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Marie Orange, Tristan Carter, François-Xavier Le Bourdonnec. Sourcing Obsidian from Tell Aswad and Qdeir 1 (Syria) by SEM-EDS and EDXRF: Methodological Implications. *Comptes Rendus. Palevol*, 2013, 12 (3), pp.173-180. 10.1016/j.crpv.2012.11.001 . hal-01743135

**HAL Id: hal-01743135**

**<https://hal.science/hal-01743135>**

Submitted on 20 Dec 2022

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Human palaeontology and prehistory (Prehistoric archaeology)

## Sourcing obsidian from Tell Aswad and Qdeir 1 (Syria) by SEM-EDS and EDXRF: Methodological implications

*Étude de provenance de l'obsidienne de Tell Aswad et Qdeir 1 (Syrie) par MEB-EDS et EDXRF: implications méthodologiques*Marie Orange<sup>a</sup>, Tristan Carter<sup>b</sup>, François-Xavier Le Bourdonnec<sup>a,\*</sup><sup>a</sup> IRAMAT-CRP2A, UMR 5060 CNRS–Université Bordeaux 3, Maison de l'Archéologie, Esplanade des Antilles, 33607 Pessac, France<sup>b</sup> Department of Anthropology/McMaster Archaeological XRF Lab, CNH 524, McMaster University, 1280 Main Street, Hamilton, LS8 4L9, Ontario, Canada

## ARTICLE INFO

*Article history:*

Received 5 October 2012

Accepted after revision 23 November 2012

Available online 1 February 2013

Presented by Yves Coppens

*Keywords:*

Obsidian

Provenance studies

SEM-EDS

EDXRF

Non-destructive

Neolithic

Syria

*Mots clés :*

Obsidienne

Études de provenance

MEB-EDS

EDXRF

Non destructif

Néolithique

Syrie

## ABSTRACT

While obsidian sourcing has long represented a powerful means of reconstructing past socio-economic interaction, the use of destructive techniques restricted most studies to analysing only a few artefacts per site. Non-destructive methods allow the characterization of much more material, thus providing more robust data upon which to base our archaeological interpretations. Here we report on one such study using EDXRF and SEM-EDS to analyse assemblages from Tell Aswad and Qdeir 1, two Syrian Neolithic sites. The study demonstrates for the first time that SEM-EDS can play an important role in discriminating Bingöl A and Nemrut Dağ sources, while the rapidity of EDXRF permits the analysis of a more statistically valid number of artefacts, providing a better impression of the assemblage. It enabled us to chart diachronic patterns in raw material procurement at Tell Aswad and detailed raw materials not recorded in a previous smaller-scale analysis of obsidian from Qdeir 1.

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## R É S U M É

Alors que les études de provenance de l'obsidienne ont longtemps représenté un moyen efficace de reconstruire les interactions socio-économiques du passé, l'utilisation de méthodes destructives a restreint la plupart de ces études à l'analyse de seulement quelques artefacts par site. Les méthodes non destructives permettent de caractériser plus de matériel, nous prodiguant ainsi des données plus « solides » sur lesquelles fonder nos interprétations. Nous présentons ici ce type d'étude, utilisant l'EDXRF le MEB-EDS pour analyser deux assemblages provenant de Tell Aswad et Qdeir 1, deux sites néolithiques syriens. Cette étude démontre deux points principaux. Premièrement, nous prouvons, pour la première fois, que le MEB-EDS peut jouer un rôle important dans la discrimination des sources de Bingöl A et Nemrut Dağ, deux des plus importantes sources du Proche-Orient durant la Préhistoire, tandis que la rapidité de l'EDXRF a permis l'analyse d'un nombre statistiquement plus représentatif d'artefacts, nous apportant une meilleure vue d'ensemble de la

\* Corresponding author.

E-mail addresses: [marie.orange24@gmail.com](mailto:marie.orange24@gmail.com) (M. Orange), [stringy@mcmaster.ca](mailto:stringy@mcmaster.ca) (T. Carter), [francois-xavier.le-bourdonnec@u-bordeaux3.fr](mailto:francois-xavier.le-bourdonnec@u-bordeaux3.fr)

(F.-X. Le Bourdonnec).

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<http://dx.doi.org/10.1016/j.crpv.2012.11.001>

série lithique en question. Cela nous a permis de noter des tendances diachroniques dans l'approvisionnement en matière première du site et de remarquer des matières premières non relevées lors de précédentes études de moins grande envergure sur l'obsidienne de Qdeir 1.

