Ferrière, L., et al., 2021, Distinguishing volcanic from impact glasses—The case of the Cali glass (Colombia): Geology, v. 49, https://doi.org/10.1130/G48925.1

Supplemental Material

Distinguishing volcanic from impact glasses - The case of the Cali glass

(Colombia)

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Contains:

- Additional information on methods
- Figures S1, S2, S3, and S4
- Tables S1, S2, S3, and S4
- References cited

Additional information on methods

Field emission gun electron probe microanalyzer (EPMA):

An accelerating voltage of 15 kV, a beam current of 20 nA, a defocused 25 μm beam diameter, and a counting time of 10 s for peak and 5 s for background were used for all element Kα lines. The following synthetic compounds Al₂O₃, Cr₂O₃, TiO₂, NaCl, KCl, and natural minerals tephroite Mn₂SiO₄, wollastonite CaSiO₃, Durango apatite Ca₅(PO₄)₅F, and Marjalahti olivine (Mg,Fe)₂SiO₄ were used as standards for Al, Cr, Ti, Na, K, Mn, Ca, Mg, Si, and Fe, respectively. The mean detection limits (in ppm) for measured elements (with SD in parentheses), are: Si 159 (3), Ti 464 (60), Cr 298 (26), Al 107 (3), Fe 206 (8), Mn 176 (7), Mg 92 (3), Ca 89 (1), Na 107 (6), and K 67 (1), respectively. Precision (relative) of analysis for major elements (Si, Al, Fe, Mg, and Ca) is typically better than 1%, but total EPMA error is 1–2%.

Instrumental neutron activation analysis (INAA):

For bulk INAA analysis, Cali glass chips (i.e., Cali-1 = 177.52 mg, Cali-2 = 189.46 mg, and Cali-3 = 206.25 mg) were placed inside small sealed polyethylene vials. The same was done for powder of international reference materials, i.e., Ailsa Craig granite AC-E (Centre de Recherches Pétrographiques et Géochimiques, Nancy, France), the carbonaceous chondrite Allende (ALL; Smithsonian Institution, Washington DC, USA), and the Devonian Ohio shale SDO-1 (USGS), but using less material (60–90 mg). Samples were then packed together with other samples in groups of 17, to which three standard samples were added.

Samples and standards were irradiated together for 8 hours in the 250 kW Triga reactor of the Atomic Institute of the Austrian Universities at a neutron flux of 2.10^{12} n cm⁻² s⁻¹. Samples and standards were then measured with coaxial Canberra HpGe detectors in three cycles (L1, L2, and L3). Cycle L1 was measured 7 days after irradiation. Each sample was measured for at least 60 minutes. Cycle L2 was done 11 days after irradiation, with ~3–4 hours measuring time for each

sample. Finally, cycle L3 was performed five weeks after irradiation and the samples were measured for at least 12 hours. Data obtained were then processed automatically by computer, and neutron flux correction was applied. Finally, the data were checked manually. More details on instrumentation, accuracy, and precision of this method can be found in Mader and Koeberl (2009).

Sr and Nd isotope analysis:

An aliquot of each glass sample was hand ground in an agate mortar to a grain size $< 63 \mu m$. The powder of the three samples (ca. 50 mg) were digested in tightly screwed Savillex beakers using an ultra-pure mixture of HF:HNO₃ (4:1) for 2-4 weeks at 100-120 °C on a hot plate. After acid evaporation repeated treatment of the residue using HNO₃ and 6 N HCl resulted in clear solutions. Element extraction (Sr, REE) was performed using AG 50W-X8 (200-400 mesh, Bio-Rad) resin and 2.5 N and 4.0 N HCl as eluants. Nd was separated from the REE group using teflon-coated HdEHP and 0.24 N HCl as eluant. Maximum total procedural blanks were < 1 ng for Sr and 50 pg for Nd, and were taken as negligible. The pure element fractions were evaporated using a Re double filament assembly and run in static mode on a Thermo-Finnigan Triton thermal ionization mass spectrometer. A mean ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratio of 0.710258 ± 0.000005 (n = 5) was determined for the NBS987 (reference value 87 Sr/ 86 Sr = 0.710248 from Faure, 2001) and a mean 143 Nd/ 144 Nd ratio of 0.511843 ± 0.000005 (n = 5) for the La Jolla (reference value 143 Nd/ 144 Nd = 0.511858 from Lugmair and Carlson, 1978) international standards during the period of investigation. Within-run mass fractionation was corrected for 88 Sr/ 86 Sr = 8.3752 and 146 Nd/ 144 Nd = 0.7219, respectively. Errors quoted represent 2 σ errors of the mean.

