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# New Data on Source Characterization and Exploitation of Obsidian from the Chikiani Area (Georgia)

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**Abstract** This paper presents the results obtained from two brief surveys carried out in 2012 and 2014 along the slopes of Mt. Chikiani in south Georgia. The scope of the surveys was to collect obsidian samples for characterization, to improve our knowledge of the raw material resources exploited in prehistoric times. The analysis of 69 samples retrieved from 20 different points have confirmed that Chikiani obsidian is to be subdivided into 3 main groups, characterised by variable percentages of barium and zirconium. The new results have important implications in the prehistory of the Caucasus and its related regions. They improve our knowledge on the exploitation of the obsidian resources, and their circulation in the territory.



**Keywords** Georgia. Lesser Caucasus. Mt. Chikiani. Obsidian outcrops. Obsidian geochemistry. LA-ICP-MS analysis.

## 1 Introduction

Recently, results originating from a large analytical program involving both obsidian source characterization and obsidian artefact sourcing, were published within the framework of the French archaeological mission 'Caucasus' (Chataigner, Gratuze 2014a; 2014b). Within that paper, the source of Chikiani was briefly discussed, and it was shown that it forms a single chemical compositional group characterized by low zirconium and high

In this paper Chapters 1, 2, 4 and 5 are by B. Gratuze; Chapters 3 and 6 by P. Biagi and B. Gratuze.

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barium (400 to 700 ppm) contents. A continuous variation of the Ba and Zr concentrations was also observed. Similar conclusions were drawn for this source by F.-X. Le Bourdonnec (Le Bourdonnec et al. 2012). Among the different Armenian archaeological sites discussed by C. Chataigner and B. Gratuze, none was supplied by the Chikiani obsidian outcrops. In contrast it was the main obsidian source for the two Georgian sites studied by F.-X. Le Bourdonnec: Bondi Cave (Tushabramishvili et al. 2012) and Ortvale Klde (Le Bourdonnec et al. 2012).

Recent unpublished works carried out at the IRAMAT-CEB in the frame of different analytical programs dealing with the obsidian supply of Azeri, Armenian and Georgian archaeological sites (most of them dating from the 5th millennium BC), have revealed the existence of an obsidian compositional groups, which had not been described before by C. Chataigner and B. Gratuze. This group is characterized by a high barium content (900 to 1,200 ppm) that appears to be significantly different from the only Caucasian obsidian group defined by C. Chataigner and B. Gratuze, which shows similar barium and zirconium contents: Tsaghkunyats 2 (Chataigner, Gratuze 2014a).

The data published by other authors (Blackman et al. 1998; Frahm 2010; Keller et al. 1996; Lebedev et al. 2008; Karapetyan et al. 2010; Le Bourdonnec et al. 2012) as well as unpublished data by C. Bressy (pers. comm.) and J. Keller (pers. comm.) tend to show the possible existence of at least two obsidian chemical groups at Chikiani: a medium barium one (400 to 750 ppm), and a high barium one (800 to 1,200 ppm). However the analytical methods used by the aforementioned authors (XRF, INAA and EPMA) do not determine all the elements, and a direct comparison between the different analytical sets of data is not always feasible.

Moreover the precise location of the samples was not always provided, and some of the analytical works were carried out on old geological collections, and not on recent fieldwork finds. The exact origin of the samples was therefore not always ascertain. Thus, in order to identify the precise location of this ‘unidentified’ high barium group, new geological surveys should be carried out. According to the published data the Chikiani area could be considered as a possible source for these artefacts, and therefore it constitutes a good starting point for new geological surveys.

## 2 High Barium Obsidian Artefacts Group Compared to Caucasian Obsidian Flows

In the frame of different projects dealing with obsidian sourcing, two French-German ANR-DFG research programs (‘Ancient Kura’ and ‘Kura in motion’, directed by B. Lyonnet and B. Helwing, study of Azeri Kura

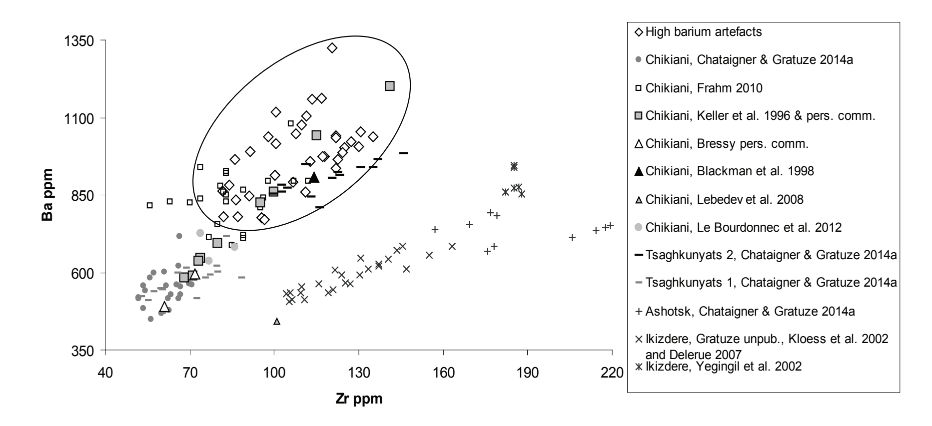


Figure 1. Binary diagram for the Zr-Ba contents of the barium rich Caucasian obsidian

Valley Chalcolithic sites dating from the second half of the 5th millennium cal BC), an English project (The BTC Pipeline Archaeological Excavations in Azerbaijan, project conducted by D. Maynard), a Georgian-Italian joint expedition (the Shida Kartli Region directed by E. Rova; Rova and Gratuze in preparation), as well as a different project carried out by one of the authors of the present paper (P.B.), a new chemical group of obsidian artefacts was identified. This group is characterized by a very high barium content (760-1,330 ppm), and a low zirconium content (80-135 ppm).

According to the data published by the aforementioned authors, only two Caucasian obsidian sources could match such a composition: Tsaghkunyats 2 as defined by C. Chataigner and B. Gratuze (2014a), and Chikiani according to some values published by J. Blackman (1998), E.E. Frahm (2010) and J. Keller (Keller et al. 1996). The zirconium and barium contents of the other rich barium obsidian sources such as Ashotsk, Ikizdere (Kloess et al. 2002, Delerue 2007) or Tsaghkunyats 1 appear fairly different from the composition of the barium rich artefacts group (fig. 1).

We were also able to observe that the values published from Chikiani split into two main groups. The data from C. Bressy (pers. comm.), some others from J. Keller (Keller et al. 1996 and Keller pers. comm.) and F.-X. Le Bourdonnec (Le Bourdonnec et al. 2012), as well as those from C. Chataigner and B. Gratuze (2014a), constitute a first group characterized by a barium content in the range of 450 to 750 ppm. Data from E.E. Frahm, J. Blackman as well as the remaining data from J. Keller (Keller et al. 1996 and Keller pers. comm.) form a second group characterized by a higher barium content in the range of 750 to 1,300 ppm. Some data from V.A. Lebedev form a third group, which is characterized by a different Ba/Zr ratio (Lebedev et al. 2008).

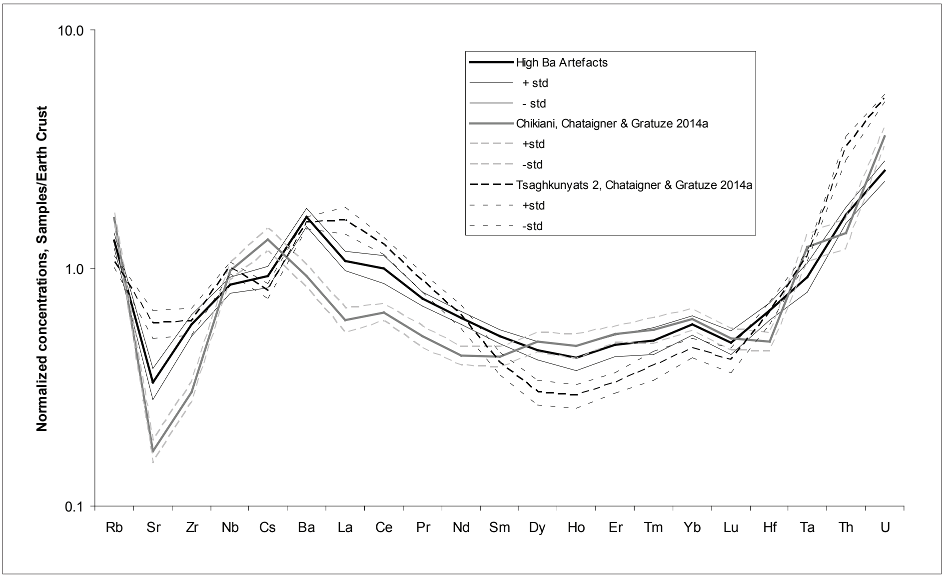


Figure 2. Rare earth element and extended trace normalized plots for the high barium obsidian artefacts compared with those for Chikiani and Tsaghkunyats 2 obsidian. Earth crust normalization from K.H. Wedepohl 1995

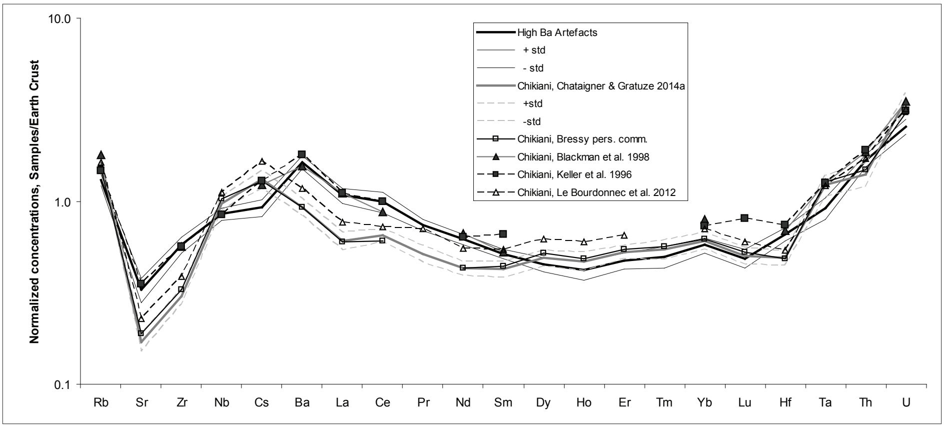


Figure 3. Rare earth element and extended trace normalized plots for the high barium obsidian artefacts compared with those of published values for Chikiani. Earth crust normalization from K.H. Wedepohl 1995

If we now compare the rare earth elements distribution pattern of the high barium artefacts with that of Chikiani and Tsaghkunyats 2 groups defined by C. Chataigner and B. Gratuze (fig. 2) we can notice several differences. The rare earth elements distribution patterns clearly show that the artefacts do not originate from the outcrops of Chikiani and Tsaghkunyats (Kamakar or Aïkasar) sampled and discussed by C. Chataigner and B. Gratuze.

As stated above, the comparison at the same degree of confidence with data published by other authors is less easy, as different analytical as well as calibration and protocol methods were used. Among the published data, only J. Blackman (Blackman et al. 1998), C. Bressy (pers. comm.), J. Keller (Keller et al. 1996), and F.-X. Le Bourdonnec (Le Bourdonnec et al. 2012) have determined the rare earth elements concentration, though, in some case, it was not made for all the samples (Keller et al. 1996; Le Bourdonnec et al. 2012) or only an average contents corresponding to several samples has been given (Blackman et al. 1998).

Despite the aforementioned differences, some interesting features can be observed (fig. 3). The first is that the different sets of data form two main distribution patterns. One is represented by the data published by J. Blackman and J. Keller (both related to obsidian with high barium contents, respectively 906 and 1,042 ppm). The second by the data from C. Bressy, and C. Chataigner and B. Gratuze (both related to obsidian with low barium contents, average of 540 ppm). The data published by F.-X. Le Bourdonnec show an intermediate pattern between the two first trends (these obsidian contain an average content of Ba of 680 ppm). It could also be observed that a fairly good agreement is obtained between rare earth element values published by J. Blackman and J. Keller (samples from Chikiani characterized by a high barium content) with those of the high barium artefacts group.

The above different sets of data show that all the Chikiani obsidian samples do not form a chemically homogenous source as stated by C. Chataigner and B. Gratuze, and F.-X. Le Bourdonnec; in contrast they point out a more complex pattern. At least two main obsidian groups could be derived from published data. The first is characterized by barium concentrations in the range of 450 to 750 ppm, the second by barium concentrations in the range of 750 to 1,300 ppm. The intermediate trend pattern shown in fig. 3 from F.-X. Le Bourdonnec's data point out a probably more complex issue.