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## 1. Introduction

Obsidian is a volcanic glass, whose excellent flaking qualities and razor-sharp edges made it a highly desired tool-making raw material for pre-metalworking prehistoric peoples. With obsidian a relatively rare resource, communities often had to procure the material over great distances, often through exchange with intermediary populations. With the product of each volcanic source (flow/emission) having a unique chemical signature, archaeologists have long been interested in sourcing their artefacts' raw materials as a means of reconstructing ancient interaction networks. This is achieved by matching the chemical signature of an obsidian artefact to that of a distinct geological source, ideally using the same analytical technique (Glascok et al., 1998).

Over the past 50 years, a variety of chemical and physical characterization techniques have been employed in Eastern Mediterranean/Near Eastern obsidian sourcing studies (Pollard and Heron, 2008), whereby virtually all of the archaeologically significant sources can now be discriminated (Carter, 2009; Chataigner, 1998; Poidevin, 1998). While this work has included numerous artefact analyses, most studies involved only a few pieces per excavation, whereby the statistical significance of these data has to be questioned. This is particularly true when one is dealing with a site that has:

- a variety of tool-making strategies represented within the obsidian assemblage;
- a multi-phase occupation;
- a range of distinct contexts within which one finds obsidian (domestic, artisanal, burial *inter alia*), for if one wished to investigate the various modes of raw material consumption through time and space then it follows that one requires a not insignificant number of artefacts for analysis.

This is the situation faced by many Near Eastern prehistorians, yet only at the central Anatolian Neolithic site of Çatalhöyük (Fig. 1) do we thus far have such a large-scale sampling strategy, with many hundreds of artefacts analysed as a means of addressing exactly these concerns (Carter et al., 2006; Carter and Shackley, 2007; Poupeau et al., 2010 *inter alia*).

The fact that most studies only included a few artefacts per site arguably pertains to two interrelated issues, namely:

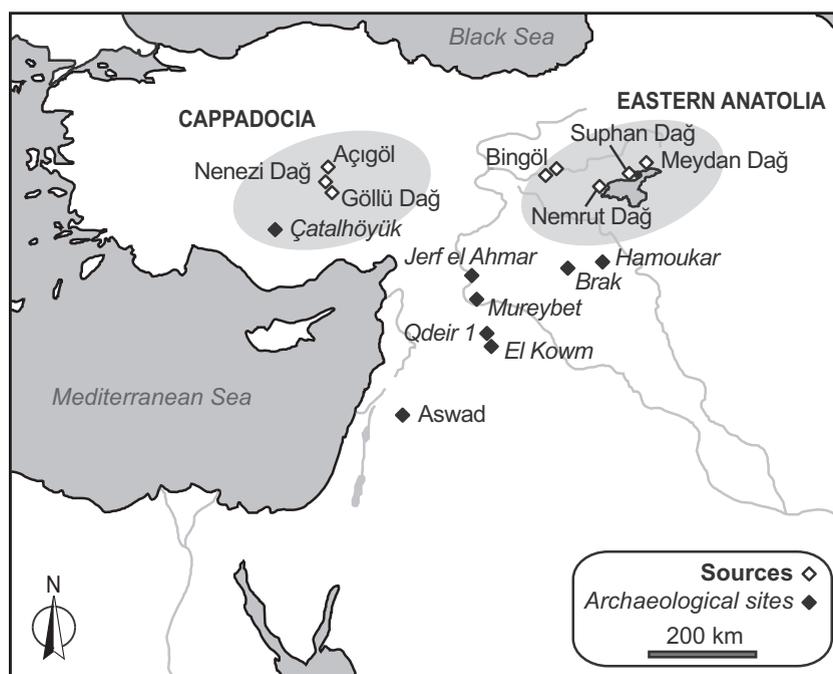
- the bureaucracy involved in exporting archaeological objects for analysis;
- the fact that so many of the early characterization techniques were partly, or wholly destructive, such as optical

emission spectroscopy (Renfrew et al., 1966), neutron activation analysis (Aspinall et al., 1972; Yellin, 1995) and inductively coupled plasma–mass spectroscopy (Abbès et al., 2003).

More recently there has been a turn towards non-destructive techniques such as EDXRF (Shackley, 1998), particle induced X-ray emission (PIXE) (Butalag et al., 2008; Le Bourdonnec et al., 2005) and SEM-EDS (Acquafredda and Muntoni, 2008) for reasons of cultural sensitivity, cost and speed of analysis, all of which is beginning to permit the characterization of significantly larger data sets (Carter and Shackley, 2007; Poupeau et al., 2010).

