6.5-7 [23]. The results of all these gemological testing values indicate that the samples were indeed agate samples.

3.2. Infrared Spectroscopy Analysis

Infrared spectroscopy is dependent on the response of short-range, molecular scale, energetic vibrations such as O-H stretching and bending. This generates characteristic spectra for particular mineral phases depending on the molecules present, for example different water species. The vibration ranges of the hydroxyl (OH) group water species, main silica mineral building components or inclusions, structural point defects, structural bonds, and coloration in silica can be determined using FT-IR spectrum in the mid-infrared region. Therefore, mid-infrared absorption spectroscopy is widely used to reveal the presence of water in gem and other mineral species. Meanwhile, the initial included waters in all mineral species can be divided into three groups, namely the hydroxyl (OH) group located at structural defects, surface hydroxyls hydrogen bonded to each other (H-O-H), and free molecular water (H₂O) [14, 33, 34].

The infrared spectra of (Bellea, Addis zemen and Bure samples are presented in figures 10, 11, and 12 respectively.

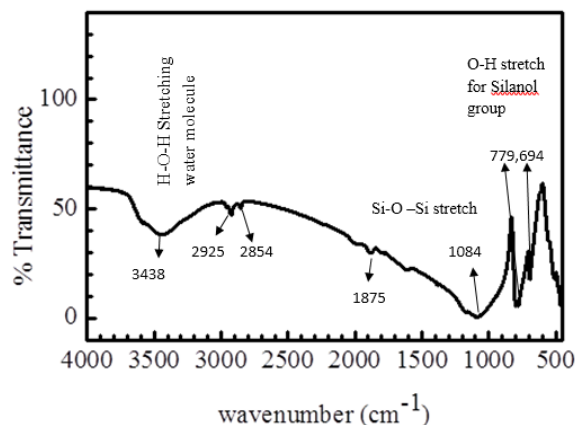


Figure11. The FT-IR spectrum of agate sample from bellea

The FT-IR spectra of the investigated samples obtained from three different places ((Belleza, Addis zemen and Bure) of Ethiopia) were analyzed within the frequency region of 400 to 4000 cm^{-1} (Fig. 11, 12 and 13). The gross features of the FT IR absorption spectra of this three agate samples were similar. However, the absolute values of the absorption bands of belleza (694, 779, 1084, 1736, 1875, 2854, 2925, 3421, 3430, 3433 and 3438 cm^{-1}) are distinctly different from those of addis zemen (693, 779, 1086, 1874, 1877, 1879, 2718, 3446, and 3576 cm^{-1}) as well as the bure (694, 797, 1082, 1687, 1878, 2924, 2963 3445 and 3586 cm^{-1}). The FT-IR spectra of these three investigated agate samples were characterized by a multi component broad absorption bands centered around 3443 cm^{-1} . This absorption band is related to the OH stretching and vibration in molecular water (H_2O). Similar results were observed in [14, 33, 34].

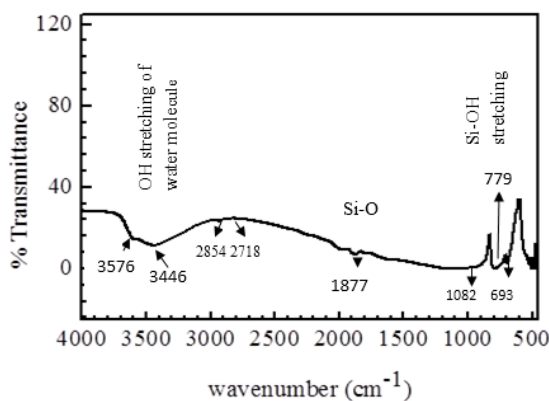


Figure12. The FTIR spectrum of agate sample from addis zemen

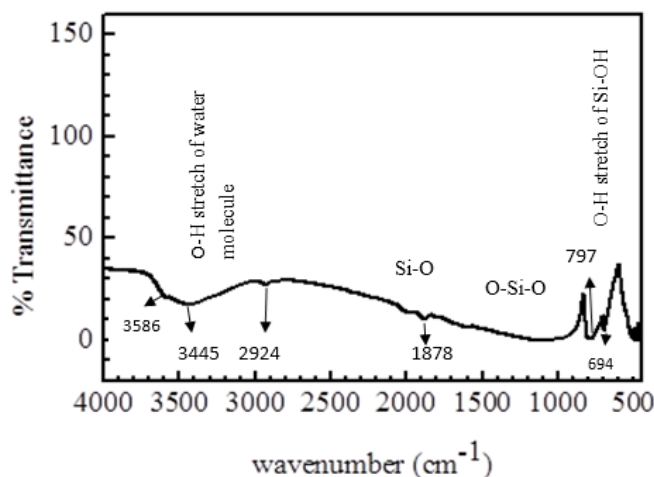


Figure13. The FTIR spectrum of agate sample from bure

According to the study conducted by Moxon T. *et al.* (2007) the sharp band present at approximately 3585–3590 cm^{-1} attributed to the structural defect of silanol (Si-OH) species. The FT-IR spectrum of belleza didn't show shoulder around 3567 cm^{-1} and this indicate that the sample has no structural defect of the silanol group species but the addis zemen and bure sample show weak shoulder around 3576 and 3586 cm^{-1} , respectively, indicating the presence of structural defects of silanol group [14,33].

