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Electron spin resonance of Fe^{3+} ion in obsidians from Mediterranean islands. Application to provenance studies

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Abstract

Archaeological artefacts made of obsidian are all the more precious for archaeologists as they are witnesses of cultural, social or 'economic' relationships between prehistoric populations. The main obsidian sources reachable in these times have been identified and characterized by chemical analysis and fission track dating. Because of iron presence (from 1% to 10% expressed in Fe_2O_3) it is possible to use Mössbauer spectroscopy and electron spin resonance (ESR) on geological samples to characterize different sources. We studied by electron spin resonance about seventy obsidians coming from six Mediterranean volcanic islands. The complex spectra are mainly due to iron in different states and site location (and sometimes isolated Mn^{2+} ions). X-band (9 GHz) spectra exhibit a signal at $g = 4.3$ with a shoulder at 9.8 ascribed to isolated Fe^{3+} in the glassy matrix with a rhombic environment (C_{2v}). Condensed clusters of Fe^{3+} ions give rise to a resonance line at $g = 2.0$ whose position and width do not depend on temperature and in addition to this signal broad resonance lines are ascribed to micro-crystallites of mixed iron oxides (hematite, magnetite and related spinels, titanates, silicates) as inclusions into the amorphous matrix of obsidian. When temperature decreases from 300 to 5 K these signals shift towards weak fields. The contribution of every signal to ESR spectrum is different from one source to the other according to the different thermodynamic conditions that occurred during obsidian formation. It is thus possible to discriminate a priori one geological source using ESR spectra. At room temperature the first differences appear at X-band, low temperatures experiments may allow to remove some ambiguities.

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1. Introduction

Obsidians are volcanic glasses, formed from magmas rich in SiO_2 (>70%), after some expansion in the margins of the flow. They are mainly constituted of a silicate glassy matrix containing

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crystalline inclusions whose composition, size, shape and number vary from one obsidian to another. According to its fracture properties, blades can be made and used as tools and also weapon as far back as Palaeolithic times.

The primary sources of these natural glasses are volcanic areas. The discovery of obsidian artefacts in archaeological sites far away from any possible sources led archaeologists on to ponder on raw material conveyance and on trade routes and (or) population migrations in prehistoric times. Linking up an artefact with a particular source first requires geographical origin determination of each obsidian, which implies that there is a one-to-one relation between a property of an obsidian and its geological source. Each obsidian has its own history which began in the magmatic chamber governed by thermodynamic conditions (pressure, temperature, chemical composition of the medium), followed by variable cooling conditions (duration, atmosphere). Thus the chemical and structural characteristics of obsidian offer clues about their geographical origin. Up to recently, obsidian provenance studies were however essentially based on their elementary composition [1–12] or formation ages [13,14]. The potentialities of structural properties remained largely to be evaluated [15]. Among the methods of element analysis, the most frequently used are neutron activation analysis (NAA) [4–6], X-ray fluorescence (XRF) [7], proton induced X-ray emission (PIXE) [8], scanning electron microscopy linked with an energy dispersion spectrometer (SEM-EDS) [9], inductively coupled plasma-mass spectrometry (ICP-MS) [10,11]. The presence of iron in appreciable amount (1–10% normalized to Fe_2O_3) can play an important role, even if it has not been used from elementary analysis. Iron can exist as ferric ions Fe^{3+} , ferrous ions Fe^{2+} , or sometimes as atomic iron Fe^0 [16]. Furthermore, it is incorporated either within the glassy matrix or within crystalline phases (oxides, silicates, titanates, etc.) which have crystallized during ‘obsidian solidification’. These various locations do not appear in elementary chemical analyses and they depend on particular thermodynamic conditions occurring during obsidian formation. On the contrary, magnetic properties (magnetization, remanence,

susceptibility), Mössbauer effect and electron spin resonance (ESR) should be able to give valuable information for the characterization of obsidians through iron behaviour [15]. Mössbauer spectroscopy is a powerful technique to study the different states of iron. It actually allows to have direct access to valence state, local environment and magnetic ordering occurring sometimes at low temperatures.