This study continues this trend, using SEM-EDS and EDXRF to characterize large numbers of obsidian artefacts from two prehistoric sites in Syria, Tell Aswad and Qdeir 1 (Fig. 1). While this article is concerned with the interpretative implications for the production of larger data sets, it also aimed to examine the use of these techniques in a Near Eastern context. Our specific interest lay in their ability to discriminate between the products of eastern Anatolian sources, not least the important peralkaline products of Bingöl and Nemrut Dağ (Fig. 1), two of the most important sources in Near Eastern prehistory, whose chemical similarity has often made them difficult to discriminate (Frahm, 2012). Previous applications of these techniques have focused primarily on archaeological case studies where central Anatolian (Cappadocian) raw materials were of primary importance (Carter and Shackley, 2007; Poupeau et al., 2010); it was thus our intention in this project to broaden the analytical remit of EDXRF and SEM-EDS through the study of assemblages that were more likely to contain tools made from eastern Anatolia obsidians.

We do not imply that this is the first use of these techniques in a Near Eastern context, as XRF was employed to characterize obsidian from the Late Chalcolithic (5th–4th millennium BC) Syrian sites of Tell Brak and Tell Hamoukar (Khalidi et al., 2009), while SEM-EDS was used to source artefacts from the PPNA – early PPNB Syrian site of Jerf el Ahmar (Abbès et al., 2003) (Fig. 1). However, in neither cases were the analysts confident in their ability to assign a specific source to those artefacts made of peralkaline obsidians, arguing that their similar geochemistry made it difficult to distinguish between the distinctive green raw materials of 'Bingöl A' and Nemrut Dağ, despite the fact that these sources are 150 km apart. The implicit suggestion was that only by using more powerful techniques such as NAA was it possible to differentiate between these raw materials (Chataigner, 1994). For archaeologists who could not employ such techniques this was a highly frustrating situation, as the inability to discriminate these raw materials likely masked important differences in their exploitation



**Fig. 1.** Archaeological sites and obsidian sources detailed in the text.

**Fig. 1.** Sites archéologiques et sources d'obsidiennes cités dans le texte.

histories and the existence of obsidian-specific exchange networks.

## 2. Tell Aswad and Qdeir 1: Background and previous sourcing studies

Tell Aswad and Qdeir 1 are two prehistoric sites in Syria (Fig. 1), excavated as part of the El Kowm-Mureybet mission, led by the *Maison de l'Orient Méditerranéen* (Lyon, France). They are both of pre-pottery Neolithic B [PPNB] date, *i.e.* early farming communities. The former is located in the Damascus basin (southern Syria) and dates to the Middle/Late PPNB, c. 8200–7500 cal BC (Stordeur and Jamous, 2009). The latter, of Final PPNB (or PPNC) date (c. 7100–5720 cal BC), is situated in the El Kowm oasis, a semi-nomadic occupation believed to be associated with the nearby permanent village site of El Kowm 2 – Caracol (Stordeur, 1993).

Both sites produced rich stone tool assemblages; while most implements were made of local chert, there are also a few of obsidian, despite the fact the nearest sources are located over 100 km to the north, in central and eastern Anatolia (Fig. 1). Available to us for analysis were 105 artefacts from Tell Aswad and 517 from Qdeir 1.

A previous analysis of 29 artefacts from Middle PPNB Tell Aswad by SEM-EDS and PIXE showed a reliance upon the south Cappadocian source of Göllü Dağ ( $n=25$ ), together with smaller quantities of eastern Anatolian products, with three artefacts of Bingöl B obsidian (or Bingöl calco-alkaline) and one of Nemrut Dağ obsidian (Delerue, 2007). A further 34 artefacts from the Middle/Late PPNB were also analysed, showing much the same pattern, with 31 pieces attributed to the Göllü Dağ, two Bingöl A/Nemrut

Dağ and one to Nemrut Dağ. Some of the artefacts analysed in our study were also characterised by Delerue (2007); unfortunately, it was not possible to tell which ones were duplicated.

For Qdeir 1, 25 artefacts were characterized by NAA (Gratuze et al., 1993), of which five were allocated to the analysts' group 1b (Bingöl A/Nemrut Dağ), 11 to Bingöl B and nine to Kayırlı (Göllü Dağ).

For our analysis we included data from an expanded range of Anatolian sources known to have been exploited by Near Eastern populations of the Early-Final PPNB (Chataigner, 1998), plus other nearby sources, including not only the raw materials previously attested at Tell Aswad and Qdeir 1, but also Açıgöl, Nenezi Dağ, Meydan Dağ and Suphan Dağ.

## 3. Analytical methods: their choice and interrelationship

A scanning electron microscope coupled with an energy dispersive spectrometer is an attractive technique for obsidian characterization analysis in the larger Mediterranean region, as a range of major and trace elements can be detailed non-destructively through surface analysis (Le Bourdonnec et al., 2010; Mulazzani et al., 2010).

