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## Characterization of Mediterranean obsidian sources by classical petrochemical methods

In memory of my father Antonino and his cousin Ottorino De fiore, with whose help I discovered Volcanology.

### ABSTRACT

*Characterization of Mediterranean obsidian sources by classical petrochemical methods*

The basic working hypothesis was that a complete investigation by classical petrochemical methods on obsidian could be sufficient to characterize the composition of this volcanic glass.

The work started by sampling Italian and Greek obsidian sources.

The Italian samples were collected at Monte Arci (Sardinia) from several flows; on the island of Lipari from prehistoric flows and, for comparison purposes, from medieval flows; on Palmarola island and on Pantelleria island, both from single sources.

The Greek samples were collected on three islands: Melos, Antiparos, and Yali. Those from Melos originate from two different and large sources: that of Aghia Nychia and that of Dhemenakion. The others come from single source.

More than five-hundred samples have been collected and analyzed.

Each source is represented by a minimum of ten samples.

The analyses were carried out by X-ray fluorescence for major, minor and some trace elements. The method in itself is of little import, but important in this case are the elements analyzed, i.e., those of the petrochemistry. In addition, the normative mineralogical composition has been calculated. The results show that accurate analyses of major and minor oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{H}_2\text{O}$ ) are sufficient to unequivocally distinguish between obsidian.

The Pantelleria obsidian has revealed a single and unmistakable composition.

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### INTRODUCTION

Obsidian is a natural glass of volcanic origin. Lava can solidify in the form of obsidian (that is, it can vetrify) when its content in silica is more than 59% (trachytic obsidian) and, therefore, its viscosity high.

Given that obsidian is a typical volcanic rock, it should be studied by classical petrochemical methods.

To date, both petrologists and those who have analyzed obsidian for archaeological purposes, have neglected investigation utilizing classical methods. Consequently, a few chemical analyses are available: Washington (1913), Georgiadis (1956), Cornaggia-Castiglioni (1963) and Assorgia et al. (1976). Previous workers concerned with the problem of characterizing the various archaeological obsidians chose to use the analytical method for trace elements, rather than quantitative analysis of the major element. Various methods have been used to analyse trace elements before neutron activation analysis (NAA) become widespread present.

Searching for the «universal method» that would make possible the characterization of obsidian from the neolithic period, the various scholars have produced a great quantity of non-comparable analyses. These methods have often solved local characterization problems but, at times, inaccurate analyses led to erroneous conclusions. Most evident from the voluminous literature on obsidian analyses in the last 20 years is that the analyses are not very representative (in statistical terms). Diagrams have been published in which a given «cluster» of obsidians is often represented by 2 or 3 samples. The composition ranges of a given element within a given cluster are rarely given. Sometimes, the boundaries for the various clusters have been arbitrarily traced to make the experimental data to coincide with expectations. Only Cornaggia-Castiglioni et al. have considered treating the problem on a statistical basis.

As geologists, we have reconsidered the obsidian problem from the viewpoint of classical petrochemical methods. Georgiadis was the first to

deal with the problem of obsidian characterization from petrochemical standpoint, although his analysis was limited to a few Aegean samples.

In the present study of characterization of obsidian we have paid considerable attention to sampling methods. Samples from the different obsidian sources had to be representative; consequently, a number of samples was collected having sizes proportional to the source size and its archaeological importance. Inevitably this involves a large number of samples, but the results, once acquired should be of general use. The elements to be analysed in each sample would have been, first of all, the major ones and then some trace elements. The accuracy of the analysis should be high, i.e. the accurate sample preparation is at a premium.

Finally, the analytical method is not by itself important, so long as it presents the necessary requisites of precision, accuracy and reproducibility.

### The samples

Care was taken to ensure that the number of samples collected for each obsidian source was proportional to the topographical size of the source itself.

The size of the single samples has been conditioned either by the natural size or by number and size of macroscopic inclusions within each single piece. It is evident that if in a piece of obsidian there are inclusions of 2-3 mm in size, with an average distance of 10 mm from each other, it would be necessary to collect samples containing at least some 20 inclusions. Otherwise, the sample would no longer be representative.

After having chosen the samples to be analysed, we passed to crushing phase using a Fritsch Pulverisette jaw crusher. The product obtained was quartered in a Carpc sampler. The final sample was ground with a Herzog HSM 100 ringmill so as to obtain a 260 mesh powder. Variable quantities (from 1 to 8 g) of this powder were mixed with 10% of Henkel wax. Pelletizing was obtained with a Herzog HTP 40 semi-automatic press, using a 4 ton force on a surface of 11.2 cm<sup>2</sup> (37.8 mm $\varnothing$ ).

The loss on ignition (LOI) and the FeO content were separately calculated, the last by the potassium permanganate colorimetric method by using Zimmermann solution.

### Instrumentation

A Siemens SRS 200 automatic sequential X-ray spectrometer, equipped with a Rh-target tube, a 10-positions sample-changer and an LC 200 interface for controlling the instrumental parameters, connected to an HP 1000 computer for calculating concentration, corrections for interelementary effects and normative mineralogical composition (*Franca viglia & Ciriachi, 1984*), was used. The correction method for interelementary effects is that reported by Franzini, Leoni and Saitta (1975).

### The method

The working hypothesis was that accurate quantity analysis of the major and minor elements contained in obsidian would be sufficient to distinguish between different sources. In addition, the normative mineralogical composition (according to the Rittmann method) should increase the probability of distinguish two very close groups.

The analytical method to apply to this case is of little importance by itself, but, intuitively, the factor of precision is very important, especially if one wishes to distinguish between very close groups and consider that minor elements of an obsidian are present in the amounts of tens to hundreds of p.p.m.

The factor of rapidity was important only at this phase of the work, which was that of the institution of a data bank.

The high number of samples to be analyzed (500) and the number of elements to be dosed per sample (23) mean that some 11,500 dosages are required. The undertaking of such a work in reasonable amount of time can be achieved only by automatic X-ray spectrometry. As is well known, the preparation of samples to be subjected to X-ray spectrometric analysis is very simple: crushing, grinding and pelletizing with specific binder. Therefore, an automatic and sequential X-ray spectrometer was used<sup>1</sup>. However, in spite of the rapidity of the instrument, measurements for a total of 650 hours were needed. Actually, the time required by the X ray spectrometer was greater due to the need to calculate the idle time while changing samples.

The following elements were analysed:

Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti and P  
trace elements being:

S, Cl, Nb, Zr, Y, Sr, Rb, Zn, Ni, Co, Cr, V and Ba.

<sup>1</sup>) All the analyses listed in this paper were performed out by the Author.

We believe that if a different analytical technique was used (e.g. AA), the time required should be multiplied by 20, even using the most rapid and automated of instruments. In other words, considering the time required for sample preparation, we would have needed a whole year to dose 23 elements in 500 samples by AA.

Nonetheless, there is nothing to prevent us from using the AA technique in the second phase of the work, when it will be a question of comparing a few unknown samples with the data bank.

Once the elementary analysis of all the samples is obtained, a computer would calculate the mineralogical normative composition and draw the classical petrochemistry diagrams.

We have chosen the Rittmann method for the computation of normative mineralogical composition instead of the older CIPW method, since the former, though more complicated, permits a better differentiation of mineralogical parageneses.

