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▶ **To cite this version:**

Marie Orange, François-Xavier Le Bourdonnec, Anja Scheffers, Renaud Joannes-Boyau. Sourcing obsidian: a new optimized LA-ICP-MS protocol. STAR: Science & Technology of Archaeological Research, 2016, 2 (2), pp.192-202. 10.1080/20548923.2016.1236516 . hal-01743034

HAL Id: hal-01743034
https://hal.science/hal-01743034

Submitted on 10 Dec 2022

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STAR: Science & Technology of Archaeological Research

ISSN: (Print) 2054-8923 (Online) Journal homepage: http://www.tandfonline.com/loi/ysta20

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To cite this article: Marie Orange, François-Xavier Le Bourdonnec, Anja Scheffers & Renaud Joannes-Boyau (2016) Sourcing obsidian: a new optimized LA-ICP-MS protocol, STAR: Science & Technology of Archaeological Research, 2:2, 192-202, DOI: 10.1080/20548923.2016.1236516

To link to this article: http://dx.doi.org/10.1080/20548923.2016.1236516

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Science and Technology of Archaeological Research

Article

Sourcing obsidian: a new optimized LA-ICP-MS protocol

Marie Orange[1*], François-Xavier Le Bourdonnec[2], Anja Scheffers[1], and Renaud Joannes-Boyau[1]

[1]Southern Cross GeoScience, Southern Cross University, Military Road, PO Box 157, Lismore, NSW, 2480, Australia
[2]IRAMAT-CRP2A, UMR 5060 CNRS-Université Bordeaux Montaigne, Maison de l'Archéologie, Esplanade des Antilles, 33607 Pessac, France

Abstract Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry [LA-ICP-MS] is one of the most successful analytical techniques used in archaeological sciences. Applied to the sourcing of lithic raw materials, it allows for fast and reliable analysis of large assemblages. However, the majority of published studies omit important analytical issues commonly encountered with laser ablation. This research presents a new advanced LA-ICP-MS protocol developed at Southern Cross GeoScience (SOLARIS laboratory, Southern Cross University, Australia), which optimizes the potential of this cutting-edge geochemical characterization technique for obsidian sourcing. This new protocol uses ablation lines with a reduced number of assayed elements (specific isotopes) to achieve higher sensitivity as well as increased precision and accuracy, in contrast to previous studies working with ablation points and an exhaustive list of measured isotopes. Applied to obsidian sources from the Western Mediterranean region, the Carpathian basin, and the Aegean, the results clearly differentiate between the main outcrops, thus demonstrating the efficiency of the new advanced LA-ICP-MS protocol in answering fundamental archaeological questions.



Statement of significance Our new LA-ICP-MS protocol, specifically tailored for the geochemical sourcing of obsidian artefacts in the Western Mediterranean area, was developed at SOLARIS (Southern Cross GeoScience, Southern Cross University, Australia) with a top-of-the-range Agilent 7700x ICP-MS coupled to a an ESI NWR 213 Laser Ablation System. Taking into account the common analytical issues encountered with the LA-ICP-MS technique, we focused on two parameters: the use of ablation lines instead of ablation points, and the development of a reduced list of measured isotopes. The use of ablation lines aims to compensate for any sample heterogeneity, achieve a higher count rate as well as a better signal stability, and also reduce laser-induced elemental fractionation. The measured isotopes have been carefully selected amongst the most efficient to discriminate between the different obsidian sources. This shortened list of isotopes achieves precise and accurate measurements with a higher sensitivity, and with the use of ablation lines, contributes to enhancing the potential of this geochemical characterization technique for obsidian sourcing.

Data availability The LA-ICP-MS results for the obsidian geological samples from the Mediterranean area are available as supplementary data.

Keywords LA-ICP-MS; Geochemistry; Lithic sourcing; Obsidian; Archaeology; Western Mediterranean

Received 9 November 2015; **accepted** 27 July 2016

1. Introduction

Geochemical characterization methods currently used for obsidian sourcing studies in archaeology include: X-Ray Fluorescence spectroscopy [XRF] (Carter and Shackley 2007; Freund 2014 *i.a.*), Particle Induced X-ray Emission spectroscopy [PIXE] (Constantinescu *et al.* 2013; Le Bourdonnec *et al.* 2015), Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry

Corresponding author: m.orange.10@student.scu.edu.au; T: +61 2 6620 3158

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[LA-ICP-MS] (Binder *et al*. 2011; Reepmeyer *et al*. 2011), Scanning Electron Microscopy coupled to energy dispersive X-ray spectroscopy [SEM-EDS] (Acquafredda and Muntoni 2008; Le Bourdonnec *et al*. 2010), and Instrumental Neutron Activation Analysis [INAA] (Santi, Renzulli, and Oddone 2010; Kuzmin and Glascock 2014). Alternative characterization methods also exist that are based on the structural or magnetic properties of obsidian (McDougall, Tarling, and Warren 1983; Stewart *et al*. 2003; Bellot-Gurlet *et al*. 2004; Carter *et al*. 2009; Frahm and Feinberg 2013). However, even non-destructive techniques have various limitations when applied to the analysis of archaeological samples (artefacts). Specifically, limitations may arise in relation to the size and shape (flatness) of the artefact (Davis *et al*. 2011), the eventual surface, and by extent geochemical alterations (see Poupeau *et al*. 2010), and even the ability to discriminate between sources of a given geographical area (depending on the elements the chosen method can measure; see *e.g*. Orange, Carter, and Le Bourdonnec 2013). Of the available methods, LA-ICP-MS is one of the most recent and most efficient tools, allowing a virtually non-destructive multi-element analysis with high accuracy and precision in a short time period (Gratuze, Blet-Lemarquand, and Barrandon 2001; Barca, De Francesco, and Crisci 2007; Barca, Lucarini, and Fedele 2012).

