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Ptghni: A new obsidian source in the Hrazdan River basin, Armenia

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ABSTRACT

Here we report our recent discovery of a new obsidian source in central Armenia. Using portable XRF, we were able to chemically identify "Ptghni" obsidian as a previously unrecognized source on the same day that we first encountered it during our field surveys. Obsidian was found in alluvial-lacustrine sediments exposed within the Hrazdan Gorge, where it had been deposited after having eroded from an upstream source. These sediments were covered by mafic lavas and later exposed by downcutting of the Hrazdan River. Based on the stratigraphy of the gorge, the lava flows – and, therefore, the sediments sandwiched between them – predate 441 ka. The composition of Ptghni obsidian does not fit into the chemical trends of known sources in the Gegham and Tsaghkunyats ranges, so its precise volcanic origin remains unknown. Comparisons to unidentified artifacts in the literature revealed no matches, but obsidian sourcing work in Armenia has largely focused on the Holocene, when the Ptghni source might no longer have been accessible. The discovery of Ptghni obsidian is crucial for research into early hominin expansions given that it was an obsidian source available for use as toolstone by hominins during the Early and/or Middle Pleistocene.

1. Introduction

The Southern Caucasus – what is now Armenia, Georgia, and Azerbaijan – is a region crucial for understanding hominin expansions throughout Eurasia. The earliest fossil evidence of hominins outside Africa occurs at Dmanisi (Georgia), where *Homo erectus* crania and skulls have been dated to ~1.8 Ma (Lordkipanadze et al., 2013). Sites of similar antiquity are anticipated elsewhere in the Southern Caucasus, including within the contemporary borders of Armenia. During the Soviet era, archaeologists found Acheulian hand axes and other Palaeolithic artifacts, including Levallois cores and tools, at surface sites across the country (Gasparyan et al., 2014a). Such discoveries inspired a recent series of archaeological surveys focused on identifying stratified Middle to Late Pleistocene sites (e.g., Gasparyan, 2010; Adler et al., 2012; Egeland et al., 2014; Gasparyan et al., 2014a, 2014b), revealing, among them, the earliest evidence of the Lower to Middle Palaeolithic transition at the site of Nor Geghi 1 at ~335–325 ka (Adler et al., 2014). One complicating factor for such surveys is the considerable degree of landscape change that has occurred over the last 2 million years. The northward push of the Arabian plate into the Eurasian plate shaped the region's geomorphological features, including mountain building, tectonic uplift, and Quaternary volcanism. Nor Geghi 1, for example, was covered by a ~200 ka mafic lava flow and later exposed as the Hrazdan River sliced into volcanic and sedimentary strata, creating a deeply incised gorge. Therefore, our international project – Pleistocene Archaeology, Geochronology, and Environment of the Southern Caucasus (PAGES) – has been mapping the Hrazdan River basin (Fig. 1A) to improve our reconstructions of the Pleistocene landscape and, in turn, chances of locating Palaeolithic sites.

Extensive Quaternary volcanism in Armenia also created one of the world's most obsidian-rich landscapes. At Palaeolithic sites in the Hrazdan River basin, obsidian comprises the majority, if not the entirety, of artifact assemblages (e.g., Nor Geghi 1, Adler et al., 2014; Lusakert Cave 1, Adler et al., 2012; Frahm et al., 2016; see also Gasparyan et al., 2014a, 2014b). Almost exclusive exploitation of obsidian also occurs at archaeological sites near the Arteni and the Syunik sources (Fig. 1A; e.g., Barozh 12, Glauberman et al., 2016). Obsidian sourcing is particularly insightful in such settings. Therefore,

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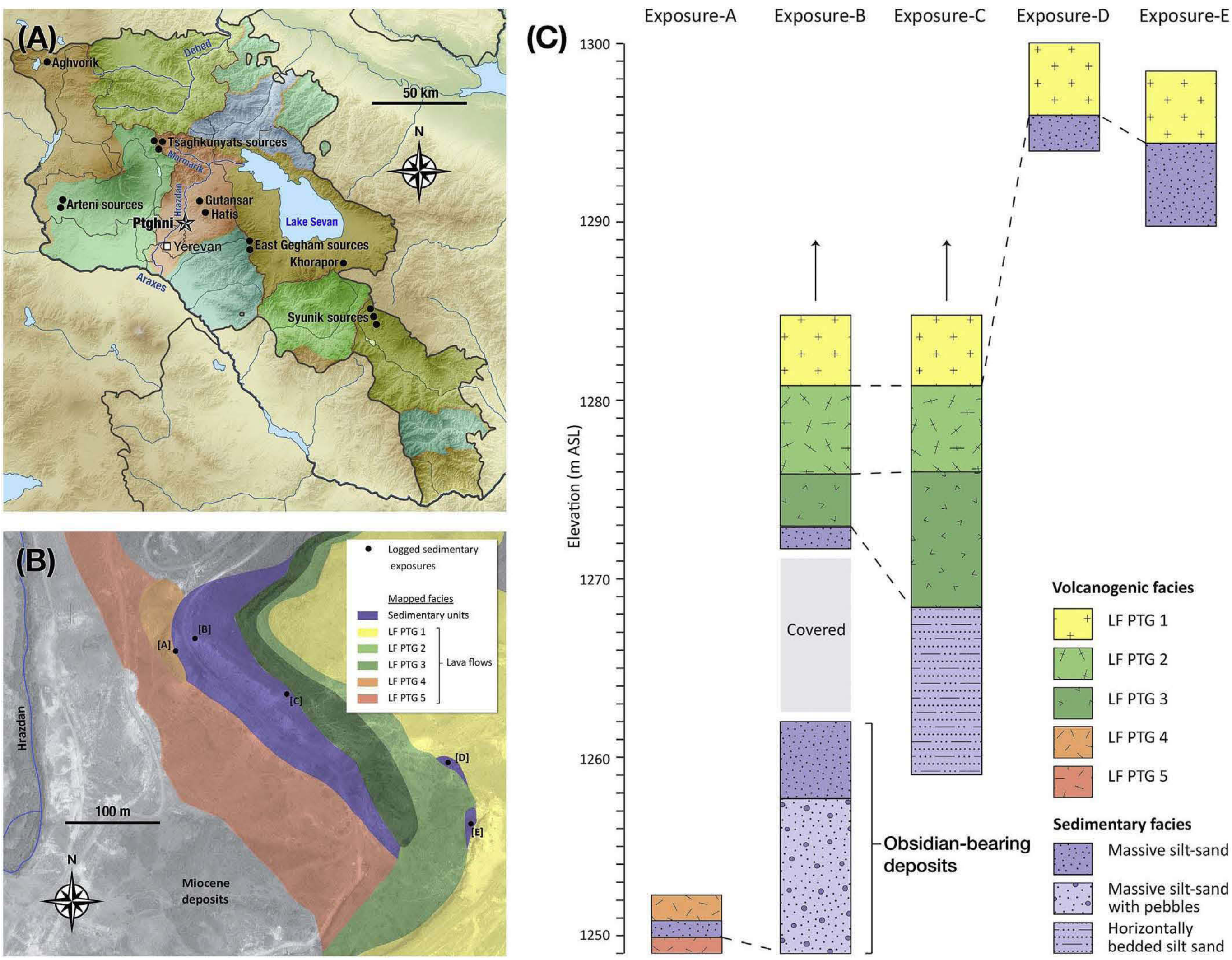

Fig. 1. (A) Known obsidian sources in Armenia in relation to the main river basins (shaded in different colors). A star denotes the location of Ptghni, and rivers of interest are also labelled. (B) Geological map of the Ptghni area showing the locations of lava flows (numbered 1 through 5) and sedimentary exposures (labelled A through E). (C) Stratigraphic sections of exposures labelled in (B). The obsidian-bearing sedimentary deposits are located in Exposure B.

since 2012, we have conducted portable X-ray fluorescence analyses (pXRF) of obsidian artifacts and geological specimens in our field lab in Armenia and in the field itself (i.e., at sites and volcanoes, Frahm et al., 2014a). The use of pXRF has enabled us to generate geochemical datasets, which include hundreds of geological specimens and thousands of obsidian artifacts, that would not have otherwise been possible or practical (e.g., Adler et al., 2014).

In 2016, the PAGES team conducted walkover surveys through and around the Hrazdan Gorge to record volcanic (i.e., mafic and felsic lava flows, pyroclastic flows) and sedimentary (i.e., alluvial and lacustrine sediments as well as paleosols developed within them) facies that date from the Early Pleistocene to the middle Holocene (~2 Ma to 8 ka). There was a particular focus on the lower stratigraphic layers to search for sites of similar age to and older than Nor Geghi 1 as well as sediments that contain palaeoenvironmental proxies. Volcanic and sedimentary sequences were documented using standard descriptive and photographic methods and precisely located using a differential global positioning system (dGPS). Additionally, the mafic lava outcrops were analyzed using pXRF to reveal their correlations and stratigraphic relationships.

