Materials Research. 2021; 24(suppl. 1): e20210033
DOI: https://doi.org/10.1590/1980-5373-MR-2021-0033

Physico-Chemical Characterization of Macusanite and Inclusions: A Volcanic Glass from Peruvian Andes

Murilo Candido de Azevedo[a*] **,** ***Luis Fernando dos Santos***[a] **,** ***Luiz Augusto Stuani Pereira***[a]**,**
Carlos Alberto Tello Sáenz[a]**,** ***Silvio Rainho Teixeira***[a]**,** ***Pedro Figueroa***[b]

[a]*Universidade Estual de São Paulo (UNESP), Departamento de fisica, Presidente Prudente, 19060-900, São Paulo, SP, Brasil.*
[b]*Universidad Nacional de San Agustin de Arequipa (UNSA), Santa Catalina, 117, Arequipa, Peru.*

Received: January 12, 2021; Revised: March 30, 2021; Accepted: June 16, 2021

Macusanite is a volcanic glass extracted from the volcanic field Macusani – Peru, formed by the fast cooling of magma. This study shows physical and chemical characterization of Macusanite samples to better understand its molecular structure, elemental composition as well as to investigate the presence of natural inclusions. The characterization of the natural glass can give valuable geological information about the magma composition, the eruption intensity and age of volcanism activity. Moreover, the use of different characterization techniques can help in mineral prospecting. Macusanite was characterized by X-Ray Diffraction/Fluorescence (XRD/XRF), Optical Microscopy, Scanning Electron Microscopy (SEM) and micro-Raman spectroscopy. The latter suggests the presence of andalusite mineral incorporated in the glass structure, while the Energy-Dispersive X-ray Spectroscopy (EDS) analysis indicates the presence of some rich calcium inclusion. Moreover, XRD shows the glass characteristic amorphous band and that the sample is in the glassy stage.

Keywords: *Volcanic Glass, Characterization, Macusanite, Mineral Inclusion.*

1. Introduction

Volcanic glass, also known as obsidian, is considered a mineraloid as it has no lattice effects like a crystalline structure. It is an amorphous, non-crystalline solid produced by the fast cooling of magma during a volcanic eruption. Moreover, some mineral inclusions may be trapped in the glass structure during its formation process.

Obsidian are mainly composed of silica (SiO_2). High silica magma has over 71-77% of SiO_2[1], which indicates a very viscous magma and, consequently, a violent volcanic eruption, in contrast with low silica magma which is very fluid. Magmas with more than 65% of silica are classified as felsic and are often explosive since lava easily obstructs the volcanic chimney. When these magmas solidifies outside the surface, like and extrusive rock, they get classified as a rhyolite. This type of obsidian can be found in deposits of tens of meters thick.

Silica can attract oxygen in magma producing the polymerization, which is a long chain of bonding molecules that increases the viscosity of the medium. Moreover, it can affect the formation of crystals by hindering the movement of ions that are responsible for the crystal growth and, consequently, few minerals are formed[2]. This behavior is more intense for felsic lavas[3].

Macusani is a volcanic field located in the province of Carabaya in Peru, with a longitude of 70 ° 27 'W. and latitude 14 ° 4 'S., at 4.3 km of altitude from sea level[4]. Glass pebbles found in volcanic rocks in the field are known as Macusanite, which was first found in fluvio-glacial sediments[5].

Macusanite was the source of some shipped stone artifacts in the archaic period, found at distances of more than 120 km from Macusani[6]. This obsidian has a translucent green appearance, but can occur in different colors[6].

Mineral characterization studies have resulted in important advances in the association between cooling magma and amorphous structure. In addition, it serves as a source of studies for improvement in radiometric dating. Some studies about its properties indicate it can be used in technological applications, such as economical adsorption of heavy metals[7,8], radioactive cations and anions, and different biomolecules due to its macroporosity, which also provides application in construction, as abrasive, acoustic, filter as well as in the agriculture field[9,10].

The Canadian company Plateau Energy Metals found large deposits of lithium and uranium in the volcanic regions near Macusani, which may have the largest lithium reserves in the world[11]. The discovery of high content of lithium in Macusanite[12] may have contributed to the exploration companies to develop projects in the region of Macusani. Moreover, this obsidian constitutes one of the greatest examples of uranium mineralization associated with pyroclastic rocks[5].

