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The first archaeometric characterization of obsidian artifacts from the archaeological site of Samshvilde (South Georgia, Caucasus)

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Abstract
This paper presents the first results about the provenance of obsidian fragments recovered in the archaeological site of Samshvilde (South Georgia, Caucasus) with the aim to obtain knowledge related to the network distribution and procurement of obsidian in Georgia. The geochemical characterization of thirty archaeological finds was obtained by the LA-ICP-MS method, an almost non-destructive technique capable of chemically characterizing the volcanic glass. A comparison of geochemical results obtained on both archaeological artefacts and geological samples collected from Chikiani outcrop in Georgia, together with literature data of southern Caucasus and eastern Turkey, allowed us to define the source of the archaeological obsidians of Samshvilde site. The majority of archaeological samples (28/30) shows a local provenance, precisely from Chikiani (Georgia) on the contrary the other two samples suggest a provenance from two different Armenian sources respectively Gegham and Akhurian volcanic system.

Keywords Obsidian · Trace elements · LA-ICP-MS · Samshvilde · Georgia

Introduction and archaeological background

Samshvilde is an archaeological complex situated in Kvemo Kartli province, in the southern-central part of Georgia. It occupies a long basalt cape that rises above the confluence of two important rivers—the Khrami and Chivchava (Fig. 1). The medieval city covered the entire length of the cape, and its layout was arranged according to the occupations and status of the population: the western part of the city, which may has been the residential area of the lower classes, was separated from the central part where nobles resided by a 4 m high and 2.5 m wide stone wall. The central district was separated from the easternmost part of the city, where high-status structures were located, by a 12 m high and 7 m wide fortification wall, forming a citadel. Such heavily fortified well-preserved defensive systems are characterized only for most important sites in the southern Caucasus.

Georgian historic tradition associates the foundation of Samshvilde with the Hellenistic period, while current archaeological project has detected proof of occupation dating back to the Neolithic times. Anyway, it is recognized that Samshvilde was founded as an urban political-economic center only in the early medieval period, in particular, during the fifth–sixth centuries (Sanadze 2016).

As the Arabs appeared in Transcaucasia during the mid-eighth century, a substantial part of eastern Georgia, including Samshvilde, was placed under the jurisdiction of the Arab Emir. This arrangement continued until the mid-ninth century when the region fell under influence of the Armenian royal Bagratuni dynasty of Shirak. In the tenth century, Samshvilde was the capital of the Armenian Kingdom of Tashir-Dzoraget, which was a vassal of the Kingdom of Ani. From the second half of the eleventh century Samshvilde was under the influence of Seljuk Turks, and this continued until 1110, when it was liberated by King of Georgia - David IV (the Builder) and placed under the jurisdiction of the Georgian State.

Various Georgian feudal families controlled Samshvilde in the late medieval and post-medieval period. First, the

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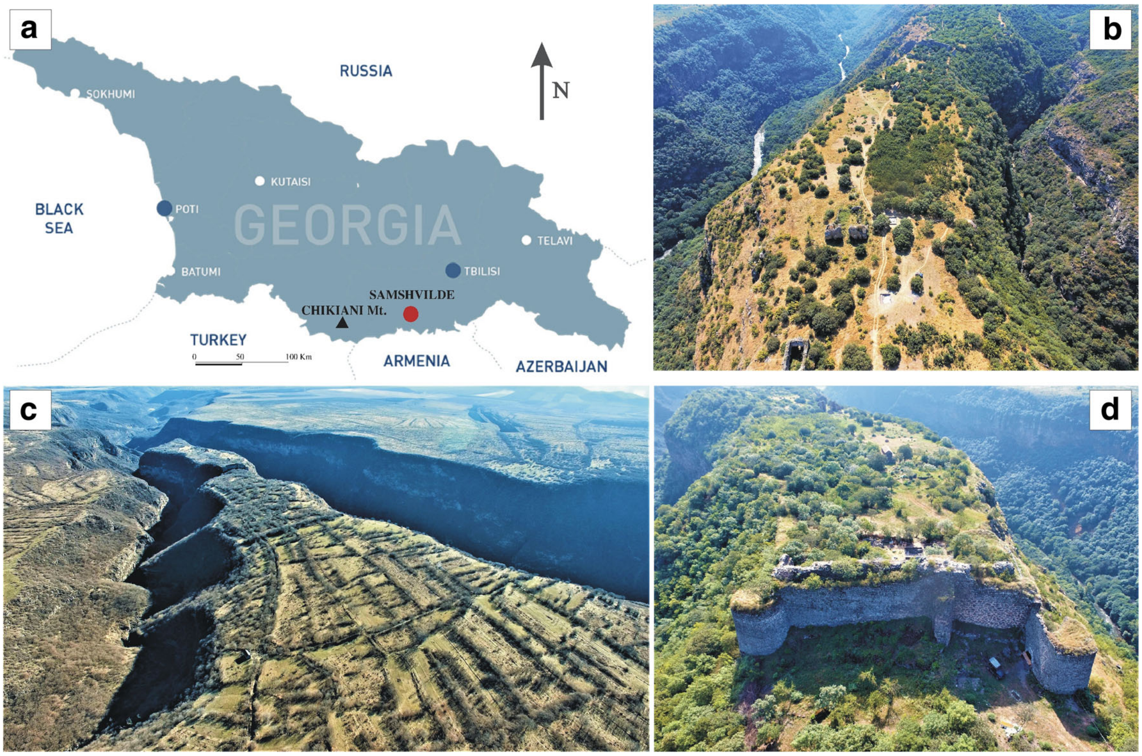

Fig. 1 **a** Georgia schematic map with indication of the archaeological site of Samshvilde (red circle). **b**–**d** panoramic view of the site

influence of the Orbeli family was dominant and later the Baratashvili-Kaplanishvili, whose tenure continued up to the seventh–eighteenth centuries. In the second half of the eighteenth century, the ethnic situation in Samshvilde and Kvemo Kartli in general changed significantly. From the beginning of the nineteenth century, Turkish-speaking populations, Germans (1818) and Greeks (1829) were settled in this region by the Russian Imperial government.

Samshvilde is a complex and multicultural archaeological site. It is perhaps surprising, therefore, that this site has never before been the subject of a full-scale archaeological and interdisciplinary investigation. Only small-scale fieldwork was carried out during the Soviet and post-Soviet period which did not provide details on the site's stratigraphy and chronology or on the distribution of cultural features and monuments.