#### *The geological sources studied.*

The geological obsidian sources chosen in this first phase of the work were as follows:

- Lipari
- Monte Arci (Sardinia)
- Palmarola (Pontine Islands)
- Pantelleria
- Melos
- Antiparos
- Yali

We cannot be sure that our sampling includes all the obsidian sources of the above-mentioned localities. It should be remembered that obsidian has always been neglected by petrologists because of its glassy structure and considered little more than a curiosity. Indeed, on pending works on vulcanites of a given area, it is not rare to find only a few hints of obsidian. We will return to this point in the chapter dedicated to the single localities mentioned above.

#### *Lipari.*

The island of Lipari is the only among Italian and Greek localities which presents true obsidianic flows. These partly obsidianic flows are those of Papesca, Forgia Vecchia and Rocche Rosse. Only the first is important for archaeological purposes, while the other two date back to medieval times. Dolomieu (1783) realized that the last volcanic event of the island was dated to the sixteenth century A.D. Buchner (1949) was the first to show that the flows of Forgia Vecchia and Rocche Rosse were much more recent than the others, from which material for making neolithic tools had

been quarried, although this suggestion was subsequently ignored. Consequently, Cornaggia Castiglioni et al. (1963), Cann & Renfrew (1964), Belluomini et al. (1970), Belluomini & Taddeucci (1971) and Gale (1981) continued to think that the two above-mentioned flows were a source of raw material in Neolithic times.

Keller (1970) published a stratigraphic profile showing (from below to above):

- lower pumices of Monte Pelato
- ancient obsidians (which outcrop in the Gabelotto valley)
- paleosol with obsidian tools dated by means of C14 from  $4810 \pm 60$  to  $1220 \pm 100$  years
- upper pumices of Monte Pelato
- recent obsidianic flows (Rocche Rosse and Forgia Vecchia).

Keller does not specify which of these last two flows is the oldest one. The same Author asserts that Neolithic obsidian tools may also come from the flow of Gabelotto, even if the quality of this obsidian is poor.

Pichler (1980), in the most recent work on the Island of Lipari, attributes all the obsidianic events of the island to what he calls «the fourth eruptive period», beginning roughly 10,000 years ago and ending some 1,400 years ago, with the two flows of Rocche Rosse and Forgia Vecchia. This Author points out how the ashes which had preceded the emission of the two mentioned flows, had covered the Greek Roman necropolis of Lipari with a 25 cm layer. Keller noticed that the same ashes cover the lava of Vulcanello, historically dated 183 B.C. There is no doubt, therefore, that the flows of Forgia Vecchia and Rocche Rosse had never been exploited in Neolithic times. Nevertheless, we carried on with the sampling of the flow of Papesca Beach and those of Forgia Vecchia, Pomiciazzo Lami and Rocche Rosse. In appendix B are listed the analytical results concerning these last three flows.

#### *Monte Arci.*

The volcanic complex of Monte Arci, in the western part of Sardinia, is probably the only location on the island to furnish obsidian. In this area, vulcanites belonging to two magmatologically and chronologically distinct moments outcrop. First, the intramiocene, which has manifested itself by a submarine volcanic activity that produced basic rocks of the calc alkaline family; second, the pliocene, which is related to conditions of tension tectonics, is responsible for melting of subaerial vulcanites with rhyolitic to basaltic chemism (*Assor-*

*gia et al., 1976*). Acidic lavas constitute a very frequent lithological type in the volcanic complex of Monte Arci. These volcanics mainly appears as lavic facies, sometimes massive, sometimes foliated, sometimes strongly vesiculated: quite frequently, there is a gradual transition from a vesiculated facies filled with bubbles to a perlitic facies where often obsidian nuclei of various dimension, ranging from less than 1 cm to several dm (Conca Cannas, Canale Perdera, Riu Solacera, Conca S'Ollastu, etc.). The first chemical analysis of an obsidian sample coming from Conca Cannas (Uras) was made by Washington (1913).

For a long time the authors, who dealt with obsidian of Monte Arci as a source of raw material in Neolithic times, thought that this obsidian was exclusively found in nearby Uras. Actually, the sources are more than one (*Puxeddu, 1956*).

Our spot investigations have allowed us to sample the well known sources of Roja Cannas or Conca Cannas (Uras), Funtana e Figù (Marrubiu), Mitza Sa tassa (Pau), S. Pinna and, finally, Cave della Ceca (Morgongiori) among the detrital ones. It is interesting to note (see tables) how the detrital deposit of Cave della Ceca resulted in a composed mixture of two types of obsidian with a considerably different chemical composition. At the moment, we have identified four different types of chemism among obsidians of Monte Arci.

From a quantitative standpoint, the Sardinian obsidians represent the major source of antiquity, after that of Melos.

Puxeddu reports of green, red or hazel-brown obsidians found by him in different places of the volcanic complex. Actually, they definitively are jaspers coming from the miocene sedimentary basement of the volcanic complex. This Author himself gave us a sample of an authentic blue obsidian found by him in an undefined locality of the volcano.

#### *Pantelleria.*

The island of Pantelleria (Sicilian Channel) is formed exclusively by vulcanites (*Rittmann, 1967*) that can be divided into two main groups: basic vulcanites and acidic vulcanites. The obsidians under examination belong to the second type and, more precisely, to the group of dark sodarhyolites (hyalopantellerites) of Fossa della Pernice, Cuddia Attalora, Contrada Khamma, Cala della Tramontana and Cala Nicà. The dark rhyolites differ from the group of the light ones because of the presence of a larger quantity of glass, to the point that all the samples show an obsidianoid appearance. The crystalline units that can be noticed

microscopically are rare: usually, they are alkali-feldspars of small dimensions.

From a chemical point of view, the obsidians of Pantelleria present some particular characteristics that would make one think they are exceptions. They are peralkaline rocks in which the quantity of alkalis ( $K_2O + Na_2O$ ) is greater than that of  $Al_2O_3$ . They are particularly distinguishable in the relative abundance of soda (*Romano, 1970*), of trivalent iron and titania and in low values of lime and magnesia. In addition, on ignition they show an average increase in weight of 0.15% which is due to the oxidation of chlorine, in this case reaching the value of 0.4%.

This phenomenon has already been noticed by Cornaggia Castiglioni in Sardinian obsidians, but it did not arise during our investigations.

A last peculiarity of the obsidian of this island is its low melting-point, obviously related to its peculiar mineralogical composition (see tables): at 730 °C a rounding of the sharp edges is observed. At 960 °C the melting is complete. The samples studied by us come from the locality of Balata dei Turchi, situated in the most southern part of the island, where obsidians is associated with light pumices.

#### *Palmarola*

The island of Palmarola belongs to an archipelago of volcanic origin which also includes the island of Ponza and Zannone, formed by the same volcanic rocks (*Barberi et al., 1967*). This island presents several big lava domes, the formation of which was due to the external projection of very viscous lava and its subsequent stagnation and formation of thick flows. One of these domes forms Monte della Tramontana, at the northern extremity of the island. It is a typical stagnation dome, where the columnar fissures are often interrupted by sub horizontal surfaces: this would seem to indicate that the building of the dome was a result of successive lava flows. On the southern side of monte della Tramontana a crust of black obsidian has been found: it represents a rapidly cooled down outer limit of the dome.

This obsidian has been the object of our sampling.

The obsidian of Palmarola is not of such high quality as that of Lipari or Melos: this is due to its small size and to its frequent inclusions.

The characteristic ratio  $K_2O/Na_2O=1$  (see tables) distinguishes it quite easily from that of Lipari ( $K_2O/Na_2O=1.15$ ), from those of Monte Arci ( $K_2O/Na_2O$  with a minimum of 1.07 to a maximum

of 1.58) and, of course, from that of Pantelleria ( $K_2O/Na_2O=0.68$ ).