Despite improved understanding of common analytical problems encountered with laser ablation (see Speakman and Neff 2005) and the adoption of adequate protocols by several specialists in the field (see *e.g*. Speakman *et al*. 2002, 2007; Glascock *et al*. 2005; Tabares *et al*. 2005), numerous LA-ICP-MS protocols for obsidian sourcing studies (*cf*. *e.g*. Gratuze 1999; Barca, De Francesco, and Crisci 2007; Eerkens, Spurling, and Gras 2008) were developed disregarding some of these issues. Many studies still use discrete ablation points, despite the fact that the use of ablation lines and rasters is a well-established means of overcoming elemental fractionation (Jackson 2001), which is one of the main issues of LA-ICP-MS analysis. Lines and rasters also allow for a higher count rate, achieve better signal stability and help compensate for sample heterogeneity (Speakman and Neff 2005). Most obsidian sourcing studies were also assaying up to 30 isotopes, when only a handful of these isotopes are typically used to discriminate between the obsidian sources and attribute the artefacts to those sources (see *e.g*. Carter *et al*. 2006; Bellot-Gurlet, Dorighel, and Poupeau 2008; Binder *et al*. 2011).

Here we present, validate, and explain the rationale underlying a protocol designed to optimize the LA-ICP-MS technique for obsidian sourcing. Geological and archaeological obsidian samples were analysed as a means of testing this new protocol, which improves analytical sensitivity, accuracy, reliability, and efficiency (*i.e*. swiftness in regard to the aforementioned factors) by focusing on two main changes: (a) the use of a reduced list of assayed isotopes, and (b) the use of ablation lines instead of ablation points, as advised in earlier methodological studies.

2. Instrumentation and protocols

2.1. Instrumentation

SOLARIS consists of an ESI (Electro Scientific Industries, Inc.) NWR 213 Laser Ablation System (solid state Nd-YAG deep UV laser [213 nm]) with a 150 mm×150 mm high performance large format cell coupled to an Agilent 7700x ICP-MS. Data was acquired and treated using MassHunter Workstation software and calibration was performed with the NIST SRM 611 international standard [National Institute of Standards and Technology; Standard Reference Material]. An internal standardization was achieved using the NIST 613 international standard, which has a similar SiO_2 content to obsidian (generally > 70 wt %; see Heide and Heide 2011), analyzed at the beginning and end of each run. Results obtained by ICP-MS on the ^{28}Si isotope are calibrated against the SiO_2 content of NIST 613 (72.1%; see Jochum *et al*. 2011).

2.2. V1 and V2 protocols

The hypothesis explored here is that a reduced number of assayed isotopes can achieve a better sensitivity. This led to the development and comparison of two different protocols: one commonly found in the literature (named V1) employs an exhaustive list of measured isotopes, the second – optimized (V2) – employs a reduced list of isotopes. The instrumental settings used for both protocols are summarized in the Table 1.

The V1 protocol included 30 specific isotopes to analyze: ^{7}Li, ^{27}Al, ^{28}Si, ^{31}P, ^{39}K, ^{43}Ca, ^{47}Ti, ^{55}Mn, ^{66}Zn, ^{69}Ga, ^{78}Se, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{146}Nd, ^{147}Sm, ^{157}Gd, ^{165}Ho, ^{166}Er, ^{178}Hf, ^{181}Ta, ^{208}Pb, ^{232}Th, and ^{238}U.

From this exhaustive list, 15 selected isotopes were measured in the V2 protocol: ^{28}Si, ^{45}Sc, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{208}Pb, ^{232}Th, and ^{238}U. These isotopes were selected on the basis of: (a) the level of accuracy obtained, (b) their occurrence in previous obsidian sourcing studies, and (c) their potential to discriminate between obsidian sources as per these previous studies. Selecting isotopes measured by other research groups helped us to compare the results of this study (isotopic contents, accuracy, or precision) to the results from other instrumentations and protocols (see 3.2.4. and 3.3.2.).

2.3. Laser ablation parameters

As previously mentioned, the use of ablation lines in LA-ICP-MS analyses has been proven to reduce element fractionation, correct for sample heterogeneity and achieve higher count rates (Speakman and Neff 2005). To our knowledge, such an ablation protocol has rarely been applied to obsidian sourcing (although see *e.g*. Speakman *et al*. 2002; Tabares *et al*. 2005). Usually, the sample ablation consists of

Table 1 LA-ICP-MS instrumental parameters for the V1 and V2 protocols.

	Instrumental settings	
	Geological samples	*Archaeological samples*
Plasma gas	Argon	Argon
Carrier gas	0.81 L/min	0.81 L/min
Laser output wavelength	213 nm	213 nm
Laser output energy	40% (≈ 0.044 mJ/pulse)	80% (≈ 0.389 mJ/pulse)
Fluence	< 3 J/cm^2	< 40 J/cm^2
Sampling depth	6.6 mm	6.6 mm
Ablation mode	Line	Line
Line length	1.2 mm	0.6 mm
Spot size	60 µm	40 µm
Scan speed	10 µm/sec	5 µm/sec
Pre-ablation	No	No
Sampling time	2:15 min	2:15 min
Ablation depth	5 µm	10 µm
Frequency	10 Hz	10 Hz
RF power	1380 W	1380 W
RF matching	1.36 V	1.36 V
Extraction lens 1 voltage	0.0 V	0.0 V
Extraction lens 2 voltage	−190 V	−190 V
Omega bias -cs	−90 V	−90 V
Omega lens -cs	9.2 V	9.2 V

several ablation points of a diameter ranging between 40 to 100 µm, with a depth reaching up to 250 µm, and an acquisition time of about 60 s per point (see *e.g.* Gratuze, Blet-Lemarquand, and Barrandon 2001; Barca, De Francesco, and Crisci 2007; Khalidi *et al.* 2010). In this study, we opted to use ablation lines in order to optimize the LA-ICP-MS technique. With our protocol designed for both geological and archaeological obsidian samples, the ablation settings have been tailored specifically for each sample type. The same instrumental parameters were utilized in both cases (see Table 1).

