

Provenance study of obsidians from the archaeological site of La Maná (Ecuador) by electron spin resonance (ESR), SQUID magnetometry and ^{57}Fe Mössbauer spectroscopy

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Published online: 6 May 2008
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Abstract Obsidians from major Ecuadorian sources (outcrops) were analyzed by electron spin resonance, SQUID magnetometry and ^{57}Fe Mössbauer spectroscopy. If the last technique allows to discriminate obsidians from the Quiscatola source, an association of ESR with SQUID magnetometry permits to differentiate obsidians from the sources of Cotopaxi volcano, from the Quiscatola and Mullumica-Callejones sources of the Chacana caldera and to infer that the 12 analyzed obsidians from the pre-Hispanic site of La Maná come from the Mullumica-Callejones source.

Keywords Obsidian · Electron spin resonance · Magnetic properties · ^{57}Fe Mössbauer spectroscopy · Obsidian provenance · Ecuador

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1 Introduction

Obsidian is a dark volcanic glass ($\text{SiO}_2 > 65\%$) used by prehistoric populations to produce various kinds of tools, arrowheads, ritual objects, etc. The ‘sources’ (outcrops) of raw material are often situated far away (up to several hundreds of kilometers) from the archaeological sites where obsidian artifacts are discovered. Thenceforward the determination of the geographical origin of ‘archaeological’ obsidians provides valuable information about the selection of lithic resources by ancient human groups and eventually about the existence of communication routes and exchange networks. This kind of ‘provenance’ study is based on the comparison of specific properties of archaeological vs. geological samples collected in potential sources (i.e. reachable at the considered archaeological periods). These comparisons may bear on the elemental compositions, the formation ages and/or the structural properties of obsidians.

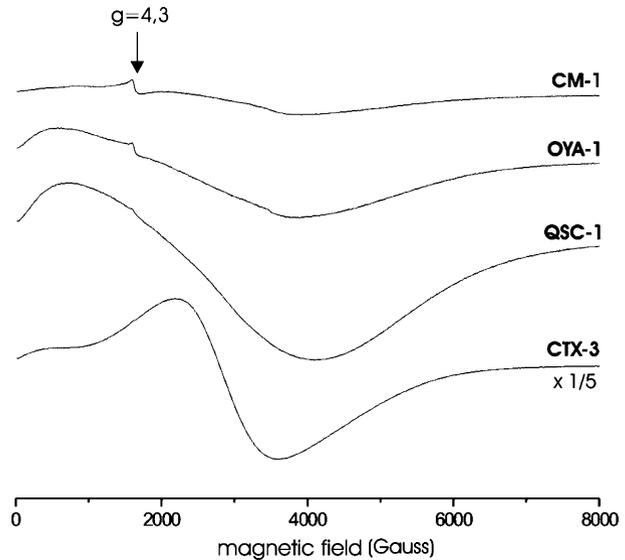
In Ecuador, earlier obsidian provenance studies were based on elemental composition [1] fission track (FT) dating [2] or both [3, 4]. We introduce here a new approach, using electron spin resonance (ESR), SQUID magnetometry and ^{57}Fe Mössbauer spectroscopy (^{57}Fe -MS), which already proved their capabilities for obsidian provenance studies in the Western Mediterranean area [5–7]. This first test-program compares archaeological samples from the pre-Hispanic site of La Maná [8] to source samples whose FT age and/or elemental composition were previously determined [2–4, 9, 10].

2 Sampling and experimental conditions

The analyzed obsidians come mostly from the Mullumica (six samples, CM and CSM) and Callejones or Oyacachi (four samples, OYA) lava flows, from the Quiscatola or Yanaurcu sources (two samples, QSC) and from the river bed of the Rio Guambi (two samples, GMB). The Rio Guambi source is a secondary deposit, where obsidians eroded from the Mullumica flow are found as rounded pebbles. The Mullumica-Callejones lava flows and the Quiscatola-Yanaurcu volcanic breccias, localized in the Sierra de Guamani (Eastern Andean Cordillera, some 30 km E of Quito, Ecuador) belong to a major volcanic structure, the Chacana caldera [10]. Six other samples (CTX) come from various pyroclastic units associated to the Cotopaxi volcano, 50 km SE of Quito. The archaeological samples come from the *tolá* (artificial mound) site of La Maná, localized between the Ecuadorian cities of La Cadena and Quevedo (about 140 km SW of Quito). This site was occupied from the Early Formative (3,600–1,800 B.C.) until the Spanish conquest (sixteenth century). In Ecuador, nearly all archaeological obsidians come from the sources of the Sierra de Guamani [1–4].

