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Magnetic properties and ^{57}Fe Mössbauer spectroscopy of Mediterranean prehistoric obsidians for provenance studies

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Abstract

Samples from the Mediterranean source-islands: Gyali, Lipari, Melos, Palmarola, Pantelleria and Sardinia (Monte Arci) had their ^{57}Fe Mössbauer spectra and magnetizations measured. The saturation magnetization (M_s) depends on the island of provenance and it reaches a maximum ~0.3 emu/g for Palmarola obsidians, indicating a larger magnetic phase content. The coercive forces (H_c) range from 46 to 372 Oe for respectively samples from Pantelleria and Palmarola islands. Our analyses show that in a M_r/M_s vs. H_c/H_m plot the data points accumulate in areas that depend on obsidian provenance (M_r, remanent magnetization; H_m, maximum applied field). The Mössbauer spectra are mainly composed of broad asymmetric doublets, which were fitted assuming two Fe^{2+} and one Fe^{3+} sites. In addition, the obsidians of Melos and Palmarola present a magnetic component attributed to magnetite and/or hematite. Binary diagrams comparing different Mössbauer hyperfine parameters for the Fe^{3+} and Fe^{2+} species gave indications of similarities and differences between obsidians of different origins. Since this kind of plot does not give an unambiguous characterization of samples from each island, a detailed analysis of the Mössbauer results is in progress using statistical method of clustering analysis as has been shown by Scorzelli et al. [Comptes Rendus Acad. Sci., Serie II, 332 (2001) 769] and Poupeau et al. [IAOS Bull. 28 (2001) 2] in previous studies.

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1. Introduction

Obsidian artifacts are present in many Neolithic sites of the Western Mediterranean basin and in its regions. However, practically all can be related to the four Italian source-islands of Lipari, Palmarola, Pantelleria and Sardinia. Revisiting the potentialities of structural description in sourcing

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studies, we showed that Mössbauer spectroscopy and electron spin resonance (ESR) [1] and magnetic properties [2] could offer viable alternatives [1].

It is shown here that variations in the magnetic properties (MP) of obsidian show also a great potential in provenance determination and thermal history of stone tools. In particular, MP offer a fast and economic approach at least for the considered area.

2. Experimental

The samples to be studied were collected mostly from outcrops, and partly from artifacts collected over wide areas from the six major obsidian source areas in the Mediterranean basin: Monte Arci (Sardinia), Palmarola, Lipari, Pantelleria, Melos and Gyali islands [3]. All samples were previously analyzed [3] by both XRF (whole rock) and SEM-EDS (glass and microliths – microphenocrysts). The room temperature Mössbauer spectra were taken in transmission geometry using a ^{57}Co/Rh source of 50 mCi. Isomer shifts are referred to α-Fe at room temperature. The spectra shown in Fig. 1 were fitted using the NORMOS program [4]. *M* vs. *H* cycles under a maximum applied field of 1.2 T were taken at room temperature using a commercial SQUID magnetometer.

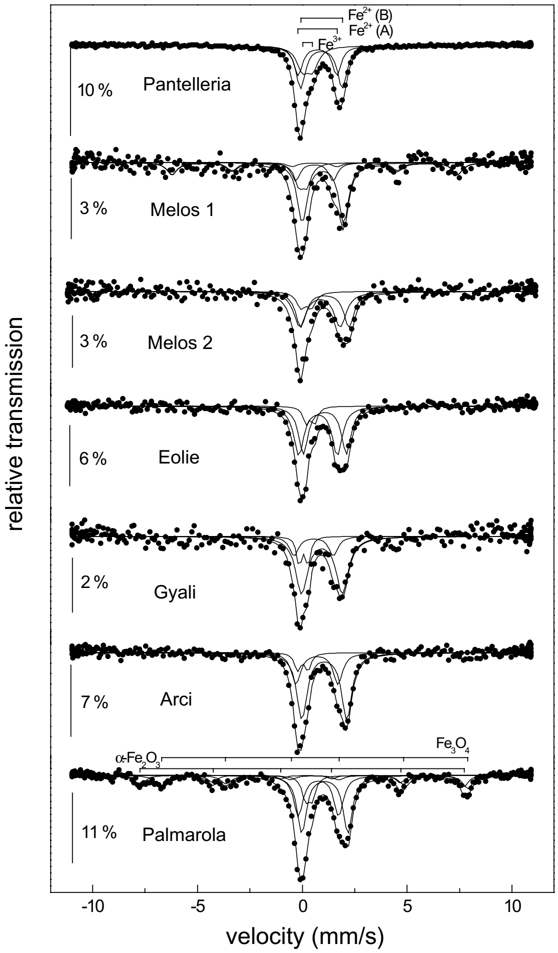

Fig. 1. Room temperature Mössbauer spectra of obsidians from Palmarola, Arci, Gyali, Pantelleria, Lipari and Melos. The solid lines correspond to the least square fitting procedure. The vertical lines on the left are indicative of the percentage of resonant absorption.