This work aims to physically and chemically characterize Macusanite samples via different methods used in material sciences (optical microscopy, scanning electron microscopy, micro-Raman spectroscopy, X-ray diffraction and X-ray fluorescence) to better understand the volcanic glass elemental

*e-mail: murilocandido_azevedo@hotmail.com

composition as well as the presence of mineral inclusions which were trapped in the glass during its formation process. Moreover, the X-ray fluorescence technique may provide geological information about the magma that originated the volcanic glass.

2. Macusanite Property Investigation

Craig et al.[6] studied the Macusanite geological settlements as well as its use as a source material for artifacts in ancient times through comparisons of various calculated ages of this mineraloid.

Macusanite pebbles have been dated by a variety of radioisotopic techniques as fission track method, potassium-argon, argon-argon, etc., which show ages of about 4 to 10 million years[5,13-15]. Since the chemical composition varies among different pebbles, this indicates they may have come from distinct volcanic eruptions and may explain why the ages are different[5,6,14]. Later volcanism led to the deposition of obsidians.

Macusanite glass has been characterized through different techniques as electrical resistance[16], micro-Raman spectroscopy[17] and atomic force microscopy[18]. Investigation of its elemental composition indicate it is mostly composed of high concentration (~ 70-73%) of SiO_2, ~ 15% of aluminum oxide (Al_2O_3) and some oxides like K_2O, Na_2O, CaO. Moreover, trace elements were also found in the glass molecular structure, e.g., H_2O, FeO, Fe_2O_3, MgO and others[4,12,19,20].

Linck[21] was one of the pioneers to investigate Macusanite and found the presence of zircon, andalusite, wollastonite, scapolite, sanidine, sillimanite, aegirine-augite and oligoclase-andesine incorporated in the glass structure. At this time, Macusanite was thought to be a tektite instead of an obsidian as both are made from a natural glass[4].

Macusanite has properties that should be similar to obsidians belonging to the rhyolite group, whose density is approximately 2.3 g/cm^3 [22,23] and hardness on the Mohs scale between 5 and 6[24]. According to Husien[22], the obsidian hardness is greater when compared to common glass, and its structure becomes more rigid with increasing Al_2O_3 content.

Obsidian reacts to water by breaking the atomic bonds of the silicate network[23], which increases the rate with the temperature. This weathering process is called hydration, and it also causes an increase in the volume of the glass.

Cracks in volcanic glass propagate as multiple micro-cracks that reach pre-existing micro-fractures and not only a single fracture. Moreover, these cracks work as pathways for fluids, favoring the water-silica interaction in the inner micro-regions of the glass.

Regarding the thermal conductivity of silica glasses, it is about 1.7 W(m·K) at T = 100 ºC. The glass strength behavior displays an elastic deformation according to the classical Hooke's law followed by a fracture once the cohesive strength exceeds. The maximum cohesive strength under tension for volcanic glasses is 30 Mpa[23].

3. Materials and Methods

3.1. Macusanite preparation

Some Macusanite pebbles of different sizes, ranging from 1 cm to 5 cm in diameter, were selected for all characterization processes, which are shown in Figure 1a. The natural glass was pulverized using a disc mill (Marconi, model MA 360) with orbital agitation of about 5 minutes, resulting in a homogenized powder (Figure 1b). Some thin glass pieces were sanded both sides with three different granulometry sandpapers: 1200, 2400 and 4000 mesh with 70 rpm during 5 minutes for each piece in a Struers model polishing machine.

These pebbles were collected in Macusani Town, Corani district, in depostis Chilcuno Chico and Caluyo Mayo. Macusanite was found either as an inclusion in pyroclastic rocks of Quenamari formation, or as a pebble at the bottom of the ravine of the volcanic environment. A panning was carried out on the banks of the river, in which pieces of various sizes were found.

3.2. Optical microscope

Possible inclusions inside Macusanite were photomicrographed via MC170 HD microscope with transmitted light and with a 10X ocular lens and a 20X objective lens, producing a total magnification of 200X. A micro-area with two visible mineral inclusions were selected and their lengths were measured. For this procedure, a thin piece was sanded so that it was flat on both sides.