ESR spectra were recorded in X-band frequency (9.75 GHz) with a commercial spectrometer (Brüker). The main experimental parameters were: microwave power 10 mW and modulation amplitude 8.0 G at 100 kHz. The magnetization curves (M vs. H cycles where M is the magnetization and H the applied field) were obtained under a maximum applied field of 1.2 T using a commercial SQUID magnetometer (Quantum Design). Mössbauer transmission spectra were collected with conventional spectrometer using a standard γ -source $^{57}\text{Co}/\text{Rh}$ (activity 50 mCi). The spectra were fitted using the NORMOS program. All measurements were performed at room temperature.

Fig. 1 Examples of X-band room temperature ESR spectra of Ecuadorian obsidians



3 Results and discussion

The X-band ESR spectra of the geological samples are mainly composed of three different signals: a broad (peak-to-peak line width ΔH_{pp} ranging from 2,000 to 3,200 G) and intense resonance line due to micro-crystallites of mixed iron oxides (hematite, magnetite and related spinels), a narrower signal ($20 \text{ G} \leq \Delta H_{pp} \leq 175 \text{ G}$) at $g_{\text{eff}} \approx 4.3$ with a shoulder at about $g_{\text{eff}} \approx 9.8$ associated to isolated Fe^{3+} ions in the glassy matrix and another line at $g \approx 2$ ascribed to Fe^{3+} condensed clusters [6] (Fig. 1). For each sample the peak-to-peak amplitude (I_{pp}) and line width (ΔH_{pp}) of these three components were measured using combined simulation and fitting procedures. As a preliminary result, the detection and quantification of the $g=4.3$ line allow one to separate the Cotopaxi obsidians from the others.

From the magnetization experiments (cycles M vs. H), several parameters were measured: the magnetization at saturation (M_S), the remanent magnetization (M_R), the coercive field (H_C) and the susceptibility (χ). Significant variations of the magnetization at saturation, from 0.009 to 0.470 emu/g and of the coercive field, ranging from 95 to 210 Oe, were observed among all the samples analyzed. These two parameters separate clearly the Quiscatola obsidians from the other Ecuadorian obsidians.

The ^{57}Fe -MS spectra of geological samples are mainly composed of doublets, associated to Fe^{3+} and Fe^{2+} in two different sites and, for some samples, sextets attributed to iron oxides (hematite and/or magnetite) (Fig. 2). Multivariate statistical analysis using cluster analysis methods in an n -dimensions space was used to differentiate the Ecuadorian obsidians from Mössbauer hyperfine parameters, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and the relative contribution of the magnetic components in the MS spectra. Only Quiscatola obsidians can be clearly distinguished from the other samples.

It is therefore possible to distinguish the Mullumica-Callejones, the Quiscatola and the Cotopaxi obsidians if an ESR- ^{57}Fe -MS or an ESR-SQUID magnetometry coupling is

Fig. 2 Typical room temperature Mössbauer spectra for Ecuadorian obsidians. The *solid lines* show the results of the fitting procedure