H2O content by Fourier-transform infrared spectroscopy (FTIR):

The exact thickness value of the three double side polished samples investigated by FTIR was measured using a digital micrometer with an accuracy of $\pm 2 \mu m$. Values are reported in Table S4.

Infrared absorption spectra were collected on a Bruker Tensor27 FTIR spectrometer, using a glowbar light source, a KBr beam splitter, a metal sample holder with a 4 mm Ø circular aperture, and a dLaTGS detector. Spectral resolution was 4 cm⁻¹. Spectra were averaged from 128 scans. Instrument control and data handling, as well as band analysis (peak height and area above background), were performed with OPUS 5.5 from Bruker.

The FTIR absorption spectra of the three samples Cali-1, Cali-2, and Cali-3 are shown in Fig. S4. The broad band at 3800–2550 cm⁻¹ with a maximum at 3577 cm⁻¹ contains the O-H stretching fundamentals of both OH and H₂O units in the glass. This band was analyzed in two ways to obtain water concentrations. Table S4 summarizes the essential parameters used.

(1) The general IR calibration of Libowitzky and Rossman (1997) employs the total integrated absorbance, i.e., the band areas of three orthogonal polarized IR measurements (here, in the isotropic case, this equals to 3 x A_i) and derives the integrated molar absorption coefficient ε_i from a linear function of the mean band position (79652 cm⁻² per mol H₂O/L at 3430 cm⁻¹ in the present case). The resulting H₂O concentrations for the three samples Cali-1, -2, and -3 are 0.48, 0.70, and 0.60 wt.% (± 10–20 rel.%).

(2) Beran and Koeberl (1997) used linear absorbances (band heights) of the fundamental O-H stretching band and a linear molar absorption coefficient ε of 75 cm⁻¹ per mol H₂O/L. Using their calibration, the water concentrations amount to 0.39, 0.56, and 0.48 wt.% (± 5 rel.%). The used ε

value was confirmed by graphical analysis of Behrens et al. (2004, their Fig. 1) resulting in ε = 78.

The very weak bands at 4515 and 5230 cm⁻¹ are assigned to the combination bands of OH and H₂O units, respectively. Based upon the work of Persikov et al. (2014), linear molar absorption coefficients ϵ of 1.36 and 1.60 cm⁻¹ (± 0.1, i.e., 5–10 rel.%) per mol H₂O/L were used for the former and the latter. The resulting H₂O concentrations assigned to both hydrous species are 0.39, 0.54, and 0.49 wt.% (OH groups) + 0.05, 0.10, and 0.08 wt.% (H₂O molecules) = 0.44, 0.64, and 0.58 wt.% (total). Due to the faint band intensities (only slightly above background noise), a large error must be expected.



Figure S1. Photograph of all the Cali glass samples collected by A.P. Crósta and F. Iwashita in July, 2018, three of which were investigated in this work (i.e., Cali-1, Cali-2, and Cali-3 as marked on the photograph). Note the different shapes, variations of size, and color of the samples.



Figure S2. (A) Microphotograph showing a close-up view of some of the alternating layers as visible on the macrophotographs of this Cali glass sample (specimen Cali-X1_NHMW) shown in Figs. 2D & E. The BSE image of the Fig. 2F was acquired from the light band visible in the central part of this microphotograph. (B) BSE image of an inclusion containing quartz and two

types of feldspars in a Cali glass sample (specimen Cali-X1_NHMW). (C) Secondary electron (SE) image of an inclusion of zircon (Zrn) and apatite (Ap) in a Cali glass sample (specimen Cali-X2_NHMW).



Figure S3. Fourier-transform infrared spectroscopy (FTIR) absorption spectra of the three glass samples (Cali-1, Cali-2, and Cali-3) investigated. Spectra were offset by each 0.05 in absorbance units for better visibility. The inset shows a magnified region of the weak OH and H₂O combination bands. While the region below 1300 cm⁻¹ is non-transparent due to the strong fundamental stretching and bending vibrations of the tetrahedral silicate units, the IR range above 1500 cm⁻¹ contains four bands that can be employed for analytical purposes. The band at 1830 cm⁻¹ is assigned to the first overtone of the silicate stretching vibration(s) and its relative height in all three samples confirms the correct measurement of thickness as reported in Table S4.

