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Identification of Obsidian Sources on Milos Greece

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Abstract

Obsidian, a natural volcanic glass, was used extensively in ancient times because of its quality as a raw material for sharp blades. As such, obsidian is of high interest for provenancing studies, since reliable provenancing can provide information about trade routes, extension of territory, long-distance contacts and the mobility of prehistoric peoples. In general, well-established databases of the characteristic elemental composition, the chemical fingerprint, are needed for reliable provenancing. On Milos Island, two sources of raw obsidian, namely Agia Nychia (Cape Bombarda) and Demenegakion are known. Recent literature claims a third source close to Agios Ioannis. In a sampling expedition with the goal to complete the Atominstitut's database on the chemical fingerprints of obsidian, samples at Agios Ioannis were collected to include this new source.

At the location, 16 scattered samples were taken for analysis, even though no direct outcrop could be identified. On the nearby island Kimolos, several more samples were found. Using instrumental neutron activation analysis (INAA), the chemical fingerprint of the samples was measured and compared to the values in the database. All samples from Agios Ioannis were identified as either from Demenegakion or Agia Nychia, indicating that no further source of obsidian exists at the location.

Keywords: *obsidian, Milos Island, INAA, chemical fingerprint, provenancing*

Περίληψη

Ο οψιδιανός, ένα φυσικό ηφαιστειακό γυαλί, χρησιμοποιήθηκε ευρέως στην αρχαιότητα σαν πρώτη ύλη για την κατασκευή αιχμηρών λεπίδων. Γι αυτό τον λόγο, ο οψιδιανός είναι ένα πολύ ενδιαφέρον υλικό για μελέτες προέλευσης, επειδή η αναγνώριση των πηγών προέλευσης μπορεί να δώσει πληροφορίες σχετικά με εμπορικές διαδρομές, επεκτάσεις κτήσεων, επαφές μακρινών αποστάσεων και την κινητικότητα των προϊστορικών ανθρώπων. Η αξιόπιστη ταυτοποίηση των πηγών προέλευσης απαιτεί, γενικά, καλά ενημερωμένες βάσεις δεδομένων σχετικών με την χαρακτηριστική χημική σύσταση (χημικό αποτύπωμα) του υλικού.

Στη νήσο Μήλο, έχουν αναγνωριστεί δύο περιοχές ως πηγές οψιδιανού, τα Άγια Νύχια (ακρωτήριο Μπομπάρδα) και το Δεμενεγάκι. Πρόσφατες βιβλιογραφικές αναφορές περιγράφουν μία τρίτη περιοχή, κοντά στην τοποθεσία Άγιος Ιωάννης. Δείγματα από αυτή την περιοχή συλλέχθηκαν κατά τη διάρκεια μίας έρευνας υπαίθρου, με σκοπό να ολοκληρωθεί η βάση δεδομένων του Atominstitut, *περιλαμβάνοντας το χημικό αποτύπωμα δειγμάτων και από την περιοχή του Αγίου Ιωάννη. Στην τοποθεσία αυτή, 16 δείγματα υλικού συλλέχθηκαν, χωρίς όμως να εντοπιστεί* in situ *γεωλογική εμφάνιση. Αρκετά δείγματα οψιδιανού βρέθηκαν και στο κοντινό νησί της Κιμώλου.*

Χρησιμοποιώντας την αναλυτική μέθοδο της νετρονικής ενεργοποίησης (INAA), ταυτοποιήθηκε το χημικό απτύπωμα των δειμάτων και έγινε σύγκρισή του με τη βάση δεδομένων. Όλα τα δείγματα που προήλθαν από την τοπθεσία του Αγίου Ιωάννη, αναγνωρίστηκαν ότι προέρχονται είτε από την θέση Αγια Νύχια, είτε από την θέση Δεμενεγάκι, υποδεικνύοντας πιθανόν, ότι δεν υπάρχει άλλη γεωλογική εμφάνιση οψιδιανού.