Although, according to the present evidence it seems possible to assign the high barium artefacts group to some of the Chikiani outcrops, they also show that it is necessary to undertake a more systematic survey, and a chemical characterization of the Chikiani obsidian flows, similarly to that made by A.K. Robin for Arteni (Robin et al. 2014).

## 3 Chikiani: Geological Description and New Sampled Sites

Located in Southern Georgia, some 85 km west-southwest of Tbilisi the Chikiani volcano, which reaches 2,417 m, raises only ca. 300 m above the shores of the nearby lake Paravani (fig. 4). Obsidian is spread all over the dome of the volcano, and extends in a large flow to the north-east. This flow belongs to an eruptive phase dated some 2.8 Ma, the southern part of the dome being ca. 400 ka younger (Lebedev et al. 2008) (fig. 5).

At Chikiani, obsidian is abundant and easy to access. The only limit to exploitation being the thick snow cover that lasts more than six months. Moreover, the Chrami river, which receives many obsidian blocks from its tributaries running down from the Chikiani slopes, carries many obsidian pebbles as far as its lower course where sites of the Neolithic Shulaveri-Shomutepe culture, dated to the 6th millennium ca. BC, are located (Badalyan et al. 2004).

The quality of the obsidian is excellent, very homogeneous and without inclusions. Several varieties are found: uniform black, banded black and red, red-brown, mottled brown and black, mottled yellow and brown, etc. The chemical analyses show that the samples taken from the Chikiani dome form a single group characterised by low zirconium and high barium contents. As observed by J. Keller (Keller et al. 1996), there is a continuous variation of Ba and Zr concentration, which corresponds to the progressive evolution of the magma between the successive flows that were emitted between 2.8 and 2.3 million years ago.

Two brief surveys were made by one of the present authors (P.B.) in October 2012 and June 2014 respectively. Their scope was to collect obsidian samples for preliminary characterization. The first survey started from the northern, lowermost foot of the mountain, moving up toward its top, and then down along the southern slope. Two specimens from six different spots were collected for characterization in 2012 (fig. 6).

A more systematic research was carried out on June 10, 2014. Following the indications provided by C. Chataigner and B. Gratuze, the eastern slope of the volcano was systematically surveyed starting from its southern foot, moving up to north-east. Obsidian samples were retrieved from 15 spots in variable sedimentary and distributive conditions, roughly between 2,165 m (sample 1) and 2,295 m (sample 12) of altitude. East of this latter point the presence of obsidian specimens seems to become more and more rare. This part of the mountain, especially between Points 8 and 12, is very rich in *kurgans* of different size and shape, and other stone structures, some of which have been built partly with obsidian boulders (fig. 7).

Obsidian pieces were collected from both thick and sparse concentrations. Differences in the appearance, colour, and texture of the samples were noticed at naked eye, which contributed the selection of the specimens to be characterised. Flakes and small bombs were collected from

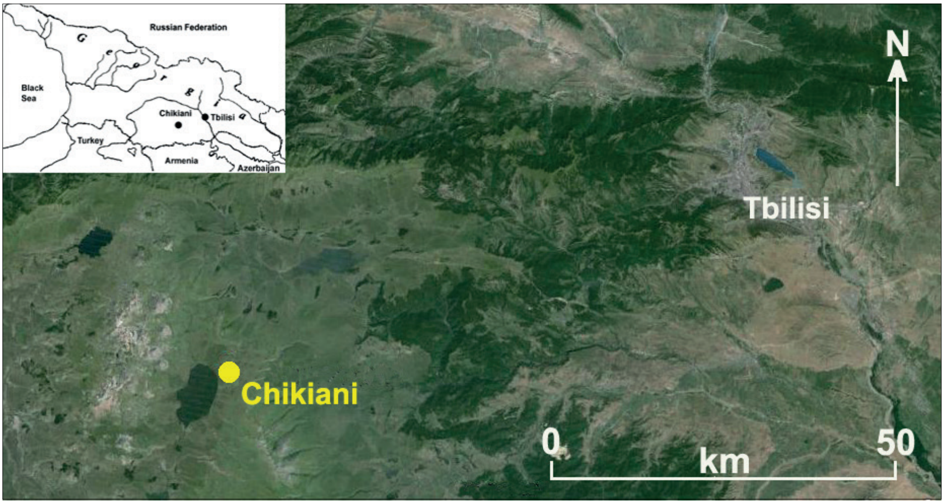


Figure 4. Location of Mt. Chikiani in south Georgia (drawing by P. Biagi)

Figure 5. Lake Paravani from the southern slopes of Chikiani with the impressive obsidian mine opened in Soviet times in the foreground (photograph by P. Biagi, 2012)

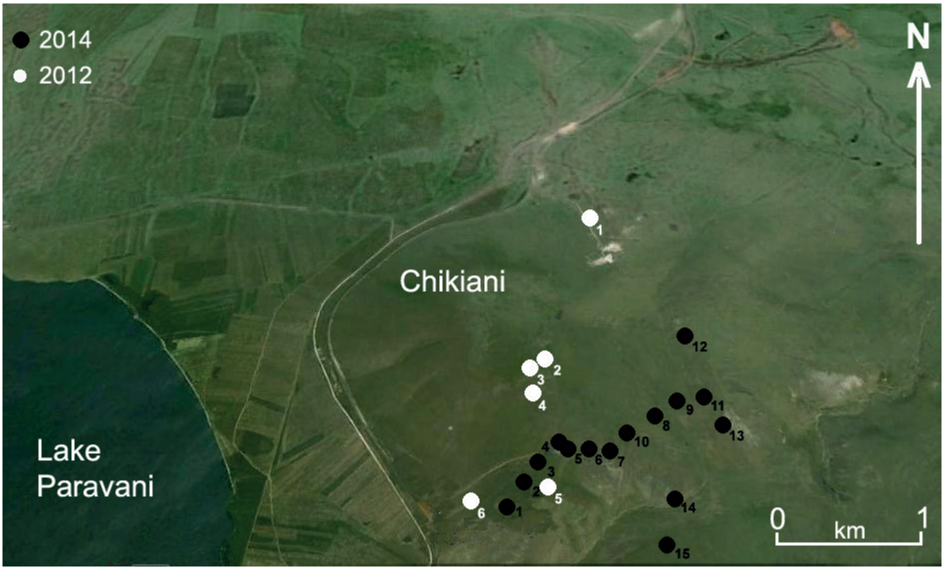


Figure 6. Chikiani. Distribution map of the Points from which samples were collected for characterization in 2012 and 2014 (drawing by P. Biagi)

Figure 7. Chikiani. Small *Kurgan* along the eastern slope of the volcano (photograph by P. Biagi, 2014)

Figure 8a-b. Chikiani. Different characeristics of Point 8 (top) and Point 6 (bottom), from which obsidian samples were retrieved (photograph by P. Biagi, 2014) both the surface of the slopes, and at the bottom of the profile of water-pits dug by Azeri transhumant shepherds. In the second case, a distinct horizon of obsidian flakes was observed, covered by ca. 1 m of colluvium (fig. 8a). Of major interest is Point 6 (fig. 8b). It yielded evidence of detached obsidian flakes with percussion bulb and *chapeau de gendarme* platform (fig. 9). Although their age cannot be defined, they show that prehistoric workshops or manufacturing areas undoubtedly exist in some areas of the mountain.

Point 15 is of unique importance (ca. 2,220 m). As clearly shown in the distribution map of fig. 6, it is located above the left, southern terrace of a small stream (fig. 10) that, turning westward, flows down into Lake Paravani. This location is quite unexpected. It roughly corresponds to the area from which Acheulian, andesite hand-axes were recovered many years ago (Кикодзе 1983; 1986; Lioubine 2002, fig. 90). Obsidian specimens from this spot are quite scattered. The general impression, supported by the morphological characteristics of the area, would suggest that they were collected from lower-lying locations.

More specimens were sampled from Point 3, along the edge of a huge obsidian mine opened for industrial purposes along the southern slope of the mountain during the Soviet period (fig. 11a). The impressive, thick obsidian deposits of the mine yield material of several colours and different texture (fig. 11b).

## 4 LA-ICP-MS analysis

The analyses of the geological and archaeological obsidian samples discussed in this paper were made at Centre Ernest-Babelon of the IRAMAT (Orléans, F) using a Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

LA-ICP-MS allows an almost non destructive analysis of the obsidian artefacts, invisible to naked eyes. The concentration of thirty-eight elements is determined for each selected sample. Among them we find elements such as zirconium, yttrium, niobium, barium, strontium, cerium, lanthanum and titanium, which appear to be the most powerful ones in order to establish discrimination between different obsidian outcrops (Chataigner, Gratuze 2014a; 2014b; Chataigner et al. 2014).

The LA-ICP-MS operates as follows. The object placed in the ablation cell is sampled by the laser beam. The diameter of the ablation crater can ranges from 4 µm to 100 µm, and its depth is around 250 µm according to the ablation duration. An argon or argon/helium gas flow carries the ablated aerosol to the injector inlet of the plasma torch, where the matter is dissociated, atomised and ionised. The ions are then injected into the vacuum chamber of a high resolution system, which filters the ions

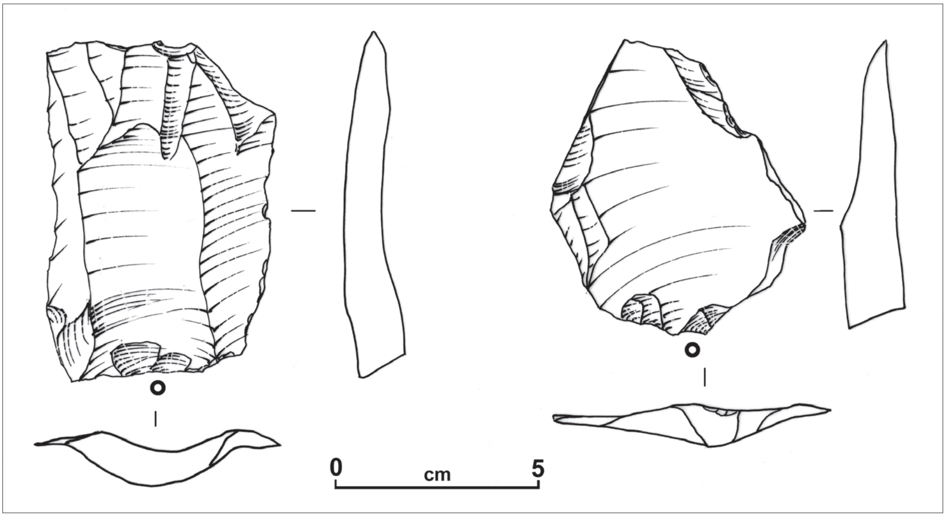


Figure 9. Chikiani. Chipped obsidian artefacts from Point 6 (drawing by P. Biagi, inking by E. Starnini)

Figure 10. Chikiani. Geomorphological characteristics of the area where obsidian samples from Point 15 were collected east of the small stream flowing down into Lake Paravani (photograph by Biagi, 2014)

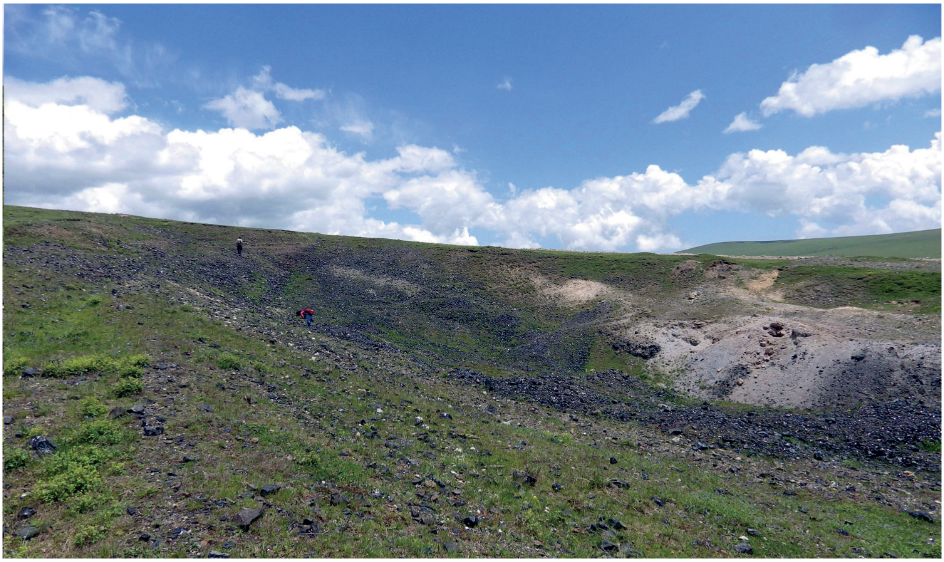

Figure 11a-b. Chikiani. Obsidian mine of Point 3 (top), and obsidian bombs and flakes from the sampled point (bottom) (photograph by P. Biagi, 2014)