In the Western Mediterranean area, it was shown that Mössbauer spectroscopy [17] and magnetic properties [18] could be used for provenance studies. Preliminary EPR data suggested this technique also might have to be considered [5]. In ESR experiments, every (structural, magnetic) situation of Fe^{3+} and (or) Fe^{2+} ions in obsidian exhibits a particular signature which should be characteristic of each source. Furthermore, the presence of other paramagnetic ions may bring additional criteria of discrimination. We present here a comprehensive EPR study bearing on obsidians from all Mediterranean source islands and a test on some obsidian artefacts from Neolithic sites of provenance previously determined. The aim of this work is to evaluate the discriminating capacities of this technique which brings us to the questions: *How are iron states reflected in ESR spectra of obsidians? Is it possible to find criteria for discrimination which are complementary or alternative to chemical analyses and dating?*

2. Experimental

2.1. Sampling

Sixty seven geological samples were studied to check the homogeneity of the ESR behaviour within a source and to reveal its discriminating potentiality. Obsidian samples come from Pantelleria, situated in the Sicilian Channel (six samples from the surrounding of Balate dei Turchi, two from Lago di Venere), Gyalì, a greek Dodecanese island (three samples), Lipari in the Aeolian Archipelago (seven samples from Gabelotto Valley), Milos in the Cyclades (one sample from Demenegaki, two from Adamas area), Palmarola in the Pontine Archipelago (four samples from

Monte della Tramontana), and Monte Arci in Sardinia (13 samples from SA chemical group – Conca Cannas sources, 11 from SB1 group – Punta Nigola Pani and Punta su Zippiri sources, eight from SB2 group – Crucis is Abis sources, 10 from SC group – Perdas Urias, Santa Pinna and Pau sources). Some archaeological artefacts whose origin was known from fission tracks dating and/or chemical composition [19] were examined and compared with the preceding results. Locations of the geological sources and the prehistoric sites are shown in Fig. 1.

Samples were ground to obtain a powder with a grain size in the range of 40–80 μm , then they were treated by acid solution (HCl 1 M/HF 0.5 M) to remove surface defects and carbonated phases.

2.2. ESR experiments

ESR spectra were recorded at X-band (9.5 GHz) or Q-band (34 GHz) with a commercial spectrometer (Brüker ESP300) equipped with a cryostat allowing a temperature range from 300 to 4.2 K. The main experimental parameters were: microwave power 10 mW, conversion time 82 ms per point, 1024 points per spectrum, time constant 5 ms, modulation amplitude 0.80 mT at 100 kHz,

receiver gain optimized according to the intensity level of the signal. The intensities were normalized to a mass of 50 mg and a gain of 10^4 . In this paper, the intensity of an ESR line is in fact the peak-to-peak amplitude of the first derivative of the absorption signal.

3. Results and discussion

The ESR of iron (and other transition ions) in silicate glasses has been the subject of several hundred of articles, two review papers seem to us to describe the situation in the glassy matrix of any obsidian [20,21].

It is known that isolated Fe^{2+} ion with electronic configuration d^6 is observable by ESR only at very low temperatures (<5 K) because of spin-orbit coupling which induces a very short relaxation time at higher temperatures [22]. The ESR signal of Fe^{3+} ion with configuration d^5 is characteristic of its local symmetry and gives rise to different signals, depending on the various forms in which this ion is involved.

Isolated Fe^{3+} ions which are diluted in a homogeneous way in the glassy matrix: it appears at X-band a line at $g_{\text{eff}} \approx 4.3$ with a shoulder at about



Fig. 1. Location of the Mediterranean sources of raw material (circles) for obsidian tool making and location of the prehistoric sites (crosses) where artefacts studied in this work were collected.

$g_{\text{eff}} \approx 9.8$ which is characteristic of a C_{2v} symmetry due to non-axial distortion of an octahedron or a tetrahedron [23]. Its line width is determined, in part, by dipolar interactions [24] and thus increases with isolated Fe^{3+} concentration following Van Vleck's relation [25]:

$$\Delta B_{\text{dip}} = 2g\beta \left[(3/5)S(S+1) \left(\sum_k r_{jk}^{-6} \right) \right]^{1/2},$$

where g is the gyromagnetic ratio of Fe^{3+} ion, β is the Bohr magneton, S is the spin of Fe^{3+} ion and r_{jk} is the distance between an ion Fe^{3+} in position j and an ion in position k , the summation is over all neighbours of ion j . Since the distance contribution to ΔB_{dip} varies as r_{jk}^{-3} , the dipolar line width can be thus considered as proportional to isolated Fe^{3+} concentration by assuming an homogeneous distribution in a continuous medium (hypothesis valid at low concentrations). Isolated Fe^{3+} concentration depends on the overall iron concentration in the obsidian, but it is also related to the cooling or annealing conditions as was shown in studies on synthetic silicate glasses [24,26]. It could thus be a discriminatory criterion between obsidian sources. A signal involving an axial symmetry (D_{4h} , D_{3d} ?) may be observed with the g values: $g_{\perp} \approx 6$ and $g_{\parallel} \approx 2$ [26].