3.3. Scanning Electron Microscope (SEM)

For the SEM analyses one pebble of Macusanite was sanded both sides and another turned into powder to investigate its topology and physical characteristics with a Backscatter electron Detector (BSD). Moreover, the elemental composition of the volcanic glass was identified and quantified with an electron-dispersive spectrometer by

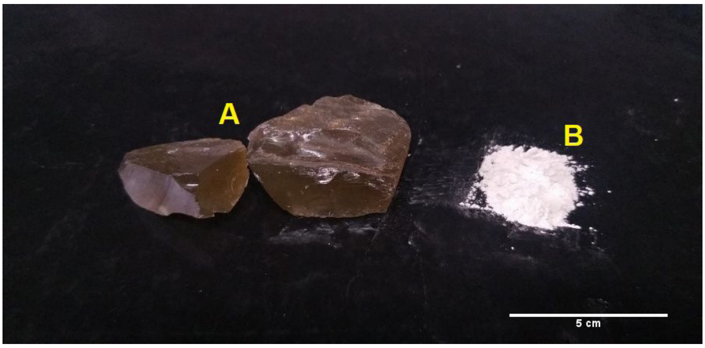

Figure 1. Macusanite pebbles (a) and their powder (b) form used in the study.

weighting the elements in the mineraloid in the compact and powder form. The measurement instrument is an EVO LS-15 microscope Zeiss with a voltage of 20 kV. The sample was coated with carbon in an evaporation process (Q150TE, Quorum). Backscattering analysis scans the surface based on the weight of the chemical elements. Because heavy elements can backscatter electrons in greater quantities than lighter ones, they appear lighter in the image[21].

3.4. Micro-raman spectroscopy

Raman spectra of Macusanite were obtained by a Raman Renishaw inVia spectrometer, equipped with a Leica optical microscope and a video camera allowing a direct visualization of the sample, 50X objective lens with a spatial resolution of 1 μm^2. The Raman spectra were collected in the region of 200-2250 cm^{-1} with a 633 nm helium-neonium laser line and 50% laser power. The measurements were performed to investigate the presence of mineral inclusions trapped in the glass.

3.5. X-Ray Fluorescence (XRF)

The X-ray fluorescence spectroscopy analysis was carried out to determine the chemical composition in weight percent (wt%) of Macusanite, using a Rh anode as the excitation source. The scans were performed in the energy range from Na to U, in qualitative and quantitative mode at room temperature in a vacuum. The measurement was carried out in a Shimadzu spectrometer (XRF-700).

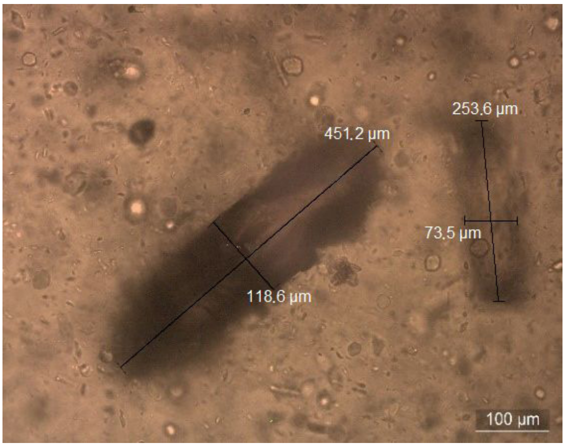

Figure 2. Photomicrograph of Macusanite with transmitted light and a total magnification of 200x.

3.6. X-Ray Diffractometry (XRD)

XRD analysis was carried out in a diffractometer (XRD 6000, Shimadzu) at room temperature with Cu-K$_{\alpha 1}$ (λ=1.5406 Å) radiation, 1º divergence and reception slits, in the continuous scan, 40 kV voltage, 30 mA current, 2 º/min scan speed, and 2θ angular range from 10º to 80º. For XRF and XRD analyses the powder sample was used.

4. Results and Discussion

Figure 2 shows a photomicrograph of two mineral inclusions trapped in the volcanic glass sample, which have dimensions of up to 450 μm on its major axis. Some other small inclusions are also visible throughout the glass surface.

