HOW TO DISTINGUISH DIFFERENT TYPES OF NATURAL GLASSES – THE ORIGIN OF CALI GLASS (COLOMBIA) REVISITED. L. Ferrière<sup>1</sup>, A. P. Crósta<sup>2</sup>, W. Wegner<sup>1,3</sup>, E. Libowitzky<sup>4</sup>, F. Iwashita<sup>5</sup>, and C. Koeberl<sup>3</sup>, <sup>1</sup>Natural History Museum Vienna, Burgring 7, A-1010 Vienna, Austria (ludovic.ferriere@nhmwien.ac.at), <sup>2</sup>Institute of Geosciences, University of Campinas, Rua Carlos Gomes, 250, 13083-855 Campinas, SP, Brazil, <sup>3</sup>Department of Lithospheric Research, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria, <sup>4</sup>Department of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria, <sup>5</sup>Geosciences Department, Universidad de los Andes, Cra 1 no 18A, 111711 Bogotá, Colombia.

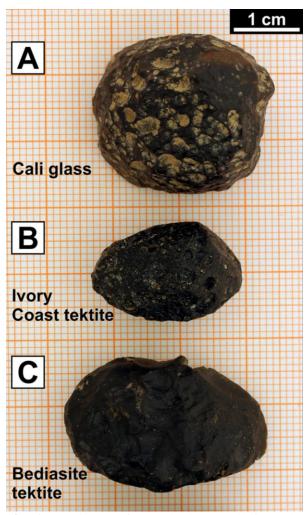
Introduction: Natural glass is rare on Earth (mostly occurring as volcanic glass, more rarely as impact glass or fulgurite) compared to crystalline rocks due to its specific formation conditions and durability aspects. It is essential to distinguish between different types of glasses because of their use for dating of geological events, to evaluate the volatile abundances of magmatic source regions, to establish pressure and temperature constraints, and 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 [e.g., 1]; 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. 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 [2, 3]. This proposed methodology could be applied for unraveling the geological context of other glasses of disputed origin.

Previous work on Cali Glass: Over the past 200 years or so, the so-called "Cali glass," also referred to in the literature as "obsidians from Cali," "calites," "calities," "colombites," "colombianites," "americanites", or "piedra de rayo" (i.e., "lightning stone") [e.g., 4–11], was described either as "obsidian," "pseudo-tektite," "possible tektite," or "tektite". It occurs in a relatively extensive area (more than 200 km long and some 30–40 km wide) along the Cauca River Valley in the Valle del Cauca department (Colombia), with the city of Cali approximately located at the central-western part of it [3].

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 and three samples collected by A.P.C. and F.I. in July 2018 at two locations west-southwest from the town of Jamundí (at 3.23639°N/76.64500°W and 3.16972°N/76.66278°W). Macroscopic investigations were conducted on all samples. Petrographic investigations were completed for five samples by optical microscope and SEM.

Major-element compositions were measured with EPMA for five samples. Major- and trace-element abundances were obtained for three samples by INAA. Sr and Nd isotopic compositions were obtained for the same three samples by TIMS. Finally, the H<sub>2</sub>O content of three double-polished samples was determined using FTIR. Additional information on the samples and methods can be found in [3].

Results: The investigated samples are dark brown and gray to black in color, with sizes ranging from 2 to 5 cm (Fig. 1A; see also [3]). Mainly spheroidal, oval, or somewhat irregular in shape (with flattened portions), they show a heavily pitted surface. A few of the samples show some layering. A few small vesicles and mineral inclusions occur, including silica, feldspar, iron oxides, zircon, and apatite. One of the investigated samples shows alternating layers with numerous (preferentially aligned) microlites. Microprobe investigations showed that the glass is chemically homogeneous in composition. The samples show no major variations in composition at the scale of one sample or between different samples. This was also confirmed by the INAA data. Compositional ranges for major-element microprobe data (in wt%) for five samples and for trace elements (Cr, Co, Rb, Sr, Zr, and Ba, in ppm), as determined with INAA for three samples, are:  $SiO_2$  (76.4–78.0),  $Al_2O_3$  (12.2–12.8), TiO<sub>2</sub> (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), Na<sub>2</sub>O (3.87–4.17), K<sub>2</sub>O (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) [2]. The  $K_2O + Na_2O$  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 [10]. The three samples for which we obtained Sr and Nd isotopic compositions, with epsilon Nd (εNd) values between 2.0 and 2.1 and ESr values between 2.4 and 2.7, showed a mantle signature, whereas all known tektites are characterized by a continental crustal signature [3]. In terms of water content, H<sub>2</sub>O concentrations for the three investigated samples are 0.39, 0.56, and 0.48 wt% (±5 rel%), respectively. For the full set of data, additional information, and figures, see [3].



**Fig. 1.** Specimens of natural glasses (all from the NHMW collection). A) Cali glass (#X2). B) Ivory Coast tektite (NHMW-O364). C) Bediasite tektite (NHMW-O168).

**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 [12, 13] or the Dakhleh glass in the Western Desert of Egypt [14], but their origins remain controversial. Based their main on visual characteristics, color, shape, and pitted surface, Cali glasses are very similar to, and difficult to distinguish from, known impact glasses, in particular tektites (Fig. 1); 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<sub>2</sub>O + Na<sub>2</sub>O contents, and the Nd and Sr isotopic ratios, typical of a mantle signature, are characteristic for a volcanic origin and unlike known tektites. With water concentrations ranging from 0.4 to 0.6 wt%, typical for obsidians, and significantly higher, by one to two orders of magnitude, than water concentrations for tektites and other impact glasses, we can definitely exclude an impact origin for the Cali glass [3]. 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 [11]), 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. With our new data set, we can end the more than one-century-long debate on the origin of the Cali glass [3]. 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.

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