Λέξεις κλειδιά: *οψιδιανός, Μήλος, χημικό αποτύπωμα, προέλευση, ανάλυση νετρονικής ενεργοποίησης*

1. Introduction

The natural volcanic glass obsidian is one of the classical subjects of archaeometric analyses. Reliable provenancing by means of the highly specific chemical composition, the “chemical fingerprint”, can provide information about trade routes, extension of territory, long-distance contacts and the mobility of prehistoric peoples.

For reliable provenancing, a well-established database of chemical fingerprints of natural obsidian sources is fundamental. On Milos Island, two well-defined sources, namely Agia Nychia (Cape Bombarda) and Demenegakion exist. In 2006, Arias et al. (2006) announced a third obsidian source on Milos, close to Agios Ioannis (see Figure 1). To complete the Atominstitut’s database on the chemical fingerprints of obsidian that contains 10 samples from Demenegakion and 7 from Agia Nychia, a sampling expedition in 2010 tried to identify the Agios Ioannis source and collect samples.

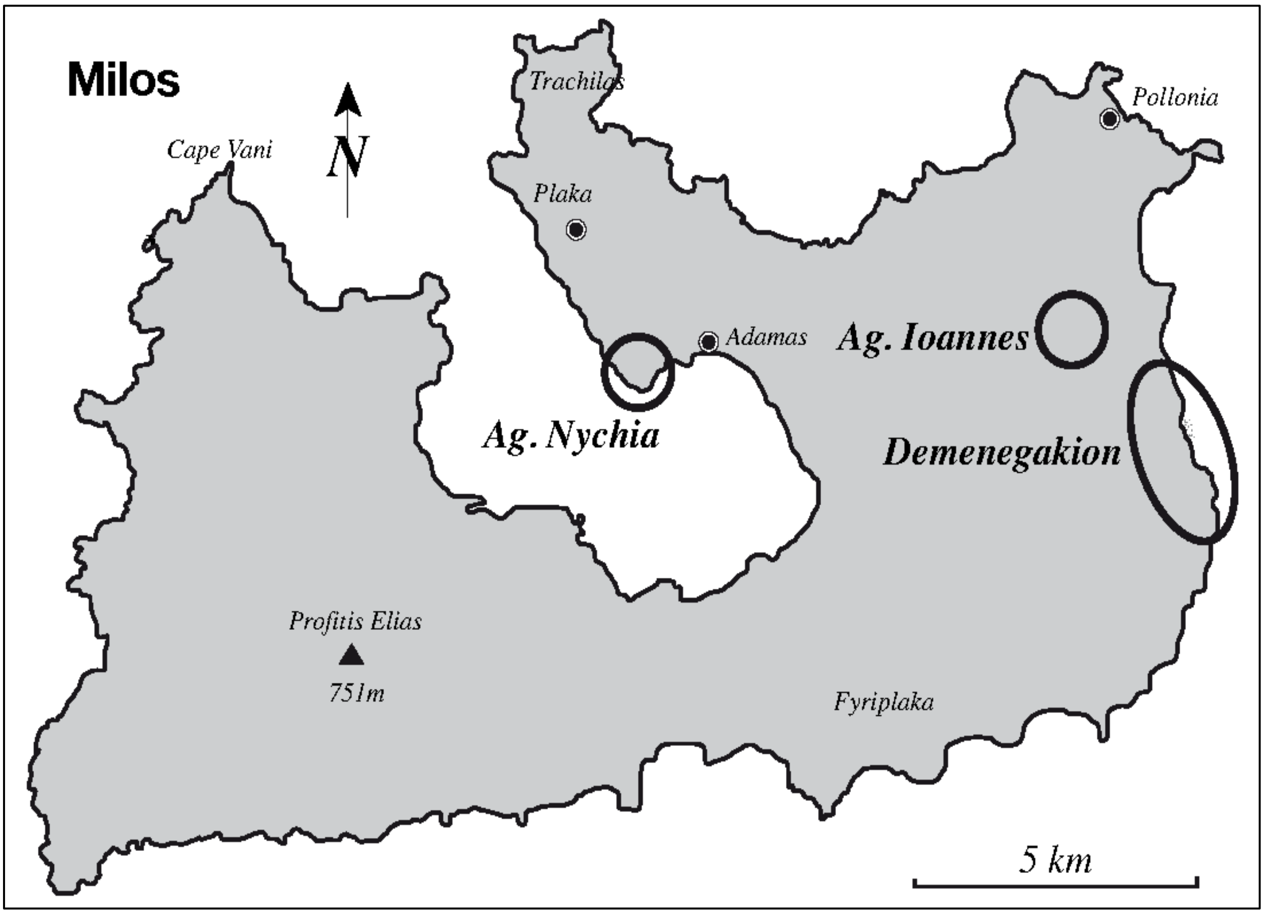

Fig. 1: Locations of obsidian sources on Milos Island.

