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Increasing data (INAA) on Ecuadorian obsidian artifacts: preliminary provenance and a clue for pre-Columbian eastward trade

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ABSTRACT

In this work we carried out INAA major (Na, K, Ca and Fe %) and trace (ppm) elements (plus Mn by FAAS analysis) of 15 obsidian samples (waste flakes) coming from an unknown archaeological site (^{14}C-AMS age of 1425 AD) located on the south-eastern flank of the back-arc Sumaco volcano (to the east of the Cordillera Real) and from two already known pre-Columbian archaeological localities: La Florida (Quito) and Milan (Cayambe). Literature compositional data of the Ecuadorian obsidian outcrops provide some constraints on the provenance of the analyzed waste flakes, even though different methods of analyses make comparisons a difficult task. Concerning the obsidian artifacts of La Florida and Milan, they come from the well known Sierra de Guamanì obsidian sources (Cordillera Real). By contrast, the obsidian fragments of the Sumaco settlement show some compositional characters compatible with obsidian erratic pebbles recently discovered in some river banks of the Amazonian foothills draining the easternmost flanks of the Antisana volcano in the Cordillera Real as well. In this way, the obsidian artifacts found at the Sumaco site reinforce the opinion that Ecuadorian source inventory is not yet exhaustive. Although the Antisana volcano seems to be the best candidate to find out additional primary outcrops of obsidian sources, it cannot be also excluded that sub-Andean and Amazonian people directly took advantage from obsidian secondary sources (e.g. river banks), rather than procurements from primary outcrops in the Cordillera Real. The new archaeological findings at the Sumaco volcano are really of paramount importance in tracing the ancient routes of a possible obsidian eastward trade toward the Amazonian region.

1. Introduction

Obsidian artifacts found in archaeological sites represent ideal material to reconstruct trade networks and cultural contacts in antiquity, as these rocks geologically occur in limited numbers of outcrops in specific volcanic provinces. Generally, starting from the Neolithic period, obsidian was used as raw material to make both cutting and ornamental artifacts, always with little dimensions, which could be transported for very long distances with respect to the source areas.

Mayer-Oakes and Bell (1960) provided a first evidence for the use of obsidian in the equatorial Andes, at about 10,000 years BC. A review on the pattern of obsidian procurement in Prehispanic Ecuador (Burger et al., 1994) indicates that the greatest number of stone tools were made of obsidian throughout the Pre-Ceramic Period (10,000–3500 BC) as found in many archaeological sites as El Inga (Ilalò region) and at the headwaters of Rio Napo. According to Salazar (1992) the use of obsidian during the Formative Period (3500–500 BC) was initially restricted to the areas of outcrops in the Cordillera Real and then spread along the Pacific coasts. This material became increasingly abundant during the Regional Development Period (500 BC–500 AD) which can be considered the phase of maximum spread of the obsidian tools in Ecuador (Salazar, 1992) then continuing during the Integration Period (500–1500 AD).

The Plio-Quaternary Ecuadorian Volcanic Arc is mainly represented by the Western Cordillera, Cordillera Real (Eastern Cordillera) and subordinately by the back-arc area located in the Sub-Andean Zone (to the east of the Cordillera Real; Barberi et al., 1988). The main sources of obsidians, employed in pre-Columbian time as raw material for making tools, are represented by glassy silicic lava flows, volcanic breccias or blocks within pyroclastic deposits of the Cordillera Real. The best known obsidian sources are well described by Bigazzi et al. (1992, 2005) and Bellot-Gurlet et al. (2008) in the Sierra de Guamanì, east of Quito (Fig. 1) and are grouped by fission track datings (Bigazzi et al., 1992) in three

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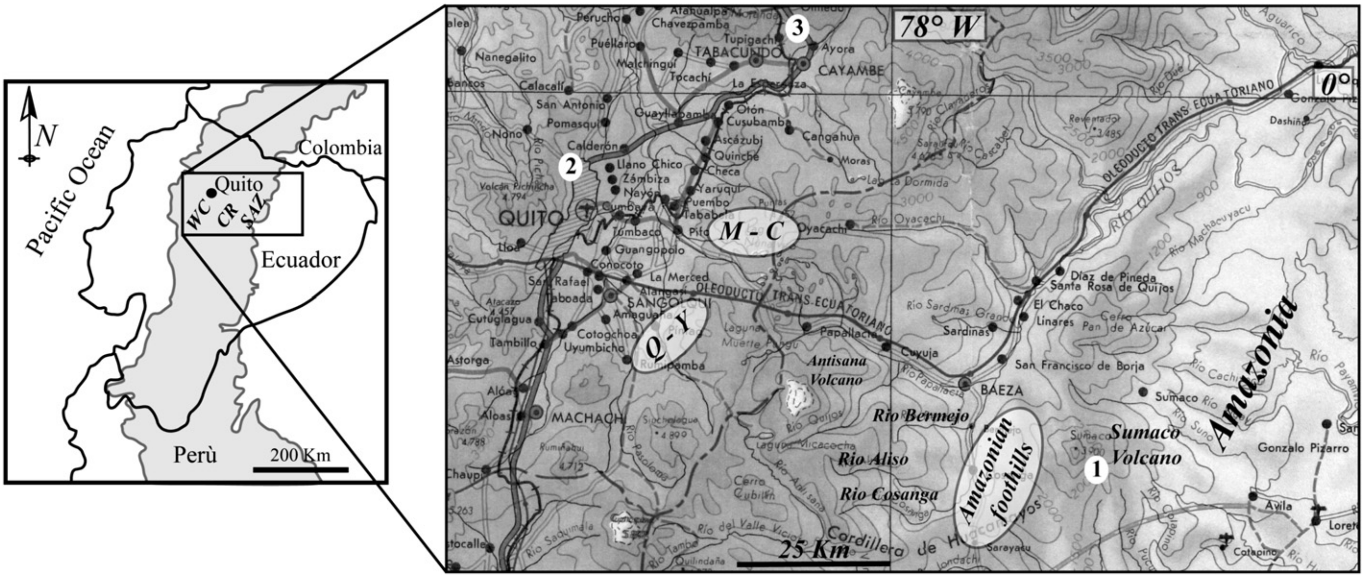