Condensed Fe^{3+} ions which form clusters of several units with an antiferromagnetic coupling are responsible for a signal at $g = 2$ [27,28]. Its line width (usually 50 mT) is almost independent of temperature and depends on dipolar and exchange contributions [22]. When the coupling leads to ferro or ferrimagnetic short range ordering, these nano-clusters may have superparamagnetic properties [29].

Iron oxides micro-crystals (about 1 μm) and single domain nano-crystals (spherical particles smaller than 100 nm) give rather wide resonance lines which move towards weak fields when temperature decreases [30]. The width of the signals attributed to crystalline inclusions may sometimes extend over the studied spectral domain.

ESR spectra of obsidians are a consequence of the variety of situations in which iron may occur (Fig. 2).

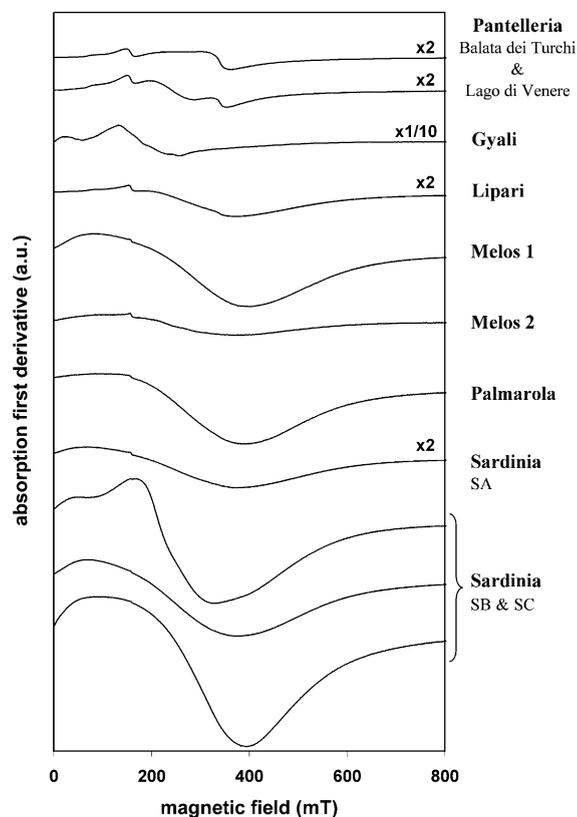


Fig. 2. Characteristic ESR X-band spectra (at room temperature, $\nu = 9.5$ GHz) of obsidian samples from respectively Pantelleria BT (Balata dei Turchi) and LV (Lago di Venere), Gyalì, Lipari, Melos 1 (Adamas) and 2 (Demenegaki), Palmarola and Sardinia SA (Conca Cannas), SB (Monte Arci West) and SC (Su Varongu).

3.1. Crystalline inclusions

At room temperature, X-band experiments show that crystalline inclusions are mainly responsible for the observed ESR spectra shapes, with the exception of Pantelleria samples whose spectra have a signal which is mainly due to the glassy matrix. The broad lines are due to various magnetic phenomena (dipolar or pseudo-dipolar broadening, exchange interaction, field anisotropy, demagnetising field, size and shape effects) [22] which may occur in each magnetic crystal inclusion. Thus, an ESR spectrum can be considered as the sum of contributions due to the micro-crystals (hematite, magnetite, pseudo-brookite, illmenite,

iron silicates, etc), each phase adding its own contribution. The diversity of these species distribution appears by simple inspection of the spectra (Fig. 2). Hence, we can easily propose a first partial discrimination among the Mediterranean obsidians.

A source easy to be recognized is Gyalì, whose spectra are characterized by a rather complex main line at relatively weak fields ($B_{\text{res}} = 180$ mT at RT). Lipari (Aeolian island) source gives rise to a broad component at $B_{\text{res}} = 260$ mT whose low intensity lets appear the signal at $g = 4.3$ – 9.8 . The samples from Melos, Palmarola, Sardinia Monte Arci South–West (SA), most of North–East (SC) and some of West zone (SB) have similar spectra, mainly constituted by an approximately isotropic line (width ~ 50 mT) which remains unresolved even when the temperature is decreased to 5 K. Singularities as multiple peaks or shoulders appear in this broad line for some Sardinian obsidians from SB and SC sources (see details Fig. 2).