Energy dispersive X-ray fluorescence (EDXRF) uses a X-ray tube to bombard the sample and produce, by the interaction of these X-rays with the electrons in the deep layers of the atom, secondary X-rays, characteristic of the elements present. It is a technique of simultaneous analysis, straightforward to use and fast.

In a previous sourcing study of Çatalhöyük obsidian, Poupeau et al. (2010) demonstrated the efficacy of EDXRF

and SEM-EDS to discriminate Anatolian obsidian sources, though it was noted that the latter was incapable of distinguishing products of two central Anatolian sources, Acıgöl and Göllü Dağ. Conversely, SEM-EDS is capable of working with small and thin samples (with low detection limits – about 0.1 wt% [see Kuisma-Kursula, 2000]) attributes that can present problems for EDXRF (Davis et al., 1998). As such, our study aimed to use the two techniques as complementary to one another. We also wished to examine the capabilities of these techniques with regard to discriminating eastern Anatolian obsidian (something we knew we would be dealing with on the basis of prior studies on the Tell Aswad and Qdeir 1 assemblages), particularly with regard to their ability to discriminate between the peralkaline obsidians of Bingöl A and Nemrut Dağ.

#### 4. Sampling and experimental procedures

##### 4.1. SEM-EDS

The study was conducted at the *Centre de recherche de physique appliquée à l'archéologie* (Bordeaux, France) using a JEOL JMS 6460 LV scanning electron microscope equipped with an energy dispersive spectrometer (Oxford Industries INCA x-sight), operating with a 20 kV accelerating potential. For each measurement, the electron beam diameter swept a surface of about  $1.5 \times 10^4 \mu\text{m}^2$ . The fluorescence X-rays emitted by the samples were collected by an Oxford X-Max EDS Silicon Drift Detector (SDD) with 20 mm<sup>2</sup> active area and a 125 eV resolution for the Mn K $\alpha$  emission line. All spectra were obtained with a real acquisition time of 90 s and a dead time of 30 to 40%. This involves spectra with more than  $10^6$  counts between 0 and 10 keV. The INCA data treatment software uses a XPP procedure  $\varphi(\rho z)$  X-ray correction models to calculate element contents as percent oxides.

Standards were used to calculate the chemical compositions (Corning B, Corning D, GaP, BCR-126 and pure mineral standards: Ti, Mn, Fe, MgO, albite). In order to check the reliability of the analysis, an obsidian geological standard was analysed at the beginning and at the end of each run.

The study involved 61 artefacts from Tell Aswad and 180 from Qdeir 1, i.e. 58% and 35% of our assemblages. After cleaning with ethylic alcohol and acetone, Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe contents were obtained for each piece following the procedure of Le Bourdonnec et al. (2010). Due to the artefacts' sizes and geometry, the elemental composition was determined as the average of two to eight 'punctual' measurements.

##### 4.2. EDXRF

This study was undertaken in the McMaster Archaeological XRF Lab [MAX Lab] using a Thermo Scientific *Quant'X* energy dispersive X-ray fluorescence spectrometer; the protocols and methods following those of Shackley (2005). The instrument is equipped with a ultra-high flux peltier air cooled Rh X-ray target with a 125 micron beryllium (Be) window, an X-ray generator operating from 4 to 50 kV/0.02 to 1.0 mA at 0.02 increments and a 2001 min<sup>-1</sup> Edwards vacuum pump for the analysis of elements below titanium

(Ti). Data are acquired with a pulse processor and analog to digital converter. Fifteen major and trace elements were recorded: Ti, Mn, Fe, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Pb and Th.

In order to evaluate these quantitative determinations, instrument data were converted to concentration estimates through reference to various standards, including those certified by the US Geological Service and Geological Survey of Japan (AGV-2, BCR-2, BHVO-2, BIR-1a, GSP-2, JR-1, JR-2, QLO-1, RGM-2, SDC-1, STM-2, TLM-1 and W-2a). The standard RGM-2 was analysed during each sample run to check machine calibration and accuracy.

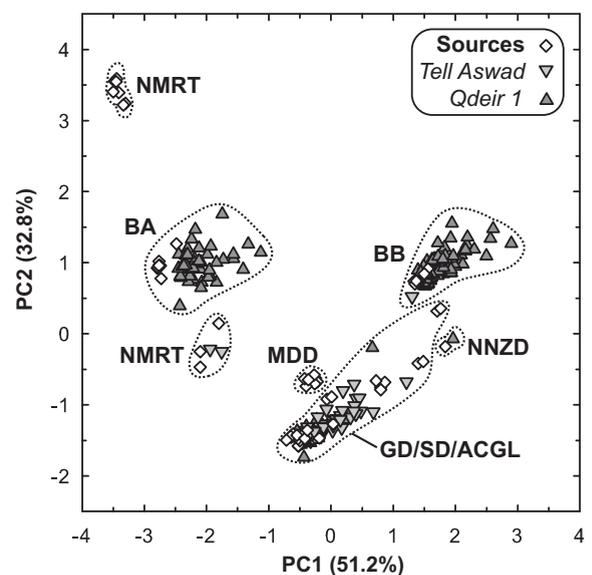
Each artefact was cleaned in an ultrasonic tank with distilled water for ten minutes. Very small artefacts, or those exhibiting anomalous concentrations, were re-run to ensure accuracy and precision.