One of the thickest volcanic-sedimentary complexes encountered during our 2016 surveys lies ~2 km southwest of Ptghni village (pronounced similar to */p tin nē/*; 40.25216° N, 44.56364° E) and ~9 km northeast of Yerevan (Fig. 1A). At this location, at least five lavas and two sequences of alluvial-lacustrine sediments are exposed in the eastern wall of the Hrazdan Gorge above Upper Miocene marine deposits. Obsidian nodules were found as isolates and stringers within lenticular beds associated with the sediments, having eroded from an upstream primary source. Based on the basin stratigraphy, the lavas – and, in turn, the alluvial-lacustrine sediments sandwiched between them – predate a lava that has been dated to 441 ± 6 ka (Adler et al., 2014). Our pXRF analyses, conducted in our field lab on the same day that this exposure was encountered during our walkover surveys, revealed that the obsidian was chemically distinct from known sources in Armenia. No unidentified obsidian artifacts in the literature match the Ptghni chemical signature; however, earlier obsidian sourcing work in Armenia has principally focused on artifacts dated to the Holocene (e.g., Keller et al., 1996; Blackman et al., 1998; Badalyan et al., 2004; Cherry et al., 2010; Chataigner and Gratuze, 2014a, 2014b), when the Ptghni source might no longer have been accessible on the landscape. The discovery of Ptghni obsidian, however, is crucial for current and future studies of early hominin occupations and expansions in the Southern Caucasus, revealing a new obsidian source that could have been used for toolstone. If indeed Ptghni obsidian has not been attainable during the Holocene, artifacts possessing its trace-element "fingerprint," even if encountered in a surface scatter or museum

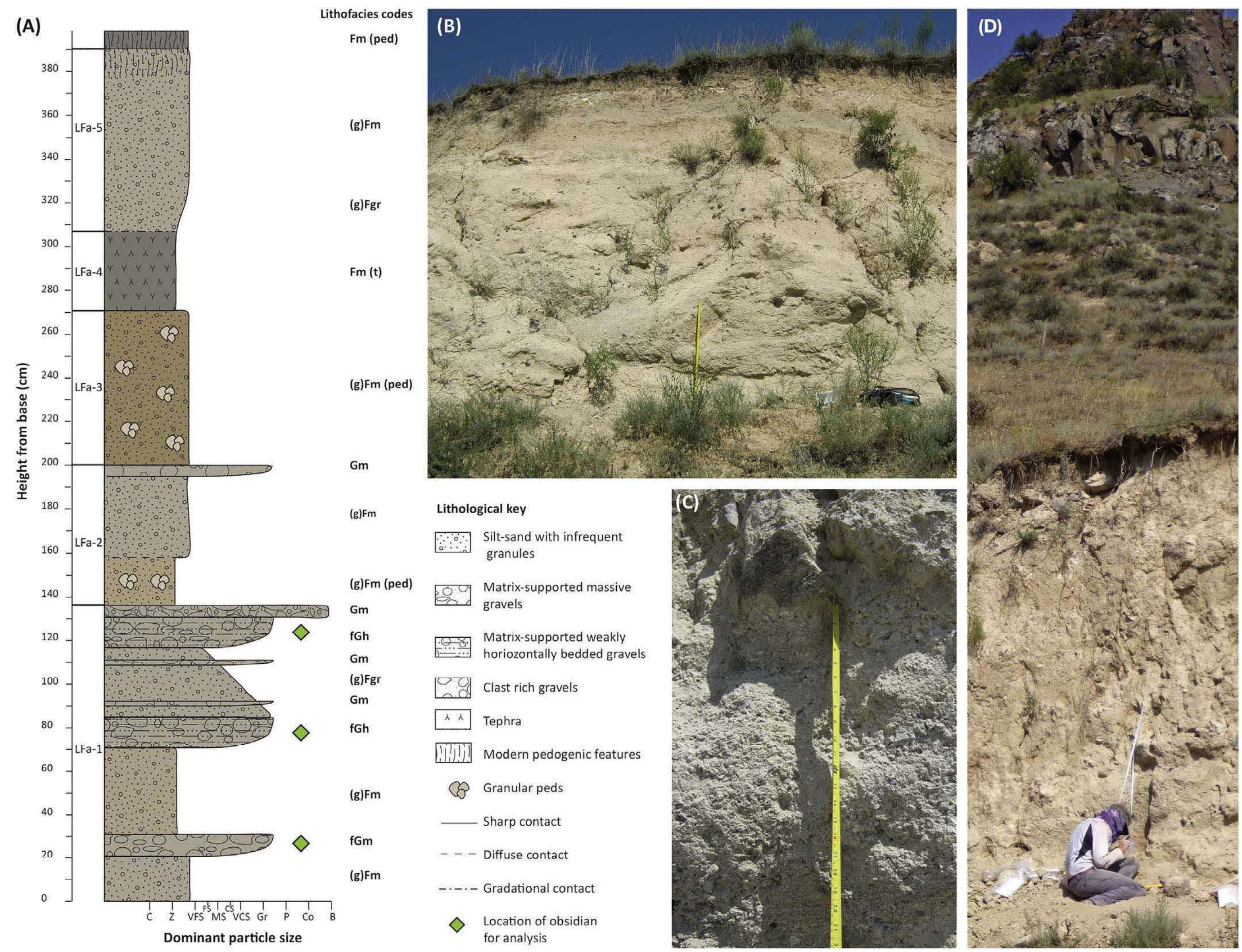

Fig. 2. Stratigraphy of Exposure B. (A) The composite sedimentological log of the section (the coded facies follow standard terminology; Graham, 1988). (B) Photograph of the logged sediment face. (C) Photograph of the beds in which obsidian nodules were recovered. (D) Photograph of the wider sequence that shows a mafic lava flow capping the obsidian-bearing sediments.

collection, might date to the Pleistocene, given our current understanding of the basin's geochronology.

2. Volcanism and obsidian in Central Armenia

The Hrazdan River is the sole drainage of Lake Sevan, and it channels overspill from the lake ~80 km northeast to southwest to a confluence with the Araxes River, ~21 km southwest of Yerevan (Fig. 1A). The river cuts through Pre-Cambrian metamorphic mudstones and Mesozoic limestones north of Karashamb village (38 km from its origin, 17 km north of Ptghni village), but thereafter it runs through a deep gorge between the Aragats and Gegham volcanic ranges to the west and east, respectively. The Aragats range is locally manifested by the Arailer stratovolcano 19 km northwest of Ptghni. Andesitic and dacitic flows of Arailer have previously been K—Ar dated to ~1.4–1.2 Ma (Lebedev et al., 2011). The Gegham range has Upper Miocene origins (Arutyunyan et al., 2007), but presently exposed deposits principally date to the Middle Pleistocene. From ~800 to ~200 ka, mafic lavas and felsic pyroclastic deposits were ejected into the Hrazdan River valley from volcanic vents along the northwestern margin of the Gegham range. Specifically, Gutansar (17 km northeast) and Hatis (15 km northeast) are the closest vents to the Ptghni exposure (Adler et al., 2014). Mapping carried out to date suggests that at least 20 mafic lavas from the Gegham range and six from Arailer have been cut by the Hrazdan River. These lavas are locally interbedded with alluvial and lacustrine deposits, some of which contain archaeological material. At present, the geochronology of these lavas is poorly constrained. Lavas from the Gegham range have been dated between ~560 and ~200 ka (Lebedev et al., 2013; Adler et al., 2014), and a single date on Aragats-derived mafic lava in north Yerevan yielded an age of 1.1 ± 0.1 Ma (Mitchell and Westaway, 1999). On stratigraphic grounds, the Ptghni lavas – and, in turn, lacustrine and alluvial deposits between them – must predate a lava dated to 441 ± 6 ka at Nor Geghi 1 (Adler et al., 2014).

The Gutansar and Hatis volcanic complexes are also the most significant obsidian sources in the Hrazdan River basin (Badalyan et al., 2004; Adler et al., 2014; Chataigner and Gratuze, 2014b; Frahm et al., 2014a). The Gutansar complex covers an area ~70 km^2 and includes the Fontan and Alapars lava domes, which probably lie along a common fault in line with the main Gutansar vent (Frahm et al., 2014b). The literature contains numerous named localities where Gutansar obsidian outcrops (e.g., Avazan, Jraber, Gyumush; Blackman et al., 1998; Chataigner and Gratuze, 2014a), but the varied localities are all parts of the same facies and have chemically indistinguishable obsidian (Keller and Seifried, 1990; Keller et al., 1996; Blackman et al., 1998; Chataigner and Gratuze, 2014a; Frahm et al., 2014b). Hatis is the taller volcano of the two, and while its obsidian outcrops cover a smaller area than Gutansar, the obsidian