The Samshvilde Archaeological Expedition of the University of Georgia, which has so far conducted six seasons of fieldwork from 2013 to 2018, is working to redress this situation. By adopting a variety of approaches to the archaeological remains at Samshvilde and its surroundings, new information on this multi-period complex could be attained. Such comprehensive surveys, involving archaeology, geophysics, anthropology, palynology, remote sensing, osteology, and archaeometry are now being conducted in Samshvilde (Berikashvili 2017). In particular, excavations have been carried out at two locations of the site. The first is inside the main fortification wall of the city, namely within the citadel (Fig. 2); the other is near the eighth century Sioni Church.

Excavations of 6 archaeological trenches (5 × 5 m each, no. 59, no. 60, no. 66, no. 67, no. 68, no. 69) at the citadel have so far unearthed archaeological deposits of 1.3 m depth belonging to the high-late medieval centuries (eleventh–thirteenth centuries). The archaeological deposits of this period overlap Islamic and pre-Islamic archaeological contexts, but on the other hand, they also are overlapped by the deposits of Ottoman periods. The archaeological finds fully correspond the mentioned historical periods and give a clear understanding for the stratigraphy of the site. It is noteworthy, that in 2018 an archaeological context (trench no. 68, Context 21) representing pit-burials have been explored under the mentioned historical deposits. According to the black polished fragments of pottery decorated with various geometric motifs, the date of the burial is defined as Late Bronze-Early Iron Age and goes back to the thirteenth–twelfth centuries B.C.

This type of pottery is well known for Late Bronze-Early Iron age sites of Eastern Georgia, such as Tskhinvalis Natsargora, Satsikhuris Gora, Treligorebi, Dmanisi, Tsiteli Gora, and Madnischalis Cemetery. The discovery of the burial of this period in Samshvilde has a big scientific value, as it is first time in the history of the site.

Artefacts from the citadel trenches are diverse and include numismatic hoard (eleventh–thirteenth centuries A.D.) consisting of 285 copper and bronze coins, ceramics, stone, glass, and bone items that date from the high and later medieval centuries, as well as the pottery of Late Bronze Age–Early Iron Age.

Fig. 2 **a**, **b** Excavations inside the main fortification wall of the city. **c** Image of the pits in the basalt bedrock inside the trenches N8-O7 where the Neolithic artifacts originate

Excavations at the Sioni section, where two trenches have been opened, have already produced important results. Remnants of a stone mortar structure and graves of the later medieval centuries were discovered to the north of the eighth century church. It is noteworthy that the thickness of archaeological deposits, at 1 m, is lower here compared to the citadel. The date of this layer is assigned to the tenth–eighth centuries on the basis of finds. An initial interpretation of the graves is that they are later and belong to Samshvildian citizens murdered during the invasion of the Turkmen leader, King of Tabriz–Jahan Shah in the fifteenth century. Regarding to this, the valuable information is given in the Armenian Chronicles of Thomas Metsoph: "...After a long-term siege Samshvilde was seized by the Turkmen Shah Jahan on the Easter day in 1440 and he punished the local population severely: "… The entire city of Samshvilde was sieged and on the day before Pentecost (Greek. Holiday of descent of the Holy Spirit) Samshvilde was seized by deceit and threats, a minaret was made from heads of 1664 people at the gate of the city and in addition to those who were captured in forests and thickets, another 9400 people were captivated … sixty people and holy souls – priests, clergymen, monks – were slaughtered like sheep at the gate of the city, the head of some of them was chopped into four parts, the head of others was smashed and some of them were forced to give up their confession and were killed…." (Thomas of Metsoph 1987).

Important results were gained from the test trenches on the same area, where obsidian and flint tools were discovered. Forms include scrapers, burins, points, arrowheads, and notched sickle blades, attributed to the final stage of the Caucasian Neolithic and chronologically placed within the Tsopa culture of Kvemo Kartli (8–6 millennia B.C.) (Berikashvili and Grigolia 2018).

The discovery of Neolithic tools in the site is a significant novelty and raises the prospect of identifying more extensive prehistoric deposits here. The oldest artefacts come from the lowest stratigraphic contexts and are composed of opaque and semi-transparent black obsidian, flint, and argillite tools. The major part of this assemblage is composed of short, wide flakes fragments of different shape. Different forms of scrapers are well preserved in this complex: end scrapers, side scrapers, and thumbnail scrapers being the most common. Micronuclei, drills, cutting tools, arrowheads, and various lamellas are also represented here (Fig. 3). The end-retouched scraper is represented by eight pieces in Samshvilde complex. All of them are formed on rough fragments and flakes and the retouched work section of each of them is arranged at the end of the tool. Only two tools have the typical form common for the end-retouched scraper. One of them is processed on a lamella-like flake whose end part is processed by coarse retouch and belongs to the category of tools with grooved. One more tool processed on an average-size flake whose one side is grooved by a steep retouch may be attributed to the same category. Among scraper tools included in the collection, depending on the processing of the blade, one is straight-bladed, three have curved blades and two may be considered as tools with indirectly retouched blades. The two latter tools are processed on a depleted nucleus and a nucleus-like flake whose

Fig. 3 Some representative samples of obsidian shards

massive blow plane is additionally flaked. The discovery of a sample resembling a pencil-form nucleus included in the complex is particularly noteworthy. Its head and end are sharpened, and probably it was used for perforating similar to a drill-like tool. Four drill-like perforating tools are discovered in Samshvilde. Among them, two drilling crests from the lower plane of the flake are processed by coarse retouch. The remaining two tools represent smaller flakes that have a

