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# Magnetic properties and electron spin resonance of Ecuadorian obsidians. Application to provenance research of archeological samples

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## Abstract

Obsidians from major Ecuadorian sources were analyzed by SQUID magnetometry and electron spin resonance (ESR). The association of these two techniques permits to differentiate obsidians from the sources of Cotopaxi volcano and from the Quiscatola and Mullumica–Callejones sources of the Chacana caldera, taking into account various parameters arising from the  $M$  vs.  $H$  cycles and the X-band ESR spectra. The analysis of 27 archeological samples coming from the prehispanic site of La Maná allowed us to infer that most of them come from the Mullumica–Callejones source.

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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 archeological sites where obsidian artifacts are discovered. Hence, the determination of the geographical origin of ‘archeological’ obsidians provides a wealth of information about the selection of lithic resources by ancient men and eventually about communication routes and exchange networks. This kind of ‘provenance’ study is based on the comparison of specific properties of archeological vs. geological samples collected in potential sources. These comparisons may be based 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) and SQUID magnetometry, which already proved their capabilities for obsidian provenance studies in the Western Mediterranean area [5–7]. This first test-program compares archeological samples from the prehispanic site of La Maná [8] to source samples whose FT age and/or elemental composition were previously determined [2–4,9,10].

## 2. Samples and experimental conditions

In Ecuador, nearly all archeological obsidians come from only two sources [1–4], 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). They belong to a major volcanic structure, the Chacana caldera [10]. Another potential obsidian source is the Cotopaxi volcano, 50 km SE of Quito. The obsidians analyzed come mostly from the Mullumica (six samples, CM and CSM) and Callejones (four samples, OYA) flows, from the Quiscatola sources (two samples) 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

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Mullumica flow are found as rounded pebbles. Six other samples (CTX) come from various pyroclastic units associated to the Cotopaxi volcano. The archeological samples come from the *tola* (artificial mound) site of La Maná, localized in the coastal plain to the West of the Andean cordilleras, between the cities of Quevedo and La Cadena. It was occupied by prehispanic groups from the Early Formative (3600–1800 B.C.) until the Spanish conquest (XVIth century).

ESR spectra were recorded in X-band frequency (9.75 GHz) with a commercial spectrometer (Bruker). The main experimental parameters were: microwave power 10 mW and modulation amplitude 1 mT at 100 kHz. Receiver gain was optimized according to the intensity level of the signal. A 25–30 mg of fine powder (granulometric fraction smaller than 37 μm) was used for ESR analyses.

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). About 30 mg of powder is required for these experiments which lasted about 3 h per sample.

### 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  $\Delta H_{pp}$  ranging from 0.2 to 0.32 T) and intense resonance line due to micro-crystallites of mixed iron oxides (hematite, magnetite and related spinels), a narrower signal ( $2 \text{ mT} \leq \Delta H_{pp} \leq 17.5 \text{ mT}$ ) at  $g_{\text{eff}} \approx 4.3$  with a shoulder at about  $g_{\text{eff}} \approx 9.8$  associated to isolated  $\text{Fe}^{3+}$  ions in the glassy matrix and another line at  $g \approx 2$  ascribed to

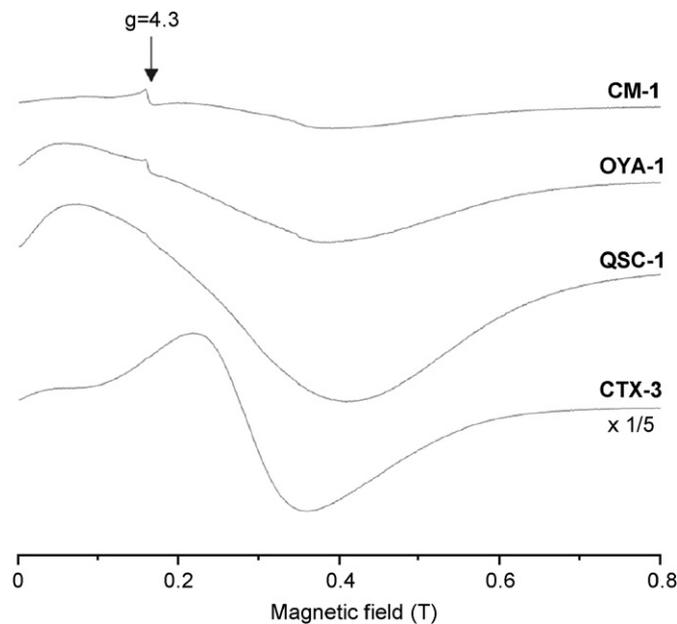


Fig. 1. Examples of X-band room temperature ESR spectra of Ecuadorian obsidians.

$\text{Fe}^{3+}$  condensed clusters [6] (Fig. 1). For each sample, the peak-to-peak amplitude ( $I_{pp}$ ) and line width ( $\Delta H_{pp}$ ) 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 coercitive field ( $H_C$ ) and the susceptibility ( $\chi$ ) (Fig. 2). Significant variations of the magnetization at saturation, from 0.009 to  $0.470 \text{ A m}^2/\text{kg}$  and of the coercitive field, ranging from 7.6 to  $16.7 \text{ kA/m}$ , were observed among all the samples analyzed. These two parameters separate clearly the Quiscatola obsidians from the other Ecuadorian obsidians. Examples of magnetization curves are given in Fig. 2.