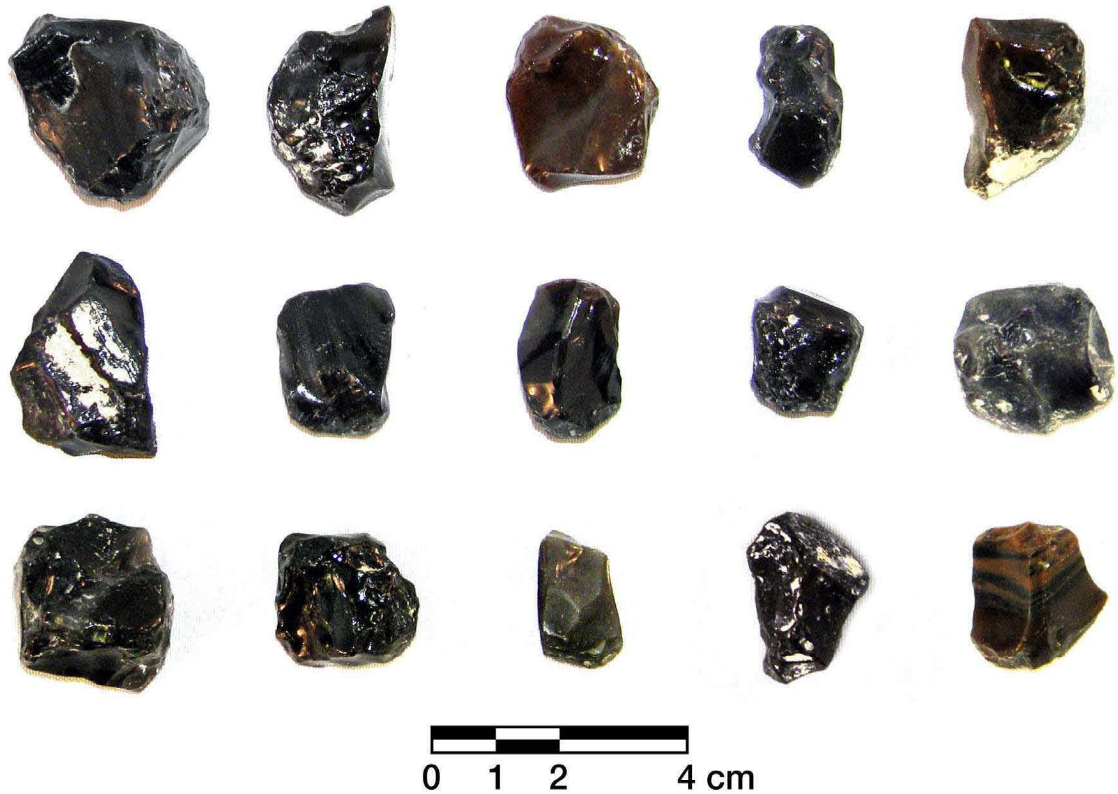

Fig. 3. Examples of Ptghni obsidian nodules and their variable appearances.

exhibits multiple chemical compositions.

The chronology of obsidian formation at both Gutansar and Hatis remains, unfortunately, ambiguous. Fission-track dates for Gutansar obsidian cluster around ~310 ± 30 ka (Wagner et al., 1976; Wagner and Weiner, 1987; Badalian et al., 2001). Lebedev et al. (2013), however, report a single K—Ar date of 1.2 ± 0.5 Ma (note the large uncertainty), which they interpret to be part of an eruptive period ~700 ka. Such a discrepancy between these two dating techniques also exists for Hatis obsidian: Komarov et al. (1972) report a fission-track date of 330 ka and a K—Ar date of 650 ka. To complicate the chronology further, Arutyunyan et al. (2007) published K—Ar dates for Hatis rhyolite and obsidian that vary between ~480 and ~700 ka. Consequently, a series of dates point to a time sometime between ~300 and ~700 ka for Gutansar and Hatis obsidians.

Three obsidian sources in the Tsaghkunyats range (Fig. 1A) – Damlik, Kamakar, and Ttvakar – are considerably older. Fission-track dates suggest an age ~4.5 Ma (Badalian et al., 2001), making them the oldest known obsidians within Armenia and meaning they were available as toolstone to the earliest Pleistocene inhabitants of the Southern Caucasus. These flows occur at elevations of ~2800 m, but colluvial processes have carried blocks and pebbles downslope to form secondary deposits at the base of the slopes, a few kilometers from their origins. The "Hankavan" source, for example, is such a secondary deposit in the Tsaghkunyats range that lies near the headwaters of the Marmarik River, a tributary of the Hrazdan River. Therefore, Tsaghkunyats obsidian pebbles might have been carried downstream by a Pleistocene predecessor of the Hrazdan River; however, to date, no such secondary deposits have been located within the Hrazdan River valley.

3. Ptghni stratigraphy

The sedimentary-volcanic sequence at Ptghni (Figs. 1B–C and 2) is a series of mafic lava flows (LF PTG 1–5) and predominantly fine-grained sedimentary facies, both alluvial and lacustrine in origin, situated atop Miocene-aged laminated sands and clay to the south. These sedimentary facies are recorded in five exposures along the eastern side of the Hrazdan valley (Exposures A–E). Exposures A–C relate to the lowest-elevation facies: a series of fine-grained alluvial sediments ~29 m in height that are laterally visible for ~200 m along a road cut. These exposures are interbedded between two lavas (LF PTG 4 and 3) that we have mapped across the Ptghni area (Fig. 1B), with a further two lavas (LF PTG 2 and 1) overlying LF PTG 3 in this location. Exposures D and E relate to higher-elevation facies that underlie LF PTG 1 to the south of Exposures A–C (Fig. 1C). Obsidian nodules occurred in and were recovered from the sedimentary facies of Exposures A to C, but none were observed in Exposures D or E. Geologically speaking, they are obsidian "clasts" that have been reworked in a sedimentary system, whereas a "nodule" tends to have been precipitated in situ, such as chert. Here "nodule" fits its usage in lithic analysis: "a relatively small rock mass that has been rounded by weathering" (Andrefsky, 2005:258). The analyzed obsidian specimens were sampled from Exposure B, which, therefore, we describe in detail here.

The sedimentary sequence at Exposure B (Fig. 2A) has five major lithofacies: LFa-1 to 5. From the base upwards, LFa-1 comprises 1.35 m of massive, very well sorted, pale brown (Munsell color 10YR/6/3) silt-fine sand with isolated granules of obsidian, tuff, and basaltic lithologies. Interbedded in these sediments are massive, weakly horizontally bedded, lenticular beds ~2–15 cm thick. The beds are clast-rich with granule-to-pebble-sized obsidian, tuff, and basalt. LFa-2 starts with a massive, well sorted, very pale brown (10YR/7/4) fine sand, 18 cm thick, with very weakly developed granular peds throughout. This, in turn, is overlain by 40 cm of massive, very well sorted, pale brown (10YR/6/3) silt-fine sand with isolated obsidian, tuff, and basaltic granules. These are then capped by a discontinuous lenticular bed of massive, clast-rich, silt-fine sand with granules/small pebbles. LFa-3 is a massive, normally graded, light yellowish brown (10YR/6/4) silt with isolated inclusions of very coarse sand/small granules. Weakly developed granular to sub-angular blocky peds occur throughout the facies.

This is overlain by LFa-4: a very well sorted, greyish brown (10YR/5/2) tephra, which grades into LFa-5, a massive, very well sorted, pale brown (10YR/6/3) silt-fine sand with isolated obsidian, tuff, and basalt granules. The sequence is then covered for ~10 m and re-exposed directly underneath LF PTG 3. These sediments comprise ~50 cm of well-sorted, buff-color silt-sand with evidence of burning at the contact with the overlying lava. Our observations suggest that the sequence is alluvial in origin, representing either overbank or levee sedimentation in a low-energy fluvial system. The observed lenticular beds are likely small, low-energy channel features that have evidence of minor, incipient pedogenesis (i.e., peds in LFa-2 and LFa-3), potentially associated with intervals of landscape stability.

The analyzed obsidian nodules were all collected from the clast-rich, lenticular beds in LFa-1 (Fig. 2A). Fig. 3 shows examples of Ptghni nodules, which, in this exposure, reach the size of pebbles (32–64 mm) with scarce cobbles (64–256 mm). These rounded to sub-angular nodules, often with indented surfaces, are sometimes called "marekanites." Like other obsidians that occur in the Hrazdan River basin, their appearance is highly variable, including black, grey, red-brown, and various combinations of all three. Such variability, which overlaps with the appearances of Gutansar, Hatis, and Tsaghkunyats obsidians (Frahm et al., 2014a), makes the visual identification of Ptghni obsidian impractical, if not impossible. The red-brown colors of some nodules indicate that the primary context (i.e., the obsidian flow or dome) must have had at least partial expression at the surface (Hughes and Smith, 1993). Such colors necessitate conversion of microscopic black magnetite crystals (Fe_3O_4) to red-brown hematite (Fe_2O_3), requiring exposure to oxygen (in the atmosphere) while hot. Hence, the nodules may have derived from obsidian that protruded to the surface rather than obsidian in the deeply buried basal zone (Hughes and Smith, 1993).