The speed and automation of this technique (approximately 3.5 h for 19 artefacts plus the standard) enabled us to analyse a major part of the two assemblages.

#### 5. Results and discussion

##### 5.1. SEM-EDS

On the basis of the artefacts' Al, Si, Ca and Fe contents the Tell Aswad material can be separated into three different geochemical groups, using a principal components analysis performed by SAS JMP Software (SAS, 2012) (Fig. 2); three groups can also be distinguished within the Qdeir 1 material, along with a fourth. The data ranges are reported in Table 1.



**Fig. 2.** Principal components analysis using Al, Si, Ca and Fe contents determined by SEM-EDS, comparing obsidians from Tell Aswad, Qdeir 1 and source samples. (NNZD: Nenezi Dağ; GD: Göllü Dağ; BB: Bingöl B; MDD: Meydan Dağ; SD: Suphan Dağ; ACGL: Acıgöl; NMRT: Nemrut Dağ).  
**Fig. 2.** Analyse en composantes principales utilisant les teneurs en Al, Si, Ca et Fe déterminées par MEB-EDS, comparant les obsidiennes de Tell Aswad, Qdeir 1 et les échantillons géologiques. (NNZD: Nenezi Dağ; GD: Göllü Dağ; BB: Bingöl B; MDD: Meydan Dağ; SD: Suphan Dağ; ACGL: Acıgöl; NMRT: Nemrut Dağ).

**Table 1**

SEM-EDS analytical data: ranges for Tell Aswad and Qdeir 1.

**Tableau 1**

Données analytiques obtenues par MEB-EDS : plages de valeurs pour Tell Aswad et Qdeir 1.

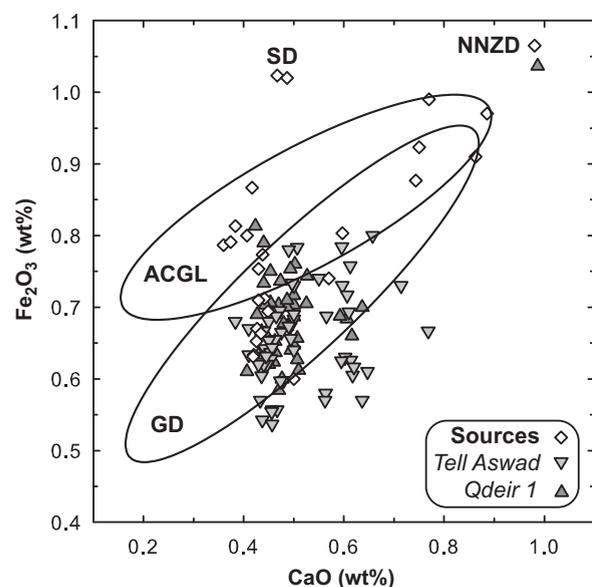
		Tell Aswad				Qdeir 1			
		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>
Calc-alkaline	Göllü Dağ	12.6–14.6	74.9–77.0	0.38–0.77	0.54–0.80	12.0–13.2	76.3–78.0	0.41–0.64	0.58–0.81
	Nenezi Dağ	–	–	–	–	14.1	74.4	0.99	1.04
	Bingöl B	15	72.3	0.58	1.31	13.6–15.7	70.7–74.6	0.65–1.15	1.34–1.91
Peralkaline	Bingöl A	–	–	–	–	10.8–12.9	73.0–74.96	0.20–0.55	3.18–4.21
	Nemrut Dağ	11.7–11.8	75.4–75.5	0.21–0.27	2.30–2.40	–	–	–	–

Contents in oxides are in weight per cent (wt%).

The first group is defined by low Fe (0.54–0.80%) and high Ca counts (0.38–0.77%), with 58 artefacts from Tell Aswad and 40 from Qdeir 1; these elemental profiles matched those of source samples from either Acıgöl or Göllü Dağ in Cappadocia (Fig. 3). The inability to discriminate between these two sources on the basis of their major elements has been noted in a previous SEM-EDS study (Poupeau et al., 2010).