2. Materials and Methods

2.1 Samples

For Instrumental Neutron Activation Analysis (INAA), a sample amount of 80-100 mg is sufficient in the case of obsidian. However, due to INAA's high sensitivity, especially for trace elements, sampling has to be performed very carefully to prevent any contamination of the samples. Since this is usually impossible in the field, whole pieces were taken and the sampling for INAA was performed under laboratory conditions at the Atominstitut (see next section). To extend the Atominstitut database , both known sources (Demenegakion and Aiga Nychia) were revisited to collect new samples. Sampling was performed in the context of a cooperation with our Greek colleagues (Sterba et al., 2010). The third source announced by Arias et al. (2006) at Agios Ioannis (see Figure 1) was visited also, following the location details as published.

At the location, many scattered obsidian pieces were found and 16 taken for sampling. Unfortunately, no direct outcrop could be identified. The pieces found showed clear signs of weathering and were dispersed over a wide area. On the nearby island Kimolos, six more samples were found at Aliki Beach (1 sample) and Prassa (5 samples). Using Instrumental Neutron Activation Analysis (INAA), the chemical fingerprint of the samples was measured and compared to the values in the database.

2.2 Experimental

All samples were cleaned with distilled water in an ultrasound bath and then crushed in an agate disc mill for homogenization. For each sample, 100-120 mg were weighed into Suprasil™ quartz vials. The vials were then irradiated for 40 hours in the TRIGA Mk II reactor of the Atominstitut at a neutron flux density of $1 \cdot 10^{13}$ $cm^{-2}s^{-1}$ together with certified reference materials NIST SRM 278 Obsidian Rock, NIST SRM 1633b CFA, CANMET reference soil SO1, BCR 142 and MC rhyolite GBW 07113.

After irradiation, the external (quartz glass) surfaces of the irradiated samples were decontaminated and packed into plastic vials that fit the automatic sample changer of the Atominstitut. Two measurements were performed to gather spectra for medium- and long-lived radionuclides. Measurement times were 1800 s and 10000 s, respectively, measurements were performed on a 222 cm^3 HPGe detector connected to a PC-based multichannel analyzer with preloaded digital filter and loss-free counting system. From those measurements, elemental concentrations for the elements Na, K, Sc, Cr, Fe, Co, Zn, As, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th and U were calculated. For further details on measurement parameters and sample preparation see Steinhauser et al. (2006).

3. Results and Discussion

The data from INAA for the samples collected at Agios Ioannis and Kimolos have been published in a different context (Eder et al., 2013, Eder, 2013).

As with many obsidian sources, the chemical fingerprints of Demenegakion and Agia Nychia are similar, as seen in Figure 2. In Figure 2, the chemical fingerprints of the two sources are plotted with their natural distribution. For clarity, all values were normalized to the average composition of the Earth's Upper Crust (Taylor and McLennan, 1985).

