Magnetite-grain-size analysis and sourcing of Mediterranean obsidians

DOI:10.1016/j.jas.2011.12.030

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Magnetite grain-size analysis and sourcing of Mediterranean obsidians

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ABSTRACT

The potential of magnetic grain-size variations as an obsidian source characteristic is investigated using geological and archaeological obsidians from five islands of the Mediterranean Sea: Lipari, Sardinia, Palmarola, Pantelleria, Melos. Four parameters are used: magnetic (χ) and anhysteretic (χ_a) susceptibilities, saturation isothermal remanent magnetizations at room ($SIRM_{293}$) and at liquid nitrogen ($SIRM_{77}$) temperature. The ratio $S_T = SIRM_{77} / SIRM_{293}$, which depends on the superparamagnetic grains relative abundance, varies little in each individual site, with the exception of Lipari which is characterized by large variations and the highest content of superparamagnetic grains. The χ_a vs. χ plot (King et al., 1982) shows some within-site dispersion of the samples; but the ratio $Q_a = \chi_a/\chi$, which is strongly influenced by the single domain grains content, is characteristic for each site. The combined use of the King and Q_a vs. S_T plots discriminates the samples from most of the sites and suggests that the grain-size analysis is a promising approach in sourcing obsidian archaeological artefacts. Moreover, the measurements of the four parameters used are simple, quick and feasible with no or little damage to archaeological finds.

Keywords: obsidian, rock-magnetism, provenance, prehistory

1. Introduction

Obsidian is a volcanic glass widely used in prehistoric ages to manufacture sharp tools such as blades, scrapers and arrow-heads. Its geological occurrence is limited to a few localities so it was a rare and precious commodity, making it an ideal material for reconstructing past trade routes between the production places and even far distant archaeological sites. ^{57}Fe Mössbauer spectroscopy, electron spin resonance and laser-ablation ICP mass spectrometry have all been successfully employed in provenance studies of archaeological finds in the western Mediterranean region (Tykot, 2002; Duttine et al., 2003; Barca et al., 2008). Unfortunately these sophisticated methods are more or less destructive, expensive and time consuming. A reconnaissance method for screening large collections of finds would therefore be extremely useful.

The use of rock-magnetism to identify the provenance of ancient obsidian tools was first proposed by McDougall et al. (1983), who analysed obsidians from prehistoric Mediterranean sources. They showed that three magnetic parameters, i.e. initial intensity of natural remanent magnetization (NRM), saturation remanent magnetization and low field bulk susceptibility, “allowed some distinction to be made between sources”. They noticed, however, that magnetic parameters usually showed high within-source scatter. Later studies (Schmidbauer et al., 1986; Urrutia Fucugauchi, 1999; Vásquez et al., 2001; Stewart et al., 2003) considered these and other parameters, such as saturation magnetization, coercivity and remanent coercive force, and basically corroborated the McDougall et al. (1983) conclusions. In recent years, promising preliminary results have been achieved using multivariate statistical analyses on collection of data from the Mediterranean Sea and around the world (Feinberg et al., 2009; Weaver et al. 2009)..The magnetic properties of black, unaltered obsidian are dominated by titanomagnetite and depend on the concentration, size, shape and spatial arrangement of its grains. Variations of these factors usually occur in the obsidian at the scale of both the outcrop and the sample making the rock neither uniform nor isotropic and resulting in varying degrees of scatter in the measured values. It is also difficult to isolate the individual factors; for example, the intensity of magnetization depends on the concentration as well as the grain-size. In principle, the size of the ferrimagnetic grains in the obsidian ranges between a few nanometres to some hundreds micrometres and they vary over all magnetic states ─ superparamagnetic (SP), single domain (SD), pseudosingle domain (PSD), multidomain (MD) ─ each characterized by very different magnetic properties. Schmidbauer et al. (1986) remarked that grains of the various sizes contribute in a different way to coercivity and remanent coercive force and inferred the occurrence of large MD grains in their specimens which were characterized by high saturation magnetization and low coercivity.

The relative abundance of the various grain-sizes as well as composition mainly depends on the eruption and emplacement processes and could therefore could itself characteristic of individual obsidian flows. It is therefore worth investigating this hypothesis further checking for any systematic difference between the obsidian sources. To be practical for provenance study, the laboratory procedure cannot range over all types of magnetic measurements, but needs to be limited to non destructive, no-damaging techniques that are fast and inexpensive, in order to screen the finds of an excavation and select samples for the more accurate, yet more demanding, geochemical analyses.