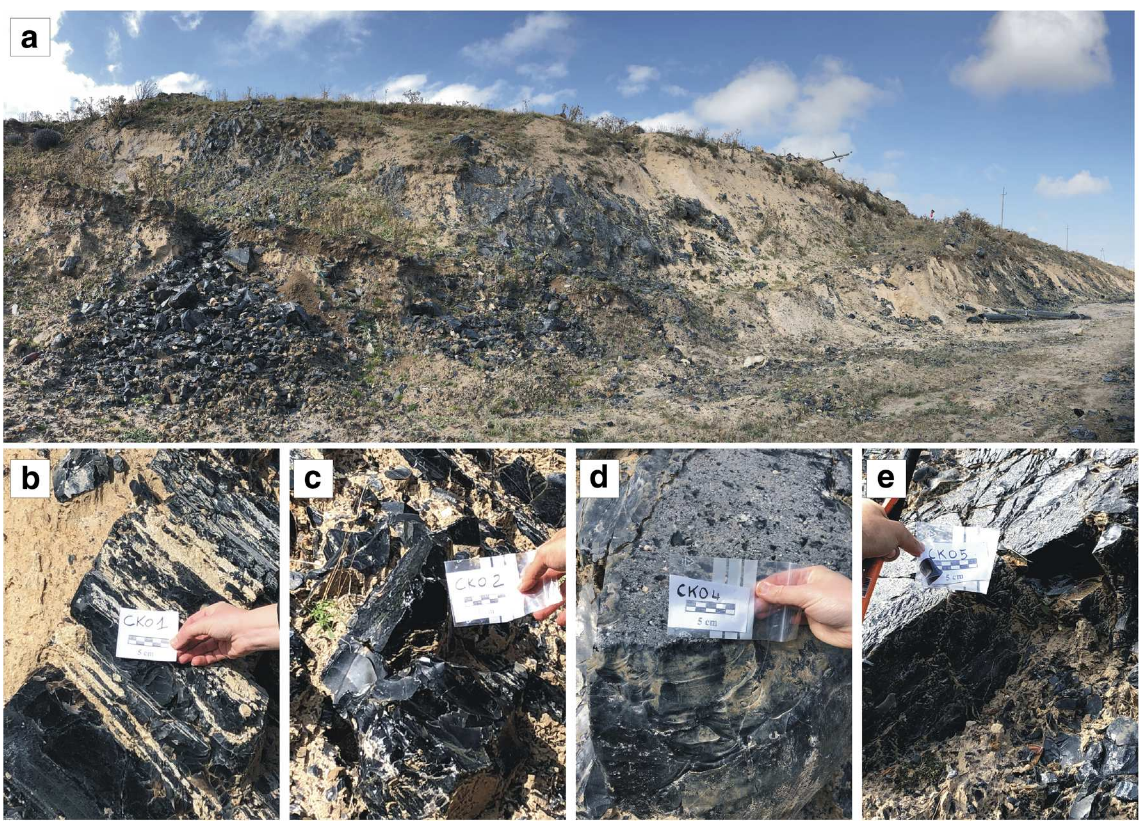

Fig. 4 **a** Chikiani obsidians outcropping. **b**–**d** Examples of obsidian sampling points

perforating crest processed by a fine retouch. Labor tools in the form of cutters are represented by three pieces in the complex. Two of them are simple cutters. One of them, in addition to the cutting flakes, has one longitudinal side and the end opposite the cutting facet blunted by a steep retouch. Another noteworthy item among Samshvilde materials is a two-side flint lamella with four cogs executed by a steep retouch on one of its longitudinal sides. This tool is basically processed from the back, and on the lower plane, the retouch is used only for the purpose of designing of sickle cogs. In addition, one of the lateral sides of lamella is designed by a fine retouch from the lower plane, suggesting that the tools must have been used placed in a wooden or bone casing, when retouching of the lateral side should serve a better use of the second similar tools placed in the handle. Cogged sickle blades appear since the inception of manufacturing industry and represent a typical tool for all monuments of the Neolithic period. One more original item found in Samshvilde complex is a two-side, knife-like obsidian lamella of rectangular form whose one side is entirely and the other side is partially processed by a creeping retouch. It is known that such tools are considered as sickle insertions for monuments of the so-called Shulaveri-Shomutepe culture. One more interesting argillite tool is included in Samshvilde complex. It is based on a two-side rectangular lamella with a broken head and a crest resembling a bird's beak is created in the end, in the angle of a specially thinned side. The retouched side of the tool with a crest has an illuminating reflection created as a result of use, suggesting that this tool must also represent an insertion of the blade of the tool to be used for reaping as a sickle. Such tools with a crest which were called "hook-shaped" due to the well-developed beaklike crest are wide spread in the Neolithic era and we consider them to be types of tools common for the so-called Mountain Neolithic culture (Grigolia 1977). Among the separate artifacts of Samshvilde, obsidian spear blade or spear blade-like tools are particularly noteworthy. It is formed on a wide lamella-like flake of an equilateral triangular form. Tools similar to Samshvilde spear blade are presented in large amount in Tsopa former settlement complex (Nebieridze 2010. 53. tab. VI 1-4), and the chronological and cultural proximity of these monuments is noteworthy. The arrowhead designed on a thin, transparent obsidian flake discovered in Samshvilde whose lower angles are rounded and the tool has acquired a heart shape seems to point to the stage and cultural proximity to Tsopa former settlement. Both sides of the arrowhead are processed by thin flakes directed to the center by blows from the edges. Unfortunately, the point part of its top is broken, but anyway, it resembles the straight stem arrowheads discovered on Beiuk Kerik former settlement of Eneolithic period in Azerbaijan.

The most significant among Samshvilde Neolithic materials are flint and argillite sickle blades, found in the so-called midden pits cut in the basalt bedrock. It is assumed that such tools must have been used in agricultural activities such as harvesting. Even though the Neolithic tools from Samshvilde did not come from intact archaeological strata, but rather derive from disturbed ones and from the pits in the basalt bedrock (Fig. 2c), the authors are confident that, because of the very specific location of the site, and the similar materials discovered in surrounding areas, the context of origin, or the location of the former Neolithic settlement, is located nearby. Thus, small but noteworthy material in the form of obsidian Neolithic production from the territory of Samshvilde city-site has a valuable scientific value. By peculiarities of the primary and secondary processing, Samshvilde material closely resembles Eastern Transcaucasia monuments dated by Neolithic period, such as Jermukhi, Selo, Nagutni I and II (Kalandadze and Tsereteli 1971; VV.AA 1991; Liubin 1966) and Delisi former settlement (Abramishvili 1978). At the same time, in terms of chronology too, this material resembles the material of Sioni former settlement discovered in Kvemo Kartli (East Georgia), which dates back to the Late Neolithic period. Discussing the above material of Samshvilde and chronological issues, particularly interesting is Tsopa former settlement located in East Georgia, which also dates back to the late Neolith (Nebieridze 2010). Undoubtedly, Samshvilde is a site belonging to Tsopa-Sioni culture which points to existence of a former settlement of the Late Neolith and Eneolith period (seventh–sixth millenniums B.C.) on the territory of the medieval city-site Samshvilde at the confluence of Khrami and Chivchava. It has already been mentioned that Samshvilde stone material derives from the disturbed cultural layer whose tools bear no trace of rolling and displacement. This makes us think that the main stratum of origin of this material, i.e., central section of Neolithic former settlement must be located on the territory of the promontory.