Fig. 1. Location of the archaeological sites of the obsidian artifacts: 1 = Sumaco volcano, 2 = La Florida – Quito, 3 = Milan – Cayambe. The two main obsidian sources of the Sierra de Guamanì (Quiscatola and Yanaurcu: Q–Y; Mullumica and Callejones: M–C) are also reported, as well as the Amazonian foothills (Sub-Andean Zone) where secondary obsidian outcrops (pebbles) were found by Bellot-Gurlet et al. (2008) along Rio Bermejo, Rio Aliso and Rio Cosanga. WC = Western Cordillera, CR = Cordillera Real and SAZ = Sub-Andean Zone are located in the inset, where the light grey area represent the Ecuadorian highlands (altitude > 500 m a.s.l.).

different periods: the oldest obsidians (1.7–1.4 Ma) cropping out at Yanaurcu, Quiscatola and Rodeo Corrales; those with intermediate age are present at El Tablon (0.85 Ma) and Yurac Paccha (0.4 Ma); the youngest (0.2 Ma) represented by the Mullumica and Callejones flows and those of Potrerillos volcano. Additional obsidian sources are represented by erratic pebbles of <10 cm diameter recently discovered along the course of some rivers (Fig. 1) of the Amazonian foothills (Bellot-Gurlet et al., 2008).

Although the presence of commercial trade of obsidian tools was already suggested by Saville (1910), only in the last two decades a useful archaeometric approach undoubtedly proved that the obsidian artifacts found in the archaeological sites of Ecuador, came from local quarries (Asaro et al., 1994; Salazar, 1992). The study of Salazar (1992) reported that the exploitation of Yanaurcu–Quiscatola sources began around 3477 ± 275 BC (corresponding to the Early Formative Period) and continued to 979 ± 59 AD (Integration Period); whereas for the Mullumica flow, the utilization began around the 2690 ± 250 BC (Early Formative Period) and continued until 1580 AD. Burger et al. (1994) indicate Yanaurcu–Quiscatola and Mullumica as the main sources of raw obsidian for most of Ecuador, on the basis of the numerous findings discovered in the Pacific coastal archaeological sites. In particular, the smoky transparent variety coming from Quiscatola flow was highly appreciated for its excellent knapping qualities. By contrast, the source area of Callejones does not appear to have been intensively exploited (Burger et al., 1994). Concerning other geologic outcrops of obsidian from Ecuador, some of them were not appropriate for the production of artifacts such as those of El Tablon flow which consists of a highly hydrated and perlitized obsidian (Bigazzi et al., 1992), and those of Potrerillos volcano which are poorly glassy and unsuitable for knapping (Asaro et al., 1994). Regarding the obsidians sources of the Amazonian foothills, they only consist of "secondary sources" being represented by pebbles discovered within some river banks (Rio Aliso, Rio Cosanga and Rio Bermejo; Fig. 1) near the Cosanga city (Bellot-Gurlet et al., 2008). Additional geological studies to unravel primary outcrops of these obsidian pebbles are therefore strongly needed.

In this work we are dealing with composition and provenance of obsidian waste flakes found in the already known Integration Period sites of La Florida (Quito) and Milan (Cayambe) and a pre-Columbian settlement found in the south-eastern flanks of the Sumaco volcano during a geological survey in the framework of a PhD thesis in volcanology and petrology (Puerini, 2009). Sumaco is an active back-arc volcano located in the Sub-Andean Zone of Ecuador and its location is just between the Cordillera Real and the Amazonian Region. Sumaco findings represent the easternmost obsidian waste flakes ever found in Ecuador.

2. Location of the archaeological sites and sample description

The studied samples derive from waste flakes (remaining after stone tool production) of three pre-Columbian Ecuadorian archaeological sites located faraway each other (Fig. 1).

The site located in the south-eastern flank of the Sumaco volcano, at 1788 m a.s.l., represents the first reported occurrence of obsidian artifacts in the Sub-Andean Zone (Fig. 1) to the east of the Cordillera Real. In this area, a possible ancient route (from west to the east), from Quito to Baeza, Sumaco volcano, Avila and Napo River, from the Western Cordillera to the rain forest passing through the Cordillera Real is reported in Cabodevilla (1998). In this framework Sumaco volcano may have been represented a very useful landmark between Andes and Amazonia. The archaeological site is constituted by a little settlement buried by the rain forest where the signs of an ancient inhabited area is now represented by the presence on the surface of scattered obsidian artifacts mixed with some chert and polished sandstone tools. Fragments of pottery and a cinerary urn were also discovered and left as they were.

Radiocarbon ^{14}C-AMS datings (Fig. 2) performed on a small charcoal sample coming from the soil (at 50 cm of depth) of the Sumaco settlement, fix between 1398 and 1451 AD (calibrated age $\pm 2\sigma$; Fig. 2) the time of this settlement (i.e. dating back to the end of the Integration Period).

The other two archaeological sites are in the Pichincha Region: La Florida (Quito) and Milan (Cayambe). The former is located on the edge of the modern Quito, in the area of the ancient city of "San Francisco de Quito" (Molestina-Zaldumbide, 1985), on the north-eastern slope of the Pichincha Volcanic Complex (Fig. 1). The

Sample	pMC*	t_{RC}*(years BP)	Calibrated Age (±1σ)	Calibrated Age (±2σ)
SMC 56-1	94.04 ± 0.37	494 ± 32	1415 - 1440 A.D. (68.2%)	1398 - 1451 A.D. (95.4%)