The SEM photomicrographs obtained using BSD are shown in Figure 3. The images were taken from the sanded surface of the sample in powder form (a) and compact form (b).

The results of the chemical composition by scanning with the EDS detector can be seen in Table 1.

Regarding the chemical composition, both samples do not present any significant difference. The results show a high prevalence of oxygen, silicon and aluminum elements, which are components of the most abundant molecules in the mineral structure (silica (SiO_2) and alumina (Al_2O_3)). Moreover, trace elements show marked depletions in F, Na, K, Ca, Fe e Cu, which is in agreement with the literature[4,12,19,20].

Figure 4 shows the dispersion of calcium through the powdered glass structure, that indicates some spot micro-areas with mineral inclusions composed of calcium. Linck[21] found some mineral inclusions in Macusanite with calcium composition: wollastonite ($CaSiO_3$), scapolite ($Na_4Al_3Si_9O_{24}Cl$ to $Ca_4Al_6Si_6O_{24}CO_3$), oligoclase-andesine ($(Na,Ca)[Al(Si,Al)Si_2O_8]$) and aegirine-augite ((Ca,Na)

Table 1. Elemental composition of Macusanite by SEM/EDS.

Element	Compact (wt%)	Powder (wt%)
O	53.94	59.66
F	2.31	2.58
Na	2.98	2.76
Al	7.08	6.20
Si	30.55	25.36
K	2.56	2.26
Ca	0.21	0.34
Fe	0.36	0.46
Cu	-	0.36
Total	100.00	

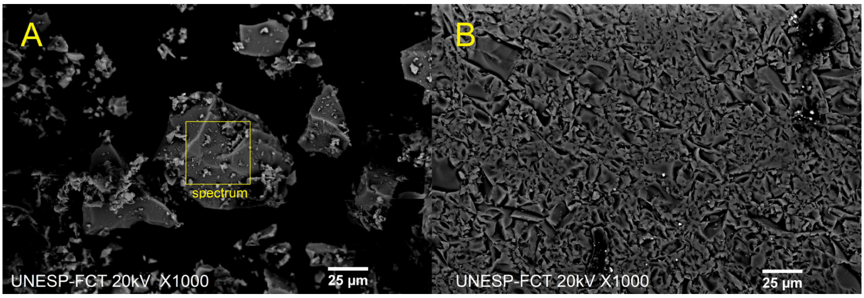

Figure 3. SEM images of Macusanite in powder (a) and compact (b) form with a total magnification of 1000x via BSD detector.

$(Fe^{3+},Mg,Fe^{2+})Si_2O_6$). The calcium-rich inclusions found by SEM-EDS may be attributed to any of the above minerals, however, further investigation is required.

Zircon grains ($ZrSiO_4$) have also been found in other Macusanite sample characterized via SEM analysis by our research group. Therefore, this microscopic technique can assist in mineral prospecting by identifying valuable inclusions. As a common accessory mineral in igneous rocks, zircon contains a large amount of uranium and thorium in levels of about tens to thousands parts per million (ppm)[25]. In addition, this mineral has a hardness of 7.5 on the Mohs scale and is resistant to various geological processes, which makes it routinely used in radioisotopic dating process, e.g. the fission-track method, U-Pb and U-Th/He dating. Moreover, in the industry of ceramics zircon is the main opacifier in ceramic applications[26].

Volcanic glasses are known in micro-Raman spectroscopy by their large band spectra as they do not have a crystalline structure[27]. Therefore, Macusanite spectrum collected with 633 nm laser is like other obsidian and silicate glasses collected with 415, 514 and 633 nm reported in the literature[28]. The Raman spectrum in Figure 5 was obtained from a crystalline inclusion (Figure 6) in Macusanite. According to Linck[21] this spectrum is similar to the andalusite (Al_2SiO_5) mineral. The spectrum was compared with the RRUFF™ Project database of Raman Spectra[29] for andalusite (see Table 2).

