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Iron (hydr)oxide nanocrystals in *raw* and *burnt* sienna pigments

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Abstract: The mineral pigments *raw sienna* and *burnt sienna*, known as bolar earths, mostly consist of iron (hydr)oxides; the two pigments, yellow and red-brown respectively, differ for thermal processing of the raw material.
Sixteen bolar earth samples from a quarry in Monte Amiata and from the Accademia dei Fisiocritici Museum were investigated by XRD, SEM-EDS, TEM-EDS, thermal treatment, TG/DTA and DRIFT.

Raw sienna is yellow to brown and prevalently contains goethite. *Burnt sienna* is red and consists of hematite obtained by dehydration of goethite at around 270°C. Chemical analyses show dominant Fe_2O_3 (53.5-71.5 wt.%), with minor SiO_2 (3.0-24.7 wt.%) and Al_2O_3 (0.8-7.1 wt.%). A very high arsenic content characterizes all the samples (with a mean of 5.6 wt.% As_2O_5). Goethite and hematite occur as finely dispersed nanocrystals, respectively 2-10 nm and 10-40 nm in size. They are enclosed in a minor amorphous silica matrix, with arsenic adsorbed on the iron (hydr)oxide nanoparticles. Due to its high arsenic content, the ochre used to produce *raw* and *burnt sienna* is an important example of an effective natural sink for arsenic.

Key-words: *raw* and *burnt* sienna, goethite, hematite, arsenic.

Introduction

Clay earth pigments generally consist of naturally-occurring metal oxide or hydroxide colorants dispersed in small quantities in a clay base. They have been used in painting since Palaeolithic times (15,000 years ago), as the cave paintings of Altamira (Spain) and Lescaux (France) testify (Pomies *et al.*, 1999). The technological processes used to produce pigments have been documented through the centuries by many authors: *Theophrast*, *Vitruvius*, *Pliny the Elder* in Antiquity, *Heraclius* ("De coloribus et artibus Romanorum") and *Cennino Cennini* ("Il libro dell'arte") in the Middle Ages, *Vannoccio Biringuccio* ("De La Pirotechnia") and *Cipriano Piccolpasso* ("Li tre libri sull'arte del vasaio") in the Renaissance.

In Italy, deposits of clay earth pigments occurred in the ochreous sediments of southern Tuscany (Monte Amiata, near Siena), which were exploited for the production of two pigments known as *raw sienna* and *burnt sienna* ("*Terra di Siena naturale*" and "*Terra di Siena bruciata*" in Italian). These names evidently refer to the provenance and technological processing of the earth, but are now used for all pigments with similar tinting properties.

Widely exploited for industrial commerce in the 19th and 20th centuries (up to 50,000 tons; Fei, 1997), the *sienna* pigments were largely used by the most important Tuscan artists of the Middle Ages and the Renaissance (*e.g.*, Duccio di Buoninsegna and Ambrogio Lorenzetti). In contrast to other clay earth pigments, *raw* and *burnt sienna* are bright colours with a high coating efficiency (Moretti, 1937; Harley, 1982; Scarzella & Natale, 1989).

Raw sienna is generally divided into *yellow earths* and *brown boles*, plus intermediate yellow to brown *bolar earths ("terre bolari"* in Italian).

After extraction from the quarry, yellow earths were dried in the sun for several days before grinding and then trading; brown boles were kept closed in shelters for a longer period (Giannetti, 1873). After heating, the raw bolar earths changed colour from light yellow to pale red and from brown to dark red.

Yellow earths and brown boles deposited as ochreous lacustrine sediments within small basins in the Middle Pleistocene trachydacitic formation of the Monte Amiata volcanic area (Ferrari *et al.*, 1996; Fig. 1). They resulted from the low-temperature, hydrothermal solute-rich fluids subsequent to the late volcanic stage. These iron-rich fluids fed small streams which flowed into the basin (as first noted by Gasperini, 1906).

Several factors, such as pH and water temperature, redox conditions, and biological and chemical activity, regulated the accumulation of the iron-rich stratified deposits, which are up to 13 meters thick. The dominant role of biological and/or chemical controls in the precipitation of bolar earths has been widely discussed in the past. Based on chemical analyses and direct observation of micro-organisms such as *Bacillus ferrooxidans* (originally

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