In the low frequency region, from 1200 cm^{-1} - 600 cm^{-1} , the investigated samples have three bands centered around 694 cm^{-1} , 779 cm^{-1} and 1084 cm^{-1} . These bands are due to the fundamental vibrations of SiO_4 tetrahedral, related with Si-O stretching vibration. There were similar observations in [14, 33, 34, 35]. Particularly, the bands occur around 1080 cm^{-1} are assigned to asymmetric Si=O=Si stretching vibration and a band around 750-800 cm^{-1} is assigned to O-Si-O bending vibration, whereas the band centered near 694 cm^{-1} is assigned to OH stretching vibration. The observed data were comparable with literature data [34]. In these investigated samples, the percent transmittance value of (Belleza, Addis zemen and Bure) were almost around 60, 29 and 35%, respectively. From this observation one can conclude that SGA absorbs the IR radiation higher than the other two and NGA is transparent to IR radiation in comparison with the other two.

Table4. Assignments of the Fourier transform infrared (FT-IR) bands of the gem-quality Agate from Amhara national regional state of Ethiopia

V(cm ⁻¹)	Assignment
Around 694	OH stretch vibration's related to silanol
779- 797	O-Si-O bending vibration
1082-1086	Asymmetric Si=O=Si stretching
Around 1687	OH bending of water
1874-1878	Si-O bending vibration
Around 2925	Si-O stretching vibration
3421-3446	OH starching of water molecule
3586	Si-OH structural defects

3.3. Powder x-Ray Diffraction Analysis

Gemological properties and mineralogical composition of natural gem-agate can be identified by different spectroscopic techniques. The mineralogical assemblage of host rocks could be determined by XRD pattern. An X-ray powder diffraction pattern was obtained for a sample of pure agate in three different zones of Amhara national regional state, Ethiopia (Fig. 14, 15 and 16 below).

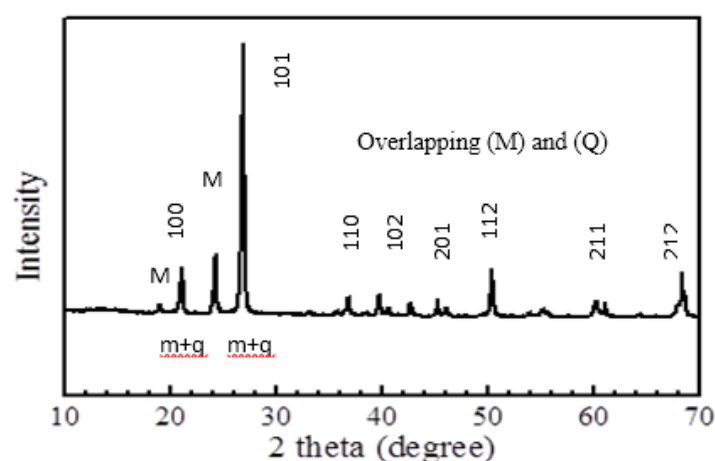


Figure14. X-ray diffraction patterns of alpha-Quartz (Q) and Moganite (M) of the (bellea)

In this study, the investigated natural agate samples in the range between 10° to 70° show some resolved peaks at $2\theta = 20.85^\circ, 26.65^\circ, 36.54^\circ, 39.46^\circ, 42.47^\circ, 45.81^\circ, 50.14^\circ, 54.87^\circ, 59.95^\circ$ and 68.32° . According to the study conducted by Paral L. *et al* and Hatipoğlu M. *et al.* (2011) and Maoxon .T *et al.* (2008) on agate using XRD the same resolved peaks at the same 2θ values were observed. The numerical data obtained from XRD analyses of (Bellea, Addis zemen and Bure samples were comparable with those studied natural agates of Australia and Turkey origin [14,32, 36].