### Melos

The island of Melos, in the Cyclades, belong to the Aegean volcanic arc (Pichler & Kussmaul, 1972) that begins at the Gulf of Aegina, extends through Santorini, Kos, Nisyros and Yali and reaches as far as Turkey.

The volcanic activity of Melos may have started between the late Pliocene and the first Quaternary (Fytikas *et al.*, 1976). Obsidian lies in two localities, 10 km apart from each other: Dhemenegakion, on the East and M. Bombarda-Aghia Nychia, not far from the chief town of Adamas. There are rhyolitic lava domes (Fytikas, 1977) that contain obsidian in their perlitic crust surface. Such an obsidian is present either in form of rounded inclusions or in the form of salbands. In both the above-mentioned localities, mine works are still visible: short galleries, trenches and stocks in open area of the mines. The source of Aghia Nychia is situated by the sea: for this reason it is possible to assume that ships docked to load the quarried volcanic glass.

The two obsidian sources are chemically similar, but clearly distinguishable (see diagrams). The archaeological obsidians from the last layer of Phylakopi come from the source of Aghia Nychia (see appendix A).

Georgiades has published three analyses on Melian obsidians without specifying from which sources of the island they come.

### Yali.

The island of Yali is one of the four volcanic islands (the others are Strongili, Pakia and Perigusa) situated some miles north east of Nisyros, whose volcanic products are petrologically linked to.

The rhyolitic obsidian from Yali may be considered as a residual liquid coming from the rhyodacites of Nisyros and, therefore, represents the final result of a fractioning process (Di Paola, 1974).

The island of Yali, with a NNE-SSW elongated shape, contains in its SW half a stratigraphic deposit of «pumice fall», while the other half is exclusively formed of obsidian flows or of perlite with rhyolitic composition.

The obsidian of Yali is often characterized by many white-grey perlitic spherulites. This peculiarity, that slightly degrades its mechanical features, has been immortalized in a Minoan obsidian rython, presently exhibited at The Museum of Iraklion (Alexiou, Platon and Guanella, 1967; Sakellara-

kis, 1978). Analyses carried out by Renfrew have demonstrated that the obsidian from which it had been shaped comes from Yali.

The island owes its name to the fact that its obsidian is sometimes transparent and colourless as glass.

According to Desio (1930), on Yali it is possible to find dark, light-brown, greengrey and bottle-green obsidians. We ourselves have not found this to the case. However, with reference to the bottle-green obsidian, we do not think it is possible to find green obsidian associated with the more ordinary black one. Since green obsidian owes its colour to the presence of aegirine (see obsidian of Pantelleria, of Bingöl and Nemrut Dag), the presence in a limited area of two magmatic types with a complete different chemical composition would be unusual.

The first chemical analysis of an obsidian from Yali was published by Bianchi (1930). Others have been published by Di Paola.

### Antiparos.

The island of Antiparos, together with the small ones of Despotiko and Strongilo, belongs to the Aegean volcanic arc.

The rhyolitic lava domes, in the most southern part of the island, present in their crust surface many spherically structured obsidians. However, it is a material of very poor quality, making it doubtful that it could ever have been used in tool making.

The 1:50,000 IGME geological map (Zachos, 1963) is rather imprecise concerning obsidian location: the dome of Mastixia (SE strip of the island) should not contain obsidian, whereas we have found it. On the other hand, we have not found it at M. Turloto, on the island of Despotiko.

From a chemical standpoint, the obsidian of Antiparos is clearly distinguishable from all the others of the Aegean and Italy. Three analyses of Antiparian obsidian have been published by Georgiades.

## Results and discussions

### 1 - Use of major elements

The analytical results for geological (or primary) obsidians are collected in tables 1,2 and 3B; analyses of several artifacts are collected in table 4. Comparative analyses for 4 types of Liparian obsidians are collected in table 5.

As a first means of distinguishing between obsidians, (apart from the  $K_2O/Na_2O$  ratio of obvious

significance) the Rittmann indices Sigma and Tau have been employed as follows:

$$\sigma = \frac{\text{Al}_2\text{O}_3 - \text{Na}_2\text{O}}{\text{SiO}_2 - 43} \quad \tau = \frac{(\text{Na}_2\text{O} + \text{K}_2\text{O})^2}{\text{TiO}_2 + \text{P}_2\text{O}_5}$$

It is clear that Sigma can become negative for values of  $\text{SiO}_2 < 43$ , but this is not the case of the obsidians, which, generally, are hypersilicic. The value of Tau can, occasionally, be negative in some hyperalkaline rocks.

The use of the  $\text{SiO}_2$ - $(\text{K}_2\text{O}/\text{Na}_2\text{O})$  plot (see fig. 1) allows an almost complete discrimination of Mediterranean obsidians, whereas the  $\text{SiO}_2/\text{K}_2\text{O}$  plot is useless in the majority of cases. The use of Rittmann indices Sigma and Tau allows a complete discrimination of all the sources studied, with the exception of the couple Antiparos/Monte Arci-Uras. Even though this distinction is purely theoretical, it is possible to obtain it by using the  $\text{SiO}_2$ - $(\text{K}_2\text{O}/\text{Na}_2\text{O})$  plot. Discrimination between the two obsidian deposits of Melos (Aghia Nychia ad Dhemenegakion) is amde possibile either by means of the  $\text{SiO}_2/\text{K}_2\text{O}$ ,  $\text{SiO}_2$ - $(\text{K}_2\text{O}/\text{Na}_2\text{O})$  plots and the Sigma-Tau plot.

The obsidians of Antiparos (if ever used by prehistoric man in tool-making) is distinguishable from the other Greek ones because of its different  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio.

The obsidian of Yali is easily distinguishable from its counterpart of Melos on the basis of the following parameters: different  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio and different Sigma and Tau values (particularly the second one).

The present study allows us to widen our knowledge of the types of Sardinian obsidians used. At least, five different flows have been now differentiated on Monte Arci. It is interesting to note how the two types named Ceca1 and Ceca2 can be found mixed with perlite in a detrital deposit.

It should be pointed out that the sources of Monte Arci-Pau and of Monte Arci-S. Pinna are almost identical in terms of the  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  value, given the Sigma and Tau values, although they are, perhaps, distinguishable on the basis of a different Sr-content.

The examination of some obsidianic artifacts showed surprising results (table 4 analysis 6): a surface sample from the Nuraghe Losa (Abbasanta) is of comenditic (peralkaline) composition. Rocks of such a composition can be found only on the islands of S. Antioco and S. Pietro, SW of Sardinia (Araña, Barberi and Santacroce, 1974). Note that around the above-mentioned Nuraghe other obsidianic artifacts have been found, all co-

ming from Monte Arci (table 4 analysis 5). Some artifacts from Nuraghe of Puisteris originate from Monte Arci, but from two different flows (table 4 analyses 3 and 4).

## 2 - Use of trace elements.

Gale (op.cit.) has shown that one parameter is not sufficient for a complete discrimination of all the primary Mediterranean obsidian sources.

The number of the obsidian sources is without doubt bound to increase and it is to be expected that probabilities of overlapping will also increase. The combination of several parameters allows us to increase the «resolution capacity» of a given method. The quantitative analysis of trace elements must, therefore, be carried out with high accuracy (either by XRF, NAA, AA, OES or other methodologies) and must present the necessary characteristics of reproducibility.

The use of some parameters not strictly quantitative (measuring, for example the gross XRF intensity of some spectral lines) may help to solve local provenance problems, as Fornaseri et al. (1977) have shown. However, it is important to notice that the technique described in these authors' article is not reproducible on XRF spectrometers of different models and different makes, the XRF answer being dependent on instrumental geometry and on the X-ray tube used. The dosage of trace elements of this work are in accordance with those published by Gale (op.cit.).