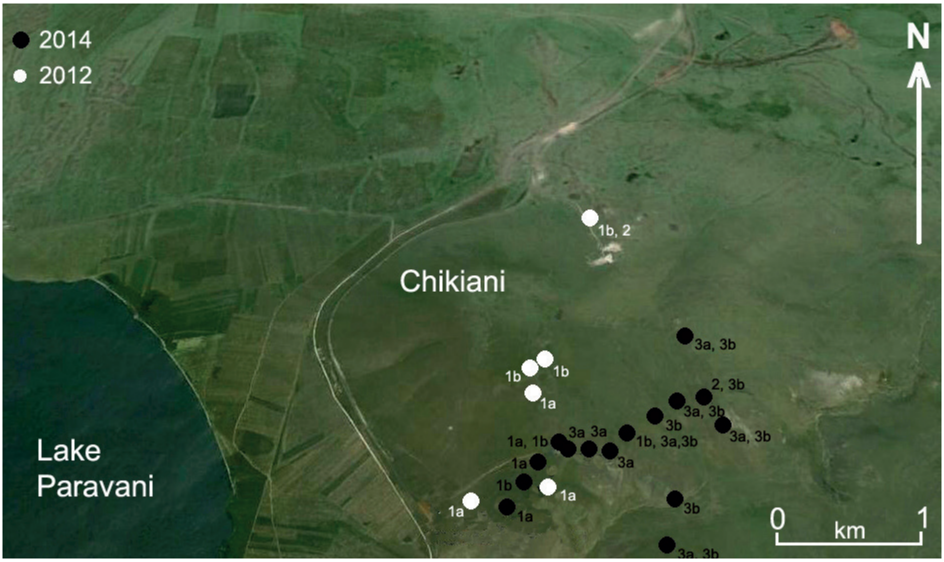


Figure 12. Chikiani. Distribution map of the different obsidian sub-groups identifies from the sampled points (drawing by B. Gratuze and P. Biagi)

depending upon their mass-to-charge ratio. The ions are then collected by a channel electron multiplier or a faraday cup. The isotope 28Si was used as an internal standard (Chataigner, Gratuze 2014a).

The standard reference materials glass Nist 610 from the National Institute for Standards and Technology and Corning B glass from Corning laboratory were used for external standardisation. The standard reference materials glass Nist 612 is regularly analysed as an unknown sample all along the analytical sequence to check possible instrumentation drifts and to insure compatibility between the different sets of analytical data. The mass spectrometer is an Element XR from Thermofisher Instrument and the ablation device are a VG UV microprobe working at 266 nm (NdYAG with quadrupled frequency) and a Resolution M50E from Resonetics (Eximer ArF laser working at 193 nm).

## 5 Results

Sixty nine obsidian samples collected from twenty different sampling areas (Figs. 6 and 12; Table 1) have been analysed. The distribution of the samples, on a Ba-Zr diagram (fig. 13), shows three main chemical groups characterized by a continuous variation of the Ba and Zr concentrations, respectively characterized by barium and zirconium contents ranging from: 432 < Ba

| Sampling point | Description | Coordinate | Sample ref |
|---|---|---|---|
| Chikiani 12 01 | Sample 1 (2 pieces) | 41°29'13"N-43°52'29"E | A & B |
| Chikiani 12 02 | Sample 2 (2 pieces) | 41°28'31"N-43°52'12"E | A & B |
| Chikiani 12 03 | Sample 3 (2 pieces) | 41°28'27"N-43°52'05"E | A & B |
| Chikiani 12 04 | Sample 4 (2 pieces) | 41°28'16"N-43°52'09"E | A & B |
| Chikiani 12 05 | Sample 5 (2 pieces) | 41°27'57"N-43°52'12"E | A & B |
| Chikiani 12 06 | Sample 3 (2 pieces) | 41°27'55"N-43°51'19"E | A & B |
| Chikiani 14 02 | Southern slope, along the earth road (2 specimens) | 41°27'58"N-43°52'05"E | A & B |
| Chikiani 14 03 | Main quarry (5 specimens) | 41°28'02"N-43°52'09"E | A, B, C, D & E |
| Chikiani 14 04 | Just above the mine, southern slope (5 specimens) | 41°28'03"N-43°52'16"E | A, B, C, D & E |
| Chikiani 14 05 | Eastern slope (4 specimens) | 41°28'02"N-43°52'19"E | A, B, C & D |
| Chikiani 14 06 | Eastern slope. Presence of tools??? (2 specimens) | 41°28'05"N-43°52'21"E | A & B |
| Chikiani 14 07 | Eastern slope (4 specimens) | 41°28'03"N-43°52'24"E | A, B, C & D |
| Chikiani 14 08 | Excavated water hole (buried level) (5 specimens) | 41°28'15"N-43°52'40"E | A, B, C, D & E |
| Chikiani 14 09 | Eastern slope (4 specimens) | 41°28'16"N-43°52'46"E | A, B, C & D |
| Chikiani 14 10 | Eastern slope (5 specimens) | 41°28'10"N-43°52'30"E | A, B, C, D & E |
| Chikiani 14 11 | Eastern slope (5 specimens) | 41°28'19"N-43°52'54"E | A, B, C, D & E |
| Chikiani 14 12 | Eastern slope (4 specimens) | 41°28'33"N-43°52'52"E | A, B, C & D |
| Chikiani 14 13 | Eastern slope, farthest point reached (5 specimens) | 41°28'10"N-43°52'59"E | A, B, C, D & E |
| Chikiani 14 14 | Eastern slope, lower down (4 specimens) | 41°27'55"N-43°52'43"E | A, B, C & D |
| Chikiani 14 15 | Eastern slope, other bank of the stream (3 specimens) | 41°27'46"N-43°52'44"E | A, B & C |

Table 1. Provenance and grouping of the analysed obsidian samples

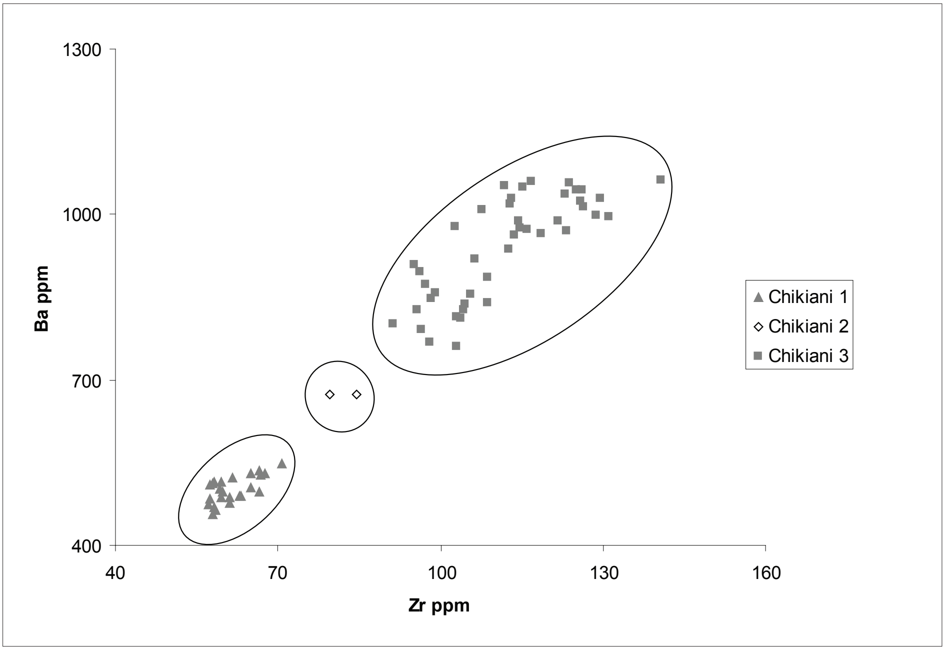


Figure 13. Binary diagram for the Zr-Ba contents of our geological corpus

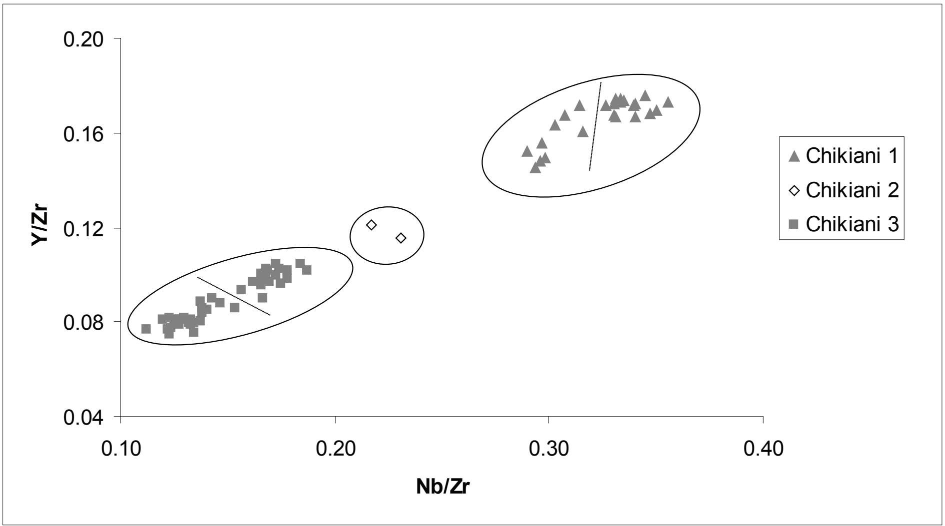


Figure 14. Binary diagram for the Y/Zr-Nb/Zr ratios of our geological corpus

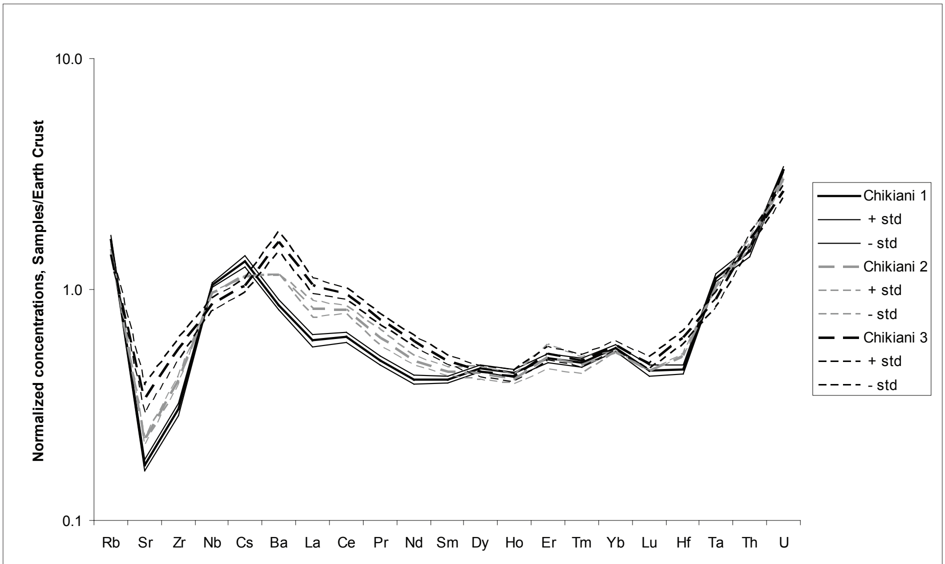


Figure 15. Rare earth element and extended trace normalized plots for the main chemical groups of our geological corpus. Earth crust normalization from K.H. Wedepohl 1995

ppm < 558 & 56 < Zr ppm < 72 for Chikiani 1; 631 < Ba ppm < 783 & 76 < Zr ppm < 85 for Chikiani 2; 760 < Ba ppm < 1,063 & 95 < Zr ppm < 141 for Chikiani 3. Similar patterns are observed for Y/Zr and Nb/Zr ratios (fig. 14) and for the rare earth elements distribution trends (Figs. 15-16).

Therefore, our new data confirm the existence of at least three main chemical groups (with some possible sub groups) at Chikiani (Tables 2, 3a and 3b). Group 1 (the lowest REE trend) is similar to that defined by the samples analysed by C. Bressy (pers. comm.), and C. Chataigner and B. Gratuze (the lowest barium content), Group 3 (the highest trend) correspond to the samples analysed by J. Blackman et al. (1998) and to the high barium samples analysed by J. Keller et al. (1996; Keller pers. comm.), and Group 2 (the intermediate trend) matches the samples analysed by F.-X. Le Bourdonnec et al. (2012) that have intermediate barium content.