2. Samples

This paper is mainly based on geological samples, collected in various islands of the Mediterranean Sea (Fig. 1) which were important centers of manufacture and export of obsidian artefacts during the Paleolithic and Neolithic periods:

– Lipari. The geological samples were collected close to Canneto as blocks in the pumiceous pyroclastic succession of the Vallone del Gabellotto formation (Tranne et al., 2002), which has been dated at 8.2 ± 0.1 ka (Siani et al., 2004). Archaeological samples from two local Neolithic sites were also provided by the Museo Archeologico Regionale di Lipari. At Contrada Diana (late 4th – early 3rd millennium bC) the prehistoric layer is covered by a sterile layer underlying a Greco-Roman necropolis (Bernabò Brea and Cavalier, 1960). No traces of huts occur at this site, although there are many open-air hearths with meal wastes together with a few dozens of finished blades, a great number of obsidian cores and countless flakes and failed blades, which can be regarded as working scraps. These finds suggest that an important obsidian workshop had existed there. The prehistoric layer of Piano Conte (about middle 3rd millennium bC) is covered by Bronze Age layers. The lithic industry consists of flint and obsidian, which occurs as flakes, cores, more or less finished blades along with some instruments showing secondary retouching. These archaeological samples can be safely regarded as coming from Lipari itself and comparison with the geological samples is helpful to assess the possible variations in magnetic properties of the obsidian within the Lipari source area.

─ Sardinia. The samples came from the four obsidian types – SA, SB1, SB2, SC – identified at the Mt. Arci volcanic complex on the basis of the chemical characteristics (Tykot, 1997).

─ Palmarola. The sampling site was located along the southeastern slopes of Mt. Tramontana (Barberi et al., 1967; Francaviglia, 1984).

─ Pantelleria. The samples came from lava flows of the Mt. Gelfiser, Cuddia Randazzo and Khaggiar eruptive cycles (Civetta et al., 1988).

─ Melos. The samples were collected from the southern side of the Adhamas, or Bombarda, dome (Arias et al., 2006).

3. Measurements and results

3.1 Hysteresis cycles.

The hysteresis cycles were obtained for at least two pilot specimens from each individual source using an Alternating Force Gradient Magnetometer (Princeton, MicroMag 2900) with a maximum applied field B = 1T. The small noise due to the silicon-oxide sample holder was separately evaluated and subtracted from the measured values. Measurements on specimens a few milligrams in mass were carried out at room temperature (293K) and in liquid nitrogen (77K). At Melos, Mt. Arci SB1 and SC the shape of two loops are similar to each other (Fig. 2) and point to a low content of SP grains. On the other hand the content is higher at the three sites of Lipari, which show a dramatic change of the hysteresis loop and a large increase of the coercive force. The loops of Palmarola, Mt. Arci SA and SB2 are mid-way between the former types, whereas those of Pantelleria show a predominat paramagnetic contribution.

3.2 Low-field and anhysteretic susceptibilities

The anisotropies of the low-field susceptibility and anhysteretic remanent magnetization (ARM) were actually measured in order to avoid the directional bias due to the large magnetic anisotropy of obsidians. The susceptibility (χ) and the ARM intensity (J_{ARM}) magnitude was computed as the radius of the sphere with the same volume as the anisotropy ellipsoid. This care proved effective, because the anisotropy degree P varied from 1.01 to 1.3 for χ, from 1.2 to 2.8 for J_{ARM}.

Magnetic susceptibility was first measured on all samples using a KLY-3 kappabridge; then an ARM was given using a D-2000 ASC equipment and measured with a JR-6 spinner magnetometer. Each sample was first tumbling demagnetized at 0.2 T to erase as much as possible of the hard NRM component. Then it was given an ARM with a steady field H = 79 A/m during the whole demagnetization cycle, and measured. The procedure was repeated in six different orientations with respect to the steady field, and in two opposite senses for each position to cancel out any unwanted contribution by unerased NRM. Finally the anhysteretic susceptibility, $\chi_a = J_{ARM}/H$, was calculated.

Both the low-field and anhysteretic susceptibilities are strongly affected by the total amount of magnetite, whereas χ is little sensitive to grain-size variation and the magnitude of χ_a increases as the grain-size decreases, since small grains acquire ARM more efficiently than large grains. The ratio $Q_a = \chi_a / \chi$ is therefore regarded as a grain-size indicator: the higher its value, the higher the relative abundance of SD to (PSD+MD) grains. The susceptibilities values (Fig. 3, 4) in the Mediterranean obsidians (Table 1) varied over three orders of magnitude: $70 \times 10^{-8} < \chi < 4000 \times 10^{-8}$ m^3kg^{-1}, $40 \times 10^{-8} < \chi_a < 46000 \times 10^{-8}$ m^3kg^{-1}. They were usually low at Pantelleria, Lipari and Mt. Arci SA, higher at Palmarola, Mt. Arci SB2 and Melos and even higher at Mt. Arci SB1 and SC. At Lipari, the Q_a values of the geological and archaeological samples are consistent to each other and plot close to the straight line $Q_a = 1$ (Fig. 3), with the exception of two samples from the Contrada Diana excavation, whose values $Q_a \approx 2.5$ are similar to those of Palmarola, Melos, Mt. Arci SA and SB2. The samples from Pantelleria have χ values similar to those of various samples from Lipari, but they are distinguishable because of the very low anhysteretic susceptibility, which makes the Q_a ratios be the lowest ($\approx 0.3 – 0.4$).