2.3.1. *Geological samples*

The geological samples were cut and embedded in an epoxy resin (Epofix, Struers), then polished down to ¼ µm (using a polycrystalline diamond solution). Before analysis, the geological samples were cleaned in distilled water in an ultrasonic bath for five minutes, then rinsed consecutively with running tap water, distilled water, and alcohol. On these polished sections, an ablation line of 1.2 mm with a scan speed of 10 µm/sec achieved a 2:15 min signal, and a spot size of 60 µm width and 5 µm depth was used to attain the best possible results. A laser output of 40% [energy per pulse ≈ 0.044 mJ] was selected.

2.3.2. *Archaeological samples*

For the archaeological samples, the protocol was adapted to minimize the impact of ablation and thus maximize the preservation of the artefact. Accordingly, the ablation line was reduced to 40 µm wide (thinner than human hair) and 0.6 mm long, making it barely visible to the naked eye and considered as virtually non-destructive. The depth of the line was increased to 10 µm in order to make up for any geochemical surface alteration (often present on artefacts; see Poupeau *et al.* 2010). To compensate for a loss of signal due to the shorter and narrower ablation line, the scan speed was lowered to 5 µm/sec and the output amplified to 80% [energy per pulse ≈ 0.389 mJ] instead of 40% as with the geological samples. Preparation of the archaeological samples before analysis involved cleaning in distilled water in an ultrasonic bath for five minutes, followed by successive thorough rinses of distilled water, alcohol, and acetone.

3. Results and discussion

3.1. Sensitivity: V1 vs. V2 protocol

In order to compare the sensitivity of our V1 and V2 protocols, a series of measurements were obtained on the same day, under similar plasma conditions on the NIST 613 SRM. For all of the isotopes common to both protocols (^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{208}Pb, ^{232}Th, and ^{238}U), a simple comparison of the raw counts shows that higher count rates were achieved with the second protocol (Table 2), and so a higher sensitivity (raw count rate/expected concentration in ppm) was established. Indeed, since fewer isotopes are selected in the V2 protocol but the total acquisition time per line stays the same (2:15 min), each isotope signal will be acquired for a longer period (2:15 min divided by 15 instead of 30). Therefore, higher count rates were achieved, resulting in higher sensitivity.

3.2. Reliability of the V2 protocol

A total of 200 geological samples and 538 archaeological samples from two sites (Orange *et al.*, *in prep.*; Mazet *et al.*, *in prep.*) was analyzed with the V2 protocol during a total of 25 runs. In order to assess the accuracy, precision, and reproducibility of our analyses,

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Table 2 Comparison of the raw counts and sensitivity results for ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{208}Pb, ^{232}Th, and ^{238}U between the V1 and V2 protocols. Certified concentrations (in ppm): GeoRem. The number of rows [Nb rows] indicates the number of measurements obtained within a single ablation line; the results displayed for each isotope represent the average count rates (in cps) for the corresponding number of 'rows'.

	Nb rows	^{66}Zn	^{85}Rb	^{88}Sr	^{93}Nb	^{133}Cs	^{137}Ba	^{146}Nd	^{147}Sm	^{208}Pb	^{232}Th	^{238}U
V1 - NIST 613 (cps)	35	351	3509	15212	5935	9046	1124	1893	1677	4873	7304	9731
V2 - NIST 613 (cps)	77	458	3844	16460	6490	10023	1247	2043	1805	5314	8230	10839
Certified concentration (ppm)		39.1	31.4	78.4	38.9	42.7	39.3	35.5	37.7	38.57	37.79	37.4
Sensitivity V1 protocol		**9**	**112**	**194**	**153**	**212**	**29**	**53**	**44**	**126**	**193**	**260**
Sensitivity V2 protocol		**12**	**122**	**210**	**167**	**235**	**32**	**58**	**48**	**138**	**218**	**290**

the NIST 613 Standard Reference Material [SRM], with a nominal composition of 72.1% SiO_2, 13.7% Na_2O, 11.9% CaO, and 2.03% Al_2O_3 (mass fraction, mg/kg), was measured at the beginning and end of each run. The BCR-2G glass standard was also analyzed to check for any matrix-induced effect in our V2 protocol.

3.2.1. *Accuracy*

A total of 50 measurements of the NIST 613 SRM were obtained at the start and end of each of the 25 analysis runs, and used to determine the accuracy of the V2 protocol. The accuracy was calculated as the relative error between the contents acquired with this protocol and reference values from the GeoRem database (Max Planck Institute's Geochemical Database for Reference Materials and Isotopic Standards), and reported in Table 3.

For ^{232}Th, the relative error does not exceed 6%, and for the majority of isotopes the relative error is below 5%, and less than 3% for five of them (^{85}Rb, ^{88}Sr, ^{137}Ba, ^{208}Pb, and ^{238}U). To further our assessment of the V2 protocol accuracy, we also compared the relative error obtained on the same number of measurements (n=8) on the NIST 613 standard between the V1 and V2 protocol. For the majority of isotopes assessed, the relative error here again calculated against the reference values of the GeoRem database is lower with the V2 protocol results than the V1 protocol results (see Table 3). This new protocol is therefore producing accurate results while achieving higher sensitivity for isotope discrimination.

3.2.2. *Precision*

To compare the precision of the analysis between the exhaustive (V1) and optimized (V2) protocols, the standard error of the mean was calculated for each of the 13 isotopes assayed in both protocols (8 measurements). The results are presented in Table 4 and show, for each isotope, a considerably lower standard error of the mean for the V2 protocol as well as a lower standard deviation – *i.e.* a higher precision of the measurements. This clearly reflects that a smaller number of isotopes assayed multiplies the measurement points, consequently increasing the precision.