	SiO ₂	AI_2O_3	MgO	FeO	MnO	CaO	Na ₂ O	K ₂ O	TiO ₂	Cr ₂ O ₃	Total
Cali-1_frag1	76.73	12.66	0.06	0.53	0.08	0.66	4.09	4.86	0.06	0.04	99.74
Cali-1_frag2_1	77.64	12.66	0.05	0.47	0.02	0.62	4.01	4.89	0.01	0.03	100.41
Cali-1_frag2_1	77.98	12.75	0.06	0.53	bdl.#	0.62	3.93	4.88	0.02	bdl.	100.77
Cali-1_Transect_pt01	76.53	12.42	0.06	0.54	0.04	0.64	4.04	4.78	0.12	bdl.	99.17
Cali-1_Transect_pt02	76.55	12.47	0.06	0.52	0.03	0.62	4.01	4.79	0.09	0.04	99.17
Cali-1_Transect_pt03	76.92	12.48	0.05	0.54	0.05	0.64	4.10	4.78	0.05	0.02	99.62
Cali-1_Transect_pt04	76.84	12.48	0.05	0.50	0.05	0.65	4.00	4.79	0.10	bdl.	99.45
Cali-1_Transect_pt05	77.02	12.43	0.06	0.56	0.03	0.65	4.02	4.78	0.10	bdl.	99.65
Cali-1_Transect_pt06	76.95	12.47	0.05	0.53	0.04	0.62	4.02	4.76	0.15	0.07	99.67
Cali-1_Transect_pt07	76.97	12.56	0.05	0.51	0.04	0.64	4.00	4.80	0.12	bdl.	99.68
Cali-1_Transect_pt08	76.79	12.46	0.04	0.50	0.02	0.62	4.06	4.81	0.14	0.01	99.44
Cali-1_Transect_pt09	77.15	12.51	0.04	0.50	0.07	0.64	4.00	4.78	0.18	0.03	99.89
Cali-1_Transect_pt10	77.39	12.40	0.07	0.58	0.02	0.63	3.94	4.80	0.00	bdl.	99.82
Cali-1_Transect_pt11	77.26	12.54	0.05	0.53	0.05	0.64	3.91	4.80	0.01	0.04	99.83
Cali-1_Transect_pt12	77.23	12.52	0.04	0.55	0.05	0.62	3.99	4.79	0.09	0.01	99.89
Cali-1_Transect_pt13	77.47	12.55	0.07	0.53	0.04	0.62	4.07	4.82	0.13	0.05	100.34
Cali-1_Transect_pt14	77.67	12.44	0.05	0.52	0.05	0.60	4.06	4.77	0.09	0.02	100.27
Cali-1_Transect_pt15	77.34	12.48	0.07	0.51	0.03	0.63	3.97	4.79	0.09	bdl.	99.90
Cali-1_Transect_pt16	77.57	12.57	0.05	0.54	0.03	0.62	3.94	4.76	0.09	bdl.	100.18
Cali-1_Transect_pt17	77.67	12.55	0.05	0.46	0.03	0.63	3.96	4.83	0.06	bdl.	100.23
Cali-1_Transect_pt18	77.48	12.45	0.04	0.50	0.05	0.64	4.00	4.87	0.12	0.02	100.17
Cali-1_Transect_pt19	77.45	12.60	0.06	0.50	0.05	0.63	3.98	4.81	0.17	0.01	100.24
Cali-2_1	77.24	12.53	0.04	0.52	0.01	0.63	4.02	4.94	0.03	0.06	100.01
Cali-2_2	76.98	12.63	0.05	0.51	0.01	0.64	4.03	4.88	0.09	bdl.	99.81
Cali-3_1	77.29	12.67	0.06	0.51	0.04	0.66	3.98	4.94	bdl.	bdl.	100.16
Cali-3_2	76.52	12.53	0.06	0.53	0.05	0.62	3.99	4.90	0.04	bdl.	99.23
Cali-3_3	76.96	12.64	0.06	0.51	0.05	0.61	4.04	4.91	0.05	0.01	99.83
Cali-X1_NHMW_1	77.77	12.60	0.05	0.50	0.04	0.61	4.10	4.76	0.19	bdl.	100.62
Cali-X1_NHMW_2	77.73	12.18	0.07	0.49	0.05	0.62	4.01	4.74	0.11	0.02	100.00
Cali-X1_NHMW_3	77.48	12.33	0.06	0.47	0.03	0.64	3.98	4.76	0.06	bdl.	99.81
Cali-X1_NHMW_4	77.50	12.28	0.06	0.47	0.04	0.63	3.97	4.77	0.02	bdl.	99.74
Cali-X1_NHMW_5	77.62	12.38	0.07	0.56	0.03	0.62	4.02	4.70	0.08	0.04	100.11
Cali-X1_NHMW_6	77.58	12.20	0.07	0.52	0.03	0.61	3.98	4.73	0.12	0.07	99.90
Cali-X1_NHMW_7	77.70	12.25	0.05	0.46	0.02	0.61	4.13	4.78	0.12	0.02	100.14
Cali-X1_NHMW_8	77.11	12.41	0.09	0.54	0.05	0.61	4.03	4.64	0.10	bdl.	99.58
Cali-X1_NHMW_9	77.64	12.45	0.07	0.56	0.04	0.62	3.96	4.71	0.04	0.04	100.11
Cali-X2_NHMW_1	77.42	12.40	0.06	0.50	bdl.	0.62	3.90	4.91	0.15	bdl.	99.97
Cali-X2_NHMW_2	76.39	12.41	0.08	0.57	0.04	0.64	4.17	4.95	0.06	bdl.	99.29
Cali-X2_NHMW_3	76.90	12.51	0.07	0.55	0.02	0.65	4.10	4.95	0.01	0.04	99.80
Cali-X2_NHMW_4	77.59	12.43	0.05	0.58	0.02	0.64	4.10	4.95	0.12	bdl.	100.49
Cali-X2_NHMW_5	76.95	12.47	0.07	0.52	0.06	0.64	4.17	4.88	0.02	bdl.	99.77
Cali-X2_NHMW_6	76.63	12.30	0.06	0.59	0.03	0.66	4.11	4.94	0.02	bdl.	99.32
Cali-X2_NHMW_7	76.53	12.40	0.07	0.58	0.05	0.64	4.01	4.93	0.13	0.04	99.37
Cali-X2_NHMW_8	77.53	12.46	0.06	0.56	0.04	0.62	3.88	4.93	0.08	0.02	100.17
Cali-X2_NHMW_9	77.91	12.51	0.06	0.56	0.01	0.64	3.87	4.96	0.11	bdl.	100.63
Cali-X2_NHMW_10	76.64	12.32	0.05	0.54	0.03	0.64	3.96	4.95	0.08	0.04	99.23