The four obsidian types (Tykot, 1997) found at Mt. Arci show very large variations both in χ and χ_a and plot in distinct areas of the King et al. (1982) plot (Fig. 4). At sites SA and SB2 the Q_a ratio shows little dispersion and values around 2.5, whereas the values are much higher at the other two sites (≈ 5 – 6 at SB1 and up to 38 at SC), which also show larger dispersion. One specimen from SB1 falls close to the SB2 field. However, it differs because of a Q_a value twice as much.

3.3 Isothermal remanent magnetization

Stepwise isothermal remanent magnetization (IRM) acquisition up to a field of 2T was measured on selected samples both at 293K and 77K. Each sample was first fitted in a small diamagnetic open box, then for each step the sample was given the field at room temperature and the IRM was measured with a 2G cryogenic magnetometre; the box was then bathed in liquid nitrogen, let to fill and cool down, given the same field in the same direction as before and measured. The general trend of the curves is similar (Fig.5) and typical of titanomagnetite: a strong increase occurs up to 0.2-0.4 T (293K) or 0.5-0.7 T (77K), then the curve smooths down toward saturation. At most sites the IRM intensity at 77K is larger than at 293K due to the contribution of SP grains, whose magnetization is not stable at room temperature. On the other hand, at Melos, Mt. Arci SB1 and SC the two curves are close to each other, and little or no magnetization increase occurs in the curve run at 77K. The occurrence of SP grains in these samples is therefore limited or negligible. These results are in full agreement with those of the hysteresis curves (Fig. 2) and show that the IRM saturation values $SIRM_{77}$ and $SIRM_{293}$ are reliable indicators of the relative content of SP grains. All samples were therefore magnetized to saturation at 1 T field at both temperatures, and the ratio $S_T = SIRM_{77} / SIRM_{293}$ was regarded as a proxy of the relative abundance of SP to larger (SD+PSD+MD) grains. The S_T values at Melos, Mt. Arci SB1 and SC were lower than 1.3 (Fig. 6) and point to a low SP grains content. At Palmarola, Pantelleria, Mt. Arci SA and SB2 they fell in the range 1.5 to 2.5. The obsidians from Lipari are conspicuous as far as the S_T, and thus the SP grains content, is characterized by a wide range and the highest values ($2.2 \leq S_T \leq 4.3$).

4. Discussion and conclusion

The hysteresis and the IRM acquisition curves confirm that a mineral of the titanomagnetite series is the main ferrimagnetic phase in all of the obsidians from the islands of Sardinia (Mt. Arci), Lipari, Palmarola, Pantelleria and Melos. The ARM and low-field susceptibility results, as summarized in the χ_a vs. χ plots (Fig. 3, 4) show that the Q_a value, and thus the relative abundance of SD to the larger (PSD+MD) grains, varies only slightly within each individual obsidian source. The plot clearly distinguishes the four obsidian types from Mt. Arci (Fig. 4). The obsidians of Lipari are well separated from those of the other sources (Fig. 3), with the exception of two samples from Contrada Diana which fall close to the Mt. Arci SA type. Data from Palmarola, Melos and Mt. Arci SB2 are dispersed through a same region in the plot. Also the relative abundance of SP to (SD+PSD+MD) grains, as given by the S_T ratio, has limited variations (Fig. 6) with the exception of Lipari, where the range is higher and similar at the three sites. The S_T values from Melos are separated from those of Palmarola and Mt. Arci SB2, which partially overlap to each other and to Mt. Arci SA and two samples from Contrada Diana. The other sites fall in distinct areas of the plot.

The grain-size analysis proposed in this paper consists of four simple and fast non-destructive measurements: low-field susceptibility, ARM intensity, SIRM intensities at 77K and 293K. The combined use of the King et al. (1982) and Qa vs. S_T plots proved effective in separating the obsidians from the distinct sources:

─ Pantelleria is characterized by very low values of both anhysteretic remanence and SIRM. Its field looks similar to that of Lipari in the King et al. (1982) plot because both are close to the origin, yet its Q_a value is less than half that of Lipari;

─ Lipari is well separated from the other sources, except for two specimens from Contrada Diana;

─ the fields of Mt. Arci SA and SB2 overlap in the Qa vs. S_T plot but are well separated in the King et al. (1982) plot. They also differ from those of SB1 and SC, which in turn are far each other in both plots;

— Palmarola, Melos and Mt. Arci SB2 overlap each other in the King et al. (1982) plot, whereas the Melos field is distinct in the Qa vs. S_T plot;

— the only unresolved overlap is between Palmarola and Mt. Arci SB2.