Andalusite is an important mineral in metamorphosed aluminous rock, such as metapelitic schist and micaceous quartzite[30]. It has an orthorhombic structure with *Pnnm* space group[31-33]. According to the factor group theory, it has 48 predicted Raman active modes[28]. The Raman spectrum of andalusite shows characteristics of an orthosilicate, the spectral bands above 800 cm^{-1} correspond to the stretching modes of SiO_4, while the bending mode of SiO_4 occurs around 360 cm^{-1} [30]. Because of the poor symmetry and poor degeneracy, there are many other Raman bands in the range from 200 to 400 cm^{-1} corresponding to the bending mode of Al^{VI}–O.

Macusanite has a considerable amount of alumina, which may explain why andalusite is not an unusual inclusion, whose chemical composition is 62.9% Al_2O_3 and 37.1% SiO_2[34].

In Biotite (silicate mineral) the presence of andalusite crystals identical to those in Macusanite were also found. Moreover, measurements performed in this mineral indicate the presence of uranium, thorium and lead, which makes andalusite also used in geological dating methods like zircon mineral[4]. Since andalusite has high resistance to thermal gradients and thermal shocks, it is greatly used in the industry for refractory construction and also in the foundry[34].

The chemical composition of Macusanite, as determined by XRF spectroscopy, is shown in Table 3. It consists mainly of 74.36% of silicon oxide (SiO_2), which is characteristic of the silica formation in bonding with the oxygen from the volcanic lava, and 18.25% of alumina (Al_2O_3). Both of them are the most predominant oxides in the glass, followed by K_2O e Fe_2O_3 and some traces as CaO, P_2O_5, etc. The measured

Table 2. Raman Shift of peaks in Macusanite inclusion and Andalusite.

Peak	Macusanite Inclusion (cm^{-1})	Andalusite (cm^{-1})[20]
1	146.15	--
2	291.67	~290
3	321.46	~320
4	357.89	~355
5	919.06	~920
6	951.56	~950
7	~1010	~1020
8	1062.08	~1065
9	2129.01	--

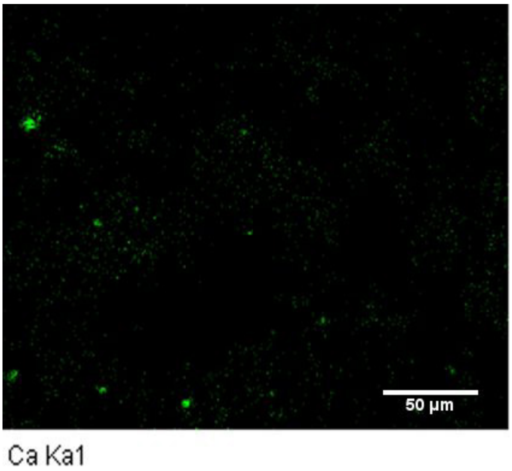

Figure 4. Calcium dispersion in Macusanite through EDS.

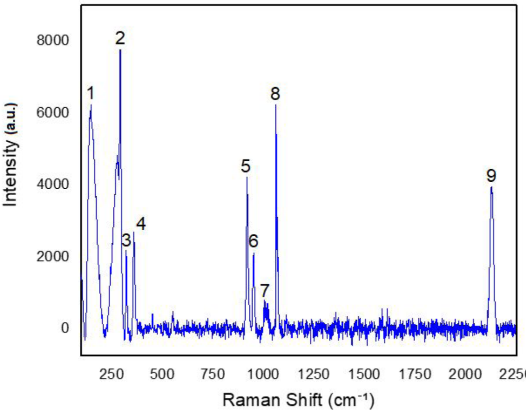

Figure 5. Raman Spectrum of Macusanite inclusion.

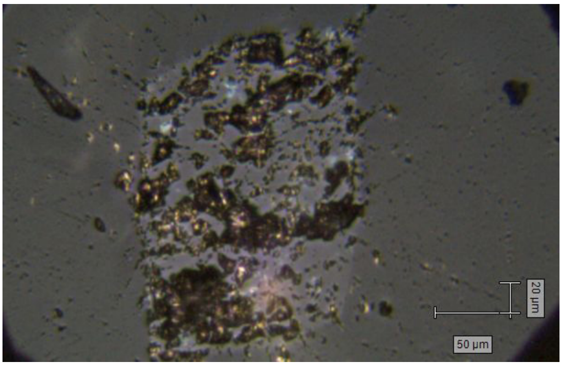

Figure 6. Macusanite inclusion.