Table 3 Comparison of the ^{45}Sc, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{208}Pb, ^{232}Th, and ^{238}U contents with uncertainty (± 1 standard deviation) obtained on the NIST SRM 613 standard between the V2 protocol (total number of measurements = 50) and the reference values recommended by the NIST and the GeoRem database. The concentrations obtained for each isotope (with the exception of ^{45}Sc, which was unassessed with the V1 protocol) and corresponding relative error are also compared between the V1 and V2 protocol for the same number of measurements (n=8). Relative error calculated in comparison with the GeoRem reference values. Concentrations are in ppm.

	NIST	GeoRem	V2 (50 measures)		V1 (8 measures)		V2 (8 measures)	
	Concentration	Concentration	Concentration (1sd)	Relative error	Concentration	Relative error	Concentration	Relative error
^{45}Sc		39.9(2.5)	38.0(1.3)	4.8%				
^{66}Zn		39.1(1.7)	41.3(3.4)	5.7%	37.2	4.9%	38.1	2.6%
^{85}Rb	31.4(0.4)	31.4(0.4)	31.0(0.9)	1.3%	32.2	2.5%	31.2	0.6%
^{88}Sr	78.4(0.2)	78.4(0.2)	78.0(3.5)	0.5%	81.1	3.4%	77.9	0.6%
^{89}Y		38.3(1.4)	36.3(1.6)	5.1%	36.4	5.0%	35.6	7.0%
^{90}Zr		37.9(1.2)	36.2(1.6)	4.4%	34.0	10.3%	35.2	7.1%
^{93}Nb		38.9(2.1)	37.2(0.8)	4.3%	38.2	1.8%	36.7	5.7%
^{133}Cs		42.7(1.8)	40.7(1.1)	4.7%	43.3	1.4%	40.6	4.9%
^{137}Ba	38.6(2.6)	39.3(0.9)	39.3(1.3)	0.05%	40.0	1.8%	39.3	0.0%
^{146}Nd	36	35.5(0.7)	33.6(0.8)	5.4%	33.1	6.8%	33.6	5.4%
^{147}Sm	39	37.7(0.8)	35.9(1.1)	4.8%	34.8	7.7%	35.8	5.0%
^{208}Pb	38.57(0.2)	38.57(0.2)	39.67(1.76)	2.85%	39.32	1.95%	37.96	1.58%
^{232}Th	37.79(0.08)	37.79(0.08)	35.54(1.30)	5.95%	35.88	5.05%	34.94	7.54%
^{238}U	37.38(0.08)	37.38(0.08)	36.41(0.59)	2.59%	38.85	3.93%	36.62	2.03%

Table 4 Comparison of the standard error of the mean (Std Err Mean) obtained on the NIST SRM 613 international standard for the 13 isotopes common to the V1 and V2 protocols (^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{208}Pb, ^{232}Th, and ^{238}U). Average contents (ave.) and standard deviations (std. dev.) obtained on 8 measurements. Contents are in ppm.

		^{66}Zn	^{85}Rb	^{88}Sr	^{89}Y	^{90}Zr	^{93}Nb	^{133}Cs	^{137}Ba	^{146}Nd	^{147}Sm	^{208}Pb	^{232}Th	^{238}U
V1	ave. (n=8)	37.2	32.2	81.1	36.4	34.0	38.2	43.3	40.0	33.1	34.8	39.3	35.9	38.8
	std. dev.	1.7	1.7	5.1	2.6	2.4	2.3	3.6	2.0	1.8	1.8	1.6	2.6	3.5
	Std Err Mean	***0.7***	***0.6***	***1.9***	***1.0***	***0.9***	***0.9***	***1.4***	***0.8***	***0.7***	***0.7***	***0.6***	***1.0***	***1.3***
V2	ave. (n=8)	38.1	31.1	77.9	35.6	35.3	36.7	40.6	39.3	33.6	35.8	38.0	35.0	36.6
	std. dev.	3.6	1.3	2.4	1.7	1.8	0.9	1.3	1.1	0.7	1.2	1.4	1.1	0.8
	Std Err Mean	***1.3***	***0.5***	***0.9***	***0.6***	***0.6***	***0.3***	***0.5***	***0.4***	***0.2***	***0.4***	***0.5***	***0.4***	***0.3***

The same conclusion would be made if it was possible to compare our data to previous studies using several ablation points (data unavailable/unpublished), since an ablation line is in fact constituted of a series of points, *i.e.* about 70 to 80 in our V2 protocol, a quantity difficult to reach in a reasonable time with punctual ablation ICP-MS analysis protocols.

As demonstrated in Table 4, only the ^{66}Zn isotope, which may have interferences with polyatomic structures (*e.g.* ^{50}Ti^{16}O; see Evans and Giglio 1993), presents a higher standard error of the mean than for the V1 protocol.

3.2.3. *Reproducibility*

The reproducibility of the analyses through time was also assessed and represents a crucial factor in archaeological studies, particularly to sourcing studies. Using the same international standard (NIST SRM 613) the evolution of the ^{66}Zn, ^{88}Sr, ^{133}Cs, ^{137}Ba, and ^{146}Nd contents was observed over a 6 month period, as illustrated in Fig. 1 (23 measurements represented). The variations frequently remain within a 2σ range, thus attesting the repeatability of these measurements.