4. Analytical procedures and assessment

We used a Thermo Scientific Niton XL3t GOLDD+ analyzer, which creates an incident X-ray beam using a 2-W Ag-anode tube and detects characteristic X-rays using a 25-mm^2 Si drift detector (SDD; energy resolution ≤ 155 eV in practice). In unison with a set of four built-in X-ray filters, the instrument's analytical settings change to "tune in" different segments of the periodic table: 40 kV and ≤ 50 μA with the "main" filter, 50 kV and ≤ 40 μA with the "high" filter, 20 kV and ≤ 100 μA with the "low" filter, and 6 kV and ≤ 200 μA with the "light" filter. Cycling through the four filters, each analysis took 300 s to attain the lowest reasonable measurement uncertainties (i.e., 60 s for the first three filters, 120 s for the light one). The incident X-ray beam is 8 mm in diameter (50 mm^2), and an internal camera aided in positioning specimens over the measurement window.

Spectra measured by XRF techniques must be "corrected" for various phenomena that occur in a specimen (e.g., absorption, attenuation, secondary and tertiary X-ray fluorescence) to convert raw counts into quantitative element concentrations. The data reported here were acquired in the "TestAll Geo" mode, which uses a dual approach to data correction. For trace elements, this mode utilizes Compton normalization, which normalizes spectra to the intensity of inelastically scattered X-rays (i.e., the Compton scattering peak) to adjust for differences in each specimen's morphology, texture, density, and so on. For elements at high concentrations, it uses a physics-based correction model known as fundamental parameters (FP). For FP, equations model the relationships between emitted X-rays and element concentrations (i.e., parameters such as mass attenuation coefficients, fluorescent and absorption X-ray edge energies, fluorescent yields, and Rayleigh and Compton cross sections). An advantage of the TestAll Geo mode is that it enables the greatest number of elements to be measured: 45 in this case. Only a subset of these elements, however, are reported here. We exclude elements that occur in volcanic rocks at undetectable concentrations and/or that could not be reliably calibrated using the available obsidian reference materials.

Although this instrument has an initial factory-set calibration, we applied a supplementary calibration based on linear regression analysis to "fine tune" the data for obsidian. In the literature, one finds two approaches to XRF calibration for obsidian. The first is to create a general silicate calibration based on powdered standard reference materials (SRMs), often from the United States Geological Survey (USGS). This approach has been favored at Berkeley's Geoarchaeological XRF Lab (Shackley, 2011) and McMaster's Archaeological XRF Lab (Carter et al., 2013). For example, three of Shackley's (2011) 16 standards are obsidians (e.g., USGS RGM-1); however, the others include basalt, andesite, and other volcanics (e.g., USGS AGV-2 and BHVO-2) as well as metamorphic and sedimentary rocks (e.g., USGS SDC-1 and SCO-1). The second calibration approach uses a collection of obsidian specimens that has been analyzed using multiple techniques. This approach is favored by the Archaeometry Laboratory at the University of Missouri Research Reactor (MURR; Glascock and Ferguson, 2012). MURR researchers analyzed a series of 40 obsidian specimens with neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS) and, in turn, used the datasets to derive energy-dispersive XRF (EDXRF) calibrations.

For the greatest rigor in documenting Ptghni obsidian for the first time, we integrated these two approaches. First, our calibration standards included 20 obsidian specimens from Southwest Asia (Armenia, Georgia, and Turkey), all characterized by (1) NAA and (2) EDXRF at MURR as well as (3) electron microprobe analysis (EMPA) at the University of Minnesota (Frahm, 2012). Second, our standards included ten USGS SRM powders typically used to calibrate EDXRF: AGV-1 (andesite), BHVO-1 (basalt), BIR-1 (basalt), DTS-1 (dunite), G-2 (granite), GSP-1 (granodiorite), QLO-1 (quartz latite), SCo-1 (shale), SDC-1 (mica schist), and SBC-1 (shale). Occasionally the SRMs have element concentrations that far exceed those found in the obsidian (e.g., 1.62% Ti in BHVO-1 is almost a full magnitude higher). Such values were excluded from our regression analysis to avoid their exertion of an undue influence on the calibration. The supplementary online material includes the resulting equations, best-fit lines, and determination coefficients for twelve elements.

Much (if not most) of the debate surrounding pXRF in archaeological science has focused on the issue of assessing calibrations (e.g., Shackley, 2010, 2011, 2012; Speakman and Shackley, 2013; Conrey et al., 2014). To demonstrate the strength of our calibration, we analyzed a powdered USGS SRM – RGM-1, rhyolitic obsidian from Glass Mountain, California – as an unknown specimen (i.e., it was excluded from the calibration). RGM-1 has long been used for this purpose (e.g., Hughes, 1988; Hughes and Lees, 1991; Shackley, 1995; Skinner and Davis, 1996; Skinner et al., 1997; inter alia). Table 1 shows (1) our RGM-1 data for eight key elements and (2) RGM-1 data from three obsidian-focused EDXRF labs in North America. Our data have excellent agreement with respect to the USGS recommended values. Given that these eight are among the most commonly reported elements for RGM-1, these are the elements on which we focus because they are the ones for which we can best demonstrate accuracy. There are other elements in which we have high confidence, such as Ca, due to high reproducibility with respect to our obsidian standards; however, their accuracy cannot be straightforwardly shown relative to RGM-1 and other analytical laboratories.

5. Results

Fig. 4 shows scatterplots using four key trace elements: Rb, Zr, and Nb versus Sr. The red circles correspond to 36 Ptghni obsidian specimens, and the grey-and-white circles correspond to other Armenian obsidians (see key for the entire list), specimens of which were analyzed under the same measurement conditions using the same instrument and calibration.

Other secondary deposits that we have identified and tested in the Hrazdan valley contain only obsidian from Gutansar. It was clear,

Table 1
Our pXRF values of USGS SRM RGM-1 (rhyolitic obsidian from Glass Mountain, California) and those from other analytical laboratories establish the accuracy of our measurements.

Laboratory	Reference	Technique	Ti (ppm)	Fe (ppm)	Zn (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	Nb (ppm)	Th (ppm)
Geochemical Research Lab	Hughes and Pavesic, 2005	EDXRF	1632 ± 36	13,160 ± 140		152 ± 4	113 ± 3	222 ± 4	9 ± 3	
	Hughes, 2007	EDXRF	1616 ± 15	13,090 ± 140		143 ± 4	105 ± 3	214 ± 4	8 ± 3	
	Roper and Hughes, 2014	EDXRF		13,160 ± 140		153 ± 4	110 ± 3	221 ± 4	11 ± 3	
	Mean		*1624*	*13,137*		*149*	*109*	*219*	*9*	
NW Research Obsidian Studies	Skinner and Davis, 1996	EDXRF	1669 ± 97	13,930 ± 770	37 ± 7	152 ± 3	107 ± 9	217 ± 8	11 ± 1	
	Skinner et al., 1997	EDXRF	1788 ± 97	14,000 ± 770	38 ± 7	150 ± 3	104 ± 9	224 ± 8	14 ± 1	
	Skinner and Thatcher, 2009	EDXRF	1576 ± 101	12,250 ± 980	41 ± 16	158 ± 4	107 ± 9	221 ± 7	10 ± 2	
	Mean		*1678*	*13,393*	*39*	*153*	*106*	*221*	*12*	
Geoarchaeological XRF Lab	Negash and Shackley, 2006	EDXRF	1680 ± 120	14,000 ± 560	39 ± 2	154 ± 3	113 ± 2	224 ± 2	8 ± 3	
	Carter and Shackley, 2007	EDXRF	1792 ± 10	14,212 ± 68	36 ± 2	153 ± 3	114 ± 3	221 ± 3	9 ± 4	14 ± 3
	Shackley, 2009	EDXRF	1480 ± 20	12,806 ± 74	32 ± 11	145 ± 2	103 ± 2	221 ± 2	7 ± 1	12 ± 4
	Mean		*1651*	*13,673*	*36*	*151*	*110*	*222*	*8*	*13*
USGS recommended values	Smith, 1995	multiple	1620 ± 120	13,020 ± 210	32	150 ± 8	110 ± 10	220 ± 20	9 ± 1	15 ± 1
This study		pXRF	1660 ± 40	12,980 ± 60	31 ± 4	151 ± 2	107 ± 2	213 ± 3	10 ± 1	14 ± 6

Mean values are italicized.