The analysis of some trace elements, such as S, Cl, Nb, Zr, Y, Sr, Rb, Zn, Co, Cr, V and Ba allows further discrimination among obsidian sources. Discrimination between Palmarola and Liparian obsidians may also be obtained by means of Cl, Nb, Zr, Sr and (above all) Rb content.

Amongst the obsidians of Monte Arci it can be noted that:

- the Ceca 1 type shows an exceptionally high Nb and Y content, in comparison with all the other obsidians an very low Sr and Ba abundances;
  - the Monte Arci-S. Pinna type can be distinguished from that of Monte Arci-Uras on the basis of its Nb, Zr, Y, Sr, Rb, V and Ba content.
- Amongst the Greek obsidians it can be seen that:
- the Antiparos type has the lowest Ba content, the highest in Rb, is impoverished in Sr and Y, but has the highest Nb content;
  - distinction between the two Melos sources may, perhaps, be obtained on the basis of their contents of Sr, Zr and V. However, from the standpoint of trace elements, the two types are practically identical.

The Yali type presents the highest content of Ba and contents of Rb, Zr and Nb that differentiates it from the Melian and Antiparian types.

The obsidian of Pantelleria, collected at Balata dei Turchi, is unique in all respect: this is easily understandable if one recalls that the magma that originated it is the only one having such a chemical composition in the Mediterranean area. Its melting point is very low (about 730 °C) in comparison with that of other obsidians (>1000 °C). Its colour is bottle-green, a peculiarity which is found only in some Anatolian and Yemeni obsidians. Aluminium, soda and ferric-iron abundances are anomalous. Amongst trace elements, high enrichment in Nb, Zr, Y, Zn and Cl can be noticed and impoverishment in Sr, Co and Cr, which are common in peralkaline rocks (*Ferrara and Treuil, 1974*).

The obsidian of Santorini (Thera), of modest quality, is to be considered as a scientific curiosity, since it probably has never been used by prehistoric man in tool-making. It originates from the Bimsstein mittlerer ignimbritic level of Günther-&Pichler (1973) and from the Bimsstein oberer pumiceous level of Neumann van Padang (1936) that should not have outcrop in prehistoric ages. As can be seen in table 3, its chemism is completely different from any other obsidian taken into consideration.

## Conclusion

This study has shown that the characterization of obsidian source should be done through the following steps:

- an adequate sampling in which the number of the samples is proportional to source size;
- accurate and comparable multielemental analyses including major, minor and several trace elements;
- measuring of their variation ranges within single sources;
- a better use of the analytical data by considering ratios between elemental abundances rather than absolute abundances themselves.

The use of some petrochemical parameters, like Rittmann's Sigma and Tau, forms part of this technique.

Newertheless, it is highly predictable that the sole use of the above mentioned petrochemical parameters will reveal itself to be insufficient to solve all the provenance problems when applied to context wider than the strictly Mediterranean ones.

Therefore, the use of petrochemical parameters should be done in connection with trace element analyses.

The final conclusion that can be drawn from the present study and all the others previously published is that a single and simple method in solving all the provenance problems does not exist.

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## APPENDIX A

Archaeological obsidians from Philakopi, Puisteris, Nerokouru and Abbasanta (table 4 and 4a)

In order to check the method proposed for obsidian characterization, samples from several archaeological sites have been analyzed.

Obsidians from Philakopi (Melos):

the values for Rittmann's Sigma and Tau and that of  $K_2O/Na_2O$  tally very well with those of the Aghia Nychia sources, being clearly different from those of the Dhemenegakion source. Curiously, trace-element abundances do not play the same clear role: the presence of Zr, Rb and V, although less evidently, allows to assign obsidians from Philakopi to the Aghia Nychia source.

Obsidian from Nerokouru (Chania, Crete):

a small sample, kindly provided by Dr. Lucia Vagnetti, from the Minoan settlement of Nerokouru has been analysed. From its analytical data it can be deduced that any sure attribution to one of the two Melian sources cannot be made. Nevertheless some resemblances, as  $K_2O/Na_2O$  ratio, Tau value and the Sr, Rb and V contents, induce us to consider the Aghia Nychia source as the most likely.

Obsidians from the Nuraghe of Puisteris (Sardinia):

five samples had been kindly provided by Dr. Ga-

briella Puddu. They clearly belong to two different flows, although from the same region, that of Monte Arci. The relatively low silica content rules out the sources of Marrubiu, Uras and that of Ceca 1. The  $K_2O/Na_2O$  ratio, the Rittmann's Sigma and Tau both show resemblances with those of the Pau and S. Pinna sources. Among trace elements only Sr enables us to assign the samples from group 3 to the S. Pinna source. Conversely, there is no doubt that the samples of group 4 belong to the Uras source, via both Rittmann's values or trace-element criteria.

Obsidians from the Nuraghe of Abbasanta or Losa (Sardinia): two randomly collected samples show two completely different compositions.

The analysis 5 of table 4 does not show a clear provenance from the S. Pinna source or from the Pau one.

The analysis 6 surprisingly shows a comenditic composition. Furthermore, trace-element abundances are very different from those of M. Arci sources. It should be noted that the sample analyzed has been obtained by mixing several small obsidian pieces. Therefore, as Hallam et alii (op.cit.) write, obsidian or pitchstone, where used in that area besides M. Arci obsidians.

The analysis 7 belongs to a small artifact from the Omodeo Lake Shore (Sardinia). The same doubts as for the analysis 5 arise: Pau or S. Pinna.

The analysis 8 belongs to an obsidian artifact from a site situated along Via Pontina, south of Rome. Its  $K_2O/Na_2O$  ratio and its Sigma value are very close to those of Palmarola sources. Trace-element abundance, namely those of Nb, Zr, Sr, Rb and V, clearly speak for a perfect identity with the Palmarola Monte della Tramontana source.

## APPENDIX B

Obsidians from the Medieval flows of Rocche Rosse, Forgia Vecchia and Pomiciazzo-Lami on Lipari.

There is no doubt today that the obsidian flows of Rocche Rosse, Forgia Vecchia and Pomiciazzo-Lami on Lipari are much younger than those from Papesca Beach and, therefore, they have nothing to do with tool making.

Nevertheless, an attempt to distinguish older obsidians from younger ones and between medieval obsidians has been made.

Samples from the three medieval flows have been analysed for major, minor and some trace

elements. The results are given in table 6 together with those of Papesca Beach for comparison.

As can be easily seen, older obsidians are virtually indistinguishable from younger ones.

In magmatological terms it can be explained by assuming that the magma originating them had undergone only very slight differentiation, the elapsed time from the first flow to the last one being small.

## APPENDIX C

Instrumental errors in XFR analyses.

Shiftings in some instrumental parameters, such as voltage (kV), current (mA), vacuum pressure, pulse-height analyser (PHA), gas-flow rate and electrical ones are a major instrumental errors source.

Siemens sequential automatic spectrometers are equipped with a ten-position sample-changer, in which all the ten samples are simultaneously air-evacuated. It is reasonable to foresee some differences between X-ray intensities measured among samples in the sample-changer and samples from different cycles. kV, mA and PHA settings and vacuum pressure are kept constant during the same measuring cycle.

However, when a given measuring cycle is repeated for a new sample-set – when the sample-changer is loaded again – all the above-mentioned parameters are resetted. Therefore, instrumental errors do occur.