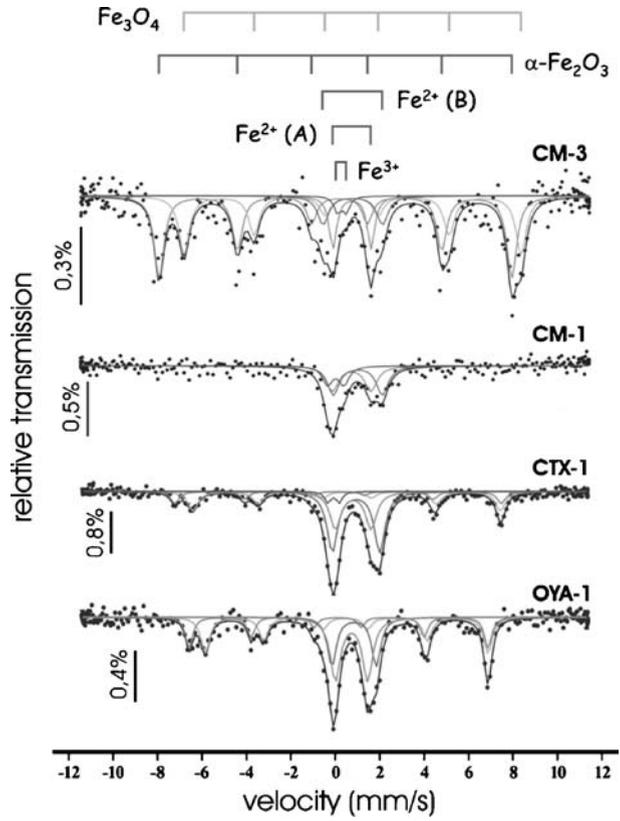
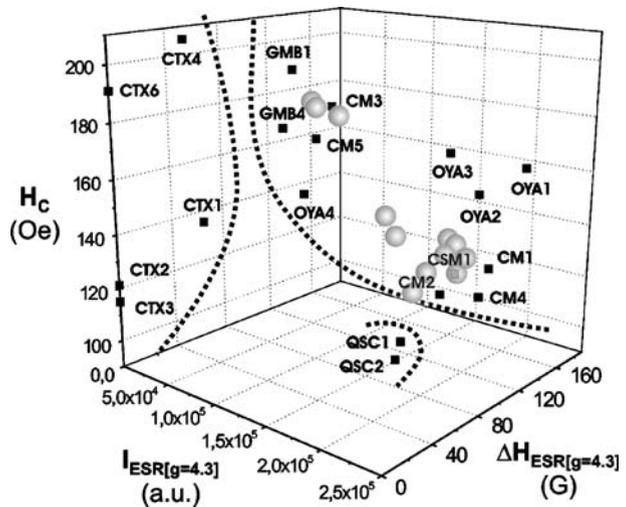


Fig. 3 3D diagram involving ESR (peak-to-peak intensity of the $g=4.3$ line, I_{ESR} , and its line width, ΔH_{ESR}) and magnetization parameters (coercive field, H_c) for Ecuadorian obsidians. The La Maná archaeological samples are represented by *gray spheres*



used. In the later case several 3D diagrams can discriminate obsidians of these sources. As an example, the Fig. 3 show that it is possible, using two ESR parameters $I_{\text{ESR}[g=4.3]}$, $\Delta H_{\text{ESR}[g=4.3]}$ and H_C , to differentiate the Cotopaxi, the Quiscatola and the Mullumica-Callejones-Guambi obsidians. The dispersion of data points for the later might be due at least partly to the fact that the Mullumica and Callejones flows result from the incomplete mixing of two parent-magmas shortly before the eruptive episodes as demonstrated by their elemental composition [10].

Twelve archaeological samples from La Maná were analyzed by ESR and by SQUID magnetometry. All these obsidians can be attributed to the Mullumica-Callejones source (Fig. 3), in agreement with their elemental composition [11].

4 Conclusion

ESR and SQUID magnetometry appear as promising techniques for obsidian provenance studies in the Ecuadorian Andean belt. These methods are particularly attractive for their low cost, simple sample preparations (powders) and short data acquisition times. Moreover, their coupled use need only an aliquot of <50 mg. Mössbauer spectroscopy of ^{57}Fe may also contribute to source discrimination, but its need of a 250-mg powder and a long data acquisition time will limit its use as a complement in doubtful cases.

An extended on-going program on obsidians from other (Peruvian to Colombian) Andean sources is in progress, which will allow us to more fully evaluate the potentials and limits of these techniques in provenance studies.

Acknowledgements This work was supported by the Centro Brasileiro de Pesquisas Físicas, Brazil. M.D. is indebted to the CNPq for financial support during his stay at CBPF.

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