Distinguishing volcanic from impact glasses—The case of the Cali glass (Colombia)

Ludovic Ferrière1*, Alvaro P. Crósta2, Wencke Wegner1,3, Eugen Libowitzky4, Fabio Iwashita5 and Christian Koeberl6

1Natural History Museum Vienna, Burgring 7, A-1010 Vienna, Austria
2Institute of Geosciences, University of Campinas, Rua Carlos Gomes, 250, 13083-855 Campinas, SP, Brazil
3Department of Lithospheric Research, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria
4Department of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria
5Geosciences Department, Universidad de los Andes, Cra 1 no 18A, 111711 Bogotá, Colombia

ABSTRACT

Natural glass occurs on Earth in different geological contexts, mainly as volcanic glass, fulgurites, and impact glass. All these different types of glasses are predominantly composed of silica with variable amounts of impurities, especially the alkalis, and differ in their water content due to their mode of formation. Distinguishing between different types of glasses, on Earth and also on the Moon and on other planetary bodies, can be challenging. This is particularly true for glasses of impact and volcanic origin. Because glass is often used for the determination of the age of geological events, even if out of geological context, as well as to derive pressure and temperature constraints, or to evaluate the volatile contents of magmas and their source regions, we rely on methods that can unambiguously distinguish between the different types of glasses. We used the case of the Cali glass, found in an extended area close to the city of Cali in western Colombia, which was previously suggested to be of impact or volcanic origin, to show that, using a multimethod approach (i.e., combining macroscopic observations, chemical and isotopic data, and H2O content), it is possible to distinguish between different formation modes. A suite of Cali glass samples was analyzed using electron microprobe, instrumental neutron activation analysis, thermal ionization mass spectrometry, and Fourier-transform infrared spectroscopy, allowing us to definitively exclude an impact origin and instead classify these glasses as a rhyolitic volcanic glass (obsidian). Our results suggest that other “unusual glass occurrences” that are claimed, but not convincingly proven, to be of impact origin should be reexamined using the same methodology as that applied here.

INTRODUCTION

Natural glass is rare on Earth compared to crystalline rocks due to its specific formation conditions and durability aspects (i.e., glass is metastable and easily altered). It is essential to distinguish between different types of glasses because of their use for dating of geological events, to evaluate the volatile abundances of magmatic source regions, to establish pressure and temperature constraints, and for many other applications. In particular, the distinction between volcanic glass versus impact glass can be challenging and may lead to erroneous interpretation of the geological context (French and Koeberl, 2010); the potential for misidentification of origin motivated our investigation of Cali glass (found in an extended area near the city of Cali in western Colombia) samples to unravel the origin of this “unusual” glass (Fig. 1). We show that, by combining a number of different analytical methods and following a relatively simple research methodological scheme, we can discriminate between a volcanic origin and an impact origin for the Cali glass. This proposed methodology could be applied to reconstruct the geological context of materials of disputed origin in the future.

Natural glass on Earth is mostly volcanic, mainly obsidian and, less commonly, tachylyte (e.g., O’Keefe, 1984). Obsidian is generally brown to black or gray in color. It commonly exhibits flow banding and contains more or fewer small vesicles and/or crystalline inclusions (microlites and/or phenocrysts), such as feldspar, pyroxene, clinopyroxene, plagioclase, magnetite, ilmenite, and olivine. A significant compositional range is known for obsidians, with silica contents from 65 to 80 wt%, and relatively high alkali contents (e.g., Tykot, 2021, and references therein).

Fulgurites are glasses formed when lightning strikes Earth’s surface, generating extremely high temperatures that are able to locally melt and fuse rock, sand, or soil (e.g., Pasek et al., 2012). It is commonly found as glassy hollow tubes and, more rarely, as patches of glass on exposed rock surfaces. This type of glass is not discussed further here, because it can easily be recognized based on macroscopic observations alone and/or on the context of occurrence.

Impact glasses are quenched melts formed by shock melting of target rocks during impact events (Stöffler, 1984; Dressler and Reimold, 2001). Due to their mode of formation, they are commonly associated with shock-metamorphosed minerals and rock fragments, and, in many cases, they contain trace amounts of a projectile component (e.g., Koeberl, 2014, and references therein). Impact glass occurs in breccia deposits within or outside the impact crater, in proximal ejecta, as glass bodies and particles in breccia, or in distal ejecta as glass particles, spherules, and as (micro)tektites. Tektites are distal impactites derived from the (near-)surface of the target rocks, with specific petrographic, chemical, and isotopic characteristics, as well as extremely low H2O content (e.g., Koeberl, 2014). They are a rare type of impact glass found in only a few distinct strewn fields on Earth, usually at hundreds to thousands of kilometers from their source crater (e.g., Koeberl, 2014). In general, they are up to a few centimeters in size, they are mainly black or green, and rarely brownish to grayish, and they commonly show a pitted or textured surface. Tektites, along with some other types of impact glasses, can resemble obsidian and thus are readily misidentified (Fig. 2).