In order to verify this statement rigorous tests have been carried out. A given amount of highly homogenized Liparian pumice was divided into nine pellets, the tenth pellet being used as an external standard. Measuring cycles for some 23 elements were repeated ten times. A total of 5400 intensities was collected and arrayed into a three-dimension matrix 23 by 9 by 10. The results are listed in table 6: it can be seen that instrumental errors accumulated during the same measuring cycle are halved in comparison with those of the subsequent cycles.

Therefore, some subtle distinctions between elemental abundances are better made if the relative X-ray intensities are measured during the same measuring cycle.



Table 1 - Average XRF-analyses and composition ranges of Sardinian geological obsidians.

	M.Arci-Pau			M.Arci-Marrubiu			M.Arci-Uras			M.Arci-S.Pinna			M.Arci-Cecal			M.Arci-Ceca2		
SiO <sub>2</sub>	71.97	72.48	72.58	72.28	73.98	75.14	73.71	74.30	74.83	72.28	72.40	72.52	74.62	75.00	75.20	71.95	72.69	73.38
Al <sub>2</sub> O <sub>3</sub>	14.24	14.37	14.46	13.29	13.71	14.50	13.68	13.83	14.01	14.23	14.34	14.45	12.59	12.68	12.80	13.83	14.07	14.59
Fe <sub>2</sub> O <sub>3</sub>	1.94	1.99	2.03	1.51	1.71	1.99	1.50	1.55	1.61	1.90	1.96	2.03	1.55	1.59	1.60	1.74	1.83	1.98
FeO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MnO	0.04	0.04	0.04	0.04	0.06	0.07	0.07	0.07	0.08	0.08	0.08	0.08	0.07	0.07	0.07	0.05	0.06	0.08
MgO	0.30	0.37	0.52	0.18	0.26	0.39	0.16	0.17	0.19	0.28	0.32	0.36	0.12	0.13	0.14	0.27	0.30	0.36
CaO	0.89	0.93	1.17	0.55	0.71	0.92	0.56	0.58	0.72	0.90	0.94	0.97	0.42	0.44	0.49	0.67	0.74	0.87
Na <sub>2</sub> O	3.54	3.31	3.66	3.52	3.63	3.81	3.63	3.70	3.78	3.54	3.58	3.63	4.27	4.29	4.32	3.69	3.74	3.85
K <sub>2</sub> O	5.50	5.56	5.63	5.01	5.24	5.79	4.71	4.97	5.18	5.47	5.65	5.84	4.51	4.57	4.68	5.34	5.39	5.50
TiO <sub>2</sub>	0.31	0.32	0.33	0.12	0.17	0.30	0.09	0.09	0.09	0.31	0.32	0.33	0.09	0.09	0.10	0.20	0.23	0.29
P <sub>2</sub> O <sub>5</sub>	0.10	0.10	0.11	0.06	0.10	0.16	0.06	0.07	0.07	0.11	0.11	0.11	0.02	0.02	0.02	0.07	0.08	0.10
H <sub>2</sub> O+	0.14	0.25	0.43	0.28	0.42	0.67	0.34	0.67	1.34	0.21	0.31	0.40	0.95	1.13	1.54	0.42	0.86	1.28

## Trace elements (p.p.m.)

S	17.0	19.6	25.0	17.7	18.9	22.0	15.2	18.1	28.8	13.2	15.8	19.6	19.4	22.1	29.8	18.7	20.7	23.4
Cl	483	571	618	611	776	836	888	916	954	523	563	585	1613	1686	1777	716	796	850
Nb	31.1	32.8	35.0	30.6	40.6	55.5	61.6	64.1	67.3	27.7	31.1	32.5	102	108	111	32.1	34.3	36.6
Zr	276	281	285	123	149	274	91	93	96	273	275	279	197	222	227	188	223	280
Y	20.2	23.6	27.7	13.4	19.6	26.6	27.9	29.3	31.6	18.4	19.7	21.8	42.0	44.2	45.8	14.3	14.9	16.4
Sr	208	214	220	46.9	84.3	180	34.9	36.4	38.1	152	156	159	1.4	4.6	7.1	87.2	107	146
Rb	184	186	188	189	253	268	268	269	271	181	184	186	293	297	306	227	235	242
Zn	60.5	61.6	63.0	54.3	60.7	73.1	67.6	68.8	70.9	60.3	62.0	64.2	73.6	74.7	76.2	54.2	55.2	56.9
Co	2.7	2.9	3.0	3.0	3.1	3.3	3.0	3.1	3.2	2.6	2.8	2.9	3.1	3.2	3.3	2.7	2.9	3.1
Cr	1.9	2.3	2.6	0.3	0.9	2.2	0.4	0.5	0.6	2.4	2.5	2.6	0.0	0.2	0.4	1.1	1.3	2.6
V	44.8	45.5	46.4	21.7	27.6	43.3	18.1	18.2	18.4	44.1	45.4	46.3	17.0	18.6	19.3	31.4	36.2	43.3
Ba	923	933	954	320	447	924	296	299	306	926	944	957	302	313	322	544	636	769

$K_2O/Na_2O$	1.54			1.44			1.34			1.58			1.07			1.44		
$\sigma$ (Rittmann)	2.85			2.54			2.40			2.90			2.46			2.81		
$\tau$ (Rittmann)	25.55			36.83			63.99			25.22			73.86			33.29		
Nr. of samples	27			30			77			18			14			6		



Table 3 - Average XRF-analyses and composition ranges of Greek geological obsidians.

	Antiparos			Yali			Melos-Dhemenegakion			Melos-Ag.Nychia			Thera
SiO <sub>2</sub>	74.67	75.31	75.63	76.23	76.83	77.21	74.96	75.28	75.75	75.61	75.94	76.42	61.27
Al <sub>2</sub> O <sub>3</sub>	12.35	12.51	12.72	12.27	12.34	12.42	13.32	13.46	13.66	12.90	13.11	13.35	15.67
Fe <sub>2</sub> O <sub>3</sub>	1.06	1.14	1.24	1.16	1.23	1.26	1.54	1.60	1.68	1.27	1.31	1.38	8.13
FeO	-	-	-	-	-	-	-	-	-	-	-	-	-
MnO	0.10	0.10	0.10	0.04	0.04	0.05	0.07	0.08	0.09	0.07	0.08	0.08	0.16
MgO	0.11	0.11	0.12	0.16	0.16	0.17	0.29	0.32	0.36	0.24	0.25	0.26	1.58
CaO	0.36	0.38	0.41	0.59	0.62	0.71	1.50	1.56	1.62	1.23	1.26	1.35	4.46
Na <sub>2</sub> O	4.33	4.40	4.55	3.81	3.85	3.99	3.93	4.06	4.15	3.90	4.00	4.09	4.36
K <sub>2</sub> O	4.12	4.34	4.53	3.98	4.06	4.14	2.96	3.03	3.08	3.17	3.24	3.45	2.43
TiO <sub>2</sub>	0.09	0.09	0.10	0.07	0.07	0.11	0.18	0.19	0.20	0.15	0.15	0.16	1.20
P <sub>2</sub> O <sub>5</sub>	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.05	0.14
H <sub>2</sub> O+	1.27	1.60	1.97	0.58	0.74	1.04	0.18	0.38	0.76	0.35	0.61	0.89	0.60