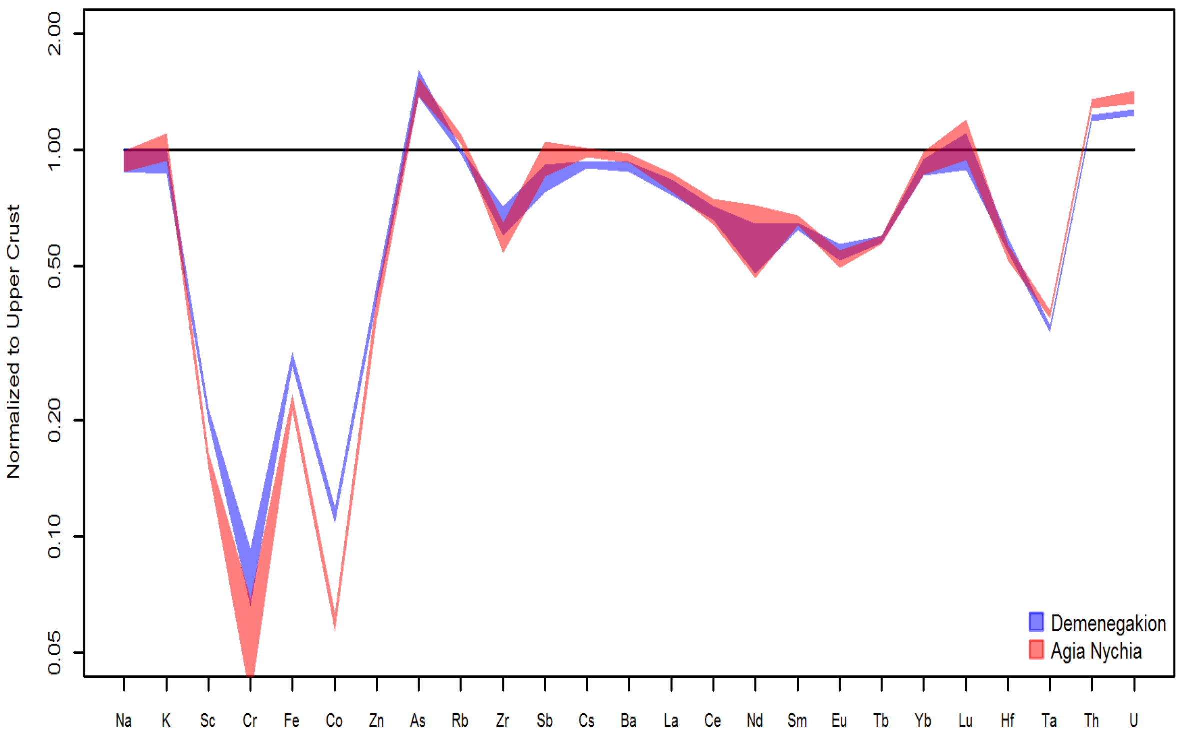

Fig. 2: Chemical Fingerprints of Obsidian from Demenegakion and Agia Nychia. All values are normalized to the average concentrations of the Earth's Upper Crust (Taylor and McLennan, 1985). Normalization is done to reduce the spread of the Y-axis to only 2 orders of magnitude.