The presence of two different eruptive phases had already been remarked by S. Nomade (Nomade et al. 2015) for the three samples analysed by F.-X. Le Bourdonnec (Le Bourdonnec et al. 2012). An age of 2.4 Ma has been assigned to the sample presenting the lowest barium content (638 ppm), and an age of 2.8 Ma to those containing 682 and 727 ppm of Ba. Nevertheless, these dates have been discussed by V.A. Lebedev in a recent paper (Lebedev, Vashakidze 2015) in which he suggests that the sample dated from 2.4 Ma, by S. Nomade, could have been heated during the eruption of a younger volcano (the Inyak Dağ, dated to 2.5-2.1 Ma). Given that the K-Ar system is thermolabile, its restart might have taken place during this thermal event, resulting in a rejuvenated age value of the obsidian dated by S. Nomade et al. (2015).

Thus, according to S. Nomade's results (Le Bourdonnec et al. 2012; Nomade et al. 2015), J. Keller observations (Keller et al. 1996), and V.A. Lebedev dates (Lebedev et al. 2008; Lebedev, Vashakidze 2015), our group 1 (1a and 1b) probably originated from the last Chikiani eruptive phase, while group 3 (3a and 3b) belong to the most ancient ones. The exact date of these eruption phases is still disputable.

If we plot the barium and zirconium concentrations published by these different authors together, the correspondence between the above groups is clear (fig. 17). The diagram shows that, before the present paper, only J. Keller (Keller et al. 1996; Keller pers. comm.) had analysed a set of samples showing the diversity of Chikiani's obsidian compositions.

If we now compare the composition of the high barium artefact groups with the new set of data obtained for Chikiani (Figs. 18 and 19), we can notice a very good agreement between group 3 (3a and 3b) and the high barium artefacts group. However, some artefacts tend to occupy an intermediate position between the sub-group 3a and group 2. Figure 20 shows a perfect match between the REE pattern of the high barium artefact groups and those of group 3 (3a and 3b), which confirms the attribution of these artefacts to the Chikiani obsidian outcrops.

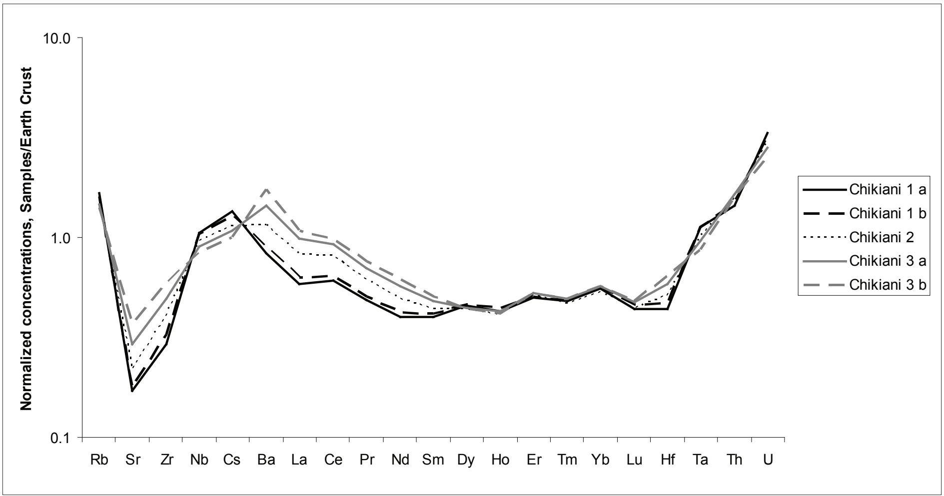


Figure 16. Rare earth element and extended trace normalized plots for the chemical sub-groups of our geological corpus. Earth crust normalization from K.H. Wedepohl 1995

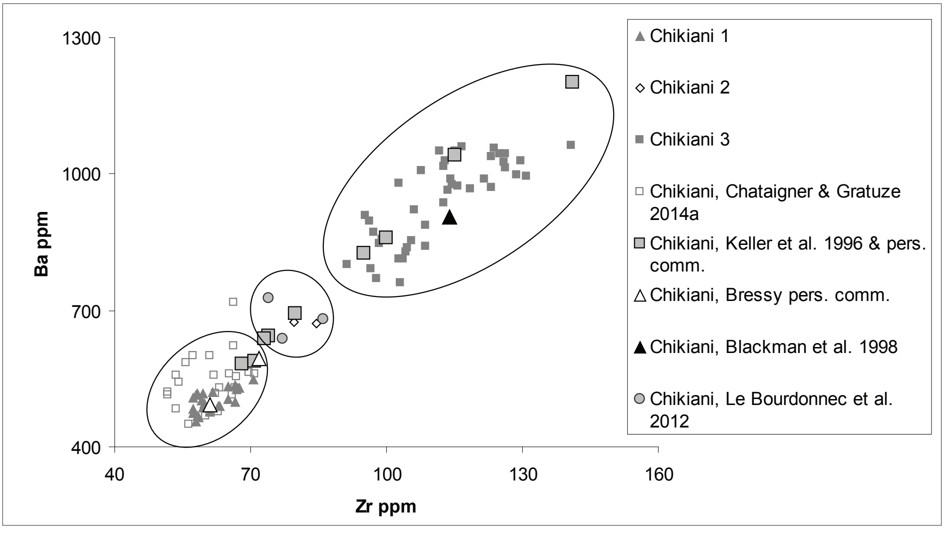


Figure 17. Binary diagram for the Zr-Ba contents of our geological corpus compared with published values for Chikiani

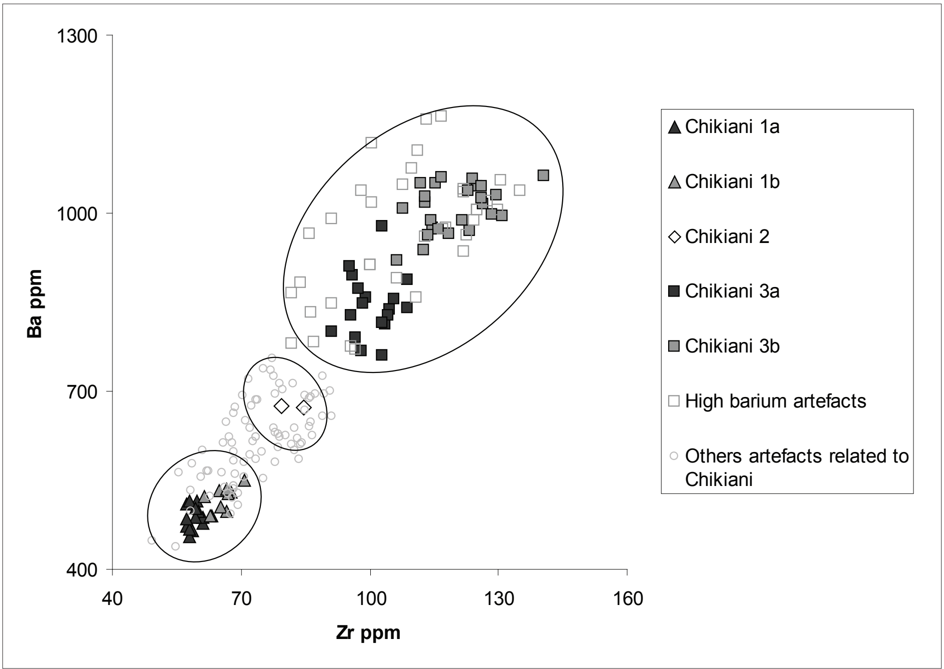


Figure 18. Binary diagram for the Zr-Ba contents of our geological corpus compared with those of archaeological artefacts originating from Chikiani (B. Gratuze unpublished values)

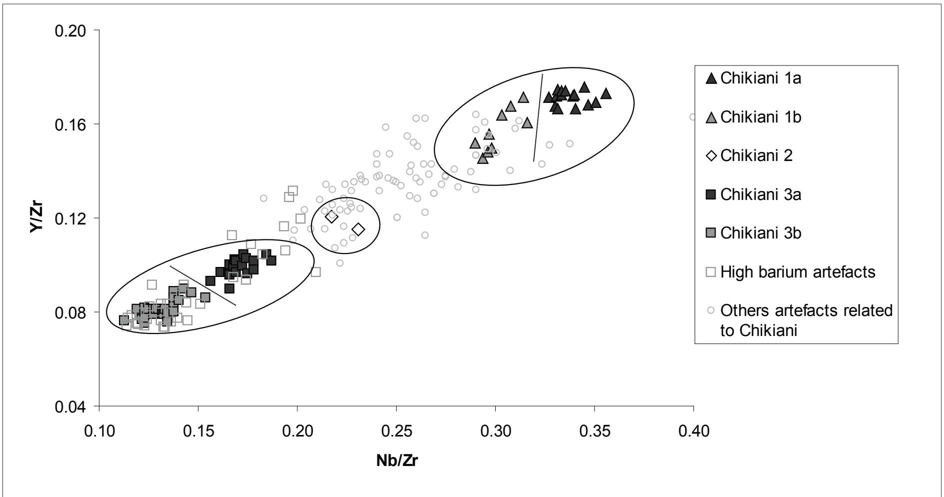


Figure 19. Binary diagram for the Y/Zr-Nb/Zr ratios of our geological corpus compared with those of archaeological artefacts originating from Chikiani (B. Gratuze unpublished values)

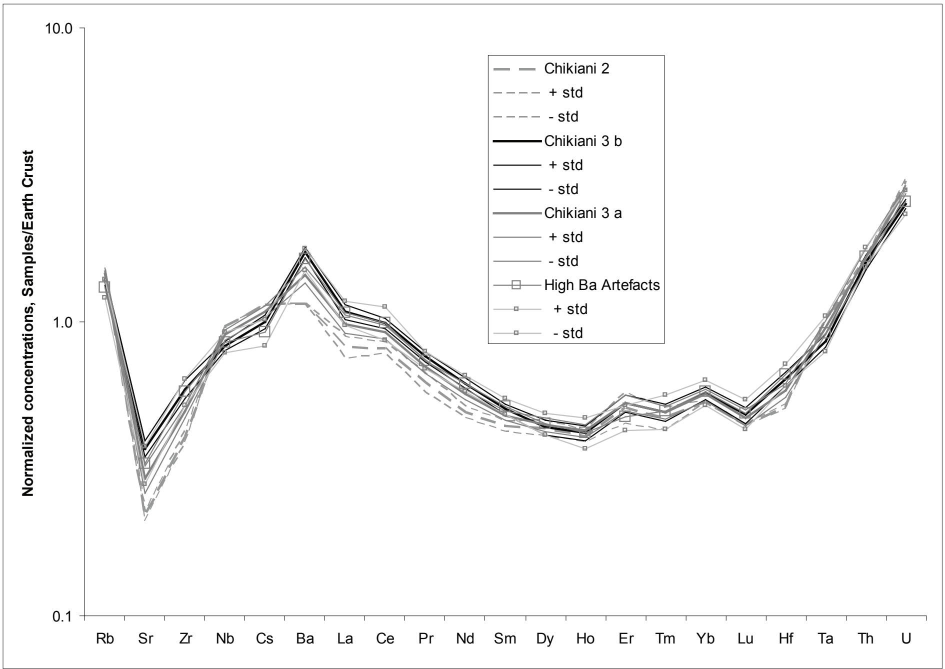


Figure 20. Rare earth element and extended trace normalized plots for group 2, 3a and 3b of our geological corpus compared with those of the high barium obsidian artefacts. Earth crust normalization from K.H. Wedepohl 1995

Plotting the other artefacts related to Chikiani in the Ba/Zr and Y/Zr-Nb/Zr diagrams, it comes out that a large majority can be better related to group 2 and sub-group 1b rather than the sub-group 1a. The Y/Zr-Nb/Zr diagram also points out that many of the above artefacts have an intermediate ratio between that defined for group 2 and sub-group 1b. This result shows that a more exhaustive survey of Chikiani area is absolutely necessary.

Table 2 summarizes the different sampling positions and samples which define our new groups and sub-groups, and gives their associated concentration range of strontium, zirconium and barium.