* pMC = % of modern carbon; t_{RC} = Conventional Age

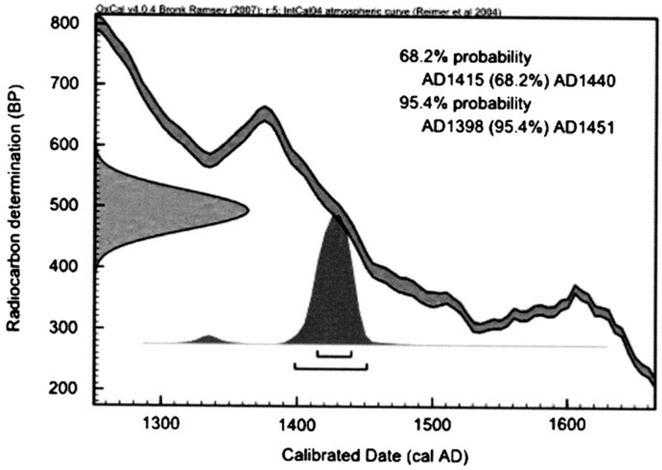

Fig. 2. Main data and computer plot of calibrated age for ^{14}C-AMS dating of the charcoal sample coming from the Sumaco volcano archaeological site.

settlement of La Florida (at about 3000 m a.s.l.) was inhabited since the Formative Period (Camino and Castillo, 1997) and was populated up to the final phase of the Integration Period (1505 AD; Doyon, 1989). At La Florida individual and multiple burial pits (“sepoltura en pozo”) with circular shape containing gold objects, ceramics, obsidians and other lithic fragments (chert, travertine, quartz and jasper), seashells of *Spondylus princeps* and pearls were discovered. From an archaeological point of view, La Florida is a very important site, because it represents the most ancient settlement referable to the “Cultura Negativo del Carchi o Capulì” (800–1500 AD) a phase included in the Integration Period (Molestina-Zaldumbide, 2006). In this period, the archaeologists suppose that important cultural and commercial influences started to spread from the Quito area to the northern and eastern regions.

The site of Milan, located to the north of the city of Cayambe (Fig. 1), is also referred to the “Cultura Negativo del Carchi” (Molestina-Zaldumbide, 1985). The archaeological area represents a typical rural Andean settlement characterized by the presence of “camellones” or “raised fields” consisting of numerous canals produced by ancient communities to mitigate damages on agriculture by the frost climate: around the Cayambe area some 5000 ha of “camellones” were detected. In these canals numerous burial pits are present, in general stratigraphically subsequent to the excavation of the “camellones”, and inside one of them, funerary objects as Inca ceramics and obsidian fragments were discovered (Molestina-Zaldumbide, 1985).

All the studied archaeological samples consist of few cm-long waste flakes, generally with a very sharp-edged rims and a maximum thickness of 2 cm (Fig. 3). The fragments coming from the site of Milan are very dark with grey lineations; whereas those from La Florida and Sumaco are transparent to smoky, with abundant dark lineations.

3. Analytical methods

INAA (Instrumental Neutron Activation Analyses) were performed at the Radiochemistry Laboratory of the University of Pavia, using the techniques described by Oddone et al. (1999). Used standards were: Obsidian Rock NIST-SRM 278 (National Bureau of Standard, 1981; Bowen et al., 1992), nitric solution of analyzed elements, high purity Al and Si (semiconductor grade). Irradiations, on 0.200–0.350 g of powdered sample, were performed at the Triga-Mark II reactor of Pavia; induced radioactivity was measured by γ-ray spectrometry using a Ge hyper-pure detector connected to a multichannel pulse height analyser and a personal computer. Data reduction was carried out using a software for spectral analysis. The determined elements are Na, K, Ca, Fe (%), and Sc, Cr, Ni, Co, Zn, Ga, Se, As, Br, Sr, Rb, Zr, Nb, Ag, Sb, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Hf, Ta, W, Th, U (ppm). Average precision is generally about 4%, except for Tb, Lu, Eu and Sb for which it ranges from 11% to 24%. Concerning the niobium it was separated from the rock matrix, in the presence of ^{95}Nb tracer, which was used to measure the fraction recovered, before irradiation to improve the sensitivity.

Mn concentrations were measured using a Perkin Elmer AAnalyst 300 atomic absorption spectrophotometer with flame atomization (FAAS) at the University of Urbino. Mn standard calibration solutions for AA Certipur® 1000 mg/l were from Merck (Germany). Lanthanum chloride 100 g/l buffer solution (Fluka) was used to suppress interferences. Recovery tests were performed with Standard Reference Material Obsidian Rock NIST-SRM 278 (USA). Milli-Q water (electrical resistivity >18.2 MΩ cm) was used for dilution reagent preparation and blanks. Samples were dried at 60 °C for 24 h and, after dry weighting, were mineralized by MDS 2100 (CEM, Italy), with a mixture of Nitric acid Suprapur® 65% (4 ml), Hydrofluoric acid Suprapur® 40% (7.5 ml), Hydrochloric acid Suprapur® 30% (1 ml), Boric acid Suprapur® 99.9999% (0.5 g) (Merck). The precision of Mn determination, based on variation in replicate analyses (2–3) on the same sample, was <5%. For each digestion cycle, one blank and one standard NIST were prepared to check all days of the sample preparation. The mean recovery was 81% ($n = 3$). Nitric acid Pro-Analysis 65% (Flukand) was used to clean glassware and vessels.