The next archaeological stage in Samshvilde is the Bronze Age. The excavations in the years 2016–2017 revealed a large amount of the pottery fragments characteristic for the Middle and Late Bronze periods in Georgia. The last phase is the Medieval period, whose archaeological contexts are best preserved on the site. The complex fortification system, religious and civil buildings, the hydrological net, and organized urban parts are the witnesses of the city's active life. Excavations inside the citadel walls revealed artifacts from the ten–fourteenth centuries, representing various types of locally made and imported pottery, stone tools, and glass items. The Sioni section yielded a rich collection of metal artifacts, including arrowheads, knives, and needles. The most notable item of the medieval artifacts is the numismatic horde discovered in 2018 containing more than 280 local and imported copper and bronze coins.

In 2018, the joined project of the University of Calabria and the University of Georgia started with the main goal to investigate the provenance of Samshvilde obsidian archaeological finds (obsidians tools), comparing them with the geological obsidian sources in the area.

The geological outcrop of obsidian sources

Georgia country is dominated by the Caucasus Mountains at the junction of the Eurasian Plate and the Afro-Arabian Plate, and rock units from the Mesozoic and Cenozoic are particularly prevalent (Adamia et al. 2011). The nearest obsidian outcrop for Samshvilde is the place called Chikian ("Chika" in Georgian language means glass, Chikiani means the place with plenty of glass) from which the field survey has started. Located about 85 km west-southwest of Tbilisi and northeast of the Paravani lake (2081 m asl), the Chikiani volcano reaches 2.417 m (Fig. 4).

This lava flow belongs to an eruptive phase dated 2.8 Ma (Blackman et al. 1998; Badalyan et al. 2004; Lebedev et al. 2008; Le Bourdonnec et al. 2012; Nomade et al. 2016). The quality of the obsidian is very good, i.e., black homogeneous obsidian, which can also turn into brown, red, or green variants. The black variety is usually translucent with no visible spherulites to the naked eyes. There are numerous obsidian boulders on the dome slopes, which are then broken down into

Table 1 List of the investigated samples and details about sampling location

Sample code	Typology	Sampling location	Stratigraphic level/unit
Artifact no. 17	Archaeological sample	Samshvilde	Trench-N8. Context-1
Artifact no. 135	Archaeological sample	Samshvilde	Trench-N8. Context-19.
Artifact no. 160	Archaeological sample	Samshvilde	Trench-N8. Context-13.
Artifact no. 162	Archaeological sample	Samshvilde	Trench-N8. Context-13.
Artifact no. 195	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 206	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 237	Archaeological sample	Samshvilde	Trench-O17. Context-1.
Artifact no. 269	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 278	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 302	Archaeological sample	Samshvilde	Trench-N8 Context-1.
Artifact no. 395	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 401	Archaeological sample	Samshvilde	Trench- N8. Context-1.
Artifact no. 429	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 434	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 436	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 479	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 481	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 483	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 484	Archaeological sample	Samshvilde	Trench-N8. Context-1
Artifact no. 485	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 493	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 494	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 496	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 519	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 571	Archaeological sample	Samshvilde	Trench-N8. Context-1.
Artifact no. 573	Archaeological sample	Samshvilde	Trench-N8. Context-19.
Artifact no. 575	Archaeological sample	Samshvilde	Trench-N8. Context-19.
Artifact no. 576	Archaeological sample	Samshvilde	Trench-N8. Context-19.
Artifact no. 580	Archaeological sample	Samshvilde	Trench-N8. Context-19.
Artifact no. 592	Archaeological sample	Samshvilde	Trench-N8. Context-19.
CK-1	Geological sample	Chikiani Mount	41° 29′ 50.28″ N
CK-2	Geological sample		43° 52′ 21.81″ E
CK-3	Geological sample		
CK-4	Geological sample		
CK-5	Geological sample		
CK-6	Geological sample		

pebbles that are carried downslope and downstream by the Paravani River to the Krami River (near Samshvilde site) which constitutes the main secondary sources (Biagi and Gratuze 2016). At Chikiani Mount (41° 29′ 50.28″ N–43° 52′ 21.81″ E, geographical coordinates have been collected by the authors during the sampling campaign by means of a portable Garmin GPS Gpsmap® 64s), obsidian is abundant and easy to access. The only limit to exploitation being the thick snow cover that lasts more than 6 months. In order to characterize this lava flow, which can be laterally followed for about 300 m, six samples have been collected from easily accessible points with an interval of about 50 m.

Samples and analytical methods

Geochemical analyses of archaeological finds and geological samples (Table 1) were carried out at the Department of Biology, Ecology and Earth Sciences, University of Calabria, Italy, using the scanning electron microscope equipped with an EDS system (EDAX GENESIS 4000) to determine the major element composition and the LA-ICP-MS for the trace element composition. The LA-ICP-MS equipment was an Elan DRCe (Perkin Elmer/SCIEX), connected to a New Wave UP213 solid-state Nd-YAG laser probe (213 nm). Samples were ablated by laser beam in a cell, and the vaporized material was then flushed (Gunther and Heinrich 1999) to the ICP, where it was quantified. Each ablation crater was generally 50 μm in diameter and nearly invisible to the naked eye. The procedures for data acquisition were those normally used in the Mass Spectroscopy Laboratory of the Department of Earth Sciences, University of Calabria (Barca et al. 2007, 2008, 2012).

Only two-point analyses were carried out on portions of archaeological fragments without roughness or alterations, and were sufficient to assign provenance. In order to remove any trace of soil, each find was cleaned by ultrasound in Millipore water. Calibration was performed on glass reference material SRM612–50 ppm by NIST (National Institute of Standards and Technology) in conjunction with internal standardization, applying SiO_2 concentrations (Fryer et al. 1995) from SEM-EDS analyses. In order to evaluate possible errors within each analytical sequence, determinations were also made on the SRM610–500 ppm by NIST and on BCR 2G by USGS glass reference materials as unknown samples, and element concentrations were compared with reference values from the literature (Pearce et al. 1997; Gao et al. 2002). Accuracy, as the relative difference from reference values, was always better than 10%, and most elements are plotted in the range ± 5%.