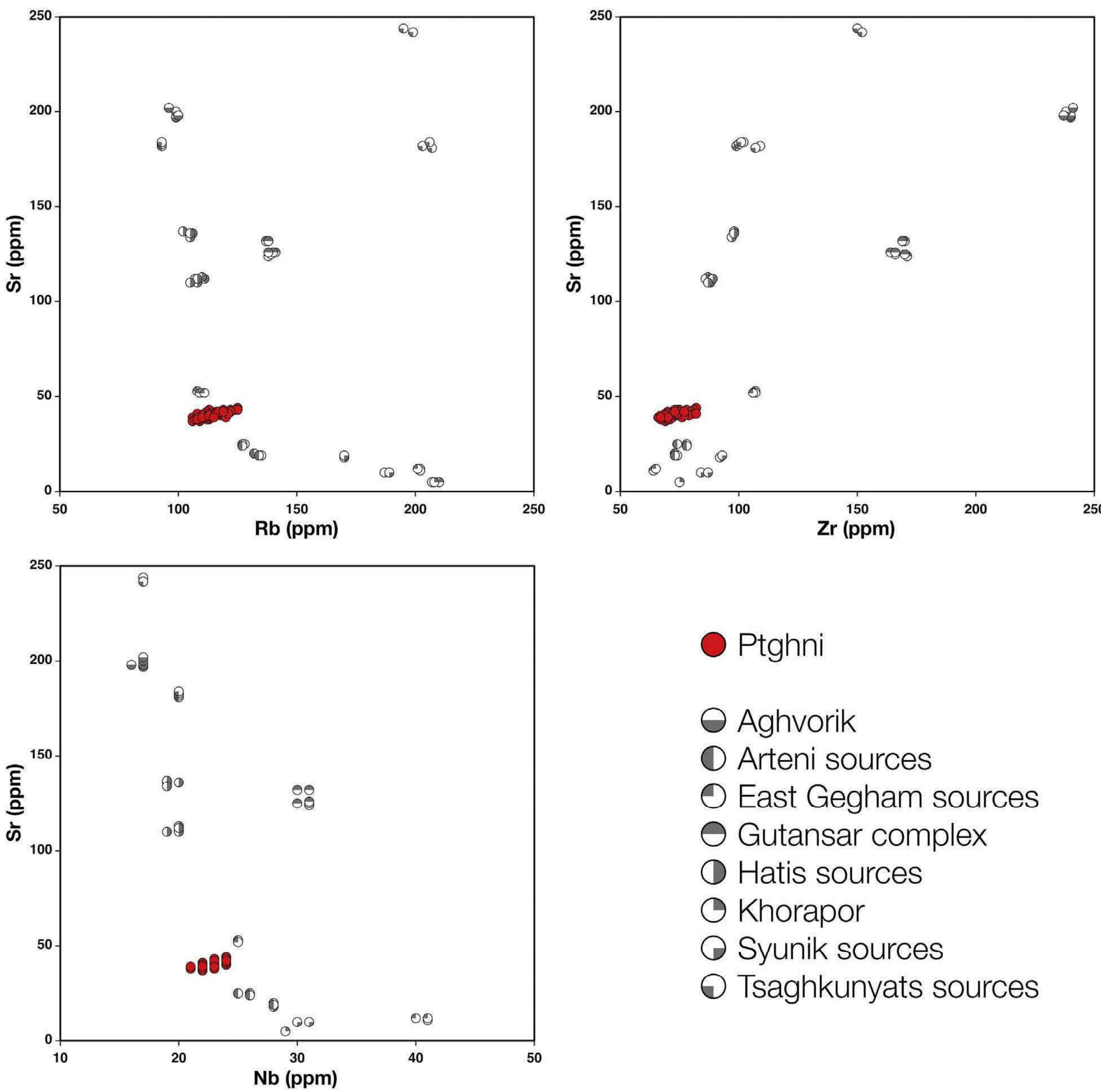

Fig. 4. Element scatterplots of Ptghni obsidian and other Armenian obsidians.

Table 2
Elemental data for select Armenian obsidian reference specimens and for Ptghni obsidian specimens. All means and standard deviations reflect three measurements per specimen.

Specimen	Ti (ppm)	Fe (ppm)	Zn (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	Nb (ppm)	Th (ppm)
Aghvorik obsidian								
AR.2009.62	1998 ± 13	12,105 ± 63	50 ± 4	99 ± 1	199 ± 1	239 ± 1	17 ± 1	17 ± 1
AR.2009.63	2004 ± 12	12,009 ± 11	52 ± 2	98 ± 3	200 ± 2	239 ± 3	17 ± 1	18 ± 1
Arteni obsidian sources								
AR.2009.41	459 ± 2	2583 ± 16	40 ± 1	134 ± 2	19 ± 1	73 ± 1	28 ± 1	16 ± 1
AR.2009.42	493 ± 12	2668 ± 28	41 ± 3	128 ± 1	25 ± 1	77 ± 2	26 ± 1	15 ± 1
East Gegham obsidian sources								
AR.2009.53	744 ± 8	3890 ± 17	44 ± 2	109 ± 1	52 ± 1	106 ± 1	25 ± 1	17 ± 1
AR.2009.54	389 ± 11	2405 ± 2	34 ± 2	201 ± 1	12 ± 1	64 ± 1	41 ± 1	28 ± 1
Gutansar volcanic complex								
AR.2009.44	1126 ± 2	5624 ± 12	43 ± 1	138 ± 1	132 ± 1	169 ± 1	31 ± 1	18 ± 1
AR.2009.45	1107 ± 2	5633 ± 83	45 ± 3	139 ± 1	125 ± 1	169 ± 3	31 ± 1	18 ± 1
AR.2009.47	1100 ± 9	5606 ± 46	45 ± 2	139 ± 1	126 ± 1	165 ± 1	31 ± 0	18 ± 1
Hatis obsidian sources								
AR.2009.48	774 ± 15	5129 ± 29	43 ± 3	105 ± 2	136 ± 1	98 ± 1	19 ± 1	17 ± 1
AR.2009.59	610 ± 21	4154 ± 44	37 ± 1	109 ± 2	111 ± 1	87 ± 1	20 ± 1	18 ± 1
Khorapor obsidian								
AR.2009.61	472 ± 10	2559 ± 21	32 ± 2	208 ± 1	5 ± 1	75 ± 1	29 ± 1	33 ± 2
Syunik obsidian sources								
AR.2009.35	566 ± 9	3188 ± 20	33 ± 4	171 ± 1	18 ± 1	95 ± 5	28 ± 1	33 ± 1
AR.2009.56	505 ± 14	2959 ± 9	36 ± 3	188 ± 2	10 ± 1	88 ± 5	30 ± 1	35 ± 1
Tsaghkunyats obsidian sources								
AR.2009.43	656 ± 1	4216 ± 102	33 ± 4	205 ± 2	182 ± 1	102 ± 4	20 ± 1	29 ± 1
AR.2009.60	655 ± 12	4252 ± 52	33 ± 3	93 ± 1	183 ± 1	104 ± 5	20 ± 1	30 ± 1
AR.2009.64	821 ± 10	5074 ± 25	34 ± 1	197 ± 2	242 ± 2	149 ± 4	17 ± 1	28 ± 1
Ptghni obsidian specimens, n = 36								
Exposure B unit 2–3	431 ± 40	2878 ± 82	30 ± 1	113 ± 2	40 ± 2	72 ± 4	23 ± 1	32 ± 1
Exposure B unit 2–3	542 ± 56	3075 ± 166	32 ± 1	120 ± 5	42 ± 2	77 ± 4	23 ± 1	34 ± 3
Exposure B unit 2–3	402 ± 40	2783 ± 140	28 ± 1	108 ± 3	39 ± 1	70 ± 2	22 ± 1	31 ± 1
Exposure B unit 2–3	513 ± 39	2988 ± 39	31 ± 2	118 ± 2	41 ± 1	73 ± 3	23 ± 1	33 ± 1
Exposure B unit 2–3	492 ± 10	2969 ± 16	30 ± 1	116 ± 2	40 ± 1	71 ± 1	23 ± 1	31 ± 1
Exposure B unit 2–3	506 ± 11	3004 ± 102	28 ± 1	118 ± 3	41 ± 1	76 ± 4	23 ± 1	32 ± 1
Exposure B unit 2–3	479 ± 4	2788 ± 96	29 ± 2	110 ± 2	39 ± 1	70 ± 1	22 ± 1	30 ± 2
Exposure B unit 2–3	470 ± 22	2902 ± 102	28 ± 2	112 ± 3	40 ± 1	79 ± 2	23 ± 1	33 ± 1
Exposure B unit 2–3	484 ± 19	2875 ± 51	30 ± 1	112 ± 1	39 ± 1	69 ± 1	22 ± 1	32 ± 2
Exposure B unit 2–3	450 ± 33	2769 ± 57	30 ± 3	111 ± 3	39 ± 1	69 ± 1	23 ± 1	30 ± 1
Exposure 1 alluvium	484 ± 32	3047 ± 136	30 ± 3	115 ± 2	41 ± 1	71 ± 1	23 ± 1	32 ± 1
Exposure 1 alluvium	488 ± 23	2965 ± 104	31 ± 1	116 ± 4	41 ± 1	75 ± 2	23 ± 1	33 ± 1
Exposure 1 alluvium	467 ± 13	2886 ± 30	32 ± 1	115 ± 2	40 ± 1	70 ± 1	23 ± 1	32 ± 1
Exposure 1 alluvium	499 ± 33	2944 ± 93	31 ± 2	116 ± 2	41 ± 1	76 ± 1	23 ± 1	32 ± 1
Exposure 1 alluvium	459 ± 85	2850 ± 199	31 ± 3	112 ± 8	40 ± 3	72 ± 8	23 ± 1	32 ± 2
Exposure 2 alluvium	511 ± 10	3043 ± 25	32 ± 1	116 ± 1	41 ± 1	73 ± 1	23 ± 1	32 ± 2
Exposure 2 alluvium	518 ± 9	3003 ± 40	31 ± 2	114 ± 2	42 ± 1	73 ± 3	23 ± 1	32 ± 1
Exposure 2 alluvium	472 ± 69	2975 ± 152	30 ± 3	117 ± 4	40 ± 1	71 ± 5	23 ± 1	32 ± 2
Exposure 2 alluvium	454 ± 71	2938 ± 85	29 ± 2	116 ± 3	40 ± 1	73 ± 1	23 ± 1	32 ± 1
Exposure 2 alluvium	528 ± 87	3093 ± 268	31 ± 3	114 ± 5	40 ± 1	72 ± 1	22 ± 1	32 ± 1
Exposure 2 alluvium	482 ± 33	2854 ± 53	32 ± 1	113 ± 2	39 ± 1	70 ± 1	23 ± 1	33 ± 1
Exposure 2 alluvium	477 ± 11	2899 ± 44	31 ± 1	116 ± 4	40 ± 1	74 ± 2	23 ± 1	33 ± 1
Exposure 2 alluvium	499 ± 13	2984 ± 79	29 ± 2	116 ± 2	41 ± 1	73 ± 1	23 ± 1	32 ± 1
Exposure 2 alluvium	499 ± 41	2969 ± 83	31 ± 1	116 ± 3	40 ± 1	73 ± 1	23 ± 1	32 ± 1
Exposure 2-log 1 unit 4	496 ± 69	2958 ± 141	30 ± 3	116 ± 7	41 ± 2	72 ± 4	23 ± 1	32 ± 1
Exposure 2-log 1 unit 4	471 ± 63	2853 ± 200	32 ± 4	114 ± 7	39 ± 3	72 ± 2	23 ± 2	31 ± 1
Exposure 2-log 1 unit 3	476 ± 16	2923 ± 70	30 ± 1	115 ± 2	41 ± 1	74 ± 3	24 ± 1	33 ± 1
Exposure 2-log 1 unit 3	540 ± 43	3081 ± 132	31 ± 2	121 ± 3	42 ± 1	74 ± 3	24 ± 1	33 ± 2
Exposure 2-log 1 unit 3	512 ± 30	2984 ± 108	31 ± 1	116 ± 3	42 ± 1	76 ± 3	23 ± 1	33 ± 1
Exposure 2-log 1 unit 3	490 ± 59	2722 ± 50	27 ± 1	111 ± 3	40 ± 1	69 ± 2	22 ± 1	31 ± 1
Exposure 2-log 1 unit 3	502 ± 45	2936 ± 175	30 ± 1	111 ± 1	39 ± 1	69 ± 1	22 ± 1	31 ± 1
Section C top alluvium	515 ± 50	3023 ± 119	31 ± 1	118 ± 3	41 ± 1	75 ± 2	24 ± 1	32 ± 1
Section C top alluvium	445 ± 17	2755 ± 100	29 ± 1	111 ± 3	39 ± 1	68 ± 1	22 ± 1	31 ± 2
Section C top alluvium	610 ± 7	3139 ± 15	31 ± 1	117 ± 1	41 ± 1	74 ± 1	23 ± 1	33 ± 1
Section C top alluvium	596 ± 32	3098 ± 83	31 ± 1	121 ± 6	39 ± 1	69 ± 2	22 ± 1	31 ± 3
Section C top alluvium	550 ± 3	2984 ± 51	32 ± 3	120 ± 1	42 ± 1	77 ± 5	24 ± 1	34 ± 1
Overall means	*495 ± 41*	*2943 ± 103*	*30 ± 1*	*115 ± 3*	*40 ± 1*	*73 ± 3*	*23 ± 1*	*32 ± 1*
%RSD	*8%*	*3%*	*4%*	*3%*	*2%*	*4%*	*2%*	*3%*