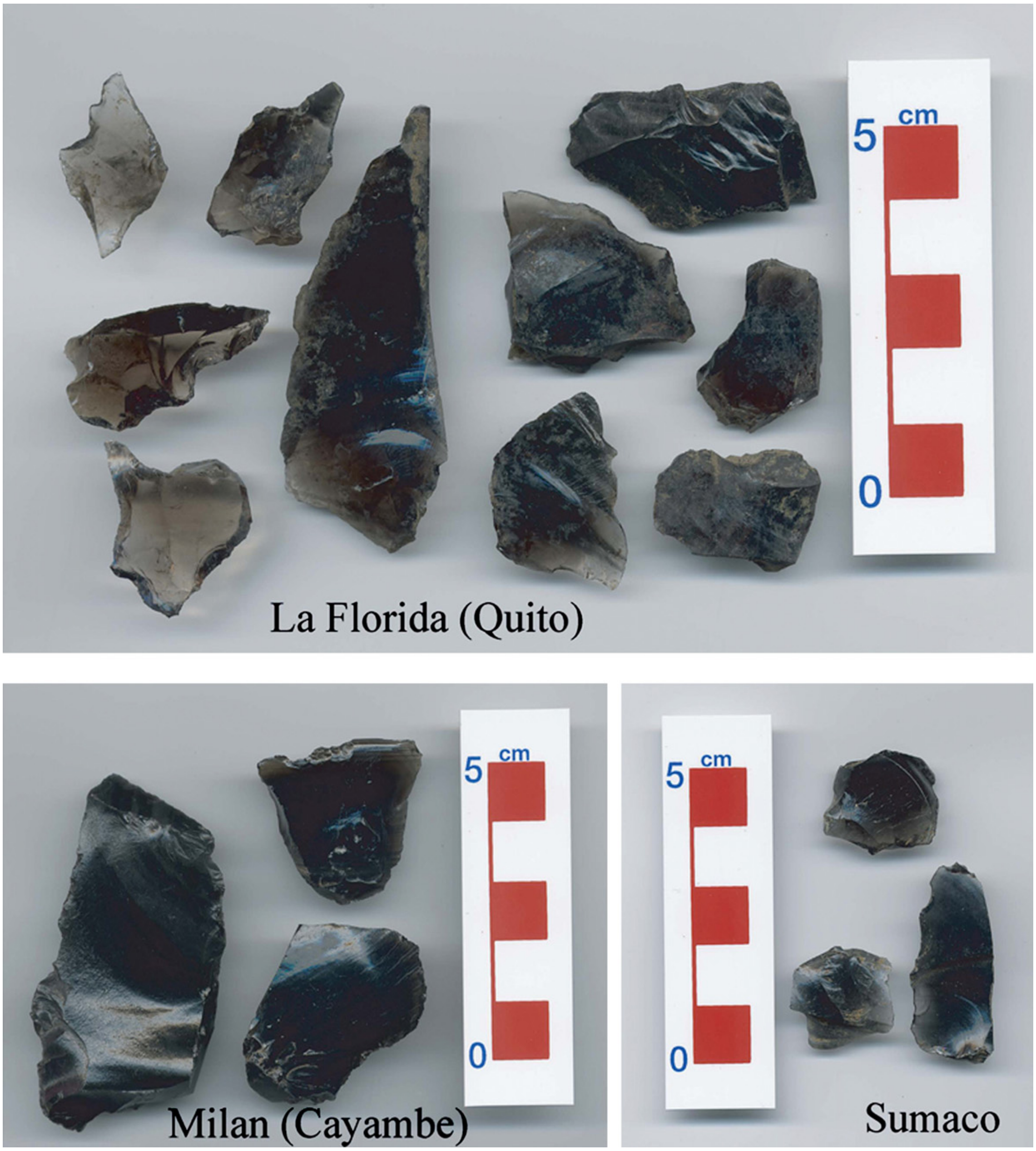

Fig. 3. Representative obsidian waste flakes coming from the studied archaeological sites.

^{14}C-AMS dating was performed at LABEC Laboratory (Florence) using an HVEE Tandetron (3 kV) accelerator on a charcoal sampled in the soil of the archaeological site of Sumaco. The carbon extraction was done by physical and chemical pre-treatment of the sample, followed by combustion and graphitisation. The radiocarbon age was determined using isotopic ratios $^{14}C/^{12}C$ and $^{13}C/^{12}C$ calculated after the mass spectrometry analyses by AMS.

4. Database of the Ecuadorian obsidian sources and artifacts

Chemical data of the Ecuadorian obsidians (sources and artifacts) all come from the Sierra de Guamanì area (Cordillera Real; Bigazzi et al., 1992, 2005; Salazar, 1992; Burger et al., 1994; Asaro et al., 1994; Dorighel et al., 1998; Bellot-Gurlet et al., 1999, 2008). They consist of a large number of obsidian samples analyzed through different methodologies: Instrumental Neutron Activation Analyses (INAA), X-Ray Fluorescence (XRF), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Flame Atomization Absorption Spectrophotometry (FAAS) and Particle Induced X-Ray Emission (PIXE). In this way, element abundances or element ratios of obsidians having the same provenance but analyzed through different techniques could significantly vary each other.

Recently, obsidians were extensively and successfully analyzed through the PIXE chemical technique (Dorighel et al., 1998; Bellot-Gurlet et al., 1999) because of high sensitivity, non-destructive character and easy implementation of this method. PIXE data coupled with Fission Track datings (Bellot-Gurlet et al., 1999, 2008) well constrained the major source groups in the Sierra de Guamanì area: Yanaurcu–Quiscatola and Mullumica–Callejones, from the oldest (1.4–1.7 Ma) to the youngest (<0.2 Ma), which can be considered the most exploited in the Prehispanic Period in the

Table 1

Na, K, Ca, Fe (%) and trace elements (ppm) of obsidian waste flakes determined by INAA analyses; Mn* (ppm) was determined by FAAS.