Results and discussion

Chemical analyses of major oxides were reported in the TAS diagram (Fig. 5, after Le Maitre et al. 2002). As shown, chemical compositions of geological obsidian samples show a homogeneous distribution; all the samples fall into the rhyolite field, with a relatively evident enrichment in alkalis and a constant SiO_2 level, confirming the provenance from trachyrhyolitic dome reported in literature data (Blackman et al. 1998; Badalyan et al. 2004).

Table 2 lists the composition of trace and rare earth elements, determined by LA-ICP-MS, both for the geological samples and archaeological finds; each trace element quantity, in the table, represents the mean value of two/three analyses.

The main potential sources for archaeological obsidians found in Georgia can be traced to different volcanic systems: obsidian from the near sources of Paravani (Chikiani) in Georgia and from the Armenian and Caucasian obsidians erupted in a collisional tectonic setting (Keller et al. 1996).

After the pioneering work of Keller et al. (1996), the knowledge about geological sources of obsidian of the Armenian and Caucasian areas has undergone significant development (Blackman et al. 1998; Le Bourdonnec et al. 2012; Chataigner and Gratuze 2014).

The study of Keller et al. (1996) provided a detailed reconstruction of the volcanological history of the Armenian and Caucasian region together with geochemical characterization of the major obsidian sources. After, many authors (Blackman et al. 1998; Le Bourdonnec et al. 2012; Chataigner and Gratuze 2014; Nomade et al. 2016) performed a chemical characterization of the different obsidian sources using

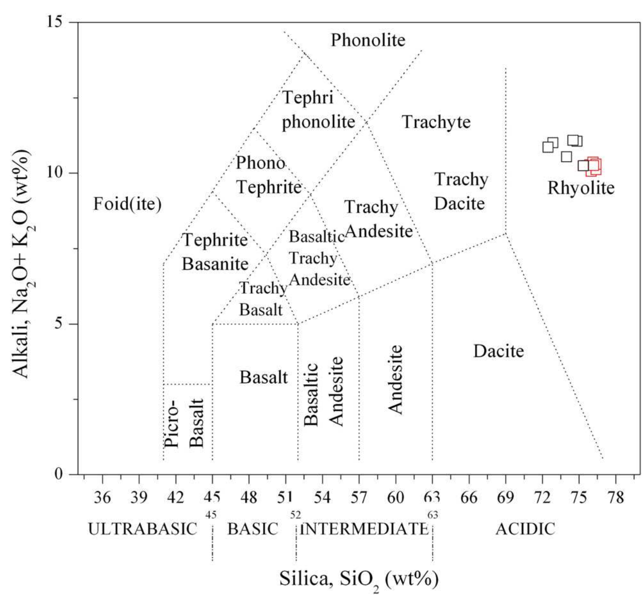

Fig. 5 Plot of obsidians chemical composition into the Total Alkali Silica (TAS) diagram (Le Maitre et al. 2002). In red color literature data from Keller et al. 1996; Chataigner and Gratuze 2014, Biagi and Gratuze 2016

Table 2 Average chemical compositions ($n = 3$) for the different obsidian shards and geological samples (concentrations are in ppm)

Sample code	Ti	Mn	Rb	Sr	Y	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
CK-1	691	396	115	64	11.5	79.2	17.5	3.8	683	24	44.4	4.15	13.37	2.66	0.38
CK-2	676	391	115	67.1	11.6	78.8	17.4	3.8	666	22.6	41.8	3.96	13.21	1.82	0.57
CK-3	684	413	123	68.7	12	80.6	17.8	4	705	24.3	45.5	4.72	15.22	1.61	0.48
CK-4	653	318	112	73.4	10.7	75.1	16.2	3.9	652	22.3	43.3	3.83	13.68	2.6	0.48
CK-5	765	351	123	78.4	11	82.8	16.6	4.1	689	24.8	46.4	4.62	13.61	2.54	0.52
CK-6	740	360	123	76.5	12.5	83.3	18.9	3.9	682	24.4	46.9	4.52	13.68	3.26	0.49
Artifact no. 17	675	400	111	71.4	12.2	70.9	16.6	3.7	623	21	38.8	3.61	12.58	2.62	0.54
Artifact no. 135	731	448	119	72.4	11.3	70.3	17.3	4	573	21.1	41.1	3.98	13.32	2.75	0.29
Artifact no. 160	928	426	124	104	11.4	95.1	18.2	4	852	29.1	54.2	4.69	15.19	1.99	0.54
Artifact no. 162	839	426	112	80.4	11.7	85.2	17.9	3.5	696	25.4	46.3	3.79	13.21	2.75	0.76
Artifact no. 195	727	429	115	74.1	11.1	77.7	18.7	4.4	698	24.9	45.5	4.78	15.86	3.62	0.51
Artifact no. 206	819	387	105	79.3	10.9	76.6	16.2	3	724	23.6	44.3	4.02	13.7	3.45	0.47
Artifact no. 237	574	425	113	83.5	12.2	95.1	18.4	3.8	741	27.9	53.3	4.92	14.81	2.11	1.02
Artifact no. 269	843	446	124	78.8	11.6	79.6	18.2	4	678	22.6	45.7	4.42	14.69	3.7	0.54
Artifact no. 278	411	445	117	68.5	12	73.9	17.3	4.9	598	20.3	42.3	3.91	15.34	3.29	1.03
Artifact no. 302	870	398	110	97.3	11.9	100	15.9	3.3	893	30.1	52.4	5.26	17.25	2.47	0.81
Artifact no. 395	363	403	104	74.7	10.2	76.7	15.4	3.1	615	21.8	40.9	3.88	14.63	1.87	0.52
Artifact no. 401	739	363	125	80.4	13	87	18.9	4.3	699	25.9	48.1	4.91	15.69	2.7	–
Artifact no. 429	904	448	120	80.6	13.1	86.7	18.1	4.1	744	26.6	48.2	4.66	12.65	5.26	0.57
Artifact no. 434	871	442	122	78.5	12.3	80.8	17.9	3.5	685	23	45.4	4.74	13.79	2.71	0.87
Artifact no. 436	722	459	119	85.6	11.7	76.8	17.3	4.3	660	25.4	44.5	4.17	15.5	2.72	0.64
Artifact no. 479	960	357	104	117	11.4	115	17.2	3.3	1048	34	58.7	6.03	17.85	2.36	0.55
Artifact no. 481	766	360	117	80.6	12	76.2	18	4.2	635	22.9	43	4.36	14.34	2.65	0.57
Artifact no. 483	724	437	124	74.7	12.6	73.3	19.8	4.3	638	23.6	44	4.17	12.75	3.08	0.45
Artifact no. 484	639	334	95	60.9	10.5	66.9	16.6	4.1	688	23.7	43.2	4.33	15.42	3.13	0.13
Artifact no. 485	1090	361	97	119	10.5	111	14.5	2.9	972	30.6	51	5.12	16.11	2.52	0.66
Artifact no. 493	1201	410	102	137	11.4	129	15.6	2.9	1130	34.8	65.7	6.6	20.36	3.61	0.64
Artifact no. 494	750	417	133	73.3	9.6	72.1	19.6	4.4	740	22.4	49.1	4.71	12.88	2.61	0.65
Artifact no. 496	677	348	116	74.9	11.8	75.1	17	4.4	633	22.8	43.6	3.8	13.54	3.03	0.5
Artifact no. 519	406	596	192	8.7	20.5	53.8	47.7	6.7	10	14.6	29.3	2.78	11.9	1.94	0.1
Artifact no. 571	704	377	106	78.9	11.4	81.5	17.2	3.9	767	25.5	47.2	4.48	13.55	2.55	0.58
Artifact no. 573	1271	373	105	137	11.5	135	14.9	3	1175	38.6	64.5	6.36	19.35	3.46	1.35
Artifact no. 575	553	602	136	2.1	41.9	155	27.5	4.9	32	27.7	59.9	6.53	24.58	4.97	0.34
Artifact no. 576	894	279	99	113	10.4	113	14.8	3.7	1007	33.2	59.1	5.91	17.19	3.25	0.74
Artifact no. 580	764	439	119	72.8	11.5	72.9	16.8	4.2	627	21.8	43.2	4.38	14.67	3.51	0.62
Artifact no. 592	720	363	121	68.6	10.9	69	19.7	5	605	23.1	44.6	3.85	13.91	3.83	0.91