The case of Lipari showed a good agreement between the geological site of Canneto and the archaeological one of Piano Conte, whereas some difference was observed at the archaeological site of Contrada Diana. Taking into account that this site was an important obsidian workshop, it is reasonable to assume that the raw material may well have come from all available sources at Lipari. Therefore, either some variations occur in the blocks within the Vallone del Gabellotto formation or another source was exploited in Neolithic times.

These results suggest that the magnetic grain-size analysis is a promising approach in sourcing obsidian archaeological artefacts. They need to be substantiated by the investigation of collections of artefacts of known source, because the geological samples come from the whole extent of a lava flow or dome, whereas only the spots with high quality material were reasonably exploited in the past (Hillis et al., 2010). Finally, it is noteworthy that the measurements of the four quantities used in the King et al. (1982) and Q_a vs. S_T plots do not require any pre-analytical treatment and, using commercial equipment, are feasible with no damage to artefacts up to 20-22 mm in size or taking very small fragments from samples of minor archaeological interest, like the obsidian cores.

Acknowledgements

We are indebted to M. Benfari, director of the Museo Archeologico Regionale di Lipari, for providing the archaeological samples, and D. Tarling for improving the original manuscript. The final text benefited by useful comments and suggestions by two anonymous reviewers.

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Figure captions

Fig. 1. Obsidian sources in the Mediterranean Sea.

Fig. 2. Hysteresis curves. Mass magnetization M vs. applied field B. Red/blue line = 293K/77K temperature. Melos, Lipari and Palmarola curves corrected for paramagnetic effect.

Fig.3. King et al. (1982) plot for Mediterranean obsidians. Anhysteretic susceptibility χ_a vs. low-field magnetic susceptibility χ .

Fig. 4. King et al. (1982) plot for Mt. Arci obsidians. Anhysteretic susceptibility χ_a vs. low-field magnetic susceptibility χ .

Fig. 5. IRM acquisition curves. Isothermal remanent magnetization M vs. applied field B. Red/blue line = 293K/77K temperature.

Fig. 6. Q_a vs. S_T plot. Q_a = anhysteretic / magnetic susceptibility (χ_a/χ), S_T = saturation isothermal remanent magnetization measured at 77K / 293K ($SIRM_{77}$ / $SIRM_{293}$). Data from Mt. Arci SC ($Q_a \approx 38$, $S_T \approx 1.25$) not shown.

Table captions

Table 1

Magnetic data for Mediterranean obsidians. Symbols: n = number of samples; χ = magnetic susceptibility; χ_a = anhysteretic susceptibility; $SIRM_{293}$, $SIRM_{77}$ = saturation isothermal remanent magnetization measured at 293K and 77K.