	Sumaco obsidian artifacts (SA)								La Florida obsidian artifacts (LFA)														Milan obsidian artifacts (MLA)							
Sample	**1**	σ	**2**	σ	**3**	σ	**4**	σ	**5**	σ	**6**	σ	**7**	σ	**8**	σ	**9**	σ	**10**	σ	**11**	σ	**12**	σ	**13**	σ	**14**	σ	**15**	σ
Na%	2.85	0.08	2.98	0.01	2.96	0.08	2.86	0.07	3.53	0.02	3.52	0.02	3.49	0.02	3.46	0.09	3.65	0.04	3.58	0.05	3.59	0.04	3.99	0.01	3.60	0.04	4.11	0.03	4.13	0.03
K%	3.25	0.07	3.27	0.02	3.27	0.03	3.29	0.03	4.67	0.04	4.91	0.05	4.39	0.03	4.36	0.07	4.02	0.02	4.03	0.03	4.36	0.03	4.75	0.06	2.48	0.02	4.37	0.07	4.28	0.07
Ca%	0.53	0.05	0.33	0.04	0.34	0.04	0.34	0.03	0.39	0.07	0.36	0.04	0.35	0.05	0.41	0.05	0.42	0.01	0.46	0.06	0.51	0.04	0.88	0.07	0.65	0.02	0.58	0.07	0.71	0.07
Fe%	0.54	0.04	0.54	0.09	0.59	0.07	0.51	0.03	0.44	0.01	0.38	0.06	0.37	0.09	0.38	0.06	0.39	0.06	0.38	0.02	0.36	0.07	0.88	0.08	0.86	0.02	1.02	0.02	0.77	0.02
ppm																														
Mn*	1432						1236		466		441										467				531		552			
Sc	1.49	0.05	2.64	0.03	2.57	0.04	2.50	0.03	1.51	0.05	1.34	0.02	1.60	0.03	1.74	0.03	1.66	0.03	1.65	0.02	1.57	0.02	1.36	0.01	1.25	0.03	1.39	0.02	1.24	0.04
Cr	2.23	0.02	3.86	0.03	3.67	0.05	3.89	0.07	2.37	0.05	2.35	0.02	2.43	0.08	2.25	0.03	2.36	0.02	2.27	0.03	2.20	0.03	3.13	0.08	2.13	0.07	3.30	0.06	1.86	0.02
Ni	3.37	0.05	3.32	0.04	3.37	0.09	3.36	0.05	2.16	0.03	2.17	0.03	2.24	0.04	2.15	0.09	2.17	0.04	2.13	0.06	2.27	0.08	11	0.03	13	0.07	12	0.03	11	0.08
Co	0.97	0.06	0.98	0.02	1.06	0.06	1.03	0.07	1.02	0.06	0.87	0.03	0.98	0.05	0.91	0.02	1.07	0.04	1.19	0.05	0.98	0.04	1.34	0.03	1.30	0.05	1.28	0.04	3.69	0.06
Zn	42	0.03	40	0.06	40	0.08	41	0.04	29	0.07	27	0.02	30	0.01	32	0.06	32	0.07	31	0.03	30	0.04	59	0.03	30	0.04	36	0.05	47	0.01
Ga	9.5	0.04	8.6	0.03	9.8	0.04	9.7	0.08	31	0.06	30	0.03	31	0.04	31	4.60	30	0.05	32	0.07	31	0.07	13	0.08	33	0.05	26	0.06	29	0.03
Se	3.19	0.07	3.16	0.03	3.18	0.03	3.16	0.05	4.87	0.07	4.87	0.02	4.66	0.03	4.90	0.09	5.02	0.03	5.02	0.03	4.65	0.04	1.85	0.06	3.48	0.07	3.42	0.03	6.11	0.03
As	4.85	0.02	4.75	0.09	4.80	0.05	4.72	0.08	11	0.04	14	0.04	14	0.04	14	0.06	12	0.03	12	0.07	9.9	0.06	2.17	0.02	4.20	0.09	5.09	0.02	3.67	0.04
Br	2.14	0.06	2.08	0.03	2.03	0.07	2.12	0.06	2.66	0.05	1.28	0.02	2.64	0.03	2.49	0.01	2.37	0.08	2.61	0.05	2.34	0.04	3.13	0.02	1.40	0.05	3.52	0.08	3.85	0.05
Sr	109	0.3	103	0.4	106	0.5	109	0.6	86	0.2	126	0.2	124	0.8	129	0.2	129	0.6	132	0.6	131	0.7	196	0.4	154	0.3	132	0.8	158	0.5
Rb	149	0.6	148	0.8	149	0.3	151	0.2	152	0.4	189	0.3	186	0.3	134	0.7	140	0.9	157	0.4	142	0.7	125	0.8	113	4.5	128	0.5	129	0.2
Zr	115	0.4	117	0.2	117	0.8	112	0.3	198	0.6	398	0.5	386	0.2	390	0.3	387	0.7	399	0.8	392	0.5	181	0.5	187	6.4	261	0.6	197	0.4
Nb	15.7	0.06	15.7	0.05	17.6	0.06	14.5	0.04	13.5	0.3	25.1	0.08	20.9	0.03	27.9	0.06	25.5	0.04	26.8	0.02	26.8	0.07	17.2	0.4	14.7	0.2	16.7	0.5	19.3	0.6
Ag	1.03	0.04	1.05	0.08	1.03	0.08	1.06	0.09	2.85	0.03	2.24	0.06	2.63	0.07	2.49	0.02	2.52	0.03	2.42	0.05	2.30	0.04	2.49	0.07	2.16	0.04	3.02	0.08	2.60	0.01
Sb	2.93	0.03	2.97	0.07	2.97	0.08	2.98	0.05	1.72	0.04	2.44	0.08	2.25	0.02	2.45	0.08	2.49	0.01	2.36	0.07	2.19	0.02	1.05	0.02	1.02	0.05	1.18	0.07	1.10	0.04
Ba	1045	0.7	1035	0.7	1035	0.5	1013	0.6	1230	0.3	1066	0.2	1177	0.1	1141	0.4	1215	0.9	1205	0.3	1234	0.9	1195	0.4	1072	0.7	1181	0.5	1383	0.8
Cs	4.96	0.02	5.14	0.04	5.13	0.02	5.02	0.01	9.31	0.06	10.19	0.06	9.67	0.04	9.94	0.04	9.18	0.09	9.64	0.02	9.95	0.08	5.08	0.02	4.49	0.04	4.72	0.06	4.81	0.08
La	10.9	0.05	10.4	0.05	10.6	0.04	10.5	0.02	36	0.02	35	0.08	36	0.05	36	0.09	36	0.01	37	0.05	40	0.08	46	0.04	44	0.06	43	0.05	45	0.06
Ce	43	0.03	42	0.06	43	0.07	43	0.04	43	0.03	42	0.04	43	0.05	42	0.08	43	0.08	42	0.03	42	0.02	45	0.06	44	0.05	43	0.02	46	0.08
Nd	12	0.09	13	0.04	12	0.05	12	0.03	24	0.06	24	0.07	23	0.05	23	0.05	23	0.01	24	0.04	23	0.03	23	0.07	23	0.04	22	0.03	20	0.06
Sm	2.97	0.05	3.02	0.03	3.10	0.06	3.07	0.08	3.71	0.05	3.65	0.01	3.71	0.06	3.90	0.05	3.76	0.07	3.70	0.08	3.69	0.05	4.10	0.01	4.08	0.08	3.88	0.02	3.58	0.05
Eu	0.68	0.03	0.69	0.05	0.70	0.02	0.69	0.01	0.49	0.01	0.50	0.04	0.47	0.05	0.48	0.07	0.47	0.02	0.46	0.03	0.47	0.02	0.47	0.04	0.47	0.01	0.49	0.01	0.46	0.08
Gd	4.18	0.03	4.19	0.06	4.23	0.02	4.15	0.06	3.94	0.09	3.90	0.06	4.15	0.04	4.14	0.05	4.11	0.04	4.10	0.07	4.11	0.02	5.44	0.06	5.16	0.07	4.88	0.03	4.69	0.02
Tb	0.59	0.06	0.58	0.07	0.58	0.04	0.59	0.07	0.61	0.03	0.59	0.09	0.59	0.03	0.62	0.03	0.60	0.03	0.61	0.06	0.60	0.07	0.83	0.05	0.82	0.03	0.80	0.09	0.82	0.02
Ho	0.92	0.07	0.91	0.02	0.88	0.02	0.90	0.05	0.90	0.07	0.89	0.05	0.91	0.04	0.90	0.03	0.87	0.09	0.90	0.05	0.90	0.04	1.23	0.07	1.21	0.05	1.13	0.04	1.22	0.07
Tm	0.32	0.04	0.31	0.03	0.31	0.03	0.30	0.03	0.34	0.07	0.33	0.05	0.33	0.02	0.33	0.02	0.33	0.08	0.32	0.06	0.32	0.01	0.44	0.05	0.43	0.02	0.40	0.02	0.40	0.06
Yb	2.08	0.02	2.06	0.01	1.97	0.02	1.95	0.08	2.13	0.03	2.11	0.03	2.16	0.01	2.18	0.04	2.21	0.05	2.12	0.03	2.16	0.03	2.62	0.03	2.50	0.09	2.32	0.08	2.24	0.08
Lu	0.28	0.01	0.29	0.03	0.28	0.03	0.28	0.05	0.29	0.03	0.29	0.06	0.29	0.01	0.30	0.02	0.30	0.03	0.30	0.03	0.28	0.02	0.33	0.04	0.32	0.04	0.32	0.05	0.33	0.03
Hf	3.51	0.03	3.00	0.06	3.46	0.08	3.44	0.07	2.70	0.05	3.70	0.07	3.28	0.09	3.00	0.02	3.58	0.07	3.56	0.02	3.41	0.02	4.41	0.05	3.49	0.06	3.78	0.03	4.29	0.03
Ta	3.46	0.07	1.36	0.03	1.50	0.04	1.52	0.09	1.66	0.04	1.61	0.02	1.58	0.01	3.23	3.02	3.48	0.05	3.49	0.05	3.49	0.05	1.72	0.06	1.21	0.04	2.55	0.05	3.11	0.02
W	1.31	0.03	1.35	0.07	1.27	0.44	1.27	0.04	1.33	0.04	1.44	0.08	1.27	0.05	1.33	0.05	1.26	0.08	1.29	0.02	1.32	0.07	1.32	0.03	1.01	0.04	1.04	0.03	1.07	0.02
Th	10.7	0.07	11.1	0.06	10.4	0.04	10.8	0.02	20	0.08	20	0.05	20	1.78	20	0.01	19	0.06	16	0.04	19	0.05	15	0.02	13	0.09	15	0.02	13	0.05
U	6.2	0.03	6.5	0.03	6.5	0.03	6.6	0.06	11	0.02	14	0.06	10	1.32	10	0.08	8.5	0.01	7.8	0.02	9.2	0.05	8.2	0.03	6.3	0.02	6.8	0.03	8.2	0.02
Nb/Zr	0.14		0.13		0.15		0.13		0.07		0.06		0.05		0.07		0.07		0.07		0.07		0.09		0.08		0.06		0.1	