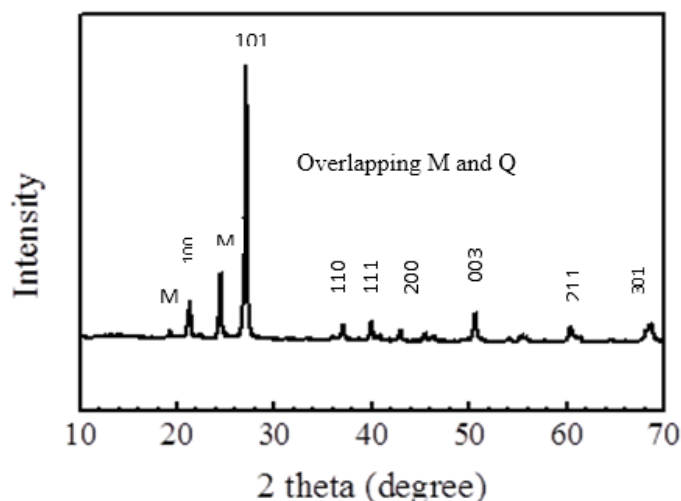


Figure15. X-ray diffraction patterns of alpha-Quartz (Q) and Moganite (M) of the addis zemen

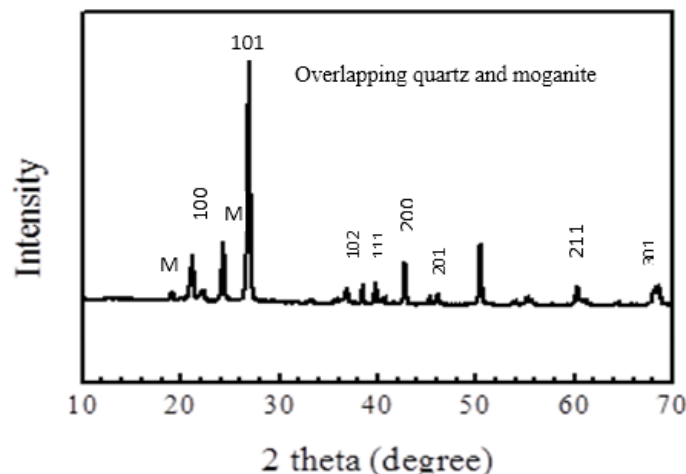


Figure16. X-ray diffraction pattern of alpha-Quartz (Q) and Moganite (M) of the bure

An agate yielded powder XRD pattern is characterized by four broad reflections, the sharp and most intense diffraction peak is pointed at $2\theta = 26.65^\circ$ - 27.00° , medium intense sharp peak observed around $2\theta = 20.00^\circ$, 24.00° and 50.14° , broad peak at $2\theta = 20.83^\circ$ and 68.85° and there is also weaker reflection band which occur at $2\theta = 55^\circ$ and 64.00° . By using XRD the same result were obtained in [14, 32, and 36]. A sharp intense peak indicates highly ordered, more crystalline than that of medium as well as weak peaks. The main and sharp peak occurred at $2\theta = 26.65^\circ$ indicating the degree of order in agate structure and the broad peak at $2\theta = 20.85^\circ$, 36.54° , 39.46° , 42.47° , 45.81° , 50.14° , 54.87° , 59.95° and 68.32° indicates the presence of microcrystalline quartz building phases, such as cryptocrystalline alpha-quartz called chalcedony, cryptocrystalline quartzine (called moganite). This demonstrate that the moganite silica phases are present at $2\theta =$ below 20° and around 24° and additionally in the overlapped diffraction bands. The observed XRD patterns of the investigated natural gem-agate samples are comparable with the literature and standard x-ray diffraction powder pattern of silicon oxide (Quartz-low), α -SiO₂ in the table 5 below [36].

When we compare the peaks of the three samples (Belleza, Addis zemen and Bure, sharp peak were observed in the bure sample. This demonstrates the bure sample is highly ordered crystalline than that of belleza and addis zemen. The belleza and addis zemen samples have similar peak intensity and this shows that the two samples have resemblance in crystalline order.

Table5. Standard x-ray diffraction powder pattern Silicon Oxide (Quartz-low), α -SiO₂ [CAS registry no. 7631-86-9]

CuK α_1	$\lambda = 1.540598\text{\AA}$ temp $25 \pm 1^\circ\text{C}$			$\alpha = 5.43088\text{\AA}$
	Internal standard Si			
d (\AA)	I ^{rel}	$\sigma = \pm 1$	h k l	2 θ ($^\circ$)
4.257	22		1 0 0	20.85
3.342	100		1 0 1	26.65
2.457	8		1 1 0	36.54
2.282	8		1 0 2	39.46
2.237	4		1 1 1	40.29
2.127	6		2 0 0	42.47
1.9792	4		2 0 1	45.81
1.8179	14		1 1 2	50.14
1.8021	1L		0 0 3	50.61
1.6719	4		2 0 2	54.87
1.6591	2		1 0 3	55.33
1.6082	1L		2 1 0	57.24
1.5418	9		2 1 1	59.95
1.4536	1		1 1 3	64.00
1.4189	1L		3 0 0	65.76
1.3820	6		2 1 2	67.75
1.3752	7		2 1 2	68.13
1.3718	8		3 0 1	68.32

3.4. Flame Atomic Absorption Spectroscopy Analysis

The geochemical investigations of agates from their parent volcanic rocks and associated silicate mineralization represent an extensive analytical characterization of agates from localities around the world. Despite the different origin of the agate samples investigated, some common geochemical characteristics were observed. The trace element signature of most agate sample is characterized by FAAS. Concerning our study, we have characterized trace element signature of natural gem agate samples from bellea, addis zemen and bure using FAAS. The results of the investigated samples are given in table 6 below.