Means and percent relative standard deviations are italicized.

during the first pXRF analysis of Ptghni obsidian, that it did not match Gutansar. As shown in Table 2, Ptghni obsidian has Zr ~60% lower than Gutansar obsidian, Sr is ~70% lower, Rb is ~20% lower, and so forth. Nor does it match the Hatis obsidians or known Tsaghkunyats sources. Furthermore, it does not match the two East Gegham sources, Geghasar and Spitakasar, which (1) lie in a different river basin, at least on the modern landscape, and (2) are much too young, having been fission-track dated to 40–80 ka and 120 ka, respectively (Badalian et al., 2001). Compositionally Ptghni is closest to one of the Arteni sources – Pokr Arteni – but it is not a match. Compared to Pokr Arteni obsidian, two elements in Table 2 (Ti and Zr) fall into the same overall range. Six trace elements, though, differ: Fe (~12% higher in Ptghni obsidian compared to Pokr Arteni), Zn (~25% lower), Rb (~12% lower), Sr (~80% higher), Nb (~15% lower), and Th (~100% higher). Each of these differences exceeds the percent relative standard deviation (%RSD) of the Ptghni obsidian analyses. Beyond those we can calibrate and assess using RGM-1, other elements exhibit differences: Ca, Pb, and U are higher in Ptghni obsidian (~12%, 40%, and 50%, respectively), but Mn is lower (~20%) than it is in Pokr Arteni obsidian.

The small obsidian nodules that we found at the Ptghni exposure are not well suited to tool production; however, the primary source (i.e., the original flow or dome) – and other secondary deposits – could have larger blocks and nodules in abundance, much like other voluminous and high-quality obsidian sources that occur throughout Armenia. To our knowledge, no previously sourced artifacts match these compositional data for Ptghni obsidian. In many cases, though, the data remain unpublished for artifacts that cannot be matched to a known obsidian source (e.g., Badalyan et al., 2010). Blackman et al. (1998) did document seven obsidian chemical types, identified in various artifact assemblages, that could not be matched to a source known to them. None, however, match Ptghni. Until recently, most obsidian sourcing work in Armenia has largely focused on sites dating to the Holocene (e.g., Blackman et al., 1998; Badalyan et al., 2004, 2010; Cherry et al., 2010; Chataigner and Gratuze, 2014b; Palumbi et al., 2014; Martirosyan-Olshansky, 2015), a time when the primary and secondary deposits of Ptghni obsidian might no longer have been accessible. It is possible, therefore, that its absence in the existing literature is a sampling issue. Prior to our own research (e.g., Adler et al., 2014; Frahm et al., 2014a, 2014b, 2016), the only Palaeolithic artifacts in Armenia to be sourced using modern analytical techniques were 18 flakes from the Epipalaeolithic site of Kalavan 1, which dates to ~17–15 ka (Chataigner and Gratuze, 2014b).

6. Discussion

The identification of Ptghni obsidian has both geological and archaeological importance for our understanding of the Hrazdan River basin during the Pleistocene, despite its primary volcanic source remaining, at present, uncertain. Geologically, the composition of Ptghni obsidian does not fit known chemical trends of either the Gegham or Tsaghkunyats obsidian sources. If it originated from either of these two ranges, it must have been produced during a different phase of volcanism to allow for such a distinct elemental composition. After Pokr Arteni, the East Gegham sources – Geghasar and Spitakasar – are chemically the next closest compositions to Ptghni obsidian (Fig. 4), but as noted above, these sources are younger and, currently, lie in a different river basin (Fig. 1A). At present, an origin in the Gegham range cannot be excluded; however, Ptghni obsidian would have to reflect a different volcanic period than those currently manifested on the surface.

Nor can we rule out an unknown source associated with Arailer volcano to the west, and as a result, we can put forward two alternative hypotheses for such a scenario. First, the sediments (and the Ptghni obsidian contained within) represent an interval that predates known volcanism in the Gegham range. The current chronology suggests that the onset of extrusive volcanism in the Gegham range occurred ~560 ka (Lebedev et al., 2013), while the chronology of Arailer volcanism, albeit based on a small number of dates, suggests an age of 1.2 Ma. Therefore, the Ptghni sediments may represent deposition earlier in the Pleistocene than observed elsewhere in the Hrazdan Gorge. This hypothesis assumes, of course, that there was not a significant hiatus between the formation of the obsidian and the onset of local fluvial activity. Thus, an alternative hypothesis is that there was indeed a hiatus such that the deposition at Ptghni occurred within the chronological framework of Gegham volcanism but still before emplacement of the Gutansar and Hatis obsidians. In either case, the lack, at present, of archaeological material in the Ptghni sediments is significant.

It is unclear in what form the Ptghni obsidian source might still exist. The appearance of the obsidian nodules (i.e., variable red-brown colors) indicates, as noted above, that this material was exposed to the atmosphere while still hot, meaning that the nodules may have derived from surface protrusions rather than the basal zone of the flow. Thus, small nodules could have eroded from the surface outcrops and been fluvially reworked and transported, whereas other parts of the obsidian flow could have stayed buried. The degree of landscape change in this region is exemplified by Nor Geghi 1, which was covered by a lava flow and later exposed as the Hrazdan River downcut by 80 m (Adler et al., 2014). Our best hopes of locating the primary source – and other secondary sources – of Ptghni obsidian involve a combination of (1) an improved geochronology of the lava flows and sedimentary deposits and (2) continued surveying, mapping, and pXRF analyses in the field. Both lines of investigation are currently being undertaken as part of the PAGES project.