Regarding the discrimination between the different barium rich Caucasian obsidian sources Chikiani, Tsaghkunyats, Ashotsk and Ikizdere, fig. 1 shows that there is an overlap between Chikiani 3 (high barium artefacts group) and Tsaghkunyats 2. However as shown by C. Chataigner and B. Gratuze (2014a), the above two sources have a different Ba/Sr ratio. It is therefore possible to resolve this overlap by plotting barium versus strontium (fig. 21, the data from E.E. Frahm and J. Blackman are not reported as strontium was not determined by these authors). In this diagram we can observe that the different Chikiani groups and sub-groups are sepa-

| Chemical groups and sub groups | Samples | Sr/Zr/Ba content range in ppm |
|---|---|---|
| Chikiani 1a | 12 04 A, 12 04 B,<br>12 05 A, 12 05 B,<br>12 06 A, 12 06 B,<br>14 03 A, 14 03 B, 14 03 C, 14 03 D, 14 03 E,<br>14 04 A, 14 04 C, 14 04 D, 14 04 E | Sr: 52 - 62<br>Zr: 57 - 63<br>Ba: 455 - 516 |
| Chikiani 1b | 12 01 A,<br>12 02 A, 12 02 B,<br>12 03 A, 12 03 B,<br>14 02 A, 14 02 B,<br>14 04 B,<br>14 10 A | Sr: 55 - 63<br>Zr: 62 - 71<br>Ba: 490 - 549 |
| Chikiani 2 | 12 01 B,<br>14 11 C | Sr: 71 - 75<br>Zr: 80 - 85<br>Ba: 673 - 674 |
| Chikiani 3a | 14 05 A, 14 05 B, 14 05 C, 14 05 D,<br>14 06 A, 14 06 B,<br>14 07 A, 14 07 B, 14 07 C, 14 07 D,<br>14 09 A ,<br>14 10 E,<br>14 12 C, 14 12 D,<br>14 13 C, 14 13 D, 14 13 E,<br>14 15 C | Sr: 73 - 117<br>Zr: 91 - 109<br>Ba: 760 - 978 |
| Chikiani 3b | 14 08 A, 14 08 B, 14 08 C, 14 08 D, 14 08 E,<br>14 09 B, 14 09 C, 14 09 D,<br>14 10 B, 14 10 C, 14 10 D,<br>14 11 A, 14 11 B, 14 11 D, 14 11 E,<br>14 12 A, 14 12 B,<br>14 13 A, 14 13 B,<br>14 14 A, 14 14 B, 14 14 C, 14 14 D,<br>14 15 A, 14 15 B | Sr: 108 - 137<br>Zr: 106 - 141<br>Ba: 920 - 1063 |

Table 2. Group attribution of the geological samples according to the chemical sub-groups

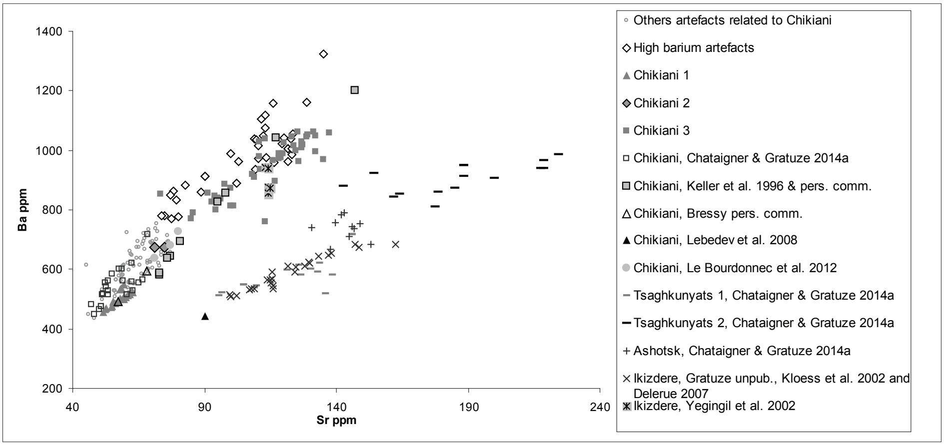


Figure 21. Binary diagram for the Sr-Ba contents of the barium rich Caucasian obsidian and the archaeological artefacts related to Chikiani

| | | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | Li | B | Ti | Mn | Fe | Zn | Rb | Sr | Y | Zr | Nb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Chikiani 1a | 12 04 A | 3.96 | 0.086 | 13.4 | 76.3 | 4.63 | 0.67 | 0.093 | 0.059 | 0.67 | 47 | 23 | 560 | 455 | 4707 | 46 | 122 | 52 | 9.8 | 59 | 20 |
| | 12 04 B | 3.74 | 0.087 | 13.7 | 76.3 | 4.50 | 0.71 | 0.094 | 0.059 | 0.67 | 47 | 23 | 561 | 458 | 4701 | 46 | 123 | 55 | 10.2 | 61 | 20 |
| | 12 05 A | 3.74 | 0.085 | 14.0 | 76.0 | 4.50 | 0.73 | 0.091 | 0.060 | 0.68 | 52 | 24 | 547 | 468 | 4789 | 46 | 126 | 56 | 10.2 | 60 | 20 |
| | 12 05 B | 3.82 | 0.086 | 13.7 | 76.2 | 4.54 | 0.67 | 0.092 | 0.062 | 0.67 | 48 | 24 | 552 | 477 | 4694 | 49 | 124 | 53 | 9.8 | 58 | 20 |
| | 12 06 A | 3.75 | 0.086 | 13.6 | 76.5 | 4.48 | 0.64 | 0.094 | 0.060 | 0.67 | 50 | 23 | 561 | 466 | 4700 | 46 | 119 | 52 | 9.8 | 58 | 20 |
| | 12 06 B | 3.59 | 0.085 | 13.1 | 76.9 | 4.55 | 0.77 | 0.11 | 0.058 | 0.74 | *46* | *23* | *679* | *452* | *5190* | *51* | *128* | *55* | *10.5* | *63* | *21* |
| | 14 03 A | 3.83 | 0.082 | 13.5 | 76.2 | 4.62 | 0.80 | 0.090 | 0.059 | 0.68 | 53 | 25 | 541 | 453 | 4755 | 57 | 133 | 58 | 10.2 | 59 | 20 |
| | 14 03 B | 3.82 | 0.080 | 13.4 | 76.4 | 4.55 | 0.77 | 0.086 | 0.059 | 0.69 | 54 | 24 | 515 | 457 | 4803 | 45 | 131 | 54 | 10.0 | 57 | 20 |
| | 14 03 C | 3.95 | 0.088 | 13.4 | 75.9 | 4.76 | 0.85 | 0.090 | 0.060 | 0.75 | *48* | *25* | *540* | *465* | *5225* | *58* | *133* | *56* | *9.9* | *57* | *20* |
| | 14 03 D | 3.64 | 0.084 | 13.8 | 76.0 | 4.69 | 0.85 | 0.090 | 0.057 | 0.61 | *49* | *30* | *539* | *442* | *4248* | *41* | *127* | *57* | *10.6* | *61* | *20* |
| | 14 03 E | 3.78 | 0.082 | 14.0 | 76.2 | 4.45 | 0.71 | 0.097 | 0.060 | 0.54 | *59* | *24* | *582* | *461* | *3763* | *44* | *130* | *59* | *10.4* | *60* | *20* |
| | 14 04 A | 3.92 | 0.086 | 13.8 | 75.7 | 4.63 | 0.76 | 0.088 | 0.060 | 0.76 | *57* | *25* | *529* | *466* | *5342* | *46* | *140* | *61* | *10.0* | *58* | *19* |
| | 14 04 C | 3.96 | 0.088 | 13.8 | 75.7 | 4.64 | 0.76 | 0.090 | 0.061 | 0.78 | *59* | *25* | *541* | *471* | *5441* | *47* | *138* | *62* | *10.2* | *60* | *19* |
| | 14 04 D | 3.86 | 0.086 | 13.8 | 75.9 | 4.58 | 0.76 | 0.090 | 0.060 | 0.76 | *58* | *25* | *537* | *465* | *5290* | *51* | *137* | *61* | *10.1* | *58* | *19* |
| | 14 04 E | 3.92 | 0.087 | 13.9 | 75.7 | 4.57 | 0.75 | 0.088 | 0.060 | 0.77 | *59* | *25* | *530* | *461* | *5389* | *50* | *137* | *60* | *9.9* | *57* | *19* |
| Chikiani 1b | 12 01 A | 3.81 | 0.098 | 13.4 | 76.3 | 4.56 | 0.69 | 0.10 | 0.058 | 0.80 | 46 | 22 | 623 | 447 | 5580 | 43 | 116 | 59 | 9.4 | 65 | 19 |
| | 12 02 A | 3.76 | 0.094 | 13.3 | 76.5 | 4.59 | 0.70 | 0.10 | 0.058 | 0.81 | 48 | 22 | 610 | 450 | 5631 | 48 | 124 | 58 | 10.0 | 68 | 20 |
| | 12 02 B | 3.69 | 0.093 | 13.7 | 76.2 | 4.61 | 0.71 | 0.10 | 0.059 | 0.76 | 44 | 22 | 607 | 458 | 5283 | 46 | 124 | 60 | 10.7 | 71 | 20 |
| | 12 03 A | 3.74 | 0.089 | 13.3 | 76.4 | 4.71 | 0.68 | 0.099 | 0.059 | 0.76 | 52 | 22 | 591 | 459 | 5346 | 47 | 120 | 55 | 10.1 | 63 | 20 |
| | 12 03 B | 3.82 | 0.098 | 13.5 | 76.2 | 4.56 | 0.72 | 0.10 | 0.059 | 0.80 | 48 | 22 | 608 | 454 | 5575 | 47 | 125 | 58 | 10.0 | 67 | 20 |
| | 14 02 A | 3.71 | 0.084 | 14.4 | 75.4 | 4.51 | 0.79 | 0.10 | 0.061 | 0.75 | *53* | *23* | *598* | *472* | *5270* | *47* | *130* | *60* | *10.9* | *65* | *20* |
| | 14 02 B | 3.68 | 0.083 | 14.5 | 75.6 | 4.39 | 0.78 | 0.099 | 0.058 | 0.73 | *53* | *23* | *594* | *453* | *5128* | *43* | *127* | *60* | *10.9* | *67* | *20* |
| | 14 04 B | 3.67 | 0.089 | 14.3 | 75.7 | 4.44 | 0.79 | 0.089 | 0.060 | 0.74 | *59* | *23* | *532* | *467* | *5195* | *46* | *130* | *63* | *10.5* | *62* | *19* |
| | 14 10 A | 3.93 | 0.089 | 14.1 | 75.3 | 4.69 | 0.81 | 0.10 | 0.061 | 0.81 | *53* | *24* | *619* | *475* | *5679* | *53* | *132* | *62* | *10.4* | *67* | *20* |
| Chikiani 2 | 12 01 B | 3.81 | 0.12 | 13.5 | 76.0 | 4.57 | 0.75 | 0.12 | 0.056 | 0.91 | 46 | 21 | 713 | 431 | 6373 | 49 | 117 | 71 | 9.2 | 80 | 18 |
| | 14 11 C | 3.60 | 0.11 | 13.5 | 76.2 | 4.51 | 0.90 | 0.12 | 0.052 | 0.88 | *42* | *21* | *699* | *405* | *6123* | *41* | *116* | *75* | *10.2* | *85* | *18* |
| Chikiani 3a | 14 05 A | 3.55 | 0.13 | 13.3 | 76.4 | 4.49 | 0.93 | 0.14 | 0.049 | 0.90 | *43* | *20* | *813* | *378* | *6266* | *46* | *109* | *93* | *10.4* | *104* | *18* |
| | 14 05 B | 3.35 | 0.12 | 13.5 | 76.3 | 4.53 | 0.85 | 0.13 | 0.049 | 0.90 | *41* | *19* | *800* | *376* | *6275* | *43* | *116* | *73* | *10.8* | *106* | *18* |
| | 14 05 C | 3.74 | 0.12 | 13.4 | 76.5 | 4.05 | 1.03 | 0.13 | 0.045 | 0.86 | *37* | *20* | *795* | *349* | *6040* | *39* | *104* | *113* | *10.6* | *103* | *18* |
| | 14 05 D | 3.42 | 0.14 | 13.6 | 76.1 | 4.35 | 0.93 | 0.14 | 0.052 | 1.11 | *43* | *19* | *827* | *403* | *7749* | *43* | *108* | *95* | *10.8* | *109* | *18* |
| | 14 06 A | 3.48 | 0.13 | 14.2 | 75.3 | 4.56 | 0.97 | 0.14 | 0.048 | 0.98 | *46* | *19* | *867* | *371* | *6823* | *41* | *111* | *101* | *10.0* | *104* | *17* |
| | 14 06 B | 3.73 | 0.12 | 13.5 | 75.9 | 4.56 | 0.88 | 0.14 | 0.051 | 0.97 | *49* | *21* | *831* | *394* | *6761* | *50* | *117* | *85* | *9.9* | *98* | *17* |
| | 14 07 A | 3.75 | 0.14 | 13.7 | 75.3 | 4.46 | 0.93 | 0.14 | 0.053 | 1.43 | *45* | *21* | *820* | *412* | *10020* | *54* | *113* | *94* | *9.3* | *91* | *17* |
| | 14 07 B | 3.77 | 0.16 | 13.4 | 75.8 | 4.53 | 1.00 | 0.14 | 0.050 | 0.99 | *41* | *21* | *822* | *388* | *6911* | *44* | *112* | *95* | *9.2* | *96* | *17* |
| | 14 07 C | 3.87 | 0.15 | 12.8 | 75.9 | 4.86 | 0.95 | 0.14 | 0.050 | 1.09 | *43* | *20* | *858* | *386* | *7650* | *49* | *120* | *91* | *8.9* | *99* | *16* |
| | 14 07 D | 3.48 | 0.12 | 14.0 | 75.7 | 4.28 | 1.03 | 0.13 | 0.047 | 0.95 | *39* | *19* | *796* | *366* | *6670* | *42* | *105* | *100* | *10.7* | *103* | *18* |
| | 14 09 A | 3.82 | 0.14 | 14.5 | 74.5 | 4.61 | 0.97 | 0.14 | 0.054 | 1.03 | *49* | *21* | *865* | *416* | *7170* | *48* | *120* | *94* | *9.6* | *98* | *18* |
| | 14 10 E | 3.73 | 0.13 | 13.9 | 75.4 | 4.61 | 0.90 | 0.14 | 0.053 | 0.94 | *49* | *20* | *810* | *407* | *6595* | *46* | *119* | *86* | *10.1* | *97* | *18* |
| | 14 12 C | 3.56 | 0.13 | 14.5 | 75.0 | 4.49 | 0.95 | 0.14 | 0.050 | 0.94 | *48* | *20* | *847* | *390* | *6586* | *41* | *111* | *96* | *10.5* | *105* | *17* |
| | 14 12 D | 3.63 | 0.15 | 14.3 | 75.0 | 4.54 | 0.97 | 0.15 | 0.052 | 1.06 | *45* | *19* | *887* | *404* | *7395* | *42* | *114* | *98* | *10.1* | *109* | *17* |
| | 14 13 C | 3.82 | 0.15 | 14.6 | 74.8 | 4.44 | 1.01 | 0.13 | 0.048 | 0.87 | *50* | *21* | *806* | *372* | *6089* | *38* | *119* | *111* | *9.9* | *103* | *17* |
| | 14 13 D | 4.22 | 0.16 | 14.0 | 75.1 | 4.16 | 0.99 | 0.14 | 0.051 | 0.99 | *48* | *21* | *812* | *398* | *6933* | *47* | *116* | *109* | *9.2* | *95* | *16* |
| | 14 13 E | 4.06 | 0.15 | 14.1 | 75.1 | 4.34 | 1.00 | 0.14 | 0.048 | 0.95 | *47* | *23* | *815* | *374* | *6645* | *44* | *115* | *117* | *9.2* | *96* | *16* |
| | 14 15 C | 3.71 | 0.14 | 14.3 | 75.1 | 4.46 | 0.97 | 0.13 | 0.049 | 0.97 | *53* | *20* | *777* | *382* | *6785* | *45* | *117* | *100* | *9.9* | *97* | *16* |
| Chikiani 3b | 14 08 A | 3.83 | 0.17 | 14.3 | 74.4 | 4.71 | 1.07 | 0.17 | 0.048 | 1.08 | *45* | *19* | *993* | *374* | *7561* | *44* | *112* | *118* | *9.7* | *116* | *16* |
| | 14 08 B | 3.56 | 0.15 | 14.7 | 74.4 | 4.69 | 1.03 | 0.17 | 0.045 | 1.06 | *49* | *18* | *1036* | *349* | *7391* | *40* | *110* | *113* | *10.0* | *123* | *16* |
| | 14 08 C | 3.86 | 0.18 | 14.3 | 74.3 | 4.48 | 1.10 | 0.17 | 0.050 | 1.30 | *43* | *19* | *1035* | *387* | *9059* | *46* | *111* | *118* | *9.1* | *114* | *16* |
| | 14 08 D | 3.74 | 0.17 | 14.7 | 74.3 | 4.44 | 1.11 | 0.17 | 0.047 | 1.15 | *45* | *18* | *1046* | *361* | *8038* | *71* | *108* | *124* | *10.2* | *126* | *16* |
| | 14 08 E | 3.78 | 0.17 | 14.6 | 74.2 | 4.42 | 1.09 | 0.17 | 0.048 | 1.30 | *44* | *19* | *1037* | *373* | *9082* | *52* | *109* | *120* | *10.2* | *126* | *16* |
| | 14 09 B | 3.78 | 0.18 | 14.4 | 74.5 | 4.43 | 1.13 | 0.17 | 0.051 | 1.19 | *44* | *19* | *991* | *395* | *8339* | *47* | *110* | *126* | *9.6* | *114* | *16* |
| | 14 09 C | 3.66 | 0.19 | 14.9 | 74.0 | 4.42 | 1.14 | 0.18 | 0.049 | 1.19 | *47* | *18* | *1068* | *379* | *8298* | *45* | *107* | *129* | *10.0* | *126* | *16* |
| | 14 09 D | 3.74 | 0.20 | 14.7 | 74.2 | 4.31 | 1.15 | 0.17 | 0.051 | 1.19 | *40* | *18* | *1043* | *393* | *8339* | *44* | *106* | *135* | *10.0* | *123* | *16* |
| | 14 10 B | 3.87 | 0.17 | 13.6 | 75.1 | 4.58 | 1.05 | 0.18 | 0.048 | 1.19 | *43* | *19* | *1067* | *369* | *8294* | *49* | *111* | *119* | *8.7* | *115* | *15* |
| | 14 10 C | 3.83 | 0.23 | 14.4 | 74.5 | 4.32 | 1.07 | 0.18 | 0.051 | 1.23 | *43* | *18* | *1088* | *397* | *8572* | *51* | *107* | *111* | *10.0* | *130* | *16* |
| | 14 10 D | 3.72 | 0.22 | 14.2 | 74.5 | 4.47 | 1.12 | 0.18 | 0.051 | 1.30 | *41* | *18* | *1098* | *395* | *9066* | *46* | *106* | *124* | *9.9* | *129* | *16* |
| | 14 11 A | 3.73 | 0.18 | 13.5 | 75.5 | 4.49 | 1.06 | 0.16 | 0.049 | 1.15 | *38* | *19* | *939* | *382* | *8045* | *45* | *107* | *108* | *9.1* | *106* | *16* |
| | 14 11 B | 3.55 | 0.17 | 13.7 | 75.7 | 4.32 | 1.06 | 0.15 | 0.049 | 1.11 | *38* | *18* | *927* | *377* | *7744* | *47* | *103* | *111* | *9.9* | *113* | *17* |
| | 14 11 D | 3.68 | 0.19 | 13.5 | 75.4 | 4.50 | 1.10 | 0.17 | 0.047 | 1.15 | *37* | *18* | *1011* | *363* | *8022* | *42* | *106* | *120* | *9.7* | *122* | *16* |
| | 14 11 E | 3.64 | 0.17 | 13.8 | 75.5 | 4.32 | 1.09 | 0.15 | 0.046 | 1.06 | *38* | *18* | *927* | *358* | *7448* | *41* | *104* | *116* | *10.2* | *119* | *16* |
| | 14 12 A | 3.90 | 0.18 | 14.2 | 74.6 | 4.49 | 1.08 | 0.18 | 0.046 | 1.13 | *44* | *18* | *1107* | *356* | *7919* | *44* | *108* | *123* | *9.4* | *125* | *15* |
| | 14 12 B | 3.73 | 0.20 | 14.6 | 74.5 | 4.31 | 1.17 | 0.18 | 0.049 | 1.10 | *39* | *18* | *1074* | *382* | *7690* | *46* | *104* | *132* | *10.6* | *131* | *16* |
| | 14 13 A | 3.82 | 0.15 | 14.7 | 74.5 | 4.41 | 1.07 | 0.15 | 0.044 | 0.98 | *46* | *20* | *906* | *344* | *6852* | *43* | *113* | *125* | *10.4* | *117* | *16* |
| | 14 13 B | 3.69 | 0.18 | 14.9 | 74.4 | 4.29 | 1.10 | 0.15 | 0.049 | 1.05 | *46* | *19* | *903* | *377* | *7338* | *40* | *112* | *127* | *10.1* | *113* | *16* |
| | 14 14 A | 4.02 | 0.19 | 14.2 | 74.1 | 4.68 | 1.11 | 0.16 | 0.049 | 1.26 | *49* | *20* | *981* | *382* | *8818* | *48* | *118* | *129* | *9.1* | *112* | *15* |
| | 14 14 B | 3.60 | 0.21 | 14.6 | 74.5 | 4.09 | 1.15 | 0.19 | 0.048 | 1.33 | *32* | *18* | *1161* | *370* | *9324* | *42* | *99* | *131* | *10.8* | *141* | *16* |
| | 14 14 C | 4.18 | 0.20 | 14.2 | 74.1 | 4.67 | 1.11 | 0.16 | 0.048 | 1.19 | *49* | *20* | *980* | *370* | *8319* | *52* | *119* | *132* | *9.2* | *115* | *15* |
| | 14 14 D | 3.78 | 0.20 | 14.6 | 74.4 | 4.31 | 1.15 | 0.16 | 0.049 | 1.22 | *48* | *19* | *976* | *381* | *8555* | *48* | *111* | *137* | *10.1* | *124* | *15* |
| | 14 15 A | 3.95 | 0.20 | 13.9 | 74.7 | 4.47 | 1.09 | 0.16 | 0.049 | 1.28 | *49* | *20* | *966* | *382* | *8931* | *53* | *112* | *127* | *8.6* | *108* | *14* |
| | 14 15 B | 4.14 | 0.22 | 13.5 | 74.6 | 4.77 | 1.11 | 0.16 | 0.048 | 1.23 | *48* | *20* | *962* | *375* | *8591* | *180* | *118* | *127* | *8.9* | *113* | *15* |
| H Ba artefacts | average | 3.79 | 0.18 | 13.6 | 75.3 | 4.22 | 0.80 | 0.16 | 0.048 | 1.07 | *35* | *21* | *941* | *373* | *7456* | *43* | *103* | *105* | *9.5* | *108* | *16* |
| | st. dev. | 0.20 | 0.03 | 0.3 | 0.5 | 0.12 | 0.22 | 0.02 | 0.005 | 0.25 | *6* | *7* | *144* | *36* | *1770* | *7* | *9* | *18* | *1.1* | *16* | *2* |
| | min | 3.50 | 0.13 | 13.0 | 74.8 | 4.07 | 0.31 | 0.11 | 0.039 | 0.57 | *12* | *12* | *671* | *302* | *4006* | *34* | *85* | *74* | *6.7* | *82* | *12* |
| | max | 4.17 | 0.24 | 14.5 | 76.6 | 4.47 | 1.02 | 0.19 | 0.057 | 1.84 | *44* | *44* | *1164* | *439* | *12865* | *58* | *129* | *135* | *12.5* | *135* | *19* |
| N612 | average | 13.3 | 0.0161 | 2.11 | 72.8 | 0.0112 | 11.7 | 0.0078 | 0.0051 | 0.0062 | 42.3 | 35.8 | 46.9 | 39.5 | 43.5 | 35.7 | 32.6 | 80.5 | 36.5 | 37.3 | 35.3 |
| | st. dev. | 0.4 | 0.0012 | 0.08 | 0.5 | 0.0030 | 0.4 | 0.0007 | 0.0001 | 0.0011 | 1.9 | 1.1 | 4.2 | 0.7 | 7.9 | 2.2 | 1.3 | 1.9 | 1.4 | 1.8 | 0.9 |