It is therefore possible to distinguish the Mullumica–Callejones, the Quiscatola and the Cotopaxi obsidians if an ESR–SQUID magnetometry coupling is used. Several 3D diagrams can discriminate obsidians of these sources. As an example, Fig. 3 shows 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

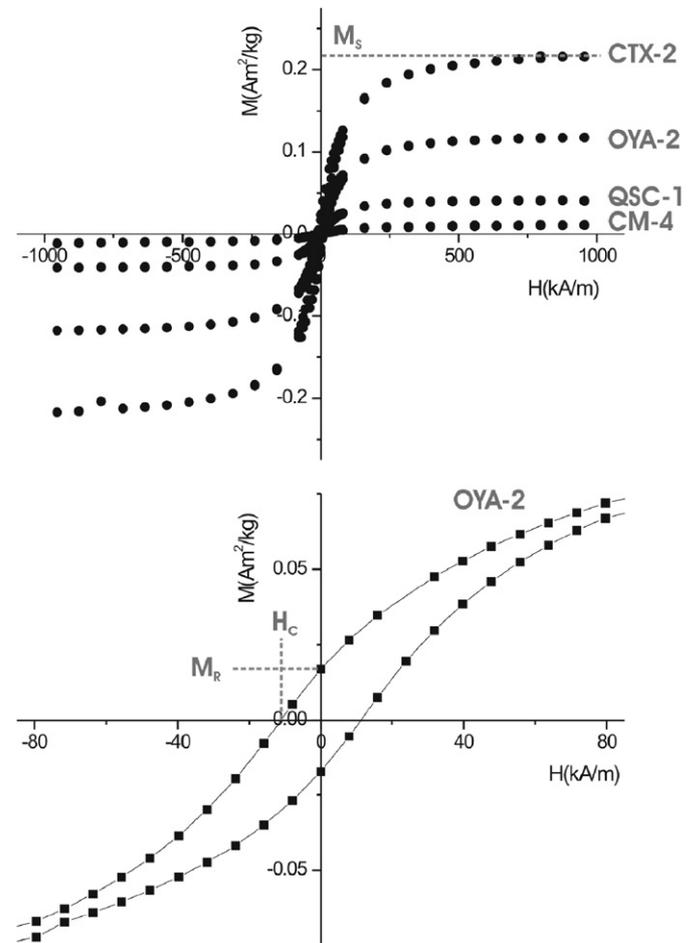


Fig. 2. Typical room temperature  $M$  vs.  $H$  cycles of Ecuadorian obsidians (maximum applied field of 1.2 T).

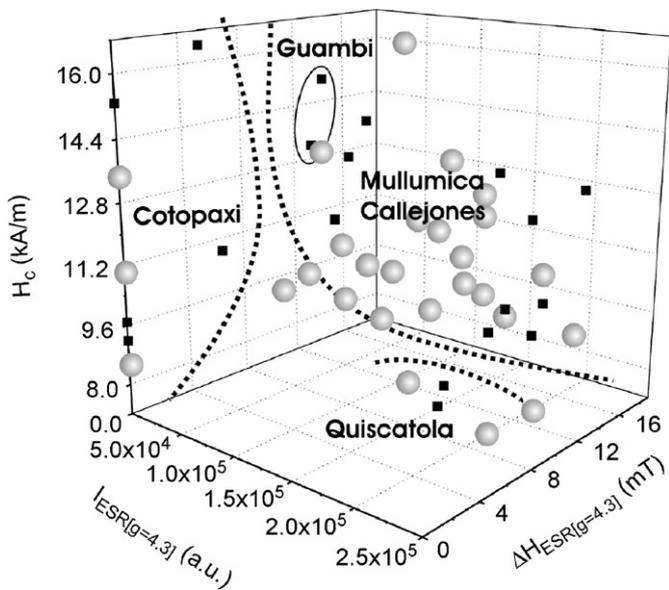


Fig. 3. 3D diagram involving ESR (peak-to-peak intensity of the  $g = 4.3$  line,  $I_{\text{ESR}}$ , and its line width,  $\Delta H_{\text{ESR}}$ ) and one of the magnetization parameters (coercive field,  $H_c$ ) for Ecuadorian obsidians. The geological samples are represented by black points and the La Maná archeological samples by gray spheres.

data points for the latter 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].

Twenty-seven archeological samples from La Maná were analyzed by ESR and by SQUID magnetometry. Almost all these obsidians can be attributed to the Mullumica–Callejones source, and only two groups of three samples each may be related to the Cotopaxi and Quiscatola sources (Fig. 3). These results are in good agreement with their elemental composition [11].

#### 4. Conclusion

ESR and SQUID magnetometry appear as promising techniques for obsidian provenance studies in the Ecu-

dorian Andean belt. These methods are particularly attractive for their low cost, simple sample preparations (powders) and short data acquisition times. Moreover, their coupled use needs only an aliquot of  $< 50$  mg. Another technique, the Mössbauer spectroscopy of  $^{57}\text{Fe}$ , may also contribute to source discrimination, but its need of at least 250 mg of powder and a long data acquisition time 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.

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