CITATION: Ferrière, L., et al., 2021, Distinguishing volcanic from impact glasses—The case of the Cali glass (Colombia): Geology, v. 49, p. 1421–1425, https://doi.org/10.1130/G48925.1
Figure 1. (A) Location map of Colombia with department boundaries, and inset of area enlarged in B. (B) Map showing area of occurrence of Cali glass (light gray).

Figure 2. Macrophotographs and backscattered electron (BSE) image of Cali glass samples. (A) Typical Ivory Coast tektite sample for comparison purposes. (B) Typical Cali glass sample with pitted surface (and remnants of soil in depressions) and broken surface showing conchoidal fracture. (C) Rare large Cali glass specimen with characteristic surface sculpture and pitting caused by chemical corrosion. (D) Cali glass sample (with clean surface) showing alternating layers. (E) Polished section of sample shown in D. (F) BSE image showing enlarged area of image in E with inclusions of silica and feldspar (Fsp), and numerous microlites and tiny iron-oxide inclusions in glass.
Water content is an important parameter for the distinction of the different types of glass; the typical range for tektites is 0.002–0.030 wt% H₂O, whereas other types of impact glasses contain 0.008–0.130 wt% H₂O, and even up to 0.166 wt% H₂O for Libyan Desert Glass (Beran and Koebel, 1997). Volcanic glasses, on the other hand, have typical H₂O contents ranging from 0.07 wt% to 2 wt% H₂O for obsidian (e.g., Stevenson et al., 2019, and references therein).

Previous Work on Cali Glass

Over the past 100 years or so, several glass samples found in a group of South American countries, including Peru, Bolivia, Ecuador, and Colombia, referred to as “americanties” in the literature (e.g., Martin, 1933), were described either as “tektites,” “possible tektites,” or “pseudo-tektites,” based on macroscopic aspects similar to confirmed tektites (Codazzi Lleras, 1925; Stutzer, 1926; Döring and Stutzer, 1928; Koomans, 1938; Martin and De Sitter-Koomans, 1956; Ocampo et al., 2017). One of these glasses, the so-called “Cali glass,” also referred to in the literature as “obsidians from Cali,” “calites,” “calitites,” “colombites,” “colombianites,” or “piedra de rayo” (i.e., “lightning stone”) (e.g., Merrill, 1911; Bellot-Gurlet et al., 2008; Ocampo et al., 2017), occurs in a relatively extensive area along the Cauca River Valley in the Valle del Cauca department, Colombia (Fig. 1). The area of occurrence is more than 200 km long and some 30–40 km wide, with the department capital city of Cali approximately located at the center-western part of it. First reported by von Humboldt in 1823 (“Ces obsidienne de Popayan ont souvent la forme de larmes ou de boules à la surface tuberculée.” [These obsidians from Popayan often have tear or ball shapes with a pitted surface.]; von Humboldt, 1823, p. 340), it was assumed to be an (unusual) type of obsidian by some authors, whereas others argued that it is a tektite (von Humboldt, 1823; Merrill, 1911; Codazzi Lleras, 1925; Stutzer, 1926; Martin, 1933; Martin and De Sitter-Koomans, 1956; Bellot-Gurlet et al., 2008; Ocampo et al., 2017). Ocampo et al. (2017) recently claimed that Cali glass is tektite glass, without any specific evidence, and in turn used it to “confirm” the impact origin of a buried 36 × 26 km diameter “crater” structure (for which no shock metamorphism evidence is reported) located in the Cauca subbasin at 3°15′ N and 76°25′ W, south-southeast of the city of Cali (Fig. 1). In addition, Ocampo et al. (2017) determined a weighted mean ⁴⁰Ar/³⁹Ar age of 3.25 ± 0.04 Ma (2σ) from three Cali glass samples.