northern region of Ecuador. Moreover, these authors highlighted the heterogeneous composition of Mullumica obsidians and the presence of obsidian artifacts with a "Mullumica-type" composition but showing ages comprised between 0.25 and 0.30 Ma. Very recently Bellot-Gurlet et al. (2008) revisited field occurrences, elemental compositions and formation ages of Ecuadorian obsidians. Numerous samples from known source areas were reconsidered and also new erratic pebbles, sampled along the Amazonian foothills rivers well to the south east of the Sierra de Guamanì (Mullumica–Callejones and Yanaurcu–Quiscatola; Fig. 1) were firstly analyzed by ICP-AES coupled by ICP-MS and PIXE. These analyses are of paramount importance in the framework of potential secondary source areas located eastwards with respect to the known (and unknown) major primary obsidian deposits.

5. Results and provenance

All the INNA (plus Mn by FAAS) analyses of the 15 obsidian fragments of Sumaco, La Florida and Milan sites are reported in Table 1. Comparison of the artifacts analysed by INAA in the present work with the literature chemical compositions of the Ecuadorian obsidian primary and secondary (erratic blocks) sources (Bigazzi et al., 1992; Asaro et al., 1994; Bellot-Gurlet et al., 1999, 2008) is a difficult task because of the lack of homogeneity of database