Table 3. Chemical composition of Macusanite by XRF spectroscopy.

Identified Oxides	(wt%)
SiO_2	74.351
Al_2O_3	18.248
K_2O	4.310
Fe_2O_3	1.077
P_2O_5	0.545
CaO	0.511
SO_3	0.364
Rb_2O	0.180
MnO	0.124
TiO_2	0.078
Cs_2O	0.026
As_2O_3	0.049
SnO_2	0.032
ZnO	0.018
Ir_2O_3	0.017
CuO	0.011
WO_3	0.010
Others	0.018

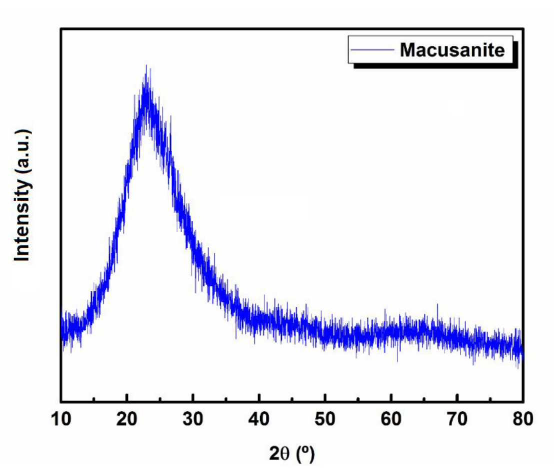

Figure 7. X-ray Diffraction analysis of Macusanite.

silica concentration is higher than the ones found in the literature, which is about 70-73%[4,12,19,20]. XRF is a technique that can help to identify the magma type that originated the glass, which in this case it is a felsic magma that causes an explosive volcanic eruption (as the concentration of silica is about 74%)[1].

Regarding the XRD analysis (Figure 7), the diffractogram does not show any presence of crystalline phases, there is only a characteristic band of an amorphous material around the position of Bragg $2\theta = 30º$. Since magma cools quickly through the glass transition temperature there is not sufficient time for the rock crystallization.

Natural glasses have short lifetime in geologic time scale, as they are unstable and tend to crystallize into a spherulite, which contains silicate crystals like quartz and feldspar. However, rhyolitic glasses can have a longer lifetime, up to approximately 60 million years[1].

The process of transforming glass from a vitreous to a crystalline phase is known as devitrification. The diffusion process of water acts as a catalyst, and at low temperatures it slows down[35]. Therefore, the glass can change in events involving water and geothermal processes.

The devitrification process can reach three stages in rhyolitic glass: i) the glassy (with some spherulites as inclusions, which are spherical semicrystalline bodies that occur in glassy rocks); ii) the spherulitic (with some mineral inclusions of quartz); and iii) the granitic texture[36].

Gimeno[37] showed that SEM can be useful for analyzing the devitrification process by revealing the growth of the crystal components, and discovered that phenocrysts, microphenocrysts and all kinds of previous crystalline materials act as nucleation sites for spherulites. Moreover, the most viscous lava like felsic ones show poor development of spherulites, unlike the less viscous magma rocks that present advanced stages of spherulites.

According to the XRD analysis, Macusanite shows a characteristic amorphous band and no presence of spherulites as inclusions, since this obsidian is no more than 10 million years. This result indicates that Macusanite is in the glassy stage and it is still young in comparison to the time needed to reach the last stage of devitrification. As the stages progress, the crystalline structure starts to become majority in the volcanic glass. Thus, the XRD can be a technique to inform the degree of crystallization of natural glasses.

5. Conclusions

The SEM and micro-Raman analyses are two non-destructive techniques that can be used to identify inclusions in volcanic glass, such as zircon and andalusite, which have already been dated to provide information about the thermal history of the mineral. Moreover, the lengths of these minerals are big enough to be dated through radioisotopic processes. Calcium-rich inclusions were detected by SEM/EDS, which may be wollastonite, scapolite, oligoclase-andesine and aegirine-augite. XRD is an important technique to analyze the degree of devitrification of a glass, showing that Macusanite age of less than 10 million years is quite young compared to time needed to reach the last stage of devitrification. Moreover, according to the XRF analysis Macusanite has a slightly higher amount of silica (74.35%) than others previously analyzed in the literature. The silica concentration indicates the magma produced the volcanic glass is felsic in origin.

6. Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, as well as the Brazilian foundations FAPESP (Fundação e Amparo à Pesquisa do Estado de São Paulo) [scholarship 2018/24203-1] and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico).

7. References

1. Friedman I, Long W. Volcanic glasses, their origins and alteration processes. J Non-Cryst Solids. 1984;67(1-3):127-33.

2. Kudo AM, Jahns RH. Igneous rock. Encyclopedia Britannica; 2020. [cited 2021 Feb 28]. Available in: https://www.britannica.com/science/igneous-rock
3. Society of Chemical Industry. It came from under the earth. Vol. 3. C&I; 2014. [cited 2021 Feb 27]. Available from: https://www.soci.org/chemistry-and-industry/cni-data/2014/3/it-came-from-under-the-earth
4. Barnes VE, George E, Mclaughlin WA, Irving F, Oiva J. Macusanite occurrence, age, and composition, Macusani, Peru: Geological Society of America Bulletin; 1970.
5. Poupeau G, Sabil N, Villa IM, Bigazzi G, Vatin-Perignon N, Flores P, et al. Fission-track and K-Ar ages of "macusanite" obsidian glasses, (SE Peru): geodynamic implications. Tectonophysics. 1992;205:295-305.
6. Craig N, Robert JS, Rachel SPF, Mark A, Luis FB, Margaret BV, et al. Macusani obsidian from southern Peru: A characterization of its elemental composition with a demonstration of its ancient use. J Archaeol Sci. 2010;37:569-76.
7. Steinhauser G, Bichler M. Adsorption of ions onto high silica volcanic glass. Appl Radiat Isot. 2008;66(1):1-8.
8. Ortega HL, Fernández HM, López CR, Autie MA, Infantes MA, Rodríguez CE. Cu2+ removal from aqueous solution with a Cuban volcanic glass mineral. International Journal of Plant. Animal and Environmental Sciences. 2015;6:174-83.
9. Cecilia JA, Autie-Pérez MA, Labadie-Suarez JM, Castellón ER, Molina AI. Volcanic glass and its uses as adsorbent. In: Aiello G, editor. Volcanoes - geological and geophysical setting, theoretical aspects and numerical modeling, applications to industry and their impact on the human health. London: Headquarters IntechOpen Limited; 2018.
10. Autie PM, Infantes MA, Cecilia J, Labadie SJ, Rodríguez CE. Separation of light liquid paraffin C5–C9 with cuban volcanic glass previously used in copper elimination from water solutions. Appl Sci (Basel). 2018;8(2):295.
11. Macusani Uranium Project. Plateau energy metals [cited 2020 Dec 9]. Available from: https://plateauenergymetals.com/macusani-uranium-project/
12. London D, Hervig RL, Morgan GB. Melt-vapor solubilities and elemental partitioning in peraluminous granite-pegmatite systems: experimental results with Macusani glass at 200 MPa. Contrib Mineral Petrol. 1988;99(3):360-73.
13. Poupeau G, Labrin E, Sabil N, Bigazzi G, Arroyo G, Vatin-Pérignon N. Fission-track dating of 15 macusanite glass pebbles from the Macusani volcanic field (SE Peru). Nucl Tracks Radiat Meas. 1993;21(4):499-506.
14. Osorio AAM, Iunes PJ, Bigazzi G, Hadler N. JC, Laurenzi MA, Norelli P, Paulo SR. Fission-track dating of Macusanite glasses with plateau and size correction methods. Radiat Meas. 2003;36(1-6):407-12.
15. Tello SCA, Curvo E, Iunes P, Soares C, Alencar I, Guedes S, et al. Fission-track dating applied to Peruvian volcanic glasses. Revista de la Facultad de Ciencias de la UNI REVCIUNI. 2012;15:71.
16. Rodrigues OVJ, Stuani PLA, Assunção SE, Tello SCA, Almeida OC. Electrical characterization of the Macusanite volcanic glass and influence of nuclear fission tracks on electrical conductivity. Radiat Phys Chem. 2020