Archaeologically, the discovery of Ptghni obsidian is important for recognizing Pleistocene hominin occupations as early as those at Dmanisi (~1.8 Ma). As late as 300 ka and as early as 700 ka (or perhaps earlier; Lebedev et al., 2013), the two West Gegham obsidian sources – Gutansar and Hatis – did not yet exist, and the two East Gegham sources – Geghasar and Spitakasar – did not exist until much later. Thus, the Tsaghkunyats range has the only obsidian sources known to have existed in central Armenia earlier in the Pleistocene. The discovery of Ptghni obsidian, however, means that there was another source that might have been exploited for toolstone by Pleistocene hominins. It is worth noting that some (but certainly not all) Lower Palaeolithic tools found in the Southern Caucasus were also produced from other fine-grained volcanics, such as dacite and basalt (e.g., Gasparyan et al., 2014a), either by design or because obsidian was not as widely available. The secondary deposit that we found is not particularly attractive as a source of lithic material. Given the nodules' occurrence in alluvial-lacustrine sediments, the primary Ptghni obsidian source likely lies somewhere in the Hrazdan River basin to the north, and it would have been exposed, at least in part, sometime during the past to allow for the erosion and transport of the nodules. The sediments exposed at Ptghni appear to represent an interval older than those at our oldest dated archaeological site, Nor Geghi 1, but so far, no artifacts have been recovered from the sedimentary deposits at Ptghni. If, however, artifacts are found in Armenia that match the chemical signature of Ptghni obsidian and if we are correct that this source was not accessible during the Holocene, it might attest to the artifacts' considerable antiquity and, in turn, their relevance to studies involving early hominin occupations and expansions in the Southern Caucasus.

7. Conclusions

Our field surveys and pXRF analyses have established that a previously unknown obsidian source exists in central Armenia, likely within the Hrazdan River basin. Using pXRF, we were able to chemically define Ptghni obsidian and to recognize it as new on the same day that it was first encountered. This meant that we were able to not only collect and analyze additional specimens but also begin our surveys for the volcanic source, all by the end of the week. Furthermore – and equally important – identifying these obsidian nodules as corresponding to a new source informed our interpretation of the volcanic and sedimentary sequence in this portion of the gorge. Without the routine use of pXRF as an interpretative tool in our field lab, we would, at least initially, have assumed these nodules reflected yet another lag deposit of Gutansar obsidian. Thus there is great value in adding such portable analytical instruments to the fieldwork toolkit.

The composition of Ptghni obsidian does not readily fit into the geochemical trends of the known Gegham or Tsaghkunyats sources. If it originated from either range, it must have been produced during a different phase of volcanism to account for such a distinct composition. Nor can we rule out a source associated with Arailer volcano, where no obsidian is currently known to exist. The variable colors and textures of Ptghni obsidian suggest that these nodules derived from surface exposures, meaning that the basal zone of the original obsidian flow could still be preserved to some extent, perhaps quite deeply. Comparisons to unidentified obsidian artifacts in the literature led to no matches, but most previous sourcing studies in Armenia have largely focused on artifacts from the Holocene. Our working hypothesis, therefore, is that the Ptghni obsidian source might no longer have been accessible during the Holocene. Nevertheless, the discovery of Ptghni obsidian is crucial for our research on early hominin occupations, establishing that there was another obsidian source in the Hrazdan River basin that might have been used for toolstone during the Pleistocene. If Ptghni obsidian was indeed unattainable in the Holocene, artifacts with its elemental signature, even if encountered in a surface scatter or museum collection, might date to the Pleistocene. Such a discovery could go a long way toward demonstrating Armenia's Early Pleistocene occupations and its role as a key expansion–contraction corridor for early hominin expansions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jasrep.2017.05.039.

References

Adler, D.S., Yeritsyan, B., Wilkinson, K., Pinhasi, R., Bar-Oz, G., Nahapetyan, S., Bailey, R., Schmidt, B.A., Glauberman, P., Wales, N., Gasparian, B., 2012. The Hrazdan Gorge palaeolithic project, 2008–2009. In: Avetisyan, P., Bobokhyan, A. (Eds.), Archaeology of Armenia in Regional Context, Proceedings of the International Conference dedicated to the 50th Anniversary of the Institute of Archaeology and Ethnography held on September 15–17, 2009 in Yerevan, Armenia. NAS RA Gitutyn Publishing House, Yerevan, pp. 21–37.

Adler, D.S., Wilkinson, K.N., Blockley, S., Mark, D., Pinhasi, R., Schmidt-Magee, B.A., Nahapetyan, S., Mallol, C., Berna, F., Glauberman, P.J., Raczynski-Henk, Y., Wales, N., Frahm, E., Jöris, O., MacLeod, A., Smith, V., Cullen, V., Gasparyan, B., 2014. Early Levallois technology and the transition from the lower to middle Palaeolithic in the southern Caucasus. Science 345 (6204), 1609–1613.

Andrefsky, W., 2005. Lithics: Macroscopic Approaches to Analysis. Cambridge Press, Second edition.

Arutyunyan, E.V., Lebedev, A.V., Chernyshev, I.V., Sagatelyan, A.K., 2007. Geochronology of Neogene–quaternary volcanism of the Geghama Highland (Lesser Caucasus, Armenia). Dokl. Earth Sci. 416, 1042–1046.

Badalian, R., Bigazzi, G., Cauvin, M.-C., Chataigner, C., Bashyan Jr., R., Karapetyan, S., Oddone, M., Poidevin, J., 2001. An international research project on Armenian archaeological sites: fission-track dating of obsidians. Radiat. Meas. 34, 373–378.

Badalyan, R., Chataigner, C., Kohl, P., 2004. Trans-Caucasian obsidian: the exploitation of the sources and their distribution. In: Sagona, A. (Ed.), A View from the Highlands: Archaeological Studies in Honour of Charles Burney. Ancient Near Eastern Studies, pp. 437–465.

Badalyan, R., Harutyunyan, A., Chataigner, C., Le Mort, F., Chabot, J., Brochier, J.-E., Balasescu, A., Radu, V., Hovsepyan, R., 2010. The settlement of Aknashen-Khatunarkh, a Neolithic site in the Ararat plain (Armenia): excavation results 2004–2009. Tüba-Ar 13, 187–220.

Blackman, M.J., Badalian, R., Kikodze, Z., Kohl, P., 1998. Chemical characterization of Caucasian obsidian geological sources. In: Cauvin, M.-C., Gourgaud, A., Gratuze, B., Arnaud, N., Poupeau, G., Poidevin, J.L., Chataigner, C. (Eds.), L'obsidienne au Proche et Moyen-Orient: Du Volcan à l'Outil, BAR International Series, pp. 205–231.

Carter, T., Shackley, M.S., 2007. Sourcing obsidian from Neolithic Catalhoyuk (Turkey) using energy dispersive X-ray fluorescence. Archaeometry 49 (3), 437–454.

Carter, T., Grant, S., Kartal, M., Coşkun, A., Özkaya, V., 2013. Networks and Neolithisation: sourcing obsidian from Körtik Tepe (SE Anatolia). J. Archaeol. Sci. 40, 556–569.

Chataigner, C., Gratuze, B., 2014a. New data on the exploitation of obsidian in the southern Caucasus (Armenia, Georgia) and eastern Turkey, part 1: source characterization. Archaeometry 56, 25–47.

Chataigner, C., Gratuze, B., 2014b. New data on the exploitation of obsidian in the southern Caucasus (Armenia, Georgia) and eastern Turkey, part 2: obsidian procurement from the Upper palaeolithic to the late bronze age. Archaeometry 56, 48–69.

Cherry, J.F., Faro, E.Z., Minc, L., 2010. Field survey and geochemical characterization of the southern Armenian obsidian sources. J. Field Archaeol. 35 (2), 147–163.

Conrey, R.M., Goodman-Elgar, M., Bettencourt, N., Seyfarth, A., Van Hoose, A., Wolff, J.A., 2014. Calibration of a portable X-ray fluorescence spectrometer in the analysis of archaeological samples using influence coefficients. Geochem.: Explor., Environ., Anal. 4 (3), 291.

Egeland, C.P., Gasparian, B., Arakelyan, D., Nicholson, C.M., Petrosyan, A., Ghukasyan, R., Byerly, R., 2014. Reconnaissance survey for Palaeolithic sites in the Debed River Valley, northern Armenia. J. Field Archaeol. 39 (4), 370–386.

Frahm, E., 2012. Non-destructive sourcing of bronze-age near eastern obsidian artefacts: redeveloping and reassessing electron microprobe analysis for obsidian sourcing. Archaeometry 54 (4), 623–642.

Frahm, E., Schmidt, B., Gasparyan, B., Yeritsyan, B., Karapetian, S., Meliksetian, Kh., Adler, D.S., 2014a. Ten seconds in the field: rapid Armenian obsidian sourcing with portable XRF to inform excavations and surveys. J. Archaeol. Sci. 41, 333–348.