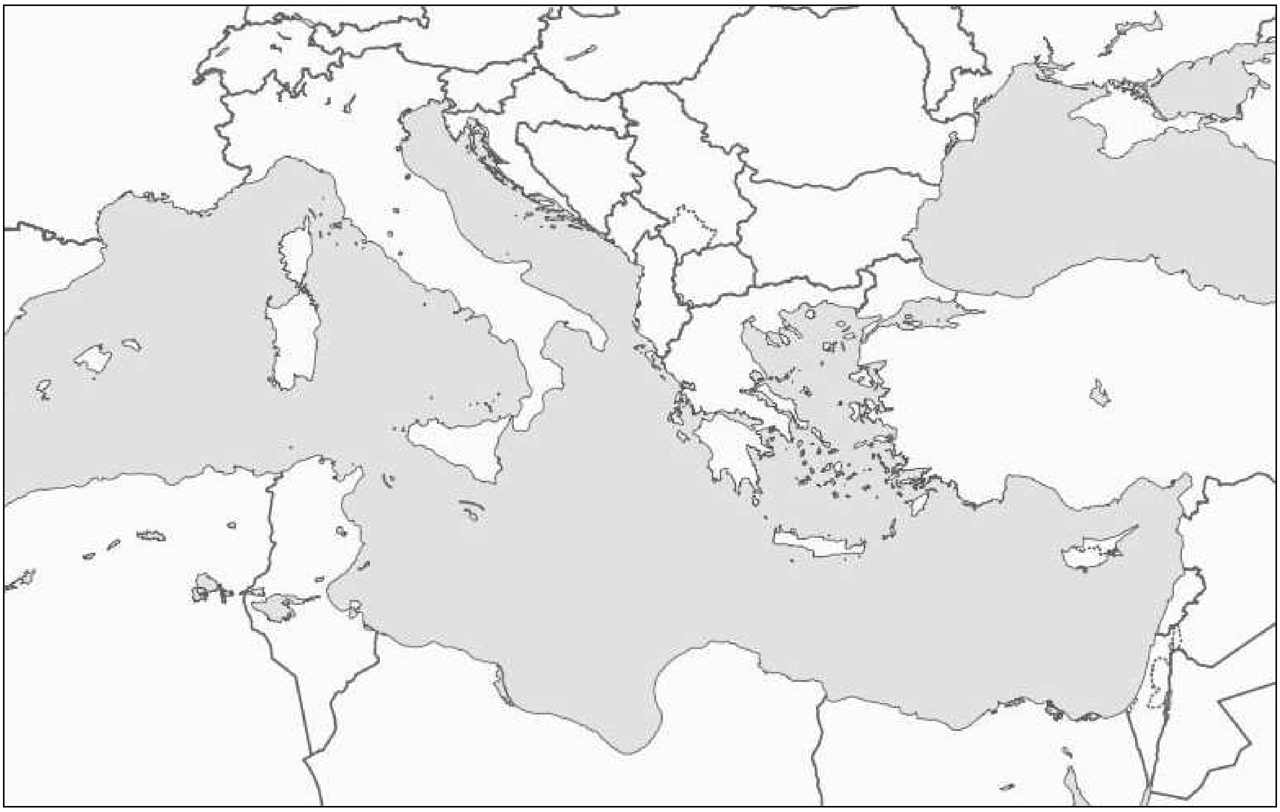
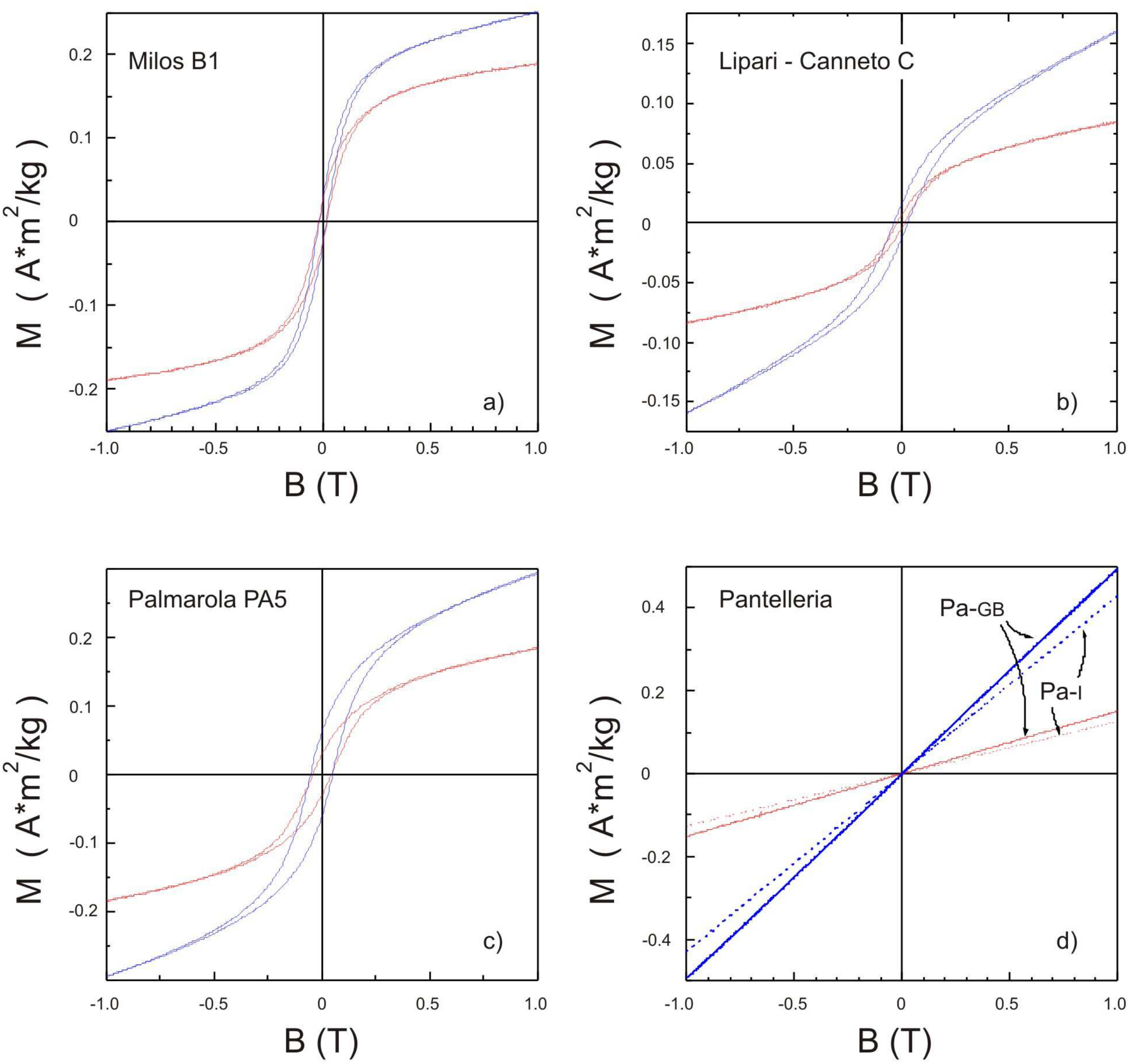