3.2.4. *Matrix-induced effect and comparison to a common protocol*

The BCR-2G standard (glass, basaltic composition; USGS, 2014) from the U.S. Geological Survey (USGS) was

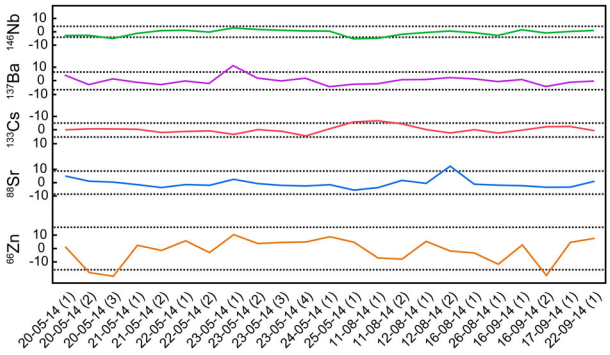


Figure 1 Evolution of the measured ^{66}Zn, ^{88}Sr, ^{133}Cs, ^{137}Ba, and ^{146}Nd contents on the NIST SRM 613 international standard over 5 months (23 measures represented). Data obtained by LA-ICP-MS with the V2 protocol. The dotted lines represent the ± 2σ dispersion.

Table 5 Comparison of the measured ^{45}Sc, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{208}Pb, ^{232}Th, and ^{238}U contents and uncertainties (± 1 standard deviation) obtained on basalt USGS standard BCR-2G (glass) in a previous LA-ICP-MS study (Barca, De Francesco, and Crisci 2007), this study, and the reference values recommended by the USGS and the GeoRem database. The relative error (Rel. error) is calculated in comparison with reference values of the GeoRem database. In bold: isotopes for which this study achieves a higher accuracy compared to a previous LA-ICP-MS study (Barca, De Francesco, and Crisci 2007). Contents are in ppm.

Isotope	USGS	GeoRem	Barca *et al.*, 2007 (n=18)	*Rel. error*	This study (*n*=4)	*Rel. error*
^{45}Sc	33(2)	33(2)	35(1)	*6%*	35(1)	*6%*
^{66}Zn	127(9)	125(5)	152(12)	*22%*	168(5)	*34%*
^{85}Rb	48(2)	47(0.5)	48(1)	*2%*	46(1)	*2%*
^{88}Sr	346(14)	342(4)	325(7)	*5%*	325(3)	*5%*
^{89}Y	**37(2)**	**35(3)**	**33(1)**	***6%***	**34(1)**	***3%***
^{90}Zr	**188(16)**	**184(15)**	**168(3)**	***9%***	**186(7)**	***1%***
^{93}Nb		12.5(1)	11.5(0.4)	*8.0%*	11.3(0.3)	*9.6%*
^{133}Cs	1.1(0.1)	1.16(0.07)	1.13(0.09)	*2.59%*	1.10(0.03)	*5.17%*
^{137}Ba	**683(28)**	**683(7)**	**642(27)**	***6%***	**674(13)**	***1%***
^{146}Nd	**28(2)**	**28.9(0.3)**	**28(1)**	***3%***	**28.6(0.8)**	***1%***
^{147}Sm	**6.7(0.3)**	**6.59(0.07)**	**6(0.3)**	***9%***	**6.6(0.2)**	***0%***
^{208}Pb	11(2)	11(1)	10.6(0.9)	*3.6%*	10.2(0.3)	*7.3%*
^{232}Th	6.2(0.7)	5.9(0.3)	5.8(0.5)	*1.7%*	6.0(0.2)	*1.7%*
^{238}U	**1.69(0.19)**	**1.69(0.12)**	**1.67(0.12)**	***1.18%***	**1.68(0.06)**	***0.59%***

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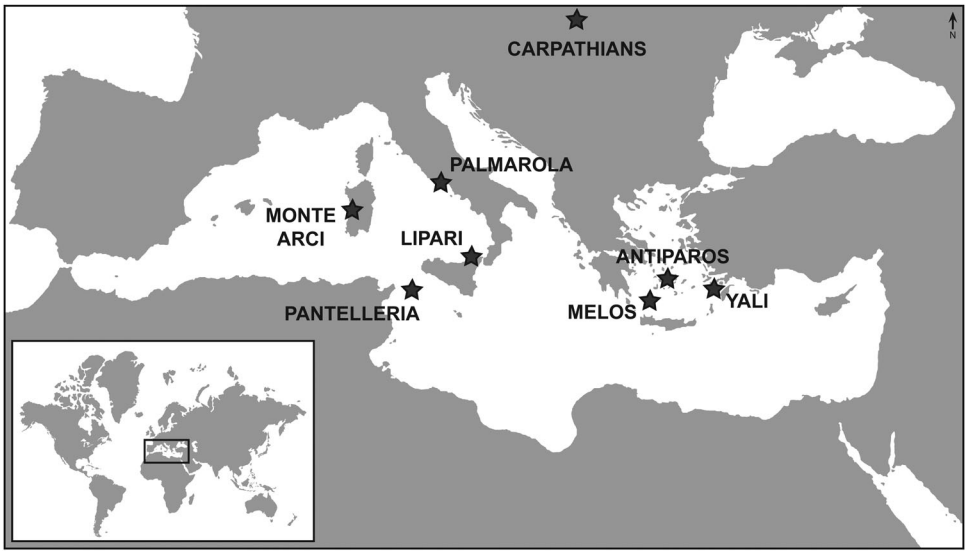


Figure 2 Map of the main obsidian sources in the Mediterranean area: Monte Arci (Sardinia), Lipari, Palmarola, Pantelleria, Yali, Melos, Antiparos, and the Carpathians.

analyzed several times to control for matrix-induced effects. The obtained average composition was compared against the USGS and GeoRem reference values, as well as against the values obtained by Barca *et al.* (2007) with LA-ICP-MS (see Table 5). The accuracy was assessed as the relative error between the measured values and the reference values from the GeoRem database. Accurate results were obtained and the relative error remains systematically below 10%, except for the zinc content which appears problematic. Comparing this study with the ablation point and exhaustive isotope list protocol (Barca, De Francesco, and Crisci 2007), four isotopes were identified (^{66}Zn, ^{93}Nb, ^{133}Cs, and ^{208}Pb) with relatively higher accuracy; however, the optimal protocol (V2) achieved considerably better results on ^{89}Y, ^{90}Zr, ^{137}Ba, ^{146}Nd, ^{147}Sm, and ^{238}U. The accuracy is comparable for the remaining isotopes (^{45}Sc, ^{85}Rb, ^{88}Sr, and ^{232}Th).