To give a quantitative picture of this qualitative inspection, diagrams have been set up involving the main relevant parameters which govern the magnetic crystal contribution of ESR spectra, i.e. the values of the resonance field, B_r , the peak-to-

peak line width, ΔB , and the peak-to-peak intensity (amplitude), $I_{\text{p-p}}$, of these isotropic broad lines. As an example, $I_{\text{p-p}}$ versus ΔB is plotted for all the samples except those from Sardinia (SB or SC) which have been yet discriminated by their ‘anomalous’ line shapes (Fig. 3). In this diagram we observe a rather good resolution, the division of SC sources into three subgroups, and unresolved ambiguities concerning the spectra of Sardinia SB, Melos and Palmarola samples. Beside the crystal inclusions it is also pertinent to compare the spectra of Fe^{3+} in glassy materials to spectra from synthetic silicate glasses [30].

3.2. Fe^{3+} ions in the glassy matrix

We observed similar spectra within each source except for those of samples from Sardinia (SB and SC groups of sources). The ESR signal at $g = 4.3$ with a shoulder at 9.8 attributed to isolated iron (III) ions in C_{2v} symmetry appeared in most of studied obsidians, although it is sometimes masked at room temperature by the more intense wide line due to crystalline inclusions involving magnetically coupled Fe^{3+} and (or) Fe^{2+} ions (Fig. 2). Pantelleria sources are well discriminated by the

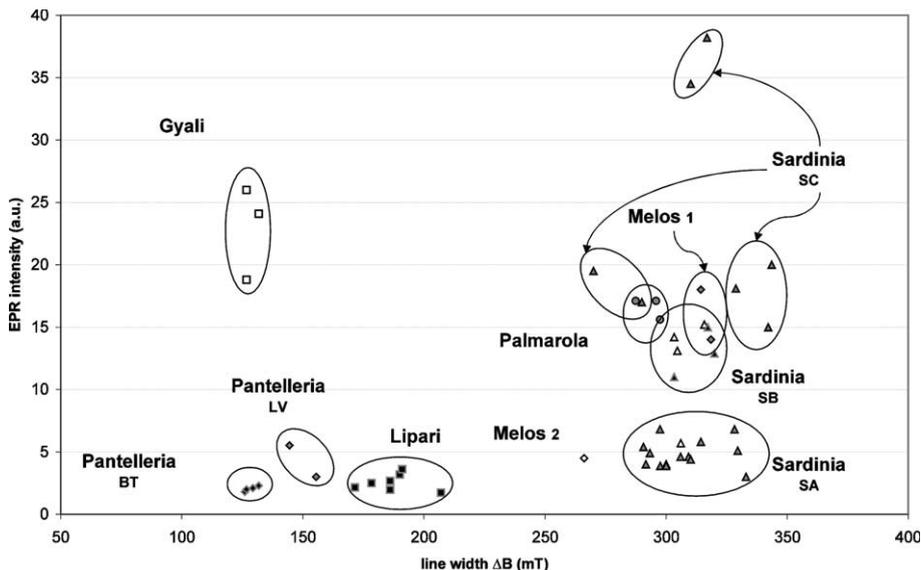


Fig. 3. Intensity (amplitude of first derivative absorption signal) versus line width of the broad signal mainly due to magnetic crystalline inclusions. All the samples were taken into account except those coming from Sardinia (SB or SC).

well-resolved signals at $g = 4.3$ – 9.8 , which are the dominant contribution to the spectrum that also includes a peak at $g = 2.0$ and an associated shoulder at $g = 2.19$. Furthermore, two subgroups can be distinguished: Salto la Vecchia and Balate dei Turchi (called here BT), and Lago di Venere (LV); the latter shows an extra broad line which is shifted towards low fields when the temperature decreases, and disappears below 200 K.

For the samples from other sources the intense broad line due to magnetically concentrated crystalline inclusions made the glassy signals difficult to be detected but they were revealed at 5 K, sometimes together with the hyperfine sextuplet of Mn^{2+} ions (Fig. 4). At 5 K all the studied obsidians exhibited the signal at 4.3–9.8. A line at $g_{\text{eff}} \approx 6$