The second group is defined by one piece from Tell Aswad and 89 from Qdeir 1, the artefacts having higher iron contents (1.34–1.91%) and higher calcium rates (0.65–1.15%). This compositional group correlates with the eastern Anatolian source of Bingöl B (Fig. 2).

The peralkaline groups comprise two artefacts from Tell Aswad and 47 from Qdeir 1 (Table 1) material that has a high iron content (2.30–4.21%) and low calcium values (0.21–0.55%). These values match those of the peralkaline products of the Bingöl A and Nemrut Dağ sources in east-



**Fig. 3.** CaO vs. Fe<sub>2</sub>O<sub>3</sub> contents determined by SEM-EDS for Tell Aswad and Qdeir 1 artefacts plus source samples from Göllü Dağ, Suphan Dağ, Nenezi Dağ and Acıgöl. 90% normal density ellipses. Source abbreviations as in Fig. 2.

**Fig. 3.** Teneurs en CaO vs. Fe<sub>2</sub>O<sub>3</sub> déterminées par MEB-EDS pour les artefacts de Tell Aswad et Qdeir 1, ainsi que pour les échantillons géologiques de Göllü Dağ, Suphan Dağ, Nenezi Dağ et Acıgöl. Ellipses normales de densité à 90%. Voir abrégés des sources en Fig. 2.

ern Anatolia, materials which have very similar chemical profiles despite being 150 km distant from one another (Fig. 1). Discriminating these sources has long been a challenge in Near East obsidian studies (though see Chataigner, 1994), with many characterization studies attributing an artefact's raw material to a "Bingöl A/Nemrut Dağ" compositional group (e.g. Abbès et al., 2003). However, it has already been demonstrated that it is possible to distinguish them through various means. For example, Poidevin (1998) already proved that, using some major elements implied in the peralkalinity of these obsidians, i.e. aluminum and iron, we can easily separate them. Unfortunately, as Frahm (2012) indicated in a recent paper, those elements were rarely or poorly measured in past studies. Our statistical analysis reveal two different geo-compositional groups for the Nemrut Dağ: one with higher (>6.50%) and one with lower (<3%) iron contents, while the aluminium content is comprised between 10.9 and 12.9%. The Bingöl A samples (*n*=2) show intermediate Fe (3.82–4.07%) and higher Al (10.8–10.9%) values. As a result, we can show here a perfect match between the Qdeir 1' artefacts and the Bingöl A source, while the two peralkaline obsidians from Tell Aswad are matching the Nemrut Dağ composition (Fe<sub>2</sub>O<sub>3</sub> < 3%) (Fig. 2 and Table 1). According to our knowledge, it is the first time that Bingöl A and Nemrut Dağ have been distinguished by SEM-EDS.

The fourth compositional group is represented by one artefact from Qdeir 1, whose chemical profile matched source materials from Nenezi Dağ in southern Cappadocia (Figs. 2 and 3), with Fe and Ca values of respectively 1.04% and 0.99% (Table 1). This raw material is not attested in the Tell Aswad assemblage; indeed it is rarely found in the Near East (Chataigner, 1998).

## 5.2. EDXRF

Using a Zr/Sr contents plot, we once again view three compositional groups amongst the Tell Aswad artefacts and four for Qdeir 1 (Fig. 4). For the first group common to both sites (respectively concerning 100 and 143 artefacts) Zr contents range from 64 to 108 ppm while the Sr values are between 9 and 20 ppm. This first group can be clearly attributed to Göllü Dağ, i.e. with EDXRF it is now possible to discriminate between the products of this source and those from Acıgöl, which was the problem we had with SEM-EDS (Figs. 3 to 5). We show here this distinction with principal components analysis using Ti, Mn, Fe, Cu, Zn, Ga, Rb, Sr, Y,