17. Zotov N. Structure of natural volcanic glasses: diffraction versus spectroscopic perspective. J Non-Cryst Solids. 2003;323:1-6.
18. Stuani PLA, Candido AM, Nakasuga WM, Figueroa P, Tello SCA. Fission-track evolution in Macusanite volcanic glass. Radiat Phys Chem. 2020
19. Elliott CJ, Moss AA. Natural glass from Macusani, Peru. Mineral Mag J Mineral Soc. 1965;35(270):423-4.
20. Macdonald R, Smith RL, Thomas JE. Chemistry of the subalkalic silicic obsidians. USA: U.S. Geological Survey. 214 p. Professional Paper 1523.
21. Linck G. Ein neuer knstallfiihrender Tektit von Paucartambo in Peru. Chem Erde. 1926;2:157-74.
22. Husien MS. Fracture behavior and mechanical characterization of obsidian: naturally occurring glass. [dissertation]. Oklahoma: Oklahoma State University; 2010.
23. van Otterloo J, Cas AF, Scutter CR. The fracture behaviour of volcanic glass and relevance to quench fragmentation during formation of hyaloclastite and phreatomagmatism. Earth Sci Rev. 2015;151:79-116.
24. Geology Page. Obsidian: what is obsidian? Why obsidian is black?. 2019 [cited 2021 Feb 28]. Available from: geologypage.com/2019/08/obsidian-what-is-obsidian-why-obsidian-is-black.html
25. Marsellos A, Garver J. Radiation damage and uranium concentration in zircon as assessed by Raman spectroscopy and neutron irradiation. Am Mineral. 2010;95(8-9):1192-201.
26. Yildiz B, Ozturk ZB. Investigation of the usage of whitening agents as an alternative to zircon in opaque frit compositions. Acta Physica Polonica Series A. 2015;127:1180-182.
27. Di Genova D, Morgavi D, Hess KU, Neuville DR, Borovkov N, Perugini D, et al. Approximate chemical analysis of volcanic glasses using Raman spectroscopy. J Raman Spectrosc. 2015;46(12):1235-44.
28. Carter EA, Hargreaves MD, Kononenko N, Graham I, Edwards HGM, Swarbrick B, et al. Raman spectroscopy applied to understanding Prehistoric Obsidian Trade in the Pacific Region. Vib Spectrosc. 2009;50(1):116-24.
29. Lafuente B, Downs RT, Yang H, Stone N. The power of databases: the RRUFF project. In: Armbruster T, Danisi RM, editors. Highlights in mineralogical crystallography. Berlin, Germany: W. De Gruyter; 2015. p. 1-30. [cited 2020 Nov 28]. Available from: https://rruff.info/Andalusite/R060212
30. Zhai K, Xue W, Wang H, Wu X, Zhai S. Raman spectra of sillimanite, andalusite, and kyanite at various temperatures. Phys Chem Miner. 2020;47(5):1-11.
31. Taylor WH. The structure of andalusite, Al_2SiO_5. Z Kristallogr Cryst Mater. 1929;71:205-18.
32. Burnham CW, Buerger MJ. Refinement of the crystal structure of kyanite. Z Kristallogr Cryst Mater. 1961;115:269-90.
33. Winter JK, Ghose S. Thermal expansion and high-temperature crystal chemistry of the Al_2SiO_5 polymorphs. Am Mineral. 1979;64:573-86.
34. Danilo F, Dirk H, Florian A, Christopher P. Andalusite based raw materials for Refractory Castable: properties and application. Paris: Imerys Refractory Minerals; 2018.
35. Marshall RR. Devitrification of natural glass. Geol Soc Am Bull. 1961;72(10):1493.
36. Lofgren G. Experimentally produced devitrification textures in natural rhyolitic glass. Geol Soc Am Bull. 1971;82(1):111.
37. Gimeno D. Devitrification of natural rhyolitic obsidian glasses: petrographic and microstructural study (SEM+EDS) of recent (Lipari island) and ancient (Sarrabus, SE Sardinia) samples. J Non-Cryst Solids. 2003;323:84-90.