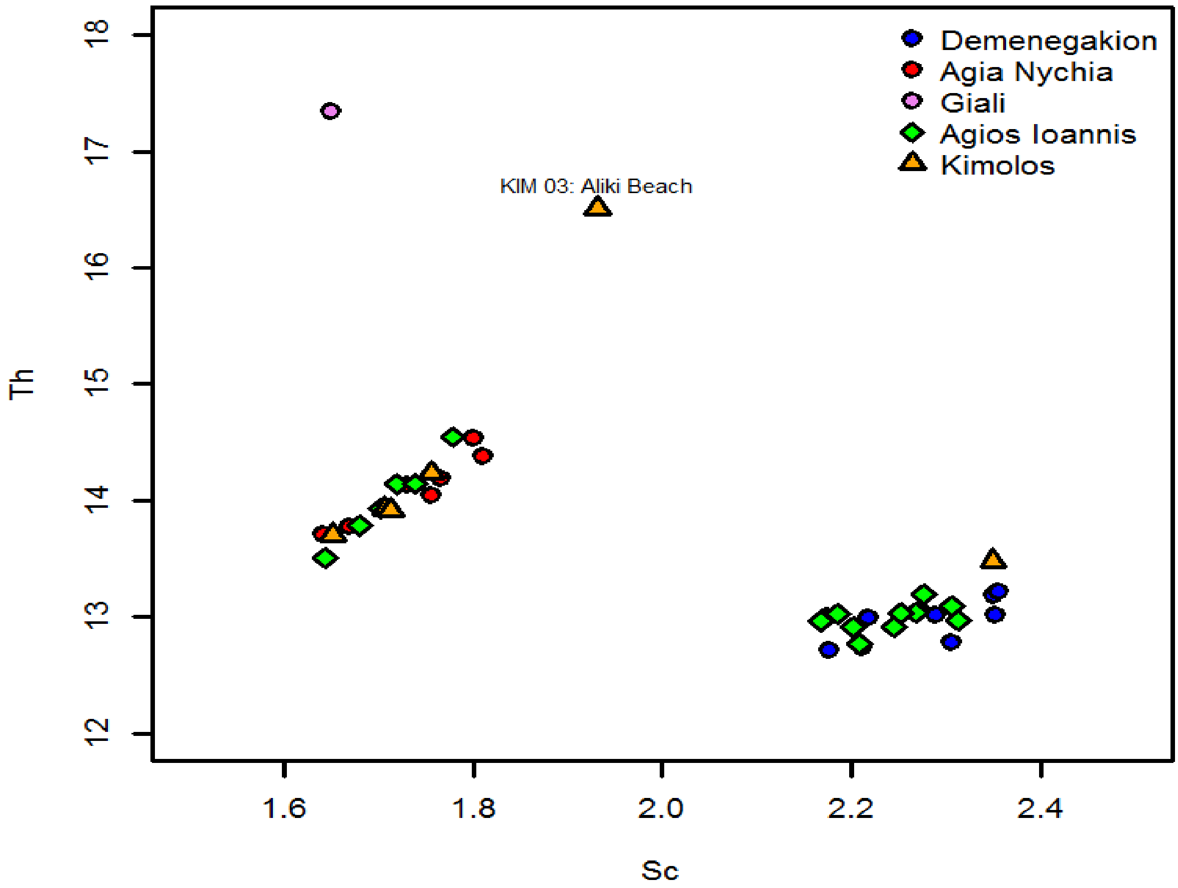

Fig. 3: Separation plot for Database and collected samples. All Agios Ioannis samples are clearly from either Demenegakion or Agia Nychia.

To differentiate the two sources more clearly, a plot of Sc vs. Th values was found to be most useful. Both Sc and Th are not only geologically relevant elements but can also be measured with very high precision using INAA and were thus selected. When the samples from Agios Ioannis are overlaid (see Figure 3), it is clear that all of them are either from Demenegakion (10 samples) or from Agia Nychia (6 samples). The presence of obsidian from both known sources on Milos further indicates that the probability for a third source, even with a composition completely similar to one of them is quite low.

The samples found at Prassa on Kimolos can also clearly be correlated to either Agia Nychia (4 samples) or Demenegakion (1 sample). Comparison with the existing database suggests that the sample found at Aliki Beach could originate from Giali (Eder et al., 2013, Bichler and Sterba, 2012, Mandl, 2001).

A close look at the data shows elevated values for Sb in most samples from Agios Ioannis. This was deemed a local contamination because of the very wide range of the concentrations measured (Eder et al., 2013, Eder, 2013). However, to make sure that the differences in the Sb concentrations are not indicative of a third source of obsidian, the data for the two sources was also analyzed by Principal Component Analysis (PCA), a multivariate statistical method (Jolliffe, 2002). For the PCA, the elements Na, K, Sc, Cr, Fe, Co, Zn, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th and U were used. After the calculation of the principal components to best separate Demenegakion and Agia Nychia, the same rotation was used on the data from the samples collected at Agios Ioannis and Kimolos. Plotting all the data clearly shows that the new samples fit into the two known sources and no other source is indicated (Figure 4). The ellipses show the 95% significance threshold for the original data from the database. Only a single sample from Agios Ioannis lies slightly outside of the ellipsis.