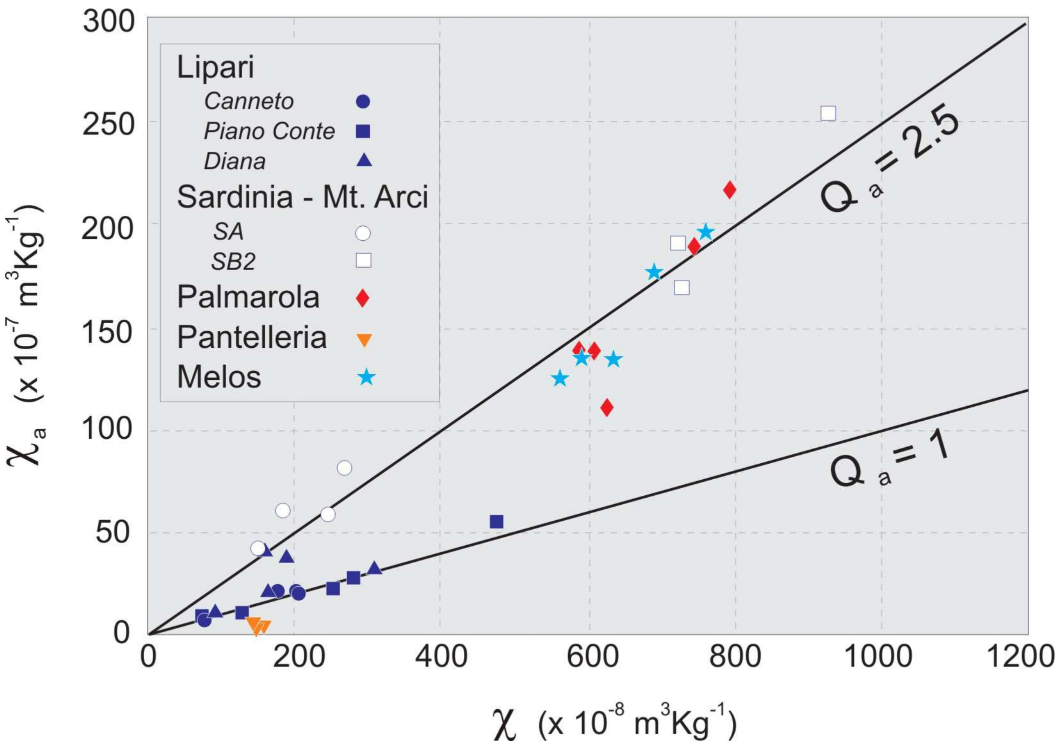