3.3. Application to obsidian sourcing studies in the Western Mediterranean

3.3.1. *Sources discrimination and provenance attribution of artefacts*

The viability of a specific method for obsidian sourcing does not only lie on its reliability (in which we entail

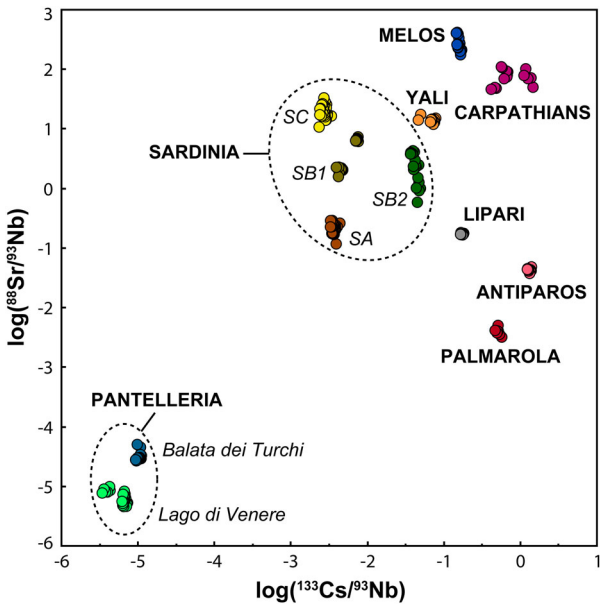


Figure 3 Comparison of log(^{133}Cs/^{93}Nb) and the log (^{88}Sr/^{93}Nb) ratios obtained by LA-ICP-MS (V2 protocol) on 200 geological samples from the Mediterranean region.

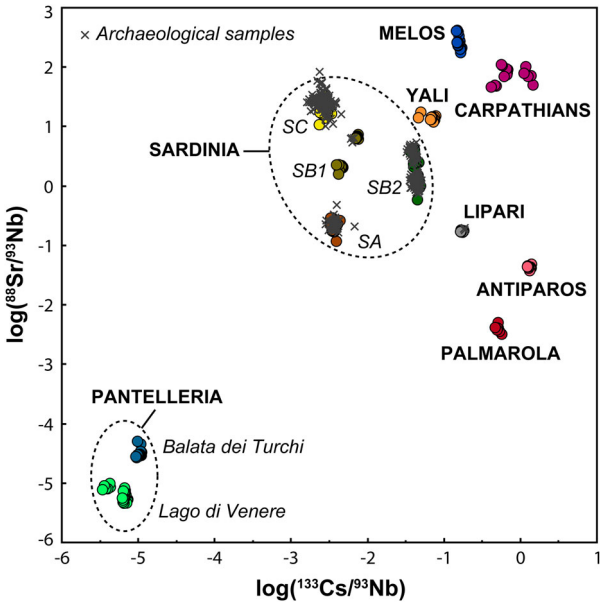


Figure 4 Comparison of log(^{133}Cs/^{93}Nb) and the log (^{88}Sr/^{93}Nb) ratios obtained by LA-ICP-MS (V2 protocol) on 200 geological samples from the Mediterranean region and 538 Neolithic archaeological samples from the Tyrrhenian area.

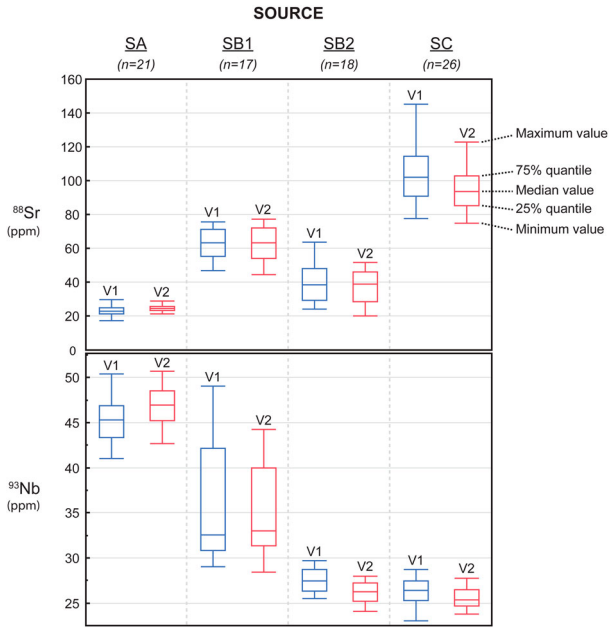


Figure 5 Dispersion of measurements for the ^{88}Sr and ^{93}Nb isotopes for the SA (n=21), SB1 (n=17), SB2 (n=18), and SC (n=26) obsidian source samples (Sardinia): comparison between exhaustive (V1) and optimized (V2) protocols. For each protocol and each source, the boxplot summarizes the minimum and maximum values (whiskers), the 25 and 75% quantiles (lower and upper limits of the boxplot), and the median value (central line within the boxplot).

sensitivity, precision, accuracy, and reproducibility; see *e.g.* Hughes 1998; Frahm 2012 for discussion), but also on its validity, *i.e.* its ability to distinguish between the relevant obsidian sources and to attribute obsidian artefacts from an assemblage to a specific source. The concept of source is defined in this context as a specific geochemical signature and not as a geographical location (see Hughes and Smith 1993). The primary known obsidian sources of the Western Mediterranean area, Carpathian basin, and Aegean area (Fig. 2) were considered in this study to assess the validity of the V2 protocol for obsidian sourcing: Sardinia (sub-types SA, SB1, SB2, and SC; Tykot 1997), Lipari (Pichler 1980), Palmarola (Tykot *et al.* 2005), Pantelleria (Balata dei Turchi and Lago di Venere; Francaviglia 1988), Yali (Milić 2014), Melos (Shelford *et al.* 1982), Antiparos (Carter and Contreras 2012) and the Carpathian sources (Bigazzi *et al.* 1990).