Table S1. Major element concentrations (in wt.%) of five Cali glass samples, as obtained by electron probe microanalyzer. Fe as FeO.

[#]bdl. = below detection limit.

Table S2. Major and trace element concentrations (in ppm, except as noted) of three Cali glass samples, as obtained by instrumental neutron activation analyses.

[ppm]	Cali-1	Cali-2	Cali-3
Na (wt%)	2.86	3.23	2.88
K (wt%)	3.69	4.09	3.99
Sc	1.03	1.17	1.03
Cr	6.65	7.66	4.24
Fe (wt%)	0.41	0.46	0.41
Со	0.30	0.38	0.29
Ni	<9	<17	<8
Zn	23	27	23
Ga	<4.83	<5.73	4.04
As	8.71	10.5	8.49
Se	0.28	<1.65	<0.75
Br	0.5	0.4	0.2
Rb	180	195	168
Sr	67	64	60
Zr	217	245	207
Sb	2.36	2.28	2.85
Cs	10.9	11.8	10.2
Ва	346	367	300
La	26	29.5	26.1
Ce	41.3	46.8	41.5
Nd	14.5	16.8	14.7
Sm	3.19	3.32	2.82
Eu	0.27	0.32	0.27
Gd	3.02	2.82	2.52
Yb	0.84	0.84	0.76
Lu	0.16	0.16	0.14
Hf	3.04	3.55	3.07
Та	1.15	1.20	1.00
W	4.28	3.04	4.34
Os (ppb)	<508	<654	<489
lr (ppb)	<1.38	<2.57	<1.16
Au (ppb)	<1.3	<1.6	<1.2
Th	32.5	34.5	29.4
U	14.4	14.5	12.0

Table S3. Strontium and neodymium isotopic composition as measured for three Cali glass samples. Values obtained for the standards NBS987 and La Jolla measured alongside are also reported here.