Fig.1



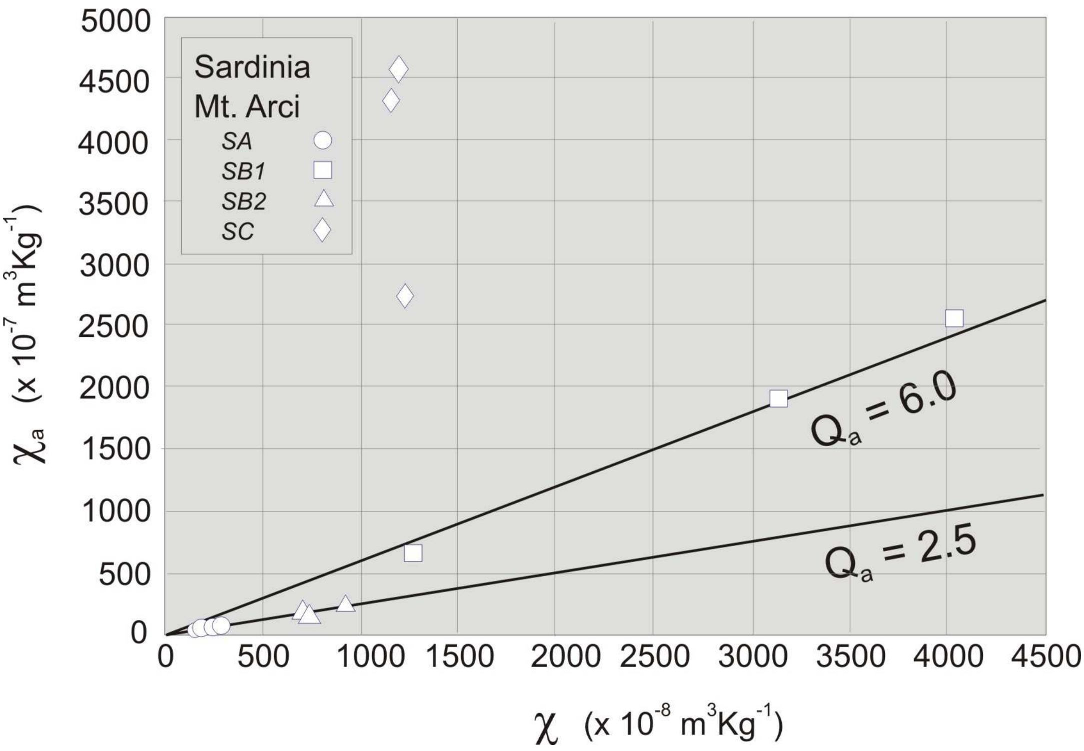
Milos B1
a)
Lipari - Canneto C
b)
Palmarola PA5
c)
Pantelleria
Pa-GB
Pa-I
d)
M (A*m2/kg)
B (T)