Using a log-ratio analysis of the compositional data (Aitchison 1982), Fig. 3 displays a comparison between the log(^{133}Cs/^{93}Nb) and the log(^{88}Sr/^{93}Nb) ratios obtained with the V2 protocol on 200 geological samples. The choice of the ^{88}Sr, ^{93}Nb, and ^{133}Cs isotopes was motivated by two reasons: (a) they are often used in the discrimination of obsidian sources in the Western Mediterranean (*cf. e.g.* Barca, De Francesco, and Crisci 2007), and (b) their variation coefficient on the totality of the Western Mediterranean sources was among the highest, therefore allowing for a clearer graphical separation of the sources. As shown by the log-ratio analysis, the sources are

Table 6 Comparison of the average ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, and ^{137}Ba contents and uncertainties (± 1 standard deviation) for the SA, SB1, SB2, and SC sub-types obtained in this study and previous studies (Tykot 2002, Barca, De Francesco, and Crisci 2007, De Francesco, Crisci, and Bocci 2008, Le Bourdonnec *et al.* 2011). Contents are in ppm.

Source	Method/Reference	^{85}Rb	^{88}Sr	^{89}Y	^{90}Zr	^{93}Nb	^{137}Ba
SA	LA-ICP-MS (Our study) (n=21)	251(11)	24(2)	30(2)	73(5)	47(2)	121(11)
	PIXE (Le Bourdonnec et al., 2011) (n=8)	253(14)	28(4)	37	78(8)	57	
	ED-XRF/NAA (Tykot 2002) (n=8)	249(3)	31(2)	37(2)	121(10)	49(3)	152(9)
	WD-XRF (De Francesco, Crisci, and Bocci 2008) (n=15)	257(2)	31(1)	37(1)	96(1)	56(1)	127(4)
	LA-ICP-MS (Barca, De Francesco, and Crisci 2007) (n=10)	270(28)	24(4)	33(4)	76(8)	49(4)	126(29)
SB1	LA-ICP-MS (Our study) (n=17)	237(10)	63(10)	23(5)	123(17)	35(5)	363(97)
	PIXE (Le Bourdonnec et al., 2011) (n=6)	250(10)	65(4)		121(6)		
	ED-XRF/NAA (Tykot 2002)*	235(4)-237 (4)-238(3)	76(16)-82 (11)-84(7)	29(3)-31 (4)-33(3)	166(17)-176 (12)-198(8)	36(4)-38 (6)-40(2)	320(20)-345 (11)-470(6)
	WD-XRF (De Francesco, Crisci, and Bocci 2008) (n=6)	245(2)	68(13)	30(5)	132(17)	45(7)	255(39)
	LA-ICP-MS (Barca, De Francesco, and Crisci 2007) (n=8)	264(55)	34(7)	20(2)	100(5)	27(3)	203(50)

(*Continued*)

Table 6 Continued.

Source	Method/Reference	^{85}Rb	^{88}Sr	^{89}Y	^{90}Zr	^{93}Nb	^{137}Ba
SB2	LA-ICP-MS (Our study) (n=18)	243(18)	38(10)	19(2)	102(14)	26(1)	207(68)
	PIXE (Le Bourdonnec et al., 2011) (n=10)	239(14)	42(9)	22(4)	108(12)	31	
	ED-XRF/NAA (Tykot 2002) (n=7)	242(8)	56(7)	26(1)	161(9)	30(3)	298(6)
	WD-XRF (De Francesco, Crisci, and Bocci 2008) (n=3)	246(1)	40(4)	21(1)	120(9)	30(1)	164(38)
	LA-ICP-MS (Barca, De Francesco, and Crisci 2007) (n=4)	249(11)	76(3)	23(2)	147(9)	33(1)	472(19)
SC	LA-ICP-MS (Our study) (n=26)	169(6)	94(12)	19(2)	199(17)	26(1)	824(76)
	PIXE (Le Bourdonnec et al., 2011) (n=20)	179(10)	148(19)	24(2)	241(23)	33(5)	
	ED-XRF/NAA (Tykot 2002)**	172(1)-173(3)	130(4)-131 (5)	27(1)-28 (1)	245(7)-247(10)	29(3)	907(20)-936 (12)
	WD-XRF (De Francesco, Crisci, and Bocci 2008) (n=11)	175(2)	134(3)	24(1)	213(3)	30(1)	899(19)
	LA-ICP-MS (Barca, De Francesco, and Crisci 2007) (n=8)	188(13)	115(20)	24(2)	237(13)	28(3)	992(151)

* The values reported here correspond to the average concentrations obtained for the SB1a, SB1b, and SB1c sub-groups defined in Tykot 2002.
** The values reported here correspond to the average concentrations obtained for the SC1 and SC2 sub-groups defined in Tykot 2002.

clearly distinguished from one another, thus confirming the validity of the V2 protocol in the geographical area considered. The validity of our protocol on the archaeological level, *i.e.* its capacity to attribute each artefact of an assemblage to a specific source, was assessed through the analysis of 538 archaeological samples from the Tyrrhenian area (Neolithic period). Fig. 4, using here again a comparison between the log(^{133}Cs/^{93}Nb) and the log(^{88}Sr/^{93}Nb) ratios, shows the clear attribution of these artefacts to the sources of the Western Mediterranean (Sardinian sources of the Monte Arci, and Lipari).

Furthermore, the optimized protocol (V2) reduces the dispersion of the measurements compared to the exhaustive protocol (V1), as illustrated in Fig. 5, where as an example the dispersion of the ^{88}Sr and ^{93}Nb contents for the same SA (n=21), SB1 (n=17), SB2 (n=18), and SC (n=26) Sardinian source samples is compared between both protocols.