Table 3a. Compositions of the geological samples analysed by LA-ICP-MS; oxides are given in weight percent, elements are given in ppm. For the high barium artefacts group only average compositions, standard deviations minimum and maximum measured values are given. Concentration obtained for glass reference material NIST 612, analysed with the geological samples are also given

| | | Cs | Ba | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Hf | Ta | Th | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Chikiani 1a | 12 04 A | 4.3 | 465 | 16.8 | 35.4 | 3.13 | 10.4 | 2.10 | 0.54 | 2.13 | 0.34 | 1.71 | 0.34 | 1.04 | 0.14 | 1.10 | 0.16 | 2.20 | 1.28 | 12.2 | 5.52 |
| | 12 04 B | 4.3 | 477 | 17.8 | 36.9 | 3.22 | 10.8 | 2.12 | 0.54 | 2.13 | 0.35 | 1.73 | 0.35 | 1.06 | 0.14 | 1.14 | 0.16 | 2.23 | 1.28 | 12.6 | 5.64 |
| | 12 05 A | 4.4 | 486 | 17.2 | 36.2 | 3.22 | 10.7 | 2.16 | 0.54 | 2.25 | 0.35 | 1.72 | 0.35 | 1.06 | 0.15 | 1.15 | 0.15 | 2.19 | 1.26 | 12.4 | 5.66 |
| | 12 05 B | 4.4 | 468 | 16.4 | 35.4 | 3.08 | 10.4 | 2.02 | 0.49 | 1.95 | 0.33 | 1.74 | 0.35 | 1.04 | 0.14 | 1.11 | 0.16 | 2.19 | 1.28 | 12.2 | 5.73 |
| | 12 06 A | 4.2 | 455 | 16.3 | 34.7 | 3.06 | 10.3 | 2.03 | 0.48 | 1.87 | 0.31 | 1.69 | 0.34 | 1.00 | 0.14 | 1.10 | 0.16 | 2.12 | 1.27 | 12.0 | 5.47 |
| | 12 06 B | *4.4* | *490* | *19.8* | *40.8* | *3.60* | *11.3* | *2.13* | *0.63* | *2.34* | *0.40* | *1.73* | *0.34* | *1.08* | *0.14* | *1.10* | *0.15* | *2.19* | *1.25* | *13.6* | *5.95* |
| | 14 03 A | 4.7 | 503 | 18.2 | 38.4 | 3.38 | 11.1 | 2.16 | 0.52 | 2.52 | 0.38 | 1.73 | 0.35 | 1.11 | 0.15 | 1.08 | 0.15 | 2.12 | 1.24 | 12.3 | 5.93 |
| | 14 03 B | 4.6 | 473 | 17.0 | 36.2 | 3.22 | 10.5 | 2.04 | 0.57 | 2.42 | 0.36 | 1.66 | 0.34 | 1.07 | 0.14 | 1.09 | 0.14 | 2.08 | 1.19 | 11.9 | 5.73 |
| | 14 03 C | *4.7* | *484* | *17.7* | *37.2* | *3.36* | *10.6* | *2.14* | *0.79* | *2.79* | *0.42* | *1.72* | *0.33* | *1.11* | *0.13* | *1.10* | *0.14* | *2.15* | *1.22* | *12.2* | *5.78* |
| | 14 03 D | *4.4* | *487* | *18.1* | *36.8* | *3.36* | *11.0* | *2.19* | *0.72* | *2.82* | *0.43* | *1.79* | *0.36* | *1.18* | *0.14* | *1.14* | *0.15* | *2.21* | *1.31* | *12.9* | *5.59* |
| | 14 03 E | *4.6* | *497* | *18.0* | *36.8* | *3.37* | *11.1* | *2.25* | *0.23* | *2.19* | *0.30* | *1.81* | *0.35* | *1.03* | *0.15* | *1.09* | *0.16* | *2.29* | *1.24* | *12.4* | *5.62* |
| | 14 04 A | *4.9* | *513* | *16.9* | *35.5* | *3.16* | *10.6* | *2.13* | *0.51* | *2.65* | *0.33* | *1.73* | *0.33* | *1.01* | *0.15* | *1.09* | *0.15* | *2.13* | *1.15* | *11.4* | *5.60* |
| | 14 04 C | *4.9* | *516* | *17.5* | *36.7* | *3.29* | *10.9* | *2.18* | *0.56* | *2.65* | *0.34* | *1.76* | *0.36* | *1.05* | *0.15* | *1.12* | *0.16* | *2.21* | *1.20* | *12.2* | *5.79* |
| | 14 04 D | *4.9* | *516* | *17.2* | *36.5* | *3.22* | *11.0* | *2.15* | *0.51* | *2.47* | *0.32* | *1.69* | *0.33* | *0.98* | *0.15* | *1.13* | *0.15* | *2.05* | *1.14* | *11.4* | *5.54* |
| | 14 04 E | *4.8* | *509* | *17.2* | *36.5* | *3.14* | *10.3* | *2.10* | *0.50* | *2.51* | *0.34* | *1.66* | *0.33* | *1.03* | *0.15* | *1.13* | *0.15* | *2.06* | *1.19* | *11.8* | *5.78* |
| Chikiani 1b | 12 01 A | 4.0 | 531 | 19.1 | 39.4 | 3.38 | 11.2 | 2.14 | 0.57 | 2.08 | 0.33 | 1.61 | 0.32 | 0.99 | 0.14 | 1.04 | 0.15 | 2.26 | 1.18 | 12.2 | 5.24 |
| | 12 02 A | 4.3 | 531 | 20.2 | 41.8 | 3.58 | 11.7 | 2.20 | 0.55 | 2.10 | 0.33 | 1.65 | 0.33 | 1.00 | 0.14 | 1.10 | 0.15 | 2.32 | 1.24 | 13.0 | 5.69 |
| | 12 02 B | 4.3 | 549 | 21.0 | 41.8 | 3.66 | 12.2 | 2.35 | 0.57 | 2.22 | 0.35 | 1.85 | 0.36 | 1.10 | 0.16 | 1.14 | 0.17 | 2.46 | 1.29 | 13.9 | 5.63 |
| | 12 03 A | 4.2 | 490 | 18.3 | 37.2 | 3.29 | 11.1 | 2.13 | 0.55 | 2.12 | 0.35 | 1.75 | 0.34 | 1.07 | 0.14 | 1.07 | 0.16 | 2.27 | 1.29 | 12.8 | 5.35 |
| | 12 03 B | 4.5 | 536 | 19.6 | 40.1 | 3.48 | 11.6 | 2.16 | 0.57 | 2.17 | 0.35 | 1.63 | 0.34 | 1.03 | 0.15 | 1.06 | 0.16 | 2.25 | 1.23 | 12.7 | 5.55 |
| | 14 02 A | *4.5* | *504* | *18.0* | *36.6* | *3.25* | *11.2* | *2.18* | *0.57* | *2.72* | *0.38* | *1.84* | *0.37* | *1.11* | *0.15* | *1.18* | *0.17* | *2.26* | *1.27* | *12.6* | *5.49* |
| | 14 02 B | *4.4* | *498* | *18.4* | *36.6* | *3.28* | *11.4* | *2.26* | *0.59* | *2.69* | *0.39* | *1.85* | *0.37* | *1.13* | *0.15* | *1.19* | *0.17* | *2.38* | *1.27* | *12.7* | *5.42* |
| | 14 04 B | *4.5* | *522* | *17.7* | *36.0* | *3.33* | *11.1* | *2.19* | *0.52* | *2.65* | *0.34* | *1.79* | *0.37* | *1.05* | *0.15* | *1.15* | *0.16* | *2.21* | *1.17* | *11.9* | *5.45* |
| | 14 10 A | *4.7* | *527* | *18.6* | *37.4* | *3.38* | *11.3* | *2.22* | *0.63* | *2.88* | *0.38* | *1.78* | *0.36* | *1.10* | *0.15* | *1.15* | *0.16* | *2.19* | *1.22* | *12.1* | *5.51* |
| Chikiani 2 | 12 01 B | 3.9 | 674 | 23.2 | 47.4 | 3.93 | 12.9 | 2.27 | 0.59 | 2.17 | 0.31 | 1.58 | 0.32 | 0.98 | 0.13 | 1.06 | 0.16 | 2.49 | 1.12 | 12.8 | 5.19 |
| | 14 11 C | *3.9* | *673* | *26.1* | *50.3* | *4.37* | *13.7* | *2.40* | *0.87* | *3.24* | *0.46* | *1.73* | *0.34* | *1.17* | *0.15* | *1.08* | *0.16* | *2.56* | *1.13* | *13.9* | *5.03* |
| Chikiani 3a | 14 05 A | *3.6* | *827* | *32.6* | *59.9* | *5.03* | *15.9* | *2.52* | *0.92* | *3.30* | *0.46* | *1.71* | *0.35* | *1.16* | *0.15* | *1.15* | *0.17* | *3.01* | *1.13* | *15.3* | *5.01* |
| | 14 05 B | *3.5* | *854* | *32.4* | *58.7* | *5.06* | *15.6* | *2.58* | *0.93* | *3.31* | *0.46* | *1.81* | *0.36* | *1.23* | *0.15* | *1.14* | *0.17* | *3.05* | *1.10* | *15.7* | *4.87* |
| | 14 05 C | *3.6* | *760* | *31.8* | *58.7* | *5.09* | *15.9* | *2.55* | *0.89* | *3.16* | *0.45* | *1.73* | *0.36* | *1.19* | *0.15* | *1.14* | *0.17* | *3.01* | *1.08* | *15.5* | *5.00* |
| | 14 05 D | *3.4* | *840* | *33.4* | *59.9* | *5.19* | *16.3* | *2.54* | *0.88* | *3.20* | *0.46* | *1.82* | *0.36* | *1.21* | *0.16* | *1.14* | *0.18* | *3.20* | *1.14* | *16.0* | *4.99* |
| | 14 06 A | *3.6* | *813* | *29.2* | *55.5* | *4.71* | *15.5* | *2.61* | *0.72* | *3.21* | *0.38* | *1.72* | *0.34* | *1.11* | *0.15* | *1.16* | *0.16* | *2.91* | *1.06* | *14.1* | *4.76* |
| | 14 06 B | *3.8* | *769* | *28.3* | *53.6* | *4.52* | *14.7* | *2.40* | *0.68* | *2.95* | *0.37* | *1.71* | *0.34* | *1.05* | *0.14* | *1.08* | *0.16* | *2.68* | *1.05* | *13.8* | *4.89* |
| | 14 07 A | *3.7* | *801* | *27.5* | *52.7* | *4.56* | *14.6* | *2.42* | *0.81* | *3.02* | *0.37* | *1.54* | *0.32* | *1.05* | *0.14* | *1.11* | *0.16* | *2.71* | *1.03* | *13.2* | *4.89* |
| | 14 07 B | *3.5* | *827* | *28.9* | *55.7* | *4.75* | *14.7* | *2.44* | *1.08* | *3.59* | *0.45* | *1.58* | *0.34* | *1.14* | *0.14* | *1.05* | *0.14* | *2.74* | *1.03* | *13.6* | *4.88* |
| | 14 07 C | *3.8* | *857* | *30.2* | *59.3* | *4.86* | *15.3* | *2.38* | *0.99* | *3.52* | *0.44* | *1.56* | *0.30* | *1.06* | *0.13* | *1.02* | *0.15* | *2.67* | *0.93* | *13.5* | *4.94* |
| | 14 07 D | *3.5* | *814* | *30.5* | *54.5* | *4.87* | *15.4* | *2.57* | *1.07* | *3.75* | *0.48* | *1.79* | *0.35* | *1.24* | *0.15* | *1.20* | *0.17* | *2.97* | *1.12* | *14.9* | *4.75* |
| | 14 09 A | *4.0* | *846* | *26.9* | *51.8* | *4.42* | *14.7* | *2.53* | *0.89* | *4.13* | *0.43* | *1.71* | *0.33* | *1.12* | *0.15* | *1.18* | *0.17* | *2.77* | *1.09* | *12.9* | *4.73* |
| | 14 10 E | *3.9* | *790* | *27.7* | *52.4* | *4.47* | *14.7* | *2.52* | *0.73* | *3.07* | *0.39* | *1.74* | *0.35* | *1.07* | *0.15* | *1.15* | *0.17* | *2.70* | *1.09* | *13.9* | *5.00* |
| | 14 12 C | *3.6* | *836* | *29.1* | *53.1* | *4.64* | *15.7* | *2.69* | *0.77* | *3.48* | *0.41* | *1.79* | *0.37* | *1.17* | *0.15* | *1.23* | *0.18* | *2.98* | *1.10* | *14.4* | *4.67* |
| | 14 12 D | *3.6* | *887* | *30.3* | *55.3* | *4.80* | *15.7* | *2.56* | *0.83* | *3.56* | *0.40* | *1.71* | *0.35* | *1.12* | *0.15* | *1.13* | *0.17* | *2.95* | *1.03* | *14.0* | *4.59* |
| | 14 13 C | *3.9* | *978* | *29.9* | *56.0* | *4.79* | *16.1* | *2.74* | *1.01* | *3.80* | *0.38* | *1.78* | *0.35* | *1.08* | *0.15* | *1.15* | *0.18* | *3.01* | *1.02* | *13.6* | *4.62* |
| | 14 13 D | *4.0* | *909* | *27.5* | *52.9* | *4.51* | *14.7* | *2.58* | *0.71* | *3.52* | *0.34* | *1.58* | *0.32* | *1.03* | *0.14* | *1.13* | *0.16* | *2.71* | *0.97* | *12.5* | *4.72* |
| | 14 13 E | *3.8* | *896* | *27.4* | *53.6* | *4.47* | *14.8* | *2.55* | *0.70* | *3.65* | *0.35* | *1.60* | *0.32* | *1.03* | *0.15* | *1.09* | *0.16* | *2.79* | *0.97* | *12.6* | *4.66* |
| | 14 15 C | *3.8* | *872* | *27.6* | *51.9* | *4.52* | *15.0* | *2.59* | *0.70* | *3.35* | *0.36* | *1.63* | *0.33* | *1.00* | *0.15* | *1.13* | *0.17* | *2.78* | *1.01* | *13.1* | *4.57* |
| Chikiani 3b | 14 08 A | *3.6* | *974* | *30.6* | *56.7* | *4.85* | *16.3* | *2.63* | *0.94* | *4.15* | *0.42* | *1.68* | *0.35* | *1.14* | *0.15* | *1.18* | *0.17* | *3.09* | *0.97* | *13.4* | *4.25* |
| | 14 08 B | *3.4* | *1037* | *32.6* | *58.7* | *5.10* | *16.9* | *2.79* | *0.90* | *4.08* | *0.43* | *1.68* | *0.34* | *1.12* | *0.15* | *1.18* | *0.18* | *3.24* | *0.97* | *13.8* | *4.22* |
| | 14 08 C | *3.5* | *987* | *30.3* | *56.4* | *4.77* | *15.8* | *2.49* | *0.95* | *4.26* | *0.41* | *1.61* | *0.32* | *1.11* | *0.14* | *1.11* | *0.17* | *2.96* | *0.93* | *12.8* | *4.29* |
| | 14 08 D | *3.4* | *1015* | *32.9* | *58.6* | *5.09* | *16.9* | *2.69* | *0.93* | *4.12* | *0.43* | *1.75* | *0.34* | *1.15* | *0.15* | *1.17* | *0.18* | *3.28* | *0.95* | *13.8* | *4.14* |
| | 14 08 E | *3.4* | *1024* | *33.3* | *58.8* | *5.16* | *17.3* | *2.83* | *0.93* | *4.33* | *0.45* | *1.74* | *0.35* | *1.20* | *0.16* | *1.22* | *0.18* | *3.21* | *0.98* | *13.7* | *4.17* |
| | 14 09 B | *3.5* | *963* | *30.2* | *55.4* | *4.85* | *16.2* | *2.60* | *0.95* | *4.20* | *0.43* | *1.67* | *0.33* | *1.16* | *0.15* | *1.13* | *0.17* | *3.04* | *0.99* | *12.9* | *4.26* |
| | 14 09 C | *3.3* | *1046* | *33.4* | *58.7* | *5.22* | *17.1* | *2.76* | *1.00* | *4.35* | *0.43* | *1.72* | *0.34* | *1.16* | *0.15* | *1.18* | *0.18* | *3.21* | *0.97* | *13.7* | *4.13* |
| | 14 09 D | *3.2* | *970* | *32.1* | *58.5* | *4.99* | *16.7* | *2.73* | *0.95* | *4.29* | *0.43* | *1.70* | *0.36* | *1.15* | *0.15* | *1.18* | *0.17* | *3.19* | *0.97* | *13.6* | *4.08* |
| | 14 10 B | *3.4* | *975* | *31.4* | *59.9* | *4.92* | *15.9* | *2.55* | *0.85* | *3.62* | *0.37* | *1.50* | *0.30* | *1.01* | *0.13* | *1.06* | *0.15* | *2.88* | *0.87* | *12.7* | *4.34* |
| | 14 10 C | *3.2* | *1029* | *34.4* | *61.6* | *5.27* | *17.3* | *2.81* | *0.92* | *3.87* | *0.43* | *1.73* | *0.35* | *1.11* | *0.15* | *1.15* | *0.17* | *3.26* | *0.97* | *13.9* | *4.23* |
| | 14 10 D | *3.3* | *998* | *33.7* | *61.1* | *5.26* | *16.8* | *2.67* | *0.92* | *3.80* | *0.40* | *1.65* | *0.33* | *1.09* | *0.14* | *1.16* | *0.17* | *3.15* | *0.92* | *13.7* | *4.24* |
| | 14 11 A | *3.4* | *920* | *31.7* | *61.2* | *5.12* | *15.7* | *2.55* | *1.14* | *3.79* | *0.47* | *1.50* | *0.31* | *1.13* | *0.13* | *1.08* | *0.14* | *2.87* | *0.96* | *13.8* | *4.65* |
| | 14 11 B | *3.3* | *936* | *33.2* | *61.9* | *5.28* | *16.5* | *2.54* | *1.07* | *3.77* | *0.48* | *1.62* | *0.34* | *1.17* | *0.17* | *1.19* | *0.16* | *3.08* | *0.98* | *14.2* | *4.57* |
| | 14 11 D | *3.3* | *988* | *35.2* | *65.3* | *5.46* | *17.3* | *2.65* | *1.14* | *3.89* | *0.48* | *1.68* | *0.32* | *1.18* | *0.15* | *1.13* | *0.16* | *3.24* | *0.95* | *14.4* | *4.44* |
| | 14 11 E | *3.3* | *966* | *34.2* | *61.0* | *5.38* | *16.7* | *2.67* | *1.16* | *3.95* | *0.50* | *1.69* | *0.35* | *1.24* | *0.15* | *1.14* | *0.17* | *3.23* | *1.02* | *14.8* | *4.46* |
| | 14 12 A | *3.3* | *1045* | *33.2* | *61.5* | *5.14* | *16.9* | *2.68* | *0.92* | *3.94* | *0.41* | *1.64* | *0.33* | *1.07* | *0.15* | *1.11* | *0.17* | *3.08* | *0.94* | *13.3* | *4.22* |
| | 14 12 B | *3.2* | *995* | *34.3* | *59.6* | *5.26* | *17.5* | *2.85* | *0.99* | *4.02* | *0.41* | *1.79* | *0.35* | *1.16* | *0.15* | *1.18* | *0.17* | *3.30* | *0.93* | *14.1* | *4.05* |
| | 14 13 A | *3.7* | *1061* | *32.3* | *57.6* | *5.15* | *17.3* | *2.87* | *0.78* | *4.11* | *0.40* | *1.77* | *0.36* | *1.15* | *0.16* | *1.21* | *0.19* | *3.23* | *1.00* | *13.9* | *4.37* |
| | 14 13 B | *3.5* | *1028* | *31.0* | *56.3* | *5.01* | *16.4* | *2.63* | *0.84* | *4.01* | *0.39* | *1.74* | *0.35* | *1.10* | *0.16* | *1.20* | *0.17* | *3.15* | *1.01* | *13.6* | *4.43* |
| | 14 14 A | *3.7* | *1051* | *30.3* | *55.8* | *4.90* | *16.0* | *2.62* | *0.89* | *4.29* | *0.36* | *1.58* | *0.31* | *0.99* | *0.14* | *1.09* | *0.16* | *2.92* | *0.89* | *12.0* | *4.22* |
| | 14 14 B | *3.1* | *1063* | *37.4* | *64.8* | *5.62* | *18.4* | *2.82* | *0.91* | *3.74* | *0.41* | *1.85* | *0.37* | *1.16* | *0.16* | *1.23* | *0.19* | *3.46* | *0.97* | *15.0* | *4.23* |
| | 14 14 C | *3.7* | *1050* | *30.8* | *58.3* | *4.94* | *16.3* | *2.59* | *0.85* | *3.93* | *0.38* | *1.55* | *0.32* | *1.05* | *0.13* | *1.10* | *0.16* | *3.03* | *0.89* | *12.3* | *4.34* |
| | 14 14 D | *3.4* | *1058* | *32.7* | *58.6* | *5.14* | *17.3* | *2.74* | *0.85* | *4.03* | *0.39* | *1.74* | *0.34* | *1.07* | *0.15* | *1.16* | *0.18* | *3.30* | *0.90* | *13.4* | *4.05* |
| | 14 15 A | *3.5* | *1008* | *29.3* | *57.1* | *4.74* | *15.8* | *2.48* | *0.77* | *3.63* | *0.33* | *1.43* | *0.29* | *0.95* | *0.13* | *1.03* | *0.16* | *2.75* | *0.88* | *12.0* | *4.33* |
| | 14 15 B | *3.8* | *1018* | *31.0* | *58.6* | *4.90* | *15.9* | *2.56* | *0.82* | *3.50* | *0.33* | *1.55* | *0.31* | *0.94* | *0.13* | *1.04* | *0.16* | *2.99* | *0.85* | *12.4* | *4.44* |
| H Ba artefacts | average | *3.3* | *976* | *30.8* | *59.1* | *4.90* | *16.8* | *2.72* | *0.64* | *2.38* | *0.30* | *1.71* | *0.34* | *1.00* | *0.15* | *1.15* | *0.17* | *3.12* | *1.04* | *13.7* | *4.58* |
| | st. dev. | *1.2* | *120* | *3.5* | *6.7* | *0.40* | *1.5* | *0.17* | *0.07* | *0.36* | *0.03* | *0.14* | *0.04* | *0.10* | *0.02* | *0.11* | *0.02* | *0.49* | *0.18* | *1.3* | *0.60* |
| | min | *1.2* | *769* | *24.7* | *51.0* | *4.20* | *13.0* | *2.40* | *0.52* | *1.88* | *0.24* | *1.47* | *0.27* | *0.82* | *0.12* | *1.00* | *0.14* | *1.90* | *0.77* | *10.1* | *3.79* |
| | max | *9.5* | *1324* | *37.1* | *87.0* | *5.77* | *20.0* | *3.04* | *0.80* | *3.05* | *0.38* | *2.15* | *0.45* | *1.24* | *0.20* | *1.43* | *0.21* | *4.11* | *1.48* | *17.2* | *6.15* |
| N612 | average | 41.6 | 36.7 | 37.0 | 38.4 | 36.4 | 34.6 | 36.3 | 36.3 | 35.0 | 36.1 | 33.7 | 36.4 | 34.8 | 34.2 | 38.3 | 34.9 | 35.0 | 31.3 | 36.9 | 36.6 |
| | st. dev. | 1.7 | 1.0 | 1.6 | 1.5 | 1.5 | 1.0 | 1.0 | 1.0 | 2.8 | 1.3 | 1.2 | 1.2 | 1.3 | 1.2 | 1.6 | 1.1 | 1.3 | 1.1 | 1.7 | 1.7 |