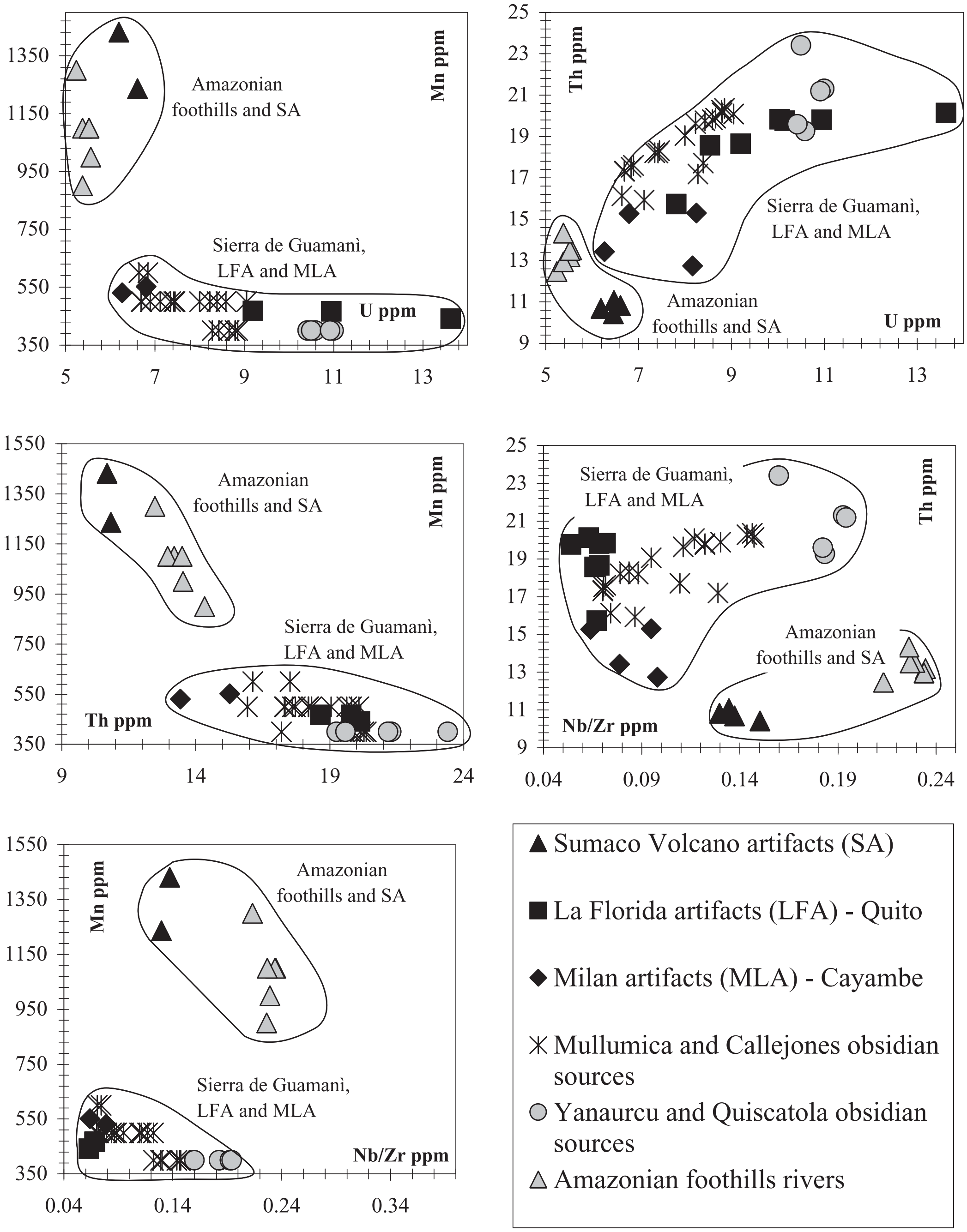

Fig. 4. Binary plots of Mn and Th *vs.* U; Mn *vs.* Th; Th and Mn *vs.* Nb/Zr for the analyzed archaeological samples (INAA) compared with literature data (ICP-MS, Bellot-Gurlet et al., 2008) of the main obsidian source areas of the Sierra de Guamanì (primary) and Amazonian foothills (secondary) outcrops.

(some elements of the obsidians are not available in literature) and different analytical techniques. In order to overcome this problem and increase the dataset with other methodologies than INAA, the samples of Sumaco, La Florida and Milan obsidian artifacts are available if requested to the first author.

5.1. La Florida and Milan

INAA major element analyses point out lower Na (3.5–3.7%), Ca (0.4–0.5%) and Fe (0.4%) contents of La Florida artifacts with respect those of Milan (Na 3.6–4.1%; Ca 0.6–0.9%; Fe 0.8–1.0%). K is between 4.0–4.9% for La Florida and 2.5–4.8% for Milan waste flakes. The above major element abundances are roughly within the compositional variation of the Sierra de Guamanì sources (e.g. Fe 0.4–1.0%; Bigazzi et al., 1992). Using some key-trace elements (Mn, U, Th and Nb/Zr ratios), the binary diagrams of Fig. 4 provide a good general provenance of La Florida and Milan artifacts from the Sierra de Guamanì sources. Also LREE (e.g. La 35–40 ppm, Ce 42–43 ppm for La Florida and La and Ce 43–46 ppm for Milan; Table 1) closely match the database (INAA) of Bigazzi et al. (1992). Sr content of La Florida and Milan obsidian artifacts (86–196 ppm; Table 1) are within the Sr range (PIXE analyses by Bellot-Gurlet et al., 1999 and ICP-MS by Bellot-Gurlet et al., 2008) of the Sierra de Guamanì sources, i.e. both Yanaurcu–Quiscatola (76–117 ppm) and Mullumica–Callejones (122–406 ppm). Mn contents of the studied obsidian waste flakes coming from La Florida and Milan sites also show values (441–552 ppm) comparable (Bellot-Gurlet et al., 1999, 2008) with those of the Yanaurcu–Quiscatola (328–400 ppm) and Mullumica–Callejones (344–600 ppm).