## Trace elements (p.p.m.)

S	16.4	19.1	24.1	8.1	10.5	13.5	14.1	17.1	23.3	14.5	18.1	28.2	31
Cl	1334	1356	1373	1070	1255	1364	487	427	650	481	495	518	1001
Nb	36.7	39.1	42.2	16.7	20.0	25.1	6.3	8.1	11.4	6.5	8.9	10.3	32.1
Zr	141	147	152	98.9	114	118	135	137	138	122	124	127	395
Y	0.0	1.6	3.6	10.9	13.8	15.2	13.2	14.9	16.5	13.4	15.3	16.6	61
Sr	0.0	1.4	3.8	78.9	84.6	90.6	145	147	149	116	117	118	302
Rb	409	412	413	145	149	154	112	114	117	118	121	123	95
Zn	42.8	43.8	45.0	43.7	44.4	45.1	47.0	48.6	51.5	45.7	46.9	50.2	83
Co	3.5	3.6	3.7	3.4	3.5	3.6	2.9	3.0	3.1	3.4	3.4	3.5	0.0
Cr	0.0	0.0	0.4	0.0	0.2	0.5	0.7	1.0	1.4	0.6	0.8	1.0	15.1
V	20.0	20.3	20.7	21.0	21.9	22.3	31.7	32.2	32.5	25.9	26.3	26.5	151
Ba	240	246	251	761	777	786	548	555	561	546	554	562	634
$K_2O/Na_2O$		0.99			1.05			0.75			0.81		0.56
$\sigma$ (Rittmann)	2.36				1.85			1.55			1.60		2.53
$\tau$ (Rittmann)	67.64				75.12			40.35			47.35		8.46
Nr.of samples	11				26			63			60		1

Table 3a - Normative (Rittmann) mineralogical composition of the geological obsidians studied.

	1	2	3	4	5	6	7
Quartz	28.3	30.2	30.2	27.3	31.6	27.9	33.3
Sanidine	60.6	62.7	64.2	62.2	65.5	63.8	41.8
Anorthoclase	0.0	0.0	0.3	0.0	0.0	0.0	0.0
Plagioclase	5.5	2.8	0.0	6.3	0.0	4.1	0.0
Aegirine	0.0	0.0	0.0	0.0	0.0	0.0	24.4
Titanaugite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hypersthene	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cordierite	4.1	2.8	4.7	2.2	0.0	0.0	0.0
Magnetite	0.3	0.3	0.2	0.3	0.3	0.3	0.0
Ilmenite	0.3	0.1	0.2	0.2	0.1	0.2	0.0
Apatite	0.2	0.2	0.1	0.2	tr.	0.2	0.1
Biotite	0.8	0.8	0.2	1.2	2.3	1.1	0.0
Zircon	tr.	tr.	tr.	tr.	tr.	tr.	0.3
Halite	tr.	tr.	tr.	tr.	tr.	tr.	0.2
C.I.	5.6	4.2	5.2	4.2	2.7	4.1	24.5
Q	30.0	31.5	31.9	28.5	32.5	29.1	44.3
A	64.2	65.5	68.1	64.9	67.5	66.6	55.7
P	5.0	3.0	0.0	6.6	0.0	4.3	0.0
F	0.0	0.0	0.0	0.0	0.0	0.0	0.0

1 = M.Arci-Pau

2 = M.Arci-Marrubiu

3 = M.Arci-Uras

4 = M.Arci-S.Pinna

5 = M.Arci-Ceca1

6 = M.Arci-Ceca2

7 = Pantelleria

Continued: Table 3a

	8	9	10	11	12	13	14
Quartz	27.8	29.0	32.3	36.9	36.5	36.9	13.9
Sanidine	68.9	60.9	65.5	51.8	25.9	30.8	18.8
Anorthoclase	0.0	7.5	0.0	8.7	0.0	0.0	0.0
Plagioclase	0.0	0.0	0.0	0.0	34.1	28.9	53.2
Aegirine	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Titanaugite	0.0	0.2	0.0	0.0	0.0	0.0	4.3
Hypersthene	0.0	1.1	0.0	0.0	0.0	0.0	6.9
Cordierite	0.0	0.0	0.0	1.6	1.8	2.2	0.0
Magnetite	0.3	0.5	0.2	0.2	0.2	0.2	1.3
Ilmenite	0.1	0.1	tr.	tr.	0.2	0.1	1.2
Apatite	0.1	0.2	0.2	0.2	0.2	0.2	0.3
Biotite	2.6	0.6	1.8	0.7	1.3	0.8	0.0
Zircon	tr.	tr.	tr.	tr.	tr.	0.1	tr.
Halite	0.2	0.1	0.2	0.1	tr.	tr.	0.2
C.I.	3.1	2.5	2.1	2.6	3.4	3.3	14.0
Q	28.7	29.8	33.1	37.9	37.9	38.2	16.2
A	71.3	70.2	66.9	62.1	26.8	31.9	21.9
P	0.0	0.0	0.0	0.0	35.3	29.9	61.9
F	0.0	0.0	0.0	0.0	0.0	0.0	0.0

8 = Palmarola  
 9 = Lipari  
 10 = Antiparos  
 11 = Yali

12 = Melos-Demenegakion  
 13 = Melos-Aghia Nychia  
 14 = Thera (Santorini)

Table 4 - XRF-analyses of archaeological obsidians.

	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	75.46	74.70	71.94	74.19	71.95	74.62	72.10	73.55
Al <sub>2</sub> O <sub>3</sub>	13.12	12.75	14.62	13.95	13.34	11.51	14.23	13.34
Fe <sub>2</sub> O <sub>3</sub>	1.59	1.35	2.36	1.87	2.26	2.76	2.33	2.26
FeO	-	-	-	-	-	-	-	-
MnO	0.06	0.06	0.04	0.06	0.04	0.13	0.04	0.08
MgO	0.27	0.29	0.35	0.17	0.39	0.13	0.29	0.12
CaO	1.30	1.42	0.91	0.59	1.11	0.15	0.95	0.51
Na <sub>2</sub> O	3.92	3.77	3.42	3.56	3.36	5.15	3.29	4.71
K <sub>2</sub> O	3.27	3.16	5.31	4.81	5.58	4.13	5.56	4.65
TiO <sub>2</sub>	0.18	0.18	0.34	0.11	0.37	0.22	0.35	0.12
P <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.08	0.05	0.08	0.02	0.08	0.02
H <sub>2</sub> O+	0.80	2.29	0.63	0.63	0.29	1.18	0.79	0.63

Trace elements (p.p.m.)

S	18	78	13	10	19	18	11	18
Cl	496	841	595	919	588	1282	565	1474
Nb	8.9	4.2	30	56	22	102	34	81
Zr	122	89	256	84	207	1010	269	330
Y	16.6	15.4	20.3	27	19	111	19	49
Sr	138	116	150	31	254	9.8	158	0.0
Rb	121	105	178	252	164	203	181	500
Zn	46	53	59	64	65	120	60	55
Co	3.2	3.5	2.5	3.1	2.8	2.4	2.6	2.8
Cr	0.0	1.9	0.6	0.0	0.0	1.2	0.9	0.0
V	27.5	27.6	38	19	47	27	45	19
Ba	556	545	295	306	920	305	919	319

1 = Melos-Philakopi (9 analyses)

2 = Nerokouru (Chania, Crete)

3 = Puisteris (Sardinia)

4 = Puisteris (Sardinia)

5 = Nuraghe Losa (Sardinia)

6 = Nuraghe Losa (Sardinia)

7 = Omodeo Lake (Sardinia)

8 = Pontina Road (Rome)



Table 4a: normative mineralogical composition  
of archaeological obsidians.