SAMPLES AND METHODS

Two sets of Cali glass samples were investigated in this study, including seven samples from the Natural History Museum Vienna (NHMW, Austria) collection (donated in the 1980s by mineral dealer Franz Gross), where “Tektites, Cali, Colombia” is written on the original label, and three samples collected by A.P. Cróstia and F. Iwashita in July 2018 at two locations west-southwest from the town of Jamundí (at 3.2363°N, 76.6450°W and 3.1697°N, 76.6628°W; Fig. 1). Macroscopic investigations were conducted on all samples. Five of them were cut, and polished thick sections were prepared. The cutting of the different samples (especially the largest ones) proceeded without any problem, whereas tektites frequently shattered during cutting due to internal residual stress release. Petrographic investigations were completed by optical microscope and a JEOL JSM-6610 scanning electron microscope at the NHMW. Major-element compositions were measured for five samples at the NHMW using a JEOL JXA-8530-F field-emission-gun electron microprobe. Major- and trace-element abundances were obtained for three samples by instrumental neutron activation analysis (INAA) at the University of Vienna. Sr and Nd isotopic compositions were obtained for the same three samples by thermal ionization mass spectrometry at the University of Vienna. Finally, the H₂O content of three double-polished samples was determined using Fourier-transform infrared spectroscopy (FTIR) at the University of Vienna. Additional information on our methods is given in the Supplemental Material.

RESULTS

Cali glass samples are generally associated with paleosurfaces covered by residual soil and/or in alluvial/colluvial deposits. In some cases, they are found at the surface, left as resistant remnants on top of the soil. The investigated samples are dark brown and gray to black in color, with sizes ranging from 2 to 5 cm (Figs. 2B and 2D; Fig. S1 in the Supplemental Material). Rare larger samples are also found (Fig. 2C). Mainly spheroidal, oval, or somewhat irregular in shape (with flattened portions), they show a heavily pitted surface (Figs. 2B–2D; Fig. S1). One of the samples is dumbbell-like in shape (“Cali-1”; Fig. S1). A few of the samples show some layering. In transmitted light, the glass is pale gray to pale brown in color. A few small vesicles and mineral inclusions occur, including silica, feldspar, iron oxides, zircon, and apatite (Fig. 2F; Fig. S2). One of the samples shows alternating layers with numerous (preferentially aligned) microcrystals (Fig. 2E; Fig. S2).

Microprobe investigations showed that the glass is chemically homogeneous in composition (Fig. 3A; Table S1). The samples show no major variations in composition at the scale of one sample (not even in the case of the layered sample investigated; Figs. 2D and 2E) or between different samples. This was also confirmed by the INAA data (Table S2). Compositional ranges for major-element microprobe data (in wt%) for five samples and for trace elements (Cr, Co, Rh, Sr, Zr, and Ba, in ppm), as determined with INAA for three samples, are: SiO₂ (76.4–78.0), Al₂O₃ (12.2–12.8), TiO₂ (below detection limit [bdl] to 0.19), FeO (0.46–0.59), MnO (bdl–0.08), MgO (0.04–0.09), CaO (0.60–0.66), Na₂O (3.87–4.17), K₂O (4.64–4.96), Cr (4.2–7.7), Co (0.3–0.4), Rb (168–195), Sr (60–67), Zr (207–254), and Ba (300–367). Figure 3A shows that the K₂O + Na₂O contents of the Cali glass are much higher than values for all known tektites, but they are in the range known for obsidians from Colombia and Ecuador (cf. Bellot-Gurlet et al., 2008). The same is also true for other major and trace elements, for which abundances are similar to those in obsidians from this region (Fig. 3B).

The three samples for which we obtained Sr and Nd isotopic compositions (Table S3), with epsilon Nd (ɛNd) values between 2.0 and 2.1 and ɛSr values between 2.4 and 2.7, showed a mantle signature, whereas all known tektites are characterized by a continental crustal signature (Fig. 4).

In terms of water content, using the same calibration as in Beran and Koebel (1997), the resulting H₂O concentrations for the three investigated samples, i.e., Cali-1, Cali-2, and Cali-3, were 0.39, 0.56, and 0.48 wt% (±5 rel%), respectively. These values were obtained using the broad band at 3800–2550 cm⁻¹ with a maximum at 3577 cm⁻¹ (i.e., the band containing the O-H stretching fundamentals of both OH and H₂O units in the glass) as visible on the FTIR absorption spectra reported in Figure S3. Water concentrations were obtained using this band in two different ways, and also using the very weak bands at 4515 cm⁻¹ and 5230 cm⁻¹, based upon the work by Persikov et al. (2014). The three different methods gave very similar results (see Table S4 and the Supplemental Material for details). The obtained values, ranging from 0.4 to 0.6 wt% H₂O, are typical for obsidians and significantly higher, by one to two orders of magnitude, than water concentrations for tektites and other impact glasses (e.g., Beran and Koebel, 1997; Stevenson et al., 2019).