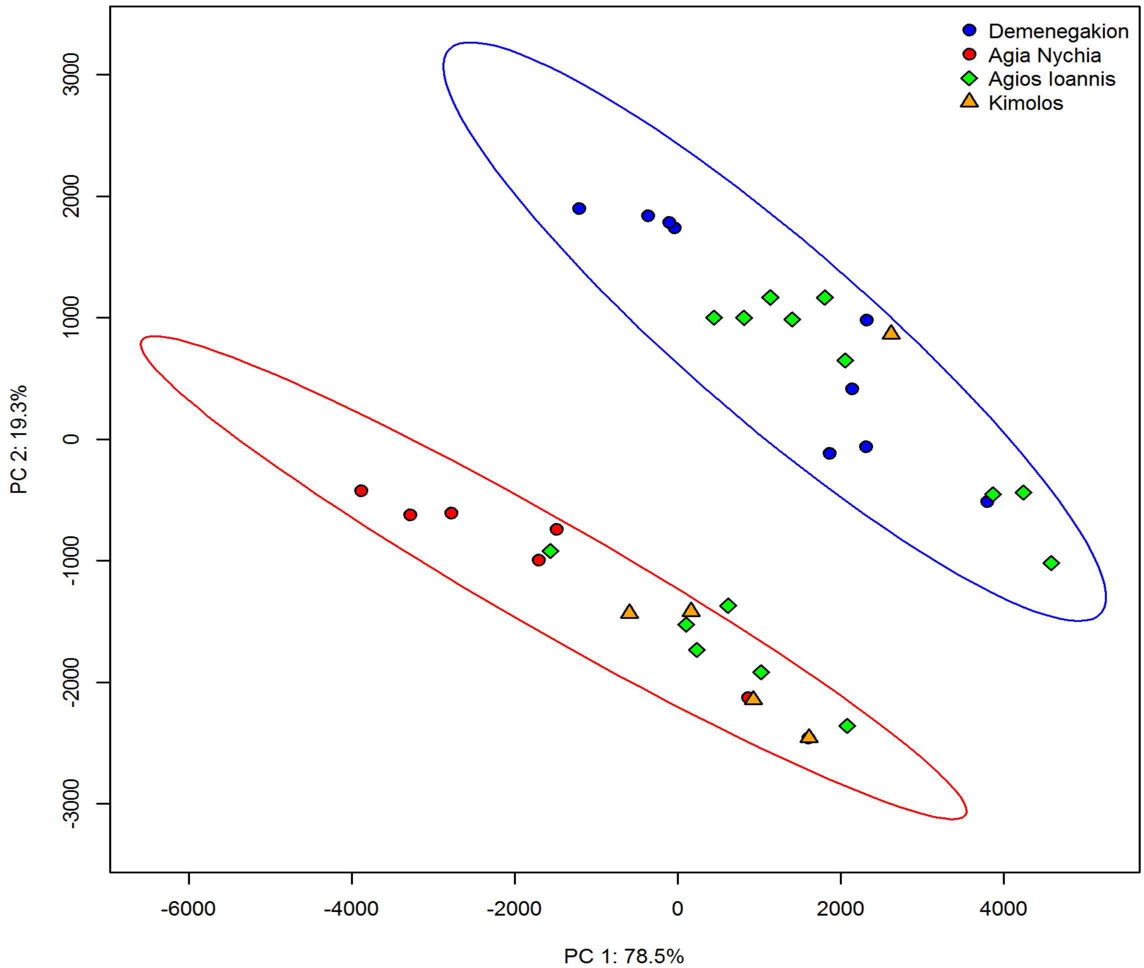

Fig. 4: Principal Component Analysis (PCA) of the data from the database for Demenegakion and Agia Nychia. Samples from Agios Ioannis and Kimolos were then predicted from the PCA and inserted. The ellipses mark the 95% confidence interval.

4. Conclusions

The Obsidian sources of Milos have been analyzed by Neutron Activation Analysis, providing a chemical fingerprint for the two known sources at Agia Nychia and Demenegakion. A third source that is mentioned in literature (Arias et al., 2006) was investigated. However, the samples collected at the location clearly belong to the two known sources and their chemical fingerprint shows no indication of a third source on Milos. This was shown not only by direct comparison of the chemical fingerprints but also by statistical means. The fact that all collected samples at Agios Ioannis could be related to either Agia Nychia or Demenegakion strongly indicates that there is no third source of obsidian in the area of Agios Ioannis.

5. Acknowledgements

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