3.3.2. *Comparison to previous studies*

Obsidian source results on Sardinian sub-types SA, SB1, SB2, and SC were also compared to published data: the obsidian samples have been analyzed by PIXE (Le Bourdonnec *et al.* 2011), ED-XRF and NAA (Energy Dispersive X-ray Fluorescence; Neutron Activation Analysis; Tykot 2002), WD-XRF (Wavelength Dispersive X-ray Fluorescence; De Francesco, Crisci, and Bocci 2008) and LA-ICP-MS (Barca, De Francesco, and Crisci 2007). The ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, and ^{137}Ba contents for each study are described in Table 6 and are in fairly good agreement. Only the measured ^{88}Sr content for the SC group is slightly lower than in the other studies, *i.e.* 82–106 ppm (taking into consideration 1 standard deviation) while other laboratories report values ranging from 95 to 167 ppm. This difference could eventually be explained by a difference in source sampling.

4. Conclusions

This study demonstrates that the new LA-ICP-MS protocol developed at Southern Cross University improves analytical reliability, validity and efficiency when applied to identifying obsidian provenance in the Western Mediterranean.

Analysis of the NIST SRM 613 international standard using the enhanced protocol (V2) demonstrated improved ability to obtain accurate and precise measurements with a higher sensitivity and within a very limited time frame (3 to 5 punctual measurement of about 60 s are usually used in previous studies, where our protocol produces a series of 70 to 80 measurement points in 2:15 min). Comparing the data obtained on the BCR-2G basalt standard (USGS) by a standard protocol using ablation points and an exhaustive list of isotopes (Barca, De Francesco, and Crisci 2007), our optimized protocol using lines and fewer isotopes obtained better or comparable results, when considering the accuracy of the measurements — V1 analysis was more accurate than V2 for only 4 of 14 isotopes. Furthermore, when the V2 protocol is applied to the Mediterranean obsidian sources, differentiation between sources is particularly distinct, thus confirming the validity of the optimized protocol (V2)

as a sourcing tool in obsidian provenance research. Further study is required to investigate the rather low precision and accuracy results of the ^{66}Zn isotope, as well as the application of the V2 protocol rationale to further obsidian sources in the Mediterranean area (*e.g.* Near East).

In conclusion, the use of a refined LA-ICP-MS protocol tailored specifically to the target material is a demonstrably effective means of optimizing this cutting-edge geochemical characterization technique. In obsidian sourcing, it is particularly important for a meticulous selection of isotopes to be measured in order to discriminate between the sources of a particular geographical area: the more judiciously selected the list of isotopes, the better results.

Conflict of interest statement

The authors confirm there are no conflicts of interest.

Author biographies

Marie Orange is a Ph.D student within Southern Cross GeoScience, Southern Cross University, Australia. Her research focuses on obsidian trade in the Western Mediterranean during the Neolithic period.

Dr. François-Xavier Le Bourdonnec is an Associate Professor of Archaeological Sciences at Bordeaux Montaigne University. His work deals with circulation and economy of prehistoric lithic raw materials.

Dr. Anja Scheffers is a professor at Southern Cross University, Australia. Her research focuses on how coastal environments have changed in the past. She is particularly interested in processes that shape and modify coastal landscapes over a variety of length and time scales and the coupling and feedback between such processes, their rates, and their relative roles, especially in the contexts of variation in climatic and tectonic influences and in light of changes due to human impact.

Dr. Renaud Joannes-Boyau is a Senior Research Fellow at Southern Cross University, Australia, in charge of the ESR dating and Laser-Ablation ICP-MS laboratories. His research involves the application of physical techniques to archaeological problematics, in particular the direct dating of fauna and hominid fossil remains as well as the investigation of isotopic signature in fossil teeth and bones to reconstruct dietary changes and diagenetic processes.

Acknowledgements

The authors wish to thank Matthew Tonge for his management of the LA-ICP-MS and his help during the analyses, as well as Mark Rosicky and Diane Fyfe for their precious help. We also thank Valerie Schoepfer, Stan Kinis, Trent McIntyre, and Dr. Scott Johnston for proofreading this paper. Marie Orange's Ph.D is funded by a Postgraduate scholarship from SCU (Southern Cross University) and part of an Australian Research Council discovery grant [DP140100919]. This research program has been financially supported by the ANR (French National Research Agency; n° ANR-10-LABX-52) and the Université Bordeaux Montaigne PSE (Politique Scientifique d'Établissement).

Supplementary data captions

Supplementary data LA-ICP-MS results for the Mediterranean obsidian sources of Antiparos, Melos, Yali, Carpathians, Pantelleria (Balata Dei Turchi, Lago Di Venere), Palmarola, Lipari, and Monte Arci (SA, SB1, SB2, SC). Contents of ^{45}Sc, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{146}Nd, ^{147}Sm, ^{208}Pb, ^{232}Th, and ^{238}U, log (^{133}Cs/^{93}Nb) and log(^{88}Sr/^{93}Nb) ratios obtained on a total 200 obsidian geological samples with the V2 protocol. The number of rows [Nb rows] indicates the number of measurements obtained within a single ablation line, after statistical treatment with removal of the outliers with JMP statistical software (SAS); the results displayed for each isotope represent the average concentration (in ppm) for the corresponding number of 'rows'.

Supplementary data can be obtained from: http://dx.doi.org/10.1080/20548923.2016.1236516

ORCiD

Marie Orange http://orcid.org/0000-0002-7344-7597
François-Xavier Le Bourdonnec http://orcid.org/0000-0002-1051-5337
Anja Scheffers http://orcid.org/0000-0002-9143-5389
Renaud Joannes-Boyau http://orcid.org/0000-0002-0452-486X

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