**Table 2**

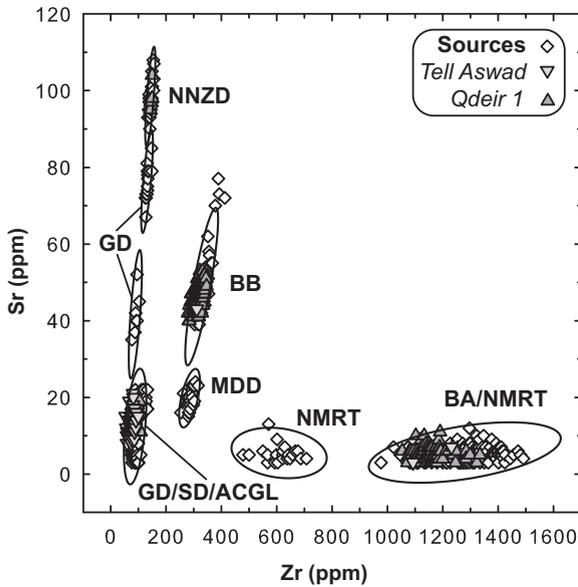
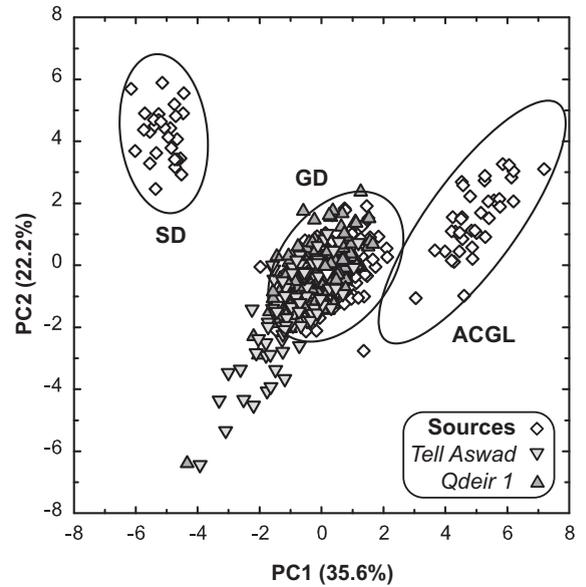
EDXRF analytical data: ranges for Tell Aswad and Qdeir 1.

**Tableau 2**

Données analytiques obtenues par EDXRF : plages de valeurs pour Tell Aswad et Qdeir 1.

		Tell Aswad		Qdeir 1	
		Sr	Zr	Sr	Zr
Calc-alkaline	Göllü Dağ	8–21	53–100	9–20	64–108
	Nenezi Dağ	–	–	95–104	142–149
	Bingöl B	43	311	40–53	279–346
Peralkaline	Bingöl A	–	–	3–11	1053–1334
	Nemrut Dağ	3–7	1092–1231	–	–

Element contents are in ppm.

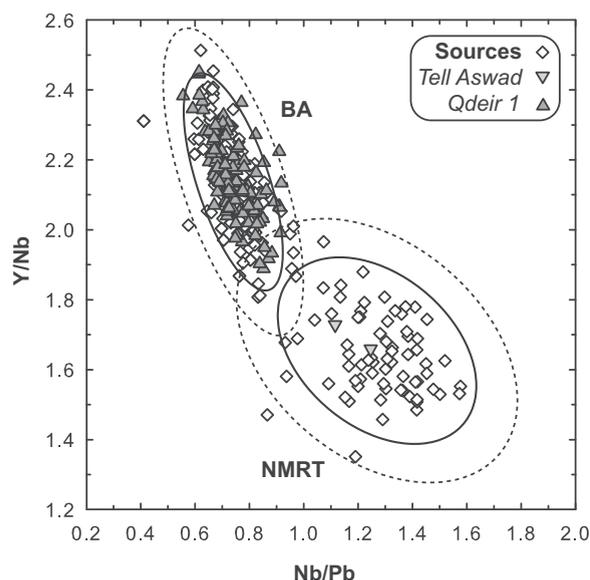
**Fig. 4.** Zr vs. Sr contents determined by EDXRF for Tell Aswad and Qdeir 1 artefacts plus source samples. 99% normal density ellipses. Source abbreviations as in Fig. 2.**Fig. 4.** Teneurs en Zr vs. Sr déterminées par EDXRF pour les artefacts de Tell Aswad et Qdeir 1, ainsi que pour les échantillons géologiques. Ellipses normales de densité à 99%. Voir abréviations des sources en Fig. 2.**Fig. 5.** Principal components analysis using Ti, Mn, Fe, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Pb and Th contents obtained by EDXRF, comparing obsidians from Tell Aswad, Qdeir 1 and source samples from Göllü Dağ, Suphan Dağ and Acigöl. Ninety-nine percent normal density ellipses. Source abbreviations as in Fig. 2.**Fig. 5.** Analyse en composantes principales utilisant les teneurs en Ti, Mn, Fe, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Pb et Th obtenues par EDXRF, comparant les obsidiennes de Tell Aswad, Qdeir 1 et les échantillons géologiques de Göllü Dağ, Suphan Dağ et Acigöl. Ellipses normales de densité à 99%. Voir abréviations des sources en Fig. 2.**Table 3**

Total number of Tell Aswad and Qdeir 1 obsidian artefacts analysed by SEM-EDS and EDXRF.

**Tableau 3**

Nombre total d'artefacts en obsidienne de Tell Aswad et Qdeir 1 analysés par MEB-EDS et EDXRF.