Table6. The Mean concentration of trace element contents in natural gem agate sample

Agate sample	Concentration of metal in mg/L(ppm)						
Site	Ca	Mg	Mn	Cu	Fe	Zn	Cd
bure	0.247	0.349	0.011	0.004	0.199	0.001	Nd
bellea	0.357	0.293	0.016	0.015	0.389	Nd	0.002
Addis zemen	0.057	0.275	0.037	0.009	0.208	0.001	Nd

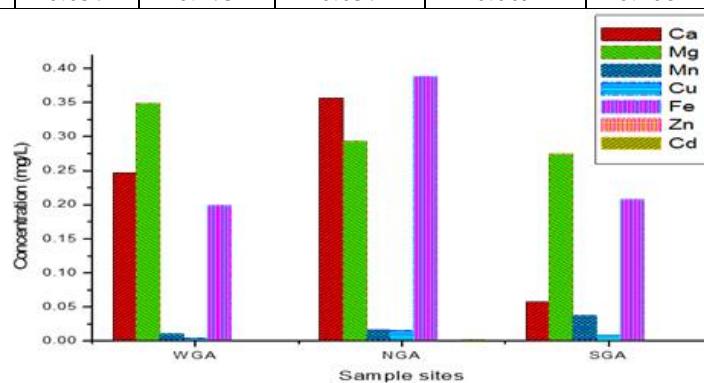


Figure17. Histogram comparing mean concentrations of metals in (bure, bellea and addis zemen)

Trace element analyses of agates, quartz incrustations and associated parent volcanic rocks are carried out to obtain more information about the geochemistry of agates. Most trace elements show variations in their concentrations comparable to those seen in rock quartzes originating from different parent rocks. However, elevated concentrations were detected for those elements that are commonly contained within micro inclusions in the agate (Cu, Ca, Fe, Mn and Mg). They are frequently concentrated in colored agate bands, obviously acting as pigments [37]. In this study, the agate sample from bure and addis zemen have a high content of magnesium (Mg) and less amount of copper (Cu) whereas the agate sample of bellea has the high content of iron (Fe) and small amount of copper (Cu). The color of agate is mainly associated with the presence of transition metals in its composition. The color of bellea agate is brown red associated with high Fe content, addis zemen agate and bure agate is a mixture of gray and white which is associated with high content of Ca and Mg. The most common solid inclusions found within the agate matrix include pyroxene, calcium rich plagioclase, and goethite, and magnesite, Mn and Cu compounds [32].

4. CONCLUSION

The samples were characterized using physical property measuring devices (Refractometer, heavy liquid method and "MOHS HARDNESS PENCILS") and Spectroscopic Techniques (FAAS, XRD and FT-IR). The performed physical property measurement had confirmed the correct identity of the agate samples. The data obtained by measuring the agate samples using spectroscopic techniques were comparable with studies conducted in different countries by different researchers. The performed physical analysis showed that the hardness value of bure agate and addis zemen agate are within the range of 6.5-7 and that of bellea agate is 7 (slightly harder than that of bellea agate and bure agate) but the refractive index and specific gravity of these investigated samples have similar value i.e., in between 1.53-1.54 and 2.4-2.7 respectively. The crystal structure were estimated using XRD studies, trace and minor elements were determined using FAAS, and the major compositional elements and water contents were confirmed by FT-IR studies. Using the FAAS Spectroscopic technique, seven elements (Ca, Mg, Cd, Cu, Fe, Mn, and Zn) were measured. The FAAS result showed that the intensity of orange color (from yellow to orange to red to "chocolate"- brown) correlates with the large amount

of Fe concentration and white color correlate with large amount of Ca concentration in the agate samples. It is also presented that the FT-IR spectroscopy could not discriminate between the difference color varieties of the studied agate samples. However, the presented FT-IR spectra data for agate samples have a significant contribution in their identification and characterization. This spectroscopic technique is important to identify their functional group in the agate formation. XRD patterns were used to determine mineralogical assemblage of host rocks. It helped to classify the base silica building components in to moganite, quartz and chalcedony

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