Frahm, E., Feinberg, J.M., Schmidt-Magee, B.A., Wilkinson, K.N., Gasparyan, B., Yeritsyan, B., Karapetian, S., Meliksetian, Kh., Muth, M.J., Adler, D.S., 2014b. Sourcing geochemically identical obsidian: Multiscalar magnetic variations in the Gutansar volcanic complex and implications for Palaeolithic research in Armenia. J. Archaeol. Sci. 47, 164–178.

Frahm, E., Feinberg, J.M., Schmidt-Magee, B., Wilkinson, K.N., Gasparyan, B., Yeritsyan, B., Adler, D.S., 2016. Middle Palaeolithic lithic procurement behaviors at Lusakert cave 1, Hrazdan Valley, Armenia. J. Hum. Evol. 91, 73–92.

Gasparyan, B., 2010. Landscape organization and resource management in the Lower Palaeolithic of Armenia. Tüba-Ar 13, 159–183.

Gasparyan, B., Adler, D.S., Egeland, C.P., Azatyan, K., 2014a. Recently discovered lower paleolithic sites of Armenia. In: Gasparyan, B., Arimura, M. (Eds.), Stone Age of Armenia. Monograph of the JSPS-Bilateral Joint Research Project, Center for Cultural Resource Studies, Kanazawa Universitypp. 37–64.

Gasparyan, B., Egeland, C.P., Adler, D.S., Pinhasi, R., Glauberman, P., Haydosyan, H., 2014b. The middle paleolithic occupation of armenia: summarizing old and new data. In: Gasparyan, B., Arimura, M. (Eds.), Stone Age of Armenia. Monograph of the JSPS-Bilateral Joint Research Project, Center for Cultural Resource Studies, Kanazawa Universitypp. 65–106.

Glascock, M.D., Ferguson, J.R., 2012. Report on the Analysis of Obsidian Source Samples by Multiple Analytical Methods. MURR Archaeometry Laboratory Report.

Glauberman, P., Gasparyan, B., Wilkinson, K.N., Frahm, E., Raczynski-Henk, Y., Haydosyan, H., Arakelyan, D., Karapetian, S., Nahapetyan, S., Adler, D.S. 2016. Introducing Barozh 12: a Middle Palaeolithic open-air site on the edge of the Ararat Depression, Armenia. ARAMAZD: Armenian Journal of Near Eastern Studies 9(2):7–20, 158–174.

Graham, J., 1988. Collection and analysis of field data. In: Tucker, M. (Ed.), Techniques in Sedimentology. Blackwell Scientific, Oxford, pp. 5–62.

Hughes, R.E., 1988. The Coso Volcanic Field reexamined: implications for obsidian sourcing and hydration dating research. Geoarchaeology 3 (4), 253–265.

Hughes, R.E., 2007. The geologic sources of obsidian artifacts from Minnesota

archaeological sites. Minnesota Archaeologist 66, 53–68.
Hughes, R.E., Lees, W.B., 1991. Provenance analysis of obsidian from two late prehistoric archaeological sites in Kansas. Trans. Kans. Acad. Sci. 94, 38–45.
Hughes, R.E., Pavesic, M.G., 2005. Proximity and provenance: a lesson from the Sterling cache, Idaho. J. Calif. Gt. Basin Anthropol. 25 (2), 221–225.
Hughes, R.E., Smith, R.L., 1993. Archaeology, geology, and geochemistry of obsidian provenance studies. In: Stein, J.K., Linse, A.R. (Eds.), Effects of Scale on Archaeological and Geological Perspectives, GSA Special Paper. 283. Geological Society of America, Boulder, Colorado, pp. 79–91.
Keller, J., Seifried, C., 1990. The present status of obsidian source identification in Anatolia and the Near East. In: PACT 25: Volcanology and Archaeology, Proceedings of the European Workshops of Ravello 25, pp. 57–87.
Keller, J., Djerbashian, E., Pernicka, E., Karapetian, S., Nasedkin, V., 1996. Armenian and Caucasian obsidian occurrences as sources for the Neolithic trade: volcanological setting and chemical characteristics. In: Archaeometry 94: Proceedings of the 29th International Symposium on Archaeometry; Ankara, 9–14 May 1994, pp. 69e86.
Komarov, A.N., Skovorodkin, N.V., Karapetian, S.G., 1972. Determination of the age of natural glasses according to tracks of uranium fission fragments (in Russian). Geochimia N6, 693–698.
Lebedev, V.A., Chernyshev, I.V., Yakushev, A.I., 2011. The initiation time and the duration of Quaternary magmatism in the Aragats neovolcanic area, Lesser Caucasus, Armenia. Dokl. Earth Sci. 437, 808–812.
Lebedev, V.A., Chernyshev, I.V., Shatagin, K.N., Bubnov, S.N., Yakushev, A.I., 2013. The Quaternary volcanic rocks of the Geghama Highland, Lesser Caucasus, Armenia: geochronology, isotopic Sr–Nd characteristics, and origin. J. Volcanol. Seismol. 7, 204–229.
Lordkipanadze, D., Ponce de León, M.S., Margvelashvili, A., Rak, Y., Rightmire, G.P., Vekua, A., Zollikofer, C.P.E., 2013. A complete skull from Dmanisi, Georgia, and the evolutionary biology of early homo. Science 342, 326–331.
Martirosyan-Olshansky, K., 2015. Provenance Study of Obsidian Artifacts from the Neolithic Settlement of Masis Blur (Armenia) Using Portable X-ray Fluorescence Spectrometry. Poster Presented at the Annual Meeting of the Society for American Archaeology. San Fransisco, CA.
Mitchell, J., Westaway, R., 1999. Chronology of Neogene and Quaternary uplift and magmatism in the Caucasus: constraints from K–Ar dating of volcanism in Armenia. Tectonophysics 304, 157–186.
Negash, A., Shackley, M.S., 2006. Geochemical provenance of obsidian artefacts from the MSA site of Porc Epic, Ethiopia. Archaeometry 48 (1), 1–12.
Palumbi, G., Gratuze, B., Harutunyan, A., Chataigner, C., 2014. Obsidian-tempered pottery in the Southern Caucasus: a new approach to obsidian as a ceramic-temper. J. Archaeol. Sci. 44, 43–54.
Roper, D.C., Hughes, R.E., 2014. Source analysis of obsidian debitage from two Early Archaic sites in Nebraska. Plains Anthropol. 59 (229), 58–68.
Shackley, M.S., 1995. Sources of archaeological obsidian in the greater American southwest: an update and quantitative analysis. Am. Antiq. 60 (3), 531–551.
Shackley, M.S., 2009. Intersource and intrasource geochemical variability in two newly discovered archaeological obsidian sources in the southern Great Basin. J. Calif. Gt. Basin Anthropol. 16 (1), 118–129.
Shackley, M.S., 2010. Is there reliability and validity in portable X-ray fluorescence spectrometry (PXRF)? In: The SAA Archaeological Record, Nov, 17–18, pp. 20.
Shackley, M.S., 2011. An introduction to X-ray fluorescence (XRF) analysis in archaeology. In: Shackley, M.S. (Ed.), X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology. Springer, pp. 7–44 (Chapter 2).
Shackley, M.S., 2012. Portable X-ray fluorescence spectrometry (pXRF): the good, the bad, and the ugly (online essay). Archaeology Southwest Magazine 26 (Spring issue).
Skinner, C.E., Davis, M.K., 1996. X-ray fluorescence analysis of an obsidian biface from the Fort Hill Site, Highland County, Ohio. In: Report 1996-48 Prepared for the Ohio Historical Society, Columbus, Ohio, by Northwest Research Obsidian Studies Laboratory, Corvallis, Oregon.
Skinner, C.E., Thatcher, J.J., 2009. Results of X-ray Fluorescence and Obsidian Hydration Studies: Site 646–0018, Malheur National Forest, Oregon, Report 2009–06. Northwest Research Obsidian Studies Laboratory, Corvallis, Oregon.
Skinner, C.E., Thatcher, J.J., Davis, M.K., 1997. X-ray fluorescence analysis and obsidian hydration rim measurement of artifact obsidian from 35-DS-193 and 35-DS-201, surveyor fire rehabilitation Project, Deschutes National Forest, Oregon. In: Report 98-96 Prepared by Northwest Research Obsidian Studies Laboratory, Corvallis, Oregon.
Smith, D.B., 1995. Rhyolite, Glass Mountain, RGM-1. U.S. Geological Survey Certificate of Analysis.
Speakman, R.J., Shackley, M.S., 2013. Commentary: silo science and portable XRF in archaeology: a response to Frahm. J. Archaeol. Sci. 40, 1435–1443.
Wagner, G.A., Weiner, K.L., 1987. Deutches Archaeologisches Institut Demircihoyuk. Die Ergebenisse des Ausgrabungen 1975–1978. In: Herausgegeben von Manfred Korfmann Band II: Naturwissenschaftliche Untersuchungen. Verlag Philipp von Zabern, Mainz, Germany, pp. 26–29.
Wagner, G.A., Storzer, D., Keller, J., 1976. Spaltspurendatierung quartärer Gesteinsgläser aus dem Mittelmeerraum. Neues Jahrb. filr Mineral. Monatsh. 2, 84–94.