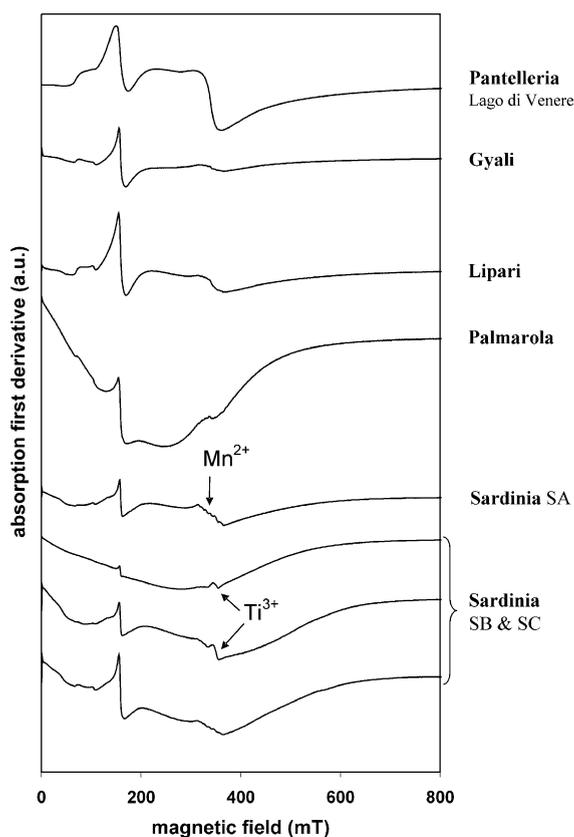


Fig. 4. Characteristic ESR X-band spectra (at 4 K, $\nu = 9.5$ GHz) of obsidian samples from respectively Pantelleria LV (Lago di Venere), Gyali, Lipari, Melos 1 (Adamas) and 2 (Demenegaki), Palmarola and Sardinia SA (Conca Cannas), SB (Monte Arci West) and SC (Monte Arci East).

was also observed for most of the samples with a very low relative intensity, and beside these signals, one can often observe a signal at $g = 2.0$ due to condensed Fe^{3+} ions with a line width B (between 46 and 53 mT) resulting from combined effect of dipolar broadening and magnetic exchange between nearest neighbour Fe^{3+} ions. According to studies of synthetic glasses, the coexistence of isolated and condensed Fe^{3+} ions depends on iron concentration and thermal treatments [29].

Some samples exhibited at 5 K a peak centred at $g = 1.93$ which unambiguously characterizes trivalent titanium Ti^{3+} in silicate glasses [30,31]. The presence of titanium(III) implies strong reducing conditions during the formation of the concerned obsidians rather than natural radiations. Actually, the defects, involving Ti^{4+} , formed by natural radiations (electron trapping on Ti^{4+}) give more complex signals with hyperfine structures due to interactions with nuclear spins of charge compensators (H^+ , Li^+ , Na^+) [32].

As was done for magnetic crystalline inclusions, it was also possible to draw diagrams involving the line width and the intensities of $g_{\text{eff}} = 4.3, 6, 2.0$ and 1.93 signals i.e. eight parameters. This procedure not only confirmed the precedent discrimination but moreover it allowed to well characterize Palmarola and Milos 1. However, such procedures were not suitable to clearly discriminate SB and SC.

3.3. Application to archaeological artefacts

Ten obsidian artefacts (mainly cutting scraps) coming from Mediterranean Neolithic sites (Fig. 1) have been studied by ESR using the procedure described above. Their provenance were determined by fission tracks dating [19] and Mössbauer spectroscopy [17]. Three archaeological samples (from Villaggio Mursia and Lampedusa) were attributed to Pantelleria BT (Balate dei Turchi), five others (from Filicudi, Serra d'Alto and Lipari Scavo) to Lipari (Gabelotto Valley), but for two samples from Isola del Giglio these methods led to ambiguity between Palmarola and Lipari. ESR study of these artefacts is in good agreement with the known provenances proposed by the methods mentioned hereinbefore. Concerning the archaeological samples from Isola del Giglio, ESR

experiments allowed us to clearly attribute one sample to Gabelotto sources (Lipari) and one other to Monte della Tramontana sources (Palmarola).

4. Conclusion

The previous results show that obsidians from certain obsidian sources of Mediterranean islands can be discriminated by ESR spectra (evaluating the relative contributions of iron in the glassy matrix and iron in the crystalline inclusions) especially Pantelleria BT and LV, Palmarola, Melos 1 and 2, Gyali, Lipari and Sardinia SA area. The case of obsidians from sources of the SB and SC chemical groups is more complex even if we have observed subdivisions already proposed from trace elements analyses. Moreover, Q-band experiments in progress (to be published) are already giving promising results to discriminate the samples of the different sources corresponding to SB and SC compositional groups.

The advantage of an approach using ESR lies in its ease of implementation, its low operating cost compared with elementary analysis methods (ICP-MS for example) and above all, its speed (about 3 min for a spectrum) in studies of a huge number of samples. It could also be used as a preliminary test before more complex studies involving chemical analyses or fission tracks dating.

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