Sample code	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ta	Pb	Th	Ba/Zr	Ba/Sr	Nb/Zr	Y/Zr
CK-1	1.2	0.32	1.81	0.38	0.86	0.21	1.15	0.16	1.43	15.2	13.7	8.6	10.67	0.22	0.145
CK-2	1.96	0.36	1.65	0.29	1.44	0.19	0.47	0.23	1.25	18.2	12.8	8.5	9.93	0.22	0.147
CK-3	2.12	0.29	1.75	0.3	0.44	0.14	2.28	0.17	1.32	21.4	13.5	8.7	10.27	0.22	0.149
CK-4	2	0.33	2.27	0.36	1.24	0.11	1.31	0.17	1.31	18	11.7	8.7	8.88	0.22	0.142

Table 2 (continued)

Sample code	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ta	Pb	Th	Ba/Zr	Ba/Sr	Nb/Zr	Y/Zr
CK-5	1.32	0.29	2.21	0.31	0.32	0.14	2.06	0.29	1.62	19.7	13.4	8.3	8.79	0.20	0.133
CK-6	1.89	0.42	2.54	0.28	2.27	0.1	1.45	–	1.3	31.2	14.1	8.2	8.92	0.23	0.151
Artifact no. 17	2.32	0.25	1.25	0.32	0.91	0.18	0.72	0.17	1.61	17	13.6	8.8	8.73	0.23	0.172
Artifact no. 135	2.14	0.18	2.35	0.4	1.5	–	1.15	0.41	1.46	19.8	13.2	8.2	7.92	0.25	0.161
Artifact no. 160	1.72	0.32	2.39	0.34	0.72	0.13	1.08	0.24	1.37	20.1	14.2	9.0	8.21	0.19	0.120
Artifact no. 162	1.26	0.27	1.17	0.59	1.14	0.17	1.11	–	0.94	21.2	12.6	8.2	8.65	0.21	0.137
Artifact no. 195	2.19	0.33	2.02	0.31	0.8	0.2	1.25	0.25	1.4	21.3	13.1	9.0	9.43	0.24	0.142
Artifact no. 206	2.12	0.31	1.5	0.45	0.97	0.16	0.6	0.18	0.93	16.1	12.9	9.5	9.13	0.21	0.143
Artifact no. 237	2.13	0.21	2.37	0.37	1.66	0.2	2.35	0.57	1.5	18.6	14.1	7.8	8.87	0.19	0.128
Artifact no. 269	3.19	0.16	1.72	0.27	1.18	0.17	1.66	0.14	1.18	15.4	13.5	8.5	8.60	0.23	0.146
Artifact no. 278	4.08	–	1.84	0.43	–	0.4	1.91	–	2	20.7	14.1	8.1	8.73	0.23	0.163
Artifact no. 302	2.38	0.24	1.43	0.43	0.88	0.29	1.9	0.25	1.21	17.9	15.6	8.9	9.18	0.16	0.119
Artifact no. 395	1.67	0.24	2.05	0.38	0.88	0.18	–	0.18	1.43	14.8	11.4	8.0	8.23	0.20	0.134
Artifact no. 401	1.27	0.05	3.39	0.17	1.56	0.32	–	–	1.6	19.8	15.2	8.0	8.69	0.22	0.150
Artifact no. 429	1.96	0.34	1.67	0.52	2.46	0.15	2.33	–	1.45	20.5	15.4	8.6	9.22	0.21	0.151
Artifact no. 434	2.72	0.43	2.35	0.57	0.94	0.25	1.33	0.33	1.08	20.9	14.8	8.5	8.72	0.22	0.152
Artifact no. 436	2.3	0.34	2.54	0.33	1.05	0.17	1.56	0.22	1.31	18.2	13	8.6	7.71	0.23	0.152
Artifact no. 479	1.76	0.24	2.26	0.3	1.53	0.13	1.88	0.25	1.14	17.4	15.5	9.2	8.95	0.15	0.100
Artifact no. 481	2.04	0.35	1.88	0.4	1.33	0.11	0.36	0.2	1.47	21.9	13.6	8.3	7.88	0.24	0.158
Artifact no. 483	2.07	0.32	2.17	0.49	1.18	0.19	1.11	0.21	1.64	20.5	13.6	8.7	8.54	0.27	0.172
Artifact no. 484	2	0.33	1.84	0.36	0.96	0.45	1.68	0.23	1.33	13.8	11.1	10.3	11.28	0.25	0.157
Artifact no. 485	1.84	0.25	1.44	0.32	1.18	0.14	1.38	0.14	0.82	14.3	14.3	8.8	8.18	0.13	0.095
Artifact no. 493	2.78	0.35	2.07	0.48	1.89	0.21	1.58	0.16	1.51	18.1	15.6	8.8	8.23	0.12	0.088
Artifact no. 494	1.96	0.22	1.33	0.46	0.97	0.23	0.79	0.19	1.24	24.4	10.8	10.3	10.10	0.27	0.133
Artifact no. 496	1.87	0.37	1.54	0.41	0.56	0.15	0.49	0.2	1.21	18.5	12.2	8.4	8.45	0.23	0.158
Artifact no. 519	2.68	0.46	2.87	0.66	2.1	0.25	1.91	0.42	4.34	22.8	23.7	0.2	1.15	0.89	0.380
Artifact no. 571	2.49	0.2	1.65	0.39	1.43	0.22	1.07	0.21	1.34	15.9	14.3	9.4	9.72	0.21	0.140
Artifact no. 573	2.07	0.3	2.81	0.47	2.06	0.32	2.32	0.44	0.98	19.7	15.4	8.7	8.57	0.11	0.085
Artifact no. 575	6.62	1.33	7.19	1.38	2.8	0.94	4.51	0.67	1.28	28.1	17	0.2	15.22	0.18	0.270
Artifact no. 576	1.99	0.32	1.81	0.42	1.23	0.19	1.34	0.24	1.07	19.4	14.2	8.9	8.89	0.13	0.093
Artifact no. 580	1.99	0.32	2.39	0.48	0.86	0.17	1.52	0.35	1.22	19.6	12.9	8.6	8.61	0.23	0.158
Artifact no. 592	1.92	0.27	1.72	0.3	0.93	0.36	0.61	0.19	1.08	18.7	11.3	8.8	8.82	0.29	0.158