		Tell Aswad		Qdeir 1	
		SEM-EDS	EDXRF	SEM-EDS	EDXRF
Calc-alkaline	Göllü Dağ	58	100	40	143
	Nenezi Dağ	–	–	1	4
	Bingöl B	1	1	89	230
Peralkaline	Bingöl A	–	–	47	102
	Nemrut Dağ	2	2	–	–
Total artefacts analysed		61	103	177	479
Total artefacts assemblage		105		517	



**Fig. 6.** EDXRF ratio plot of Nb/Pb vs. Y/Nb for Tell Aswad, Qdeir 1 and source samples from Bingöl A and Nemrut Dağ. 99% (dotted line) and 90% (solid line) normal density ellipses. Source abbreviations as in Fig. 2.  
**Fig. 6.** Diagramme binaire Nb/Pb vs. Y/Nb comparant les artefacts de Tell Aswad et Qdeir 1 aux échantillons géologiques de Bingöl A et Nemrut Dağ. Ellipses normales de densité à 99% (ligne en pointillés) et 90% (ligne continue). Voir abréviations des sources en Fig. 2.

Zr, Nb, Ba, Pb and Th contents. The second common group, involving one piece of Tell Aswad and 230 of Qdeir 1, has higher Zr (279–346 ppm) and Sr (40–53 ppm) concentrations (Table 2). The chemical signatures of these artefacts match those of samples from the Bingöl B source.

Peralkaline obsidian is documented at each site, as evidenced by those artefacts with very high Zr values (1053–1334 ppm) and low Sr contents (3–11 ppm), with 102 artefacts from Qdeir 1 and two from Tell Aswad. EDXRF further allows us to distinguish Bingöl A and Nemrut Dağ products *via* a ratio plot of Nb/Pb vs. Y/Nb (Fig. 6), whereby all the Qdeir 1 artefacts can be attributed to the former source, while the two pieces of Tell Aswad were sourced to the latter.

The fourth compositional group is only attested at Qdeir 1 with four artefacts, whose Zr values range between 142 and 149 ppm and Sr values of 95–104 ppm, which match source samples from Nenezi Dağ (Fig. 4).

## 6. Conclusion

In summary, three raw materials were documented at Tell Aswad and four at Qdeir 1 (Table 3). In the first case, most of the tools were made of obsidian from Göllü Dağ in southern Cappadocia, followed by a lesser reliance on raw materials from the eastern sources of Bingöl B and Nemrut Dağ. The occupants of Qdeir 1 used the same raw materials, though here the situation is reversed, with eastern products dominant, mainly Bingöl B, and smaller quantities of southern Cappadocian obsidian, which at this site also included a handful of Nenezi Dağ products.

It has also been demonstrated for the first time that:

- EDXRF can successfully discriminate the Cappadocian sources of Göllü Dağ and Acıgöl;
- both EDXRF and SEM-EDS are capable of discriminating the eastern peralkaline source materials from Bingöl A and Nemrut Dağ.

While we have only analysed a few eastern Anatolian source samples for the former technique, re-running the same artefacts on EDXRF and gaining the same results provides us with confidence in this assertion.

Another significant result of our work has been to highlight the intellectual impact of working with larger data sets. By analysing entire assemblages, we have been able to provide a major archaeological contribution on both sites: thus in Tell Aswad we shown that Bingöl B obsidian was already consumed during the Middle/Late PPNB, while in Qdeir 1 we revealed for the first time the use of Nenezi Dağ obsidians. These data were not revealed in previous small-scale studies; the implication is clearly that to reconstruct obsidian exchange networks large sample sizes are required.

In summary, we have established that both SEM-EDS and EDXRF can make important contributions to obsidian characterization studies in a Near Eastern context, not least due to their non-destructive capabilities. However, while source distinction with EDXRF is clear, it remains that SEM-EDS has a problem in differentiating the source products of Acıgöl and Göllü Dağ in Cappadocia; the former technique is also significantly faster. Nevertheless, we have demonstrated in this study that the SEM-EDS can distinguish sufficiently clearly the eastern Anatolian sources, thus adding to its value in Near Eastern sourcing studies.

## Acknowledgements

The authors thank Frédéric Abbès for providing the obsidian assemblages and Yannick Lefrais for his management of the CRP2A scanning electron microscope. We also thank Pierre Machut and Brigitte Spiteri for the help during sample preparation for SEM-EDS analysis. The MAX Lab was established and is currently operated by a *Canada Foundation for Innovation Leader's Opportunity Fund/Ontario Research Fund*. Orange's time at the MAX Lab was funded by Aquimob (mobility grant allocated by the Region Aquitaine). This project was partly coordinated by the University of Bordeaux and has received support from the National Agency for Research under the 'future investment' program (ANR-10-52-LabX) while Carter's involvement was covered by a Standard Research Grant of the *Social Sciences and Humanities Research Council*, Canada.

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