3. Results and discussion

The room temperature Mössbauer spectra in Fig. 1 of the above cited obsidian samples are mainly composed by a broad asymmetrical doublet. This doublet was best fitted under the assumption of two symmetrical Fe^{2+} quadrupole signals with different degree of distortion, and a smaller fraction of a Fe^{3+} doublet. These signals are mostly assigned to iron forming part of glass silicates that have different coordination. We identify the Fe^{2+} signals that have an isomer shift (IS) ranging from 0.62 to 0.94 mm/s and, in addition, a quadrupole splitting (QS) ranging from 1.53 to 2.00 mm/s with iron having a tetrahedral coordination (Site A), while the ferrous signal with a IS in the range 1.02 to 1.28 mm/s and a QS ranging from 1.98 to 2.30 mm/s is associated with a octahedral coordination (Site B). It is worth noting that a small percentage of these Fe^{2+} and Fe^{3+} doublets may account for small particles of iron oxides that behave superparamagnetically at room temperature [5]. In some cases, the superposition of Fe^{3+} sites prevents resolution (as in one of the Gyali obsidians). On the other hand, the largest Fe^{3+} concentration is observed for the samples from Pantelleria (≈30% of the resonant absorption).

The Mössbauer spectra of obsidians from Palmarola and Melos (Melos1, from volcanic domes of the Nihia area, from pyroclastes of Mandrakie headland, Adamas, Prophet Ilias and from conglomerates of Adamas beach) also show a minor magnetic component, which we attribute to iron oxides. These magnetic components were taken into account in the fitting procedure when its relative area was greater than 5%. In the case of obsidians from Palmarola, two magnetic sites were resolved and identified with magnetite (Fe_3O_4) (hyperfine field 4.2 T $\leqslant H_{hf} \leqslant$ 4.4 T) and hematite (Fe_2O_3) ($H_{hf} \approx$ 4.8 T), while for Melos only the Fe_3O_4 magnetic signal was detected.

In an attempt to have a preliminary indication of the provenance of these obsidians we used binary plots of different Mössbauer hyperfine parameters. From previous results [1] it is known that binary diagrams are not the best graphical representation to illustrate the differentiation of obsidians from different source islands. Although these plots gave indications of similarities and differences between samples from different origins, it does not allow an unambiguous characterization of obsidians from each island.

The difficulties of representing in two dimensions the correlation between the Mössbauer and magnetization parameters are overcome by using statistical method of clustering analysis in an n-dimensional space. This analysis is in progress and will be published elsewhere.

The magnetic parameters of the samples were obtained from the M vs. H cycles (Fig. 2). The remanent magnetization, M_r, is the amount of magnetization that remains once the sample has been magnetized and the external field turned off. The coercive force, H_c, is the reverse magnetic field strength necessary to demagnetize the sample after being magnetized with a magnetic field H_m, which was $H_m = 1.2$ T in our case. The magnitude of magnetization of saturation (M_s) was obtained by linear extrapolation of the paramagnetic contribution to $H = 0$.

The magnetic response is due to the paramagnetic contribution of the isolated Fe ions in the glassy matrix superimposed on the contribution of

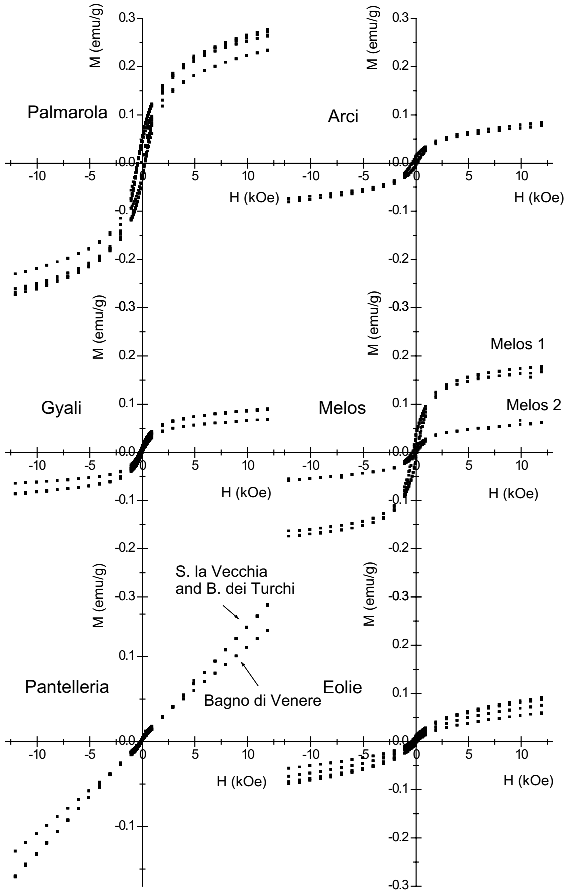

Fig. 2. Magnetization (M) vs. applied field (H) cycles at room temperature of samples from different origins in Palmarola, Gyali, Melos, Pantelleria and Eolie islands and Monte Arci.

magnetically ordered phases, mainly due to ferrimagnetic Fe_3O_4, as evidenced by the hysteresis shown in Fig. 2. The M_s of the samples depends on the island and it reaches a maximum of ~0.3 emu/g for the of Palmarola obsidian samples, due to a larger amount of the magnetic phase. This result is in accordance with the larger relative area of the magnetic signals observed in their Mössbauer spectra.