DISCUSSION AND CONCLUSIONS

The confirmation of an impact origin for a given glass sample, or glass occurrence, can be challenging. Several examples other than the Cali glass have been suggested to be of impact origin, such as the Edeowie glass in South Australia (Haines et al., 2001), or the Dakhle glass.
in the Western Desert of Egypt (Osinski et al., 2007), but their origins remain controversial.

Based on their main visual characteristics, color, shape, and pitted surface, Cali glasses (Figs. 2B–2D) are very similar to, and hardly distinguishable from, known tektites (Fig. 2A); however, they also look like typical obsidian samples that were subjected to corrosion.

The petrographic characteristics of the studied samples, such as the presence of layering and microlites, the chemical compositions, with extremely low FeO content and high K$_2$O + NaO contents (Fig. 3A), and the Nd and Sr isotopic ratios, typical of a mantle signature (Fig. 4; Table S3), are characteristic for volcanic origin and unlike known tektites.

Our water concentration data, ranging from 0.4 to 0.6 wt% H$_2$O, typical for obsidians, further allow us to definitely exclude an impact origin for the Cali glass. Furthermore, if the Cali glass were to be considered as a tektite, it should not occur in close proximity to its (assumed) source crater (Fig. 1), as claimed by Ocampo et al. (2017).

The confirmation that Cali glass is a rhyolite volcanic glass (obsidian) corroborates the geographic location in which it is found. The Cauca River Valley is located between the Western and Central Colombian Cordilleras, two mountain ranges with numerous active and inactive volcanos. Therefore, we conclude that the Cali glass was produced in a volcanic eruption during the Pliocene (based on the age estimate from Ocampo et al., 2017), deposited relatively close to its source, and then subjected to dissolution, erosion, and fluvial processes in a tropical environment, explaining its current distribution over a relatively large area (Fig. 1).

With our new data set, we can end the more than one-century-long debate on the origin of the Cali glass. Our straightforward analytical methodology is also suitable for examining other “unusual glass occurrences,” as well as glass samples returned to Earth from the Moon and future Mars missions, in order to determine the geological process(es) at the origin of their formation.

ACKNOWLEDGMENTS

This paper is dedicated to the memory of the American geologist George P. Merrill (1854–1929) for his early work on Cali glass and in the quest to follow the inscription on his gravestone, “Search for truth is the noblest occupation of man, its publication a duty” (a quote originally from Madame de Stael).