5.2. Sumaco

INAA major elements of Sumaco obsidian artifacts show lower Na (2.9–3.0%), K (3.3%) and Ca (0.3–0.5%) with respect La Florida and Milan samples. Fe is 0.5–0.6%. The Sumaco obsidian artifacts are characterized by very high values of Mn (1236 and 1432 ppm), with respect all the other findings and this element abundance strongly support a provenance compatibility with the samples coming from the obsidian erratic pebbles recently discovered along the Aliso, Bermejo and Cosanga Rivers (Amazonian foothills) which are all Mn-rich (between 900 and 1300 ppm; Bellot-Gurlet et al., 2008). It is worth to note that, among the Ecuadorian database, only the secondary source obsidians from the Amazonian foothills are characterized by such high Mn values. Differences in Mn contents among the Ecuadorian obsidian outcrops could be considered an example of intrasource differentiation as in the case considered by Glascock et al. (1999) where some obsidian sources (New Mexico) located very close each other, show Mn from 588 ± 12 ppm to 1200 ± 30 ppm. LRRE and Sr of the Sumaco artifacts (La 10–11 ppm, Ce 42–43 ppm; Sr 103–109 ppm; Table 1) are also comprised within the compositional variation of the Amazonian foothills secondary sources (La 7–25 ppm; Ce 17–47 ppm; Sr 86–186 ppm; Bellot-Gurlet et al., 2008). Other abundances of key-trace elements, such as low Th, U and relatively high Nb/Zr ratios confirm a good geochemical correspondence between the Sumaco artifacts and the obsidian pebbles of the Amazonian foothills (Fig. 4).

6. Discussion and final remarks

Obsidian ancient trade was well established in Ecuador among the Andean people of the Cordillera Real and between them and people of the Pacific coast, whereas an eastward trade toward the sub-Andean and Amazonian people was never documented. The westward trade is in fact testified by several specimens of *Spondylus* shells found in the highlands, representing the item counterpart of obsidian artifacts in the past commercial exchanges (Salazar, 1992). The studied obsidian artifacts from La Florida and Milan indicate a provenance from the Sierra de Guamanì, thus confirming an obsidian trade between the inhabitants of the Andean Cordilleras. The archaeometric study of the obsidian artifacts from the Sumaco settlement, located well eastward of the Cordillera Real, is instead of paramount importance in tracing pre-Columbian routes of the obsidian trade and movement of people from and to the Amazonian region. The ^{14}C-AMS radiocarbon age of the charcoal included in the soil of the archaeological site of Sumaco volcano, dates back the

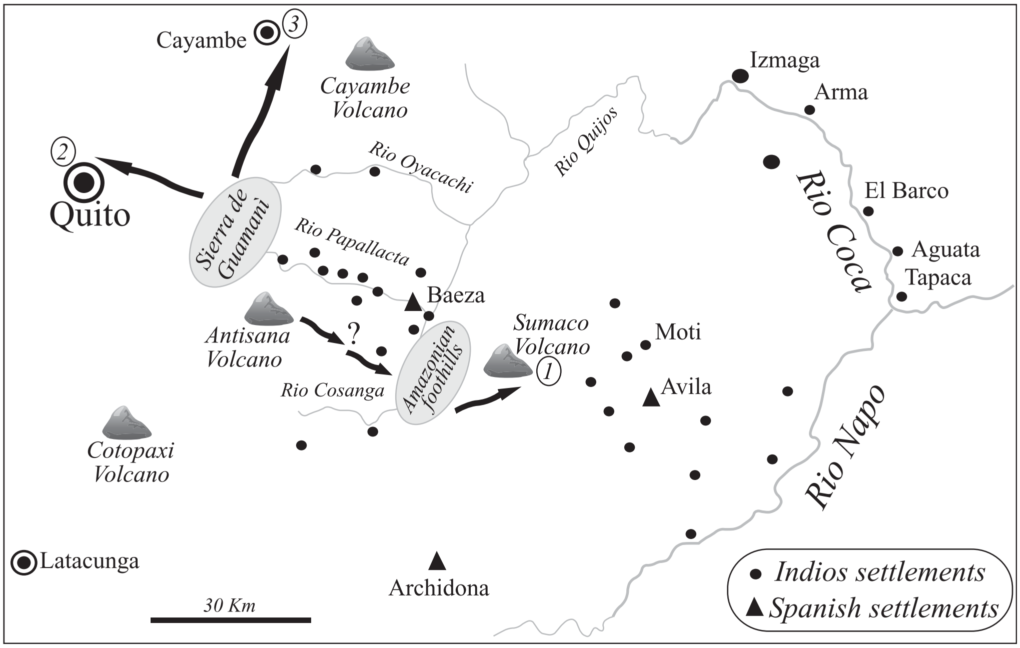

Fig. 5. Geographic-historical map (from Cabodevilla, 1998; modified) showing pre-Columbian obsidian trade (arrows) according to the artifacts studied in the present work.

settlement at 1425 ± 26 AD corresponding to the end of the Integration Period. Sumaco artifacts seem to be geochemically compatible with secondary sources represented by obsidian pebbles recently found by Bellot-Gurlet et al. (2008) in some rivers of the Amazonian foothills (Sub-Andean Zone). This preliminary inference would need to be confirmed with geochemical comparison of source and artifacts samples made with the same analytical technique. In addition, new prospecting and mapping of obsidian sources would strongly need as well as a better evaluation of the secondary obsidian sources, in the framework of procurement strategies in ancient time. The secondary sources discovered in the river banks of the Amazonian foothills could really represent the most likely potential obsidian sources for an eastern commercial trade (toward the Amazonia). The obsidian findings discovered in the Sumaco archaeological settlement seem to support the hypothesis reported by Bellot-Gurlet et al. (2008) which considered their new discovery of obsidian secondary sources in the Amazonian foothills an important landmark in tracing ancient men procurement strategies. Nevertheless, primary outcrops linked to these pebbles have to exist and the eastern flanks of the Antisana volcano are the best candidates. It is worth to note that a pioneer petrographic work of Vom Rath (1875) cited the presence of obsidianaceous rocks at the Antisana volcano.

During the Spanish invasion, different routes from the Andes to the Sub-Andean Zone and the Amazonia were discovered. Among them, the itinerary which joined Quito–Baeza–Sumaco–Avila and Napo River (Cabodevilla, 1998) could have well represented an eastern obsidian trade (both from primary or secondary sources) toward the Amazonian region (Fig. 5).

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