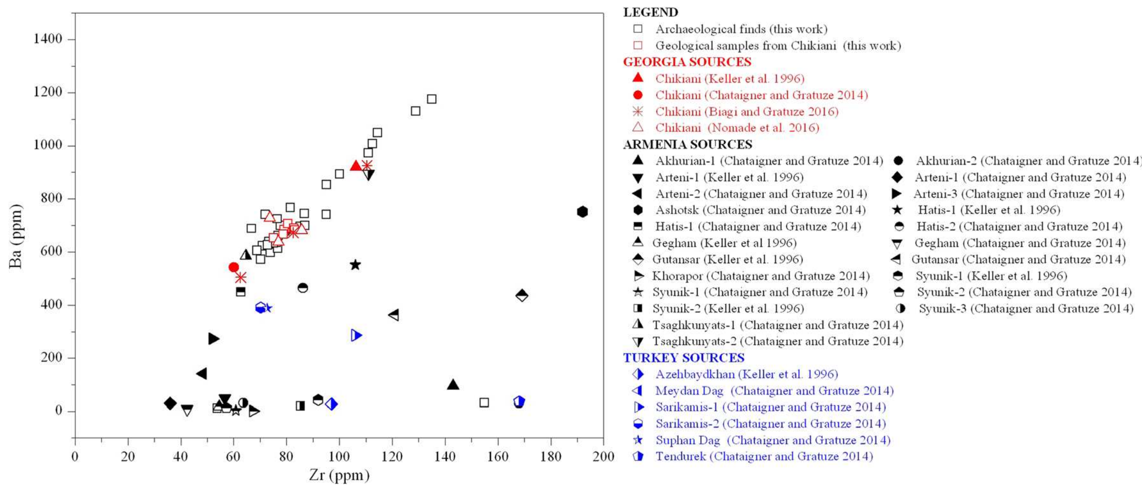

Fig. 6 The binary diagram of the Zr–Ba contents of archaeological finds and geological sources and comparison to literature average values

different analytical approaches (PIXE, INAA and LA-ICP-MS). The Chikiani outcrop has been the object of several studies (Chataigner and Gratuze 2014; Le Bourdonnec et al. 2012; Tushabramishvili et al. 2012; Keller et al. 1996) that showed the possible existence of at least two obsidian chemical groups, a medium barium and high barium (Biagi and Gratuze 2016).

Even if acquired with different analytical methods, data are quite comparable and overlapping. All these data represent a key database to refer for assigning the provenance of archaeological obsidians.

The results obtained on the archaeological fragments of Samshvilde site were compared with literature data of Georgian, Armenian, and Caucasian geological sources (Keller et al. 1996; Blackman et al. 1998; Le Bourdonnec et al. 2012; Chataigner and Gratuze 2014) and with new data from Chikiani outcrops here presented. The diagram Zr vs Ba, as suggested by Keller et al. (1996), permits the separation among Armenian and Caucasian geological sources. In the diagram Zr vs Ba (Fig. 6), twenty-eight archaeological shards fall into the area of the Chikiani and Tsaghkunyats sources.

The remaining two finds plot in two different areas of the diagram, indeed the find no. 519 shows low contents of Zr (54 ppm) and Ba (10 ppm), while the artifact no. 575 shows concentrations of Zr (155 ppm) higher than Chikiani source while the content of Ba (32 ppm) is lower than the Chikiani source.

The sample no. 519, falls within the field of different Armenian geological sources (Arteni, Gegham, and Syunik) and, for this reason, it is difficult to assign a sure provenance. The sample no. 575 plots near the field of two different sources, Akhurian (Armenia) and Tendurek (Turkey).

The diagram Ba/Zr vs Ba/Sr (Fig. 7) confirms undoubtedly the geochemical similarity between the twenty-eight artifacts and the Chikiani source indicating a clear Georgian provenance.