The samples from Pantelleria have a smaller magnetic response, being mainly due to the paramagnetic ions in the matrix. In addition, we distinguish two populations: (i) Bagno di Venere, where a small hysteresis is visible ($M_r = 1.2 \times 10^{-3}$ emu/g, $H_c = 46$ Oe) and (ii) Salto la Vecchia and

Balata dei Turchi that do not show hysteresis (Fig. 2). This agrees with previous XRF analysis [3].

The magnetic responses of the samples from Arci, Gyali, Eolie indicate the presence of a small percentage of magnetic phases, as evidenced by M_s's values. The range of H_c's values is probably due to the presence of magnetic grains of different sizes and may depend on the provenance.

Amongst Melos obsidians, we resolve two populations from the magnetic measurements: Melos 1 and Melos 2 (see Ref. [3]), the latter having a smaller percentage of magnetic phases (Fig. 2). The Mössbauer spectra show for Melos 1 a magnetic resolved component; while for Melos 2 the presence of magnetic components is below the resolution limit. The discrimination of these two different populations was also detected by the XRF analyses.

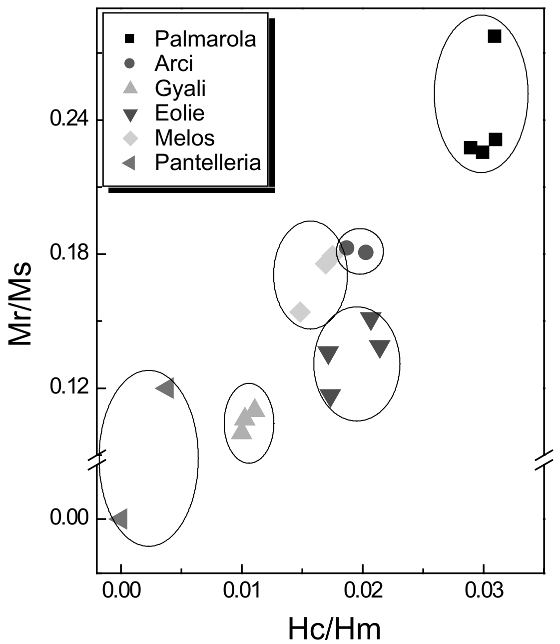

Fig. 3. Plot of the remanent magnetization M_r relative to the saturation magnetization M_s against the coercive force H_c normalized by the maximum applied field, $H_m = 1.2$ T. These parameters were determined from the M vs. H curves shown in Fig. 2. Data belonging to three of the Pantelleria obisidian samples overlap at the origin of the plot, i.e. $M_r = 0$ and $H_c = 0$ for these samples.

To distinguish different regions of provenance we plotted the relative saturation magnetization M_s/M_r vs. the coercive force H_c normalized by the maximum applied field (Fig. 3). We observe that the data corresponding to obsidian specimens from different source-islands are located, with only few exceptions, in discrete areas of the plot indicating different magnetic sources.

We are currently analyzing the classification of the obsidians from different sources using discriminant functions calculated from a multivariate analysis combining the Mössbauer hyperfine parameters, the relative areas of the magnetic phase and the Fe^{3+}/Fe^{2+} ratio, and the hysteresis parameters to apply this alternative approach to provenance studies.

4. Conclusions

Our investigation suggests that Mössbauer and magnetization measurements can be used as alternative methods to classify the source islands of obsidians for provenance studies. By means of Mössbauer spectroscopy we discriminate obsidians from Pantelleria as those containing the largest Fe^{3+} concentration. The Mössbauer spectra of obsidians from Palmarola and Melos also show magnetic components corresponding to magnetite and/or hematite. Binary diagrams of Mössbauer hyperfine parameters discriminates populations from Pantelleria and Palmarola but the same diagram does not allow the differentiation of obsidians from Gyali, Monte Arci, Lipari and Eoli.

From magnetic properties we distinguish obsidians from Palmarola and Pantelleria as those showing the largest and lowest magnetization, respectively. In addition, we distinguish two populations of both Pantelleria and Melos. By means of binary diagrams M_s/M_r vs. H_c/H_m, we were able to discriminate – with only few exceptions – obsidian specimens from different Mediterranean source-islands.

We have shown that the combination of structural and magnetic characterization of obsidians offers a valuable perspective in provenance studies. A better discrimination of different Mediterranean source islands using the Mössbauer and magnetization parameters can be obtained by using a multiparametric statistical method that is in progress.

Acknowledgements

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