Fig.2



Lipari
Canneto
Piano Conte
Diana
Sardinia - Mt. Arci
SA
SB2
Palmarola
Pantelleria
Melos
$Q_a = 2.5$
$Q_a = 1$
χ_a (x 10^{-7} m^3Kg^{-1})
χ (x 10^{-8} m^3Kg^{-1})
0
50
100
150
200
250
300
0
200
400
600
800
1000
1200

Fig.3



Sardinia
Mt. Arci
SA
SB1
SB2
SC
$Q_a = 6.0$
$Q_a = 2.5$
χ_a (x 10^{-7} m^3Kg^{-1})
χ (x 10^{-8} m^3Kg^{-1})

Fig.4

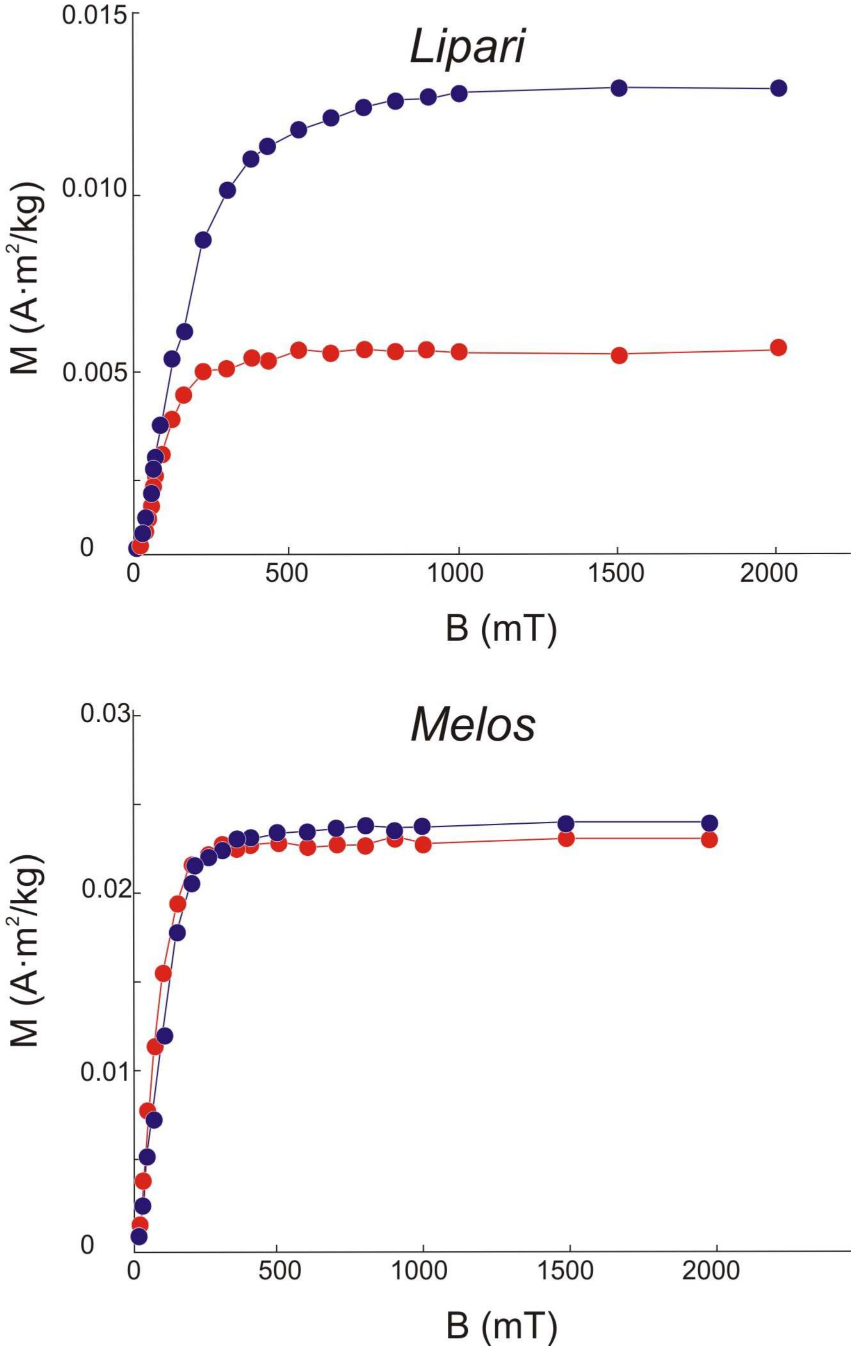
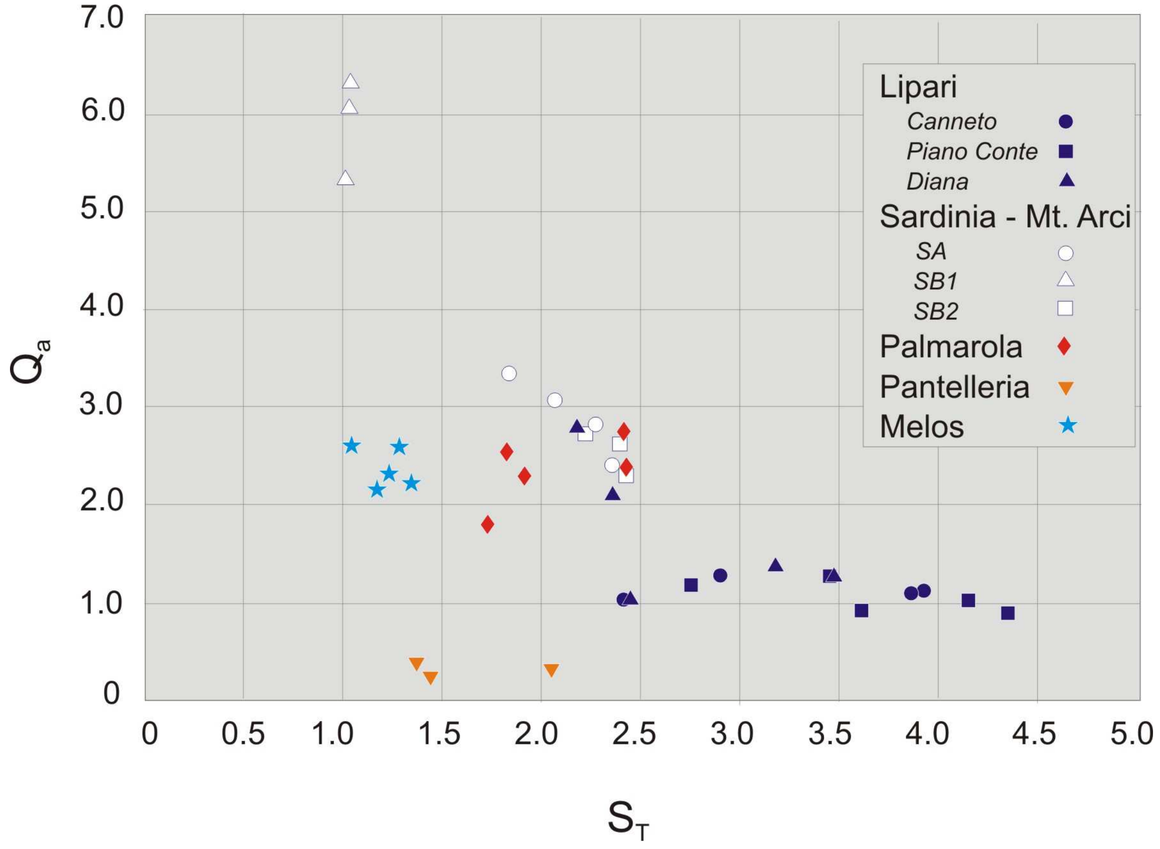

Lipari
0.015
0.010
0.005
0
M (A·m²/kg)
0
500
1000
1500
2000
B (mT)
Melos
0.03
0.02
0.01
0
M (A·m²/kg)
0
500
1000
1500
2000
B (mT)

Fig. 5



Lipari
Canneto
Piano Conte
Diana
Sardinia - Mt. Arci
SA
SB1
SB2
Palmarola
Pantelleria
Melos
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Q_a
S_T

Fig. 6