	1	2	3	4	5	6	7	8
Quartz	37.0	38.2	27.6	31.2	29.8	30.5	28.5	26.6
Sanidine	30.8	29.5	59.0	59.7	56.3	62.6	59.9	70.3
Anorthoclase	0.0	0.0	0.0	2.5	0.0	0.0	0.0	0.0
Plagioclase	28.8	29.3	6.7	0.0	9.2	0.0	6.3	0.0
Aegirine	0.0	0.0	0.0	0.0	0.0	6.2	0.0	0.0
Titanaugite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
Hypersthene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1
Cordierite	2.0	1.4	5.2	5.6	0.0	0.0	0.0	0.0
Magnetite	0.2	0.2	0.3	0.3	0.3	0.2	0.3	0.6
Ilmenite	0.1	0.2	0.3	0.0	0.2	0.1	0.3	0.1
Apatite	tr.	tr.	0.2	0.1	0.2	tr.	0.2	tr.
Biotite	1.1	1.2	0.7	0.7	3.9	0.0	1.0	0.5
Zircon	tr.	tr.	tr.	tr.	tr.	0.1	tr.	tr.
Halite	tr.	0.1	tr.	0.1	tr.	0.1	0.2	0.2
C.I.	3.4	2.8	6.7	6.0	4.6	6.5	5.2	2.9
Q	38.3	39.4	29.6	33.4	31.3	32.7	30.0	27.4
A	31.9	30.4	63.2	66.6	59.1	67.3	63.3	72.6
P	29.8	30.2	7.2	0.0	9.6	0.0	6.7	0.0
F	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$K_2O/Na_2O$	0.83	0.84	1.55	1.35	1.71	0.80	1.69	0.99
$\sigma$ (Rittmann)	1.59	1.51	2.63	2.25	2.70	2.72	2.69	2.87
$\tau$ (Rittmann)	46.00	44.90	26.67	64.94	22.40	26.50	25.44	61.64



Table 6 - Instrumental errors in XRF analyses.

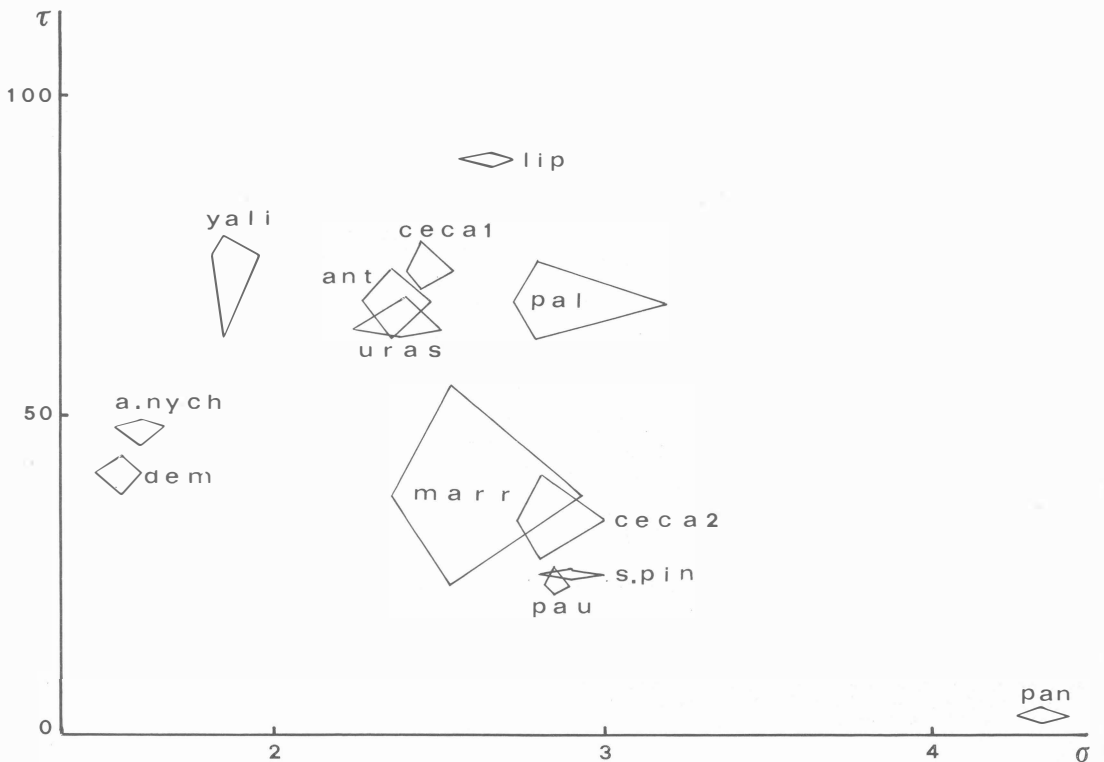
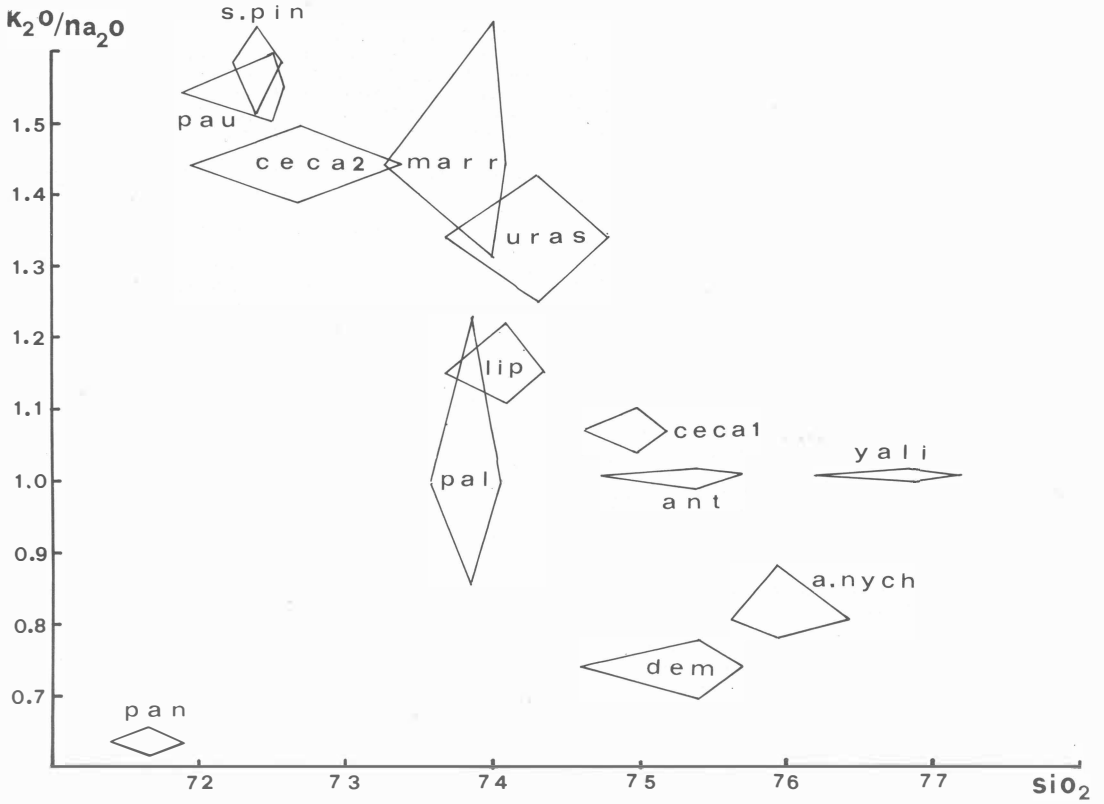
	%	$\sigma_e$	$\sigma_{e\%}$	$\sigma_i$	$\sigma_{i\%}$
SiO <sub>2</sub>	71.21	$\pm 0.06$	(0.09)	$\pm 0.04$	(0.06)
Al <sub>2</sub> O <sub>3</sub>	12.75	$\pm 0.03$	(0.25)	$\pm 0.02$	(0.16)
Fe <sub>2</sub> O <sub>3</sub>	2.02	$\pm 0.03$	(1.38)	$\pm 0.01$	(0.46)
MnO	0.065	$\pm 0.001$	(0.97)	$\pm 0.0005$	(0.48)
MgO	0.17	$\pm 0.002$	(0.96)	$\pm 0.001$	(0.48)
CaO	0.72	$\pm 0.07$	(1.03)	$\pm 0.02$	(0.29)
Na <sub>2</sub> O	3.82	$\pm 0.03$	(0.76)	$\pm 0.02$	(0.51)
K <sub>2</sub> O	4.76	$\pm 0.03$	(0.66)	$\pm 0.01$	(0.22)
TiO <sub>2</sub>	0.088	$\pm 0.02$	(1.13)	$\pm 0.01$	(0.56)
P <sub>2</sub> O <sub>5</sub>	0.016	$\pm 0.01$	(5.18)	$\pm 0.005$	(2.59)