Also, it confirms the double provenance for the other two analyzed fragments, which again plot in two distinct areas. In

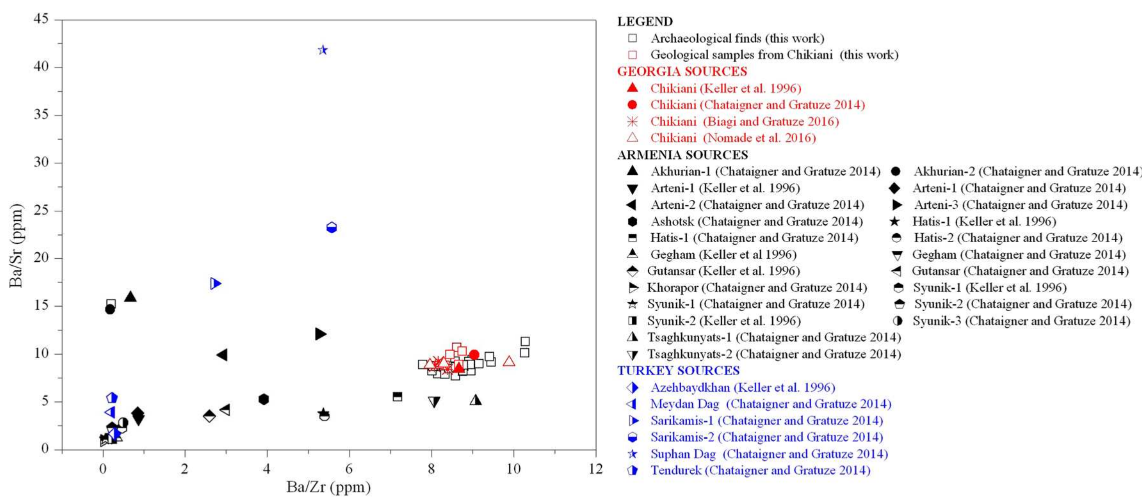

Fig. 7 The binary diagram of the Ba/Sr–Ba/Zr ratios of archaeological finds, geological sources, and comparison to literature average values

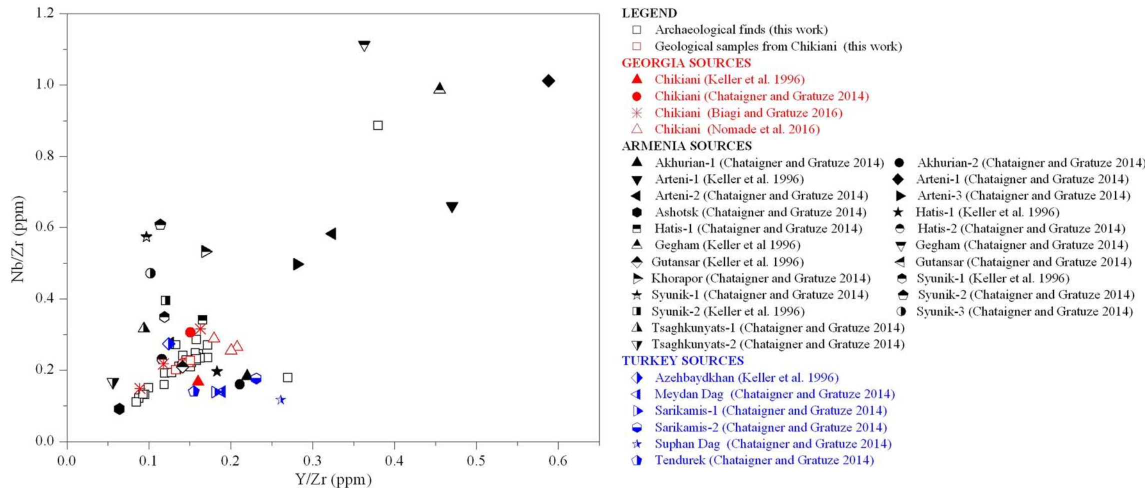

Fig. 8 The binary diagram of the Nb/Zr-Y/Zr ratios of archaeological finds, geological sources, and comparison to literature average values

detail, the sample no. 575 plots very near to the geological Armenian source of Akhurian; on the contrary, the sample no. 519 is of doubt provenance. The diagram Y/Zr vs Nb/Zr (Fig. 8) was used in order to determine a more clear source. In particular, this geochemical diagram allowed to discriminate the correct source of the no. 519 archaeological find, showing a clear similarity with the geological Gegham source.

In conclusion, the majority of analyzed finds shows a clear Chikiani provenance, only two samples overlaps, respectively, the geological obsidian of Gegham analyzed by Keller et al. (1996) and by Chataigner and Gratuze (2014), and the Akhurian source (Chataigner and Gratuze 2014).

Conclusions

Generally, South Caucasus, especially South Georgia and Armenia are rich in obsidian. Since 1990s, more than twenty obsidian sources and outcrops, stretching across more than 300 km of the rugged Lesser Caucasus ranges, have been identified (Keller et al. 1996). Equally significant are the studies that propose exchange models, which attempt to explain the social and economic patterns behind the procurement and consumption of raw materials (Badalyan et al. 2004). The present study confirms that the prehistoric populations of Samshvilde and surroundings supplied themselves with several obsidian' sources.

It is not surprising that in ancient times, communities procured obsidian from the source closest to their base. This "time-distance" model argues that the distance factor should not be calculated as the crow flies, but instead, on the maximum time acceptable to procure the raw materials (Sagona 2018).

It is also notable that the Khrami River, which cuts a course through the Chikiani Range, distributes large quantities of obsidian cobblestones down its course, so communities in the surrounding of Samshvilde and in nearby villages did not have to visit the source itself, but collect obsidians, brought by the river in the local ravines.

Anyway, most of the obsidian explored here derives from the Chikiani source, but some also are exported from Armenian sources. From the Neolithic period some clear pattern of obsidian procurement and consumption are beginning to emerge. Although communities may have preferred obsidian from a specific source, their artifacts show a more varied procurement pattern. This pattern changed later, during the Early Bronze Age, when villagers in the Caucasus increasingly exploited Hatis obsidian.

Long-distance trade networks and a formative organizational system to cope with the demand for raw materials were actively functioning, and it seems that the obsidian was one of the important raw materials among others.

It is quite likely that the Samshvilde inhabitants, as well as the villagers around, were actively drawn into the trade interaction with southern regions. Indeed, the nature of this interaction has yet to be determined more accurately.

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