	⁸⁷ Sr/ ⁸⁶ Sr	εSr [#]	¹⁴³ Nd/ ¹⁴⁴ Nd	εNd*	
Cali-1	0.704671 ± 4	2.4	0.512746 ± 4	2.1	
Cali-2	0.704689 ± 5	2.7	0.512747 ± 3	2.1	
Cali-3	0.704675 ± 6	2.5	0.512742 ± 3	2.0	
NBS987	0.710258 ± 5				
La Jolla			0.511843 ± 5		
[#] Epsilon Sr (ϵ Sr) = [((⁸⁷ Sr/ ⁸⁶ Sr) _{sample} / (⁸⁷ Sr/ ⁸⁶ Sr) _{UR}) - 1] x 10,000. Using a present day ⁸⁷ Sr/ ⁸⁶ Sr uniform reservoir (UR) value of 0.704500.					

*Epsilon Nd (ϵ Nd) = [((¹⁴³Nd/¹⁴⁴Nd)_{sample} / (¹⁴³Nd/¹⁴⁴Nd)_{CHUR}) - 1] x 10,000. Using a present day ¹⁴³Nd/¹⁴⁴Nd chondritic uniform reservoir (CHUR) value of 0.512638. Table S4. Parameters used for the determination of the water concentrations.

	Band used (cm ⁻¹)	Cali-1	Cali-2	Cali-3			
Thickness (μm) [#]		101	95	115			
Integrated absorbance (cm ⁻¹)*	3577	169	230	240			
Integrated absorption coefficient (cm ⁻²)	3577	16733	24211	20870			
Molar absorption coefficient (cm ⁻² per mol H ₂ O/L) $^{\$}$	3577	79652	79652	79652			
Values obtained using the same approach as in Libowitzky & Rossman (1997) [± 10–20 rel.%] $^{\$}$							
H2O (wt.%)	3577	0.48	0.70	0.60			
Linear absorbance	3577	0.381	0.518	0.538			
Linear absorption coefficient (cm ⁻¹)	3577	37.72	54.53	46.78			
Molar absorption coefficient (cm ⁻¹ per mol H ₂ O/L)	3577	75	75	75			
Values obtained using the same approach as in Beran & Koeberl (1997) [± 5 rel.%]							
H ₂ O (wt.%)	3577	0.39	0.56	0.48			
Linear absorbance	(OH) 4515	0.007	0.009	0.010			
Linear absorption coefficient (cm ⁻¹)	(OH) 4515	0.69	0.95	0.87			
Molar absorption coefficient (cm ⁻¹ per mol H ₂ O/L)	(OH) 4515	1.36	1.36	1.36			
Values obtained using the same approach as in Persikov et al. (2014) [± 5–10 rel.%]							
H2O (wt.%)	(OH) 4515	0.39	0.54	0.49			
Linear absorbance	H ₂ O 5230	0.001	0.002	0.002			
Linear absorption coefficient (cm ⁻¹)	H ₂ O 5230	0.10	0.21	0.17			
Molar absorption coefficient (cm ⁻¹ per mol H ₂ O/L)	H ₂ O 5230	1.60	1.60	1.60			
Values obtained using the same approach as in Persikov et al. (2014) [± 5–10 rel.%]							
H ₂ O (wt.%)	H ₂ O 5230	0.05	0.10	0.08			
H ₂ O (wt.%)	(OH) + H₂O	0.44	0.64	0.58			

[#]Thickness (at ± 2) as obtained using a digital micrometer (and further confirmed by linear absorbance of silicate overtone at 1830 cm⁻¹).

*Range of integration (at ±2): 3800–2550 cm⁻¹, mean wavenumber: 3430 cm⁻¹

§General, wavenumber-dependent IR calibration A_{i,tot} = 3 * A_i

For water calculations an average density of 2.34 g/cm³ was used, based on the extensive compilation on rhyolitic glasses of Newman et al. (1986).

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