Table 3b. Compositions of the geological samples analysed by LA-ICP-MS; elements are given in ppm. For the high barium artefacts group only average compositions, standard deviations minimum and maximum measured values are given. Concentration obtained for glass reference material NIST 612, analysed with the geological samples are also given

rated from the other obsidian sources with the exception of some values published by Z. Yegingil (Yegingil et al. 2002) for Ikizdere. We can also notice that data published by S.A. Lebedev show a different barium/strontium ratio as it is the case for barium/zirconium. The distinction between these different Caucasian barium rich obsidian sources can thus be easily obtained by using the two graphs shown above.

## 6 Discussion

The characterization of the Chikiani specimens collected during the 2012 and 2014 surveys contribute to the redefinition of the complex pattern of procurement and exchange of Caucasian obsidian in prehistory suggested just a few years ago (see f.i. Chataigner, Barge 2010; Badalyan 2010).

According to the available data, Mt. Chikiani sources were exploited throughout quite a long period, at least from the Early Neolithic (Nebieridze 1972), as shown by the characterization of three samples from Kobuleti, near Batumi, along the Black Sea coast of Georgia (B. Gratuze unpublished data, 2013), to the Middle Bronze Age (Badalyan 2010, 32). The supply zone undoubtedly covers quite a wide territory. In fact Chikiani obsidians have been recovered from a site located ca 500 km south-east of the source (Chataigner, Barge 2010, fig. 6). Nevertheless, at present little is still known of the modes of exploitation of the different Chikiani flows, and even less of the precise location of the exploitation zones during the different periods.

The new characterizations presented in this paper, according to which three Chikiani obsidian groups have been identified for the first time, help interpret the complexity of the role played by Caucasian obsidian exploitation and its modes of circulation inside and outside the territory (Biagi et al. 2014, 7). At present we know only a few cases from which obsidians from different sources were utilised during the same period of occupation at the same site (see f.i. Lyonnet et al. 2012, 176). In contrast, it is unfortunate that very little is known of the obsidians from important Neolithic and later settlements like Aruchlo for example (Gatsov, Nedelcheva 2008; Hansen et al. 2013), located further east along the course of the Chrami river, a watercourse whose relevance has already been pointed out in chapter 3.

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