We thank G. Batic for sample preparation. B. Gruber,
REFERENCES CITED
Albin, E.F., Norman, M.D., and Roden, M., 2000, Major and trace element compositions of geontiages: Clues to the source of North American tektites: Meteoritics & Planetary Science, v. 35, p. 795–806, https://doi.org/10.1111/j.1945-5100.2000.tb01463.x.
Bellot-Gurlet, L., Dorighel, O., and Poupeau, G., 2008, Obsidian provenance studies in Colombia and Ecuador: Obisidian sources revisited: Journal of Archaeological Science, v. 35, p. 272–289, https://doi.org/10.1016/j.jas.2007.03.008.
Beren, A., and Koeberl, C., 1997, Water in tektites and impact glasses by Fourier-transformed infrared spectrometry: Meteoritics & Planetary Science, v. 32, p. 211–216, https://doi.org/10.1111/j.1945-5100.1997.tb01260.x.
Blum, J.D., Papanastassiou, D.A., Koeberl, C., and Mader, D., 2007, Evidence for a ∼200–100 ka meteorite impact in the Western Desert of Egypt: Earth and Planetary Science Letters, v. 253, p. 378–388, https://doi.org/10.1016/j.epsl.2006.10.039.
Koeberl, C., 2014, The geochemistry and cosmochemistry of impacts, in Holland, H.D., and Turekian, K.K., eds., Treatise on Geochemistry (2nd ed.), Volume 2: Planets, Asteroids, Comets and the Solar System: Oxford, UK, Elsevier, p. 73–118, https://doi.org/10.1016/B978-0-08-095975-7.00130-3.
Koeberl, C., Brandstätter, F., Niedermayr, G., and Kurat, G., 1998, Moldavites from Austria: Meteoritics, v. 23, p. 325–332, https://doi.org/10.1111/j.1945-4510.1998.tb00917.x.
Koeberl, C., Bottomley, R., Glass, B.P., and Storzer, D., 1997, Geochemistry and age of Ivory Coast tektites and microtektites: Geochimica et Cosmochimica Acta, v. 61, p. 1745–1772, https://doi.org/10.1016/S0016-7037(97)00024-6.
Koomans, C.M., 1938, On tektites and pseudo-tektites from Dutch East Indies and Philippines: Leidse Geologische Mededelingen, v. 10, p. 63–81.
Le Maitre, R.W., ed., 2002, Igneous Rocks: A Classification and Glossary of Terms, Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks: Cambridge, UK, Cambridge University Press, 236 p., https://doi.org/10.1017/CBO9780511535581.
Martin, R., 1933, Are the “americanites” tektites?: Leidse Geologische Mededelingen, v. 6, p. 123–132.
Martin, R., and De Sitter-Koomans, C., 1956, Pseudo-tektites from Colombia and Peru: Leidse Geologische Mededelingen, v. 20, p. 151–164.
Merrill, G.P., 1911, On the supposed origin of the moldavites and like sporadic glasses from various sources: Proceedings of the United States National Museum, v. 40, p. 481–486, https://doi.org/10.5479/si.00963801.40-1833.481.
Ngo, H.H., Wasserburg, G.J., and Glass, B.P., 1985, Nd and Sr isotopic compositions of tektite material from Barbados and their relationship to North American tektites: Geochimica et Cosmochimica Acta, v. 49, p. 1479–1485, https://doi.org/10.1016/0016-7037(85)90297-2.
Ocampo, A., et al., 2017, Pliocene impact crater discovered in Colombia: Geological evidences from tektites, in Lunar and Planetary Science Conference XLVIII: Houston, Texas, Lunar and Planetary Institute, abstract 2532.
O’Keefe, J.A., 1984, Natural glass: Journal of Non-Crystalline Solids, v. 67, p. 1–17, https://doi.org/10.1016/0022-3093(84)90137-6.
Osinski, G.R., Schwarz, H.P., Smith, J.R., Kleindienst, M.R., Haldemann, A.F.C., and Churcher, C.S., 2007, Evidence for a ∼200–100 ka meteorite impact in the Western Desert of Egypt: Earth and Planetary Science Letters, v. 253, p. 378–388, https://doi.org/10.1016/j.epsl.2006.10.039.
Pasek, M.A., Block, K., and Pasek, V., 2012, Fulgurite morphology: A classification scheme and clues to formation: Contributions to Mineralogy and Petrology, v. 164, p. 477–492, https://doi.org/10.1007/s00410-012-0753-5.
Perrisski, E.S., Bukhitiyarov, P.G., Nekrasov, A.N., and Bondarenko, G.V., 2014, Concentration dependence of water diffusion in obsidian and dactitic melts at high-pressures: Geochemistry International, v. 52, p. 365–371, https://doi.org/10.1134/S0016702914050085.
Schnetzler, C.C., and Pinson, W.H., Jr., 1963, The chemical composition of tektites, in O’Keefe, J.A., ed., Tektites: Chicago, Illinois, University of Chicago Press, p. 95–129.
Shaw, H.F., and Wasserburg, G.J., 1982, Age and provenance of the target materials for tektites and possible impactites as inferred from Sm-Nd and Rb-Sr systematics: Earth and Planetary Science Letters, v. 60, p. 155–177, https://doi.org/10.1016/0012-821X(82)90061-2.
Stevenson, C.M., Rogers, A.K., and Glasscock, M.D., 2019, Variability in obsidian structural water content and its importance in the hydration dating of cultural artifacts: Journal of Archaeological Science, Reports, v. 23, p. 231–242, https://doi.org/10.1016/j.jasrep.2018.10.032.
Stöfler, D., 1984, Glasses formed by hypervelocity impact: Journal of Non-Crystalline Solids, v. 67, p. 465–502, https://doi.org/10.1016/0022-3093(84)90171-6.
Stutzer, O., 1926, Kolumbiana Glas-Meteorite (Tektite): Centralblatt für Mineralogie, Geologie und Paläontologie, v. A, p. 137–145.
Sun, S.-S., and McDonough, W.F., 1989, Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes, in Saunders, A.D., and Norry, M.J., eds., Magmatism in the Ocean Basins: Geological Society [London] Special Publication 42, p. 313–345, https://doi.org/10.1144/GSL.SP.1989.042.01.19.
Tykot, R.H., 2021, Obsidian in prehistory, in Richet, P., ed., Encyclopedia of Glass Science, Technology, History, and Culture (1st ed.): New York, American Ceramic Society and John Wiley & Sons, p. 1237–1248, https://doi.org/10.1002/9781118801017.ch111.
von Humboldt, A., 1823, Essai Géognostique sur le Gisement des Roches dans les Deux Hémisphères: Paris, Édition F.G. Levrault, 379 p.
Zindler, A., and Hart, S., 1986, Chemical geodynamics: Annual Review of Earth and Planetary Sciences, v. 14, p. 493–571, https://doi.org/10.1146/annurev.earth.14.050186.002425.

Printed in USA