Trace elements (p.p.m.)

S	19	$\pm 3.5$	(18.93)	$\pm 1.0$	(5.41)
Cl	2470	$\pm 32$	(1.28)	$\pm 8.2$	(0.33)
Nb	32	$\pm 2.6$	(7.97)	$\pm 0.4$	(1.23)
Zr	128	$\pm 1.8$	(1.45)	$\pm 1.1$	(0.89)
Y	45	$\pm 2.6$	(5.84)	$\pm 1.4$	(3.14)
Sr	13	$\pm 2.4$	(17.88)	$\pm 1.2$	(8.94)
Rb	306	$\pm 3.9$	(1.26)	$\pm 2.1$	(0.68)
Zn	55	$\pm 0.5$	(0.98)	$\pm 0.5$	(0.98)
Ni	2.2	$\pm 0.02$	(1.00)	$\pm 0.01$	(0.50)
Co	2.8	$\pm 0.11$	(3.83)	$\pm 0.05$	(1.74)
Cr	0.6	$\pm 0.04$	(6.68)	$\pm 0.03$	(5.01)
V	15	$\pm 0.4$	(2.55)	$\pm 0.2$	(1.27)
Ba	284	$\pm 5.5$	(1.94)	$\pm 2.3$	(0.81)

$\sigma_e$  = errors between measuring cycles.

$\sigma_i$  = errors during the same measuring cycle.



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## RÉSUMÉ

*Caractérisation de Gîtes d'obsidienne méditerranéens par les méthodes classiques de la pétrochimie.*

L'hypothèse de travail était qu'une étude complète avec les méthodes classiques de la pétrochimie appliquées aux obsidiennes suffisait pour caractériser la composition de ces verres volcaniques à des fins archéologiques.

On a commencé par l'échantillonnage des gîtes d'obsidienne italiens et grecs. Les échantillons italiens proviennent de différentes coulées du Monte Arci (Sardegna), des coulées préhistoriques de l'île de Lipari et, par comparaison, de celles du moyen âge, de l'île de Palmarola et de l'île de Pantelleria.

Les échantillons grecs ont été recueillis à l'île de Milos, d'Antiparos et de Yali. Ceux de Milos proviennent de deux différentes localités: Haya Nychia et Dhemenegakion.

On a recueilli, au total, près de 500 échantillons. Chaque localité est représentée par un minimum de dix échantillons.

Les échantillons choisis ont été analysés aux rayons X (FRX) pour le dosage des éléments majeurs, mineurs et en trace. La méthode analytique en question n'est pas d'importance capitale, mais on veut souligner les éléments dosés, c'est à dire, ceux de la pétrochimie. Le calcul de la composition minéralogique normative à la méthode de Rittmann s'est révélé de grande aide. Les résultats obtenus nous montrent que des oxydes majeurs et mineurs sont suffisants, dans la plupart des cas, pour distinguer d'une façon non équivoque un gîte d'obsidienne des autres.

Enfin, l'obsidienne de Pantelleria s'est révélée d'une composition unique.

## RIASSUNTO

L'ipotesi di lavoro è stata che una completa applicazione dei metodi della petrochimica classica allo studio delle ossidiane fosse sufficiente a caratterizzare la composizione di questi vetri vulcanici a fini archeologici.

Il lavoro è iniziato dalla campionatura dei giacimenti di ossidiana italiani e greci.

I campioni italiani provengono da diverse colate del Monte Arci (Sardegna), dalle colate preistoriche di Lipari e, per confronto, da quelle altomedievali; dall'isola di Palmarola e dall'isola di Pantelleria, invece da una sola fonte. I campioni greci sono stati raccolti su tre isole: Milos, Antiparo e Yali. Quelli di Milos provengono da due grandi e distinti giacimenti: Aghia Nychia e Dhemenegakion.

Complessivamente sono stati raccolti oltre cinquecento campioni.

Ogni località è rappresentata da almeno dieci campioni.

I campioni sono stati sottoposti ad analisi per fluorescenza X per il dosaggio degli elementi maggiori, minori ed alcuni in tracce.

Il metodo analitico in se stesso è irrilevante, mentre essenziali sono gli elementi dosati, quelli della petrochimica. È stata anche calcolata la loro composizione mineralogica normativa.

I risultati ottenuti dimostrano che accurati dosaggi degli ossidi maggiori e minori ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{H}_2\text{O}$ ) sono sufficienti a distinguere inequivocabilmente un giacimento di ossidiana da un altro.

L'ossidiana di Pantelleria ha rivelato una composizione inconfondibile.

## ZUSAMMENFASSUNG

*Kennzeichnung der Mittelländischen Vorkommen von Obsidian durch klassische Methoden der Petrochemie.*

Die Hypothese wurde gestellt, dass eine vollständige Anwendung der klassischen Methoden der Petrochemie für die Obsidiane genügen würde die Zusammensetzung dieser vulkanischen Gläser zu kennzeichnen.

Die Arbeit hat mit der Bemusterung der italienischen und griechischen Vorkommen von Obsidian begonnen. Die italienischen Mustern sind auf verschiedenen Strömen des Monte Arci (Sardinien), auf prähistorischen Strömen von Lipari, auf der Palmarolainsel und der Pantelleriainsel gesammelt worden. Die griechischen Mustern sind auf der Miloinsel in zwei Lokalitäten (Aya Nychia und Dhemenegakion) und auf der Insel von Yali gesammelt worden.

Insgesamt sind über 500 Mustern gesammelt worden. Jede Lokalität ist mit mindestens 10 Mustern vertreten.

Die ausgewählten Mustern sind auf RFA, auf den Inhalt der Haupt- und Minderelemente und einiger Spurenelemente analysiert worden.

Die analytische Methode ist an sich nicht wichtig, aber man möchte die Bedeutung unterstreichen, die Elemente der klassischen Petrochemie zu dosieren. Die Berechnung der normativen mineralogischen Komposition, nach der Methode von Rittmann, hat sich als grosse Hilfe in der Unterscheidung der verschiedenen Obsidiane erwiesen.

Die erlangten Resultate zeigen dass sorgfältige Dosierungen der hauptsächlichsten und mindere Oxide meistens ausreichend sind, unmissverständliche eine Lagerung von Obsidian von einer anderen zu unterscheiden.

Ausserdem hat der Obsidian von Pantelleria eine unverwechselbare Komposition gezeigt.