Magiber Magnetismo da Ibéria

Mineralogia magnética das estalagmites da Gruta da Cerâmica, Portugal

Magnetic mineralogy of stalagmites from the Cerâmica Cave, Portugal.

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Resumo
Os espeleotemas são potenciais candidatos para reconstruções paleomagnéticas e paleoclimáticas. No caso de os minerais magnéticos possuírem uma origem litogénica ou pedogénica, a sua concentração nas camadas de calcite das estalagmites é influenciada por parâmetros paleoclimáticos e paleoambientais, como precipitação, vegetação e erosão do solo. Neste estudo, investigamos a mineralogia magnética de estalagmites da Gruta da Cerâmica, Ansião, Centro de Portugal, assim como de sedimentos do interior da gruta e de subsuperfície. Foram realizadas análises as propriedades magnéticas, da composição isotópica de carbono e oxigénio, além da composição química através a fluorescência de raio-X. Os resultados indicam que a magnetite e a hematite são os principais minerais magnéticos presentes nas estalagmites, enquanto os sedimentos da gruta e da cobertura sedimentar contem essencialmente magnetite. Sugerimos que a hematite seja primária, sendo concentrada na estalagmite através de um processo de filtragem durante o transporte através do solo e do sistema cárstico ou seja secundária e formada pela oxidação química de minerais magnéticos primários depositados na superfície da estalagmite. valores mais negativos de isótopos de oxigénio e carbono estão associados a maiores concentrações de magnetite, sugerindo uma origem primária para a magnetite cuja concentração é possivelmente controlada por fatores climáticos e ambientais.

Abstract
Speleothems are potential candidates for paleomagnetic and paleoclimatic reconstructions. In case the magnetic minerals have a lithogenic or pedogenic origin, their concentration in the calcite layers of the stalagmites is influenced by paleoclimatic and paleoenvironmental parameters, such as precipitation, vegetation, and soil erosion. We investigated the magnetic mineralogy of stalagmites from the Cerâmica Cave, Ansião, Central Portugal, as well as cave sediments and sediments from the subsurface. Analyzes of the isotopic composition of carbon and oxygen were conducted, in addition to the chemical composition through X-ray fluorescence. The results indicate that magnetite and hematite are the main magnetic minerals present in stalagmites, while the sediments of the cave and the sedimentary cover are more dominated by magnetite. We suggest that hematite is either primary, being concentrated in the stalagmite through a process of filtering during transport through the soil and the karst system or is secondary and formed by chemical oxidation of primary magnetic minerals deposited onto the stalagmite surface. more negative oxygen and carbon isotope values are associated with higher concentrations of magnetite, suggesting a primary origin for magnetite whose concentration is possibly controlled by climatic and environmental factors.

Palavras-chave: *espeleotemas, magnetismo de rocha, isótopos estáveis, hematite.*
Key words: *speleothem, rock magnetism, stable isotopes, hematite*

Introduction

Speleothems are secondary cave deposits formed in karst environments. They provide valuable sources of information about past climate changes when accurately dated using radiometric methods (Fairchild & Baker, 2012). In addition, speleothems contain magnetic minerals, primarily lithogenic or pedogenic magnetite, transported from the upper soils and deposited within the calcite layers according to the Earth's magnetic field direction (Lascu & Feinberg, 2011; Font et al., 2014). Other authors suggested that secondary magnetic minerals can be formed in the stalagmites by chemical processes or by crystallization alteration of primary minerals during or after their deposition into calcite layers (Perkins & Maher, 1992; Perkins, 1996; Strauss et al., 2013). In the case where magnetite minerals contained in the stalagmites are primary, their nature, grain size, and concentration are influenced by environmental and climatic factors acting on the surface soils, including precipitation, moisture availability, and vegetation cover (Bourne et al., 2015; Jaqueto et al., 2016; Burstyn et al., 2022). Examination of concentration-dependent magnetic properties alongside climate proxies such as carbon and oxygen isotopes may thus provide valuable information about past climate changes. For example, Bourne et al. (2015) and Burstyn et al. (2022) showed a correlation between increased precipitation and higher concentrations of magnetite trapped in the calcite laminae of stalagmites. In stalagmites from Brazil, Jaqueto et al. (2016) proposed that vegetation, soil erosion, and aridity are the primary factors influencing stable isotope composition and magnetite content. Here we study the magnetic mineralogy of speleothems of the Cerâmica Cave from Central Portugal, as well as of the host carbonates, cave sediments, and sedimentary cover and soils, to investigate the nature and origin of the magnetic particles present in the stalagmites. In addition, we compare the magnetic data of the speleothems with their oxygen and carbon isotope composition to investigate possible connections between climate and environmental forcing parameters and the magnetic mineralogy of the speleothems.

Geological Context and Sampling

We analyzed four stalagmites from the Cerâmica Cave (39.92702; -8.51788 – WGS84) along with cave sediments (5 samples) and sedimentary cover (3 samples) from the subsurface. The stalagmites were oriented *in situ* using a magnetic compass and subsequently cut vertically into several slices using non-magnetic blades. In the stalagmite's central slices, plate-like specimens of 2x2x0.5cm were cut along the growing axis, where calcite laminae are horizontal. The Cerâmica Cave is located in the Sicó Massif, Ansião, western-central Portugal, and is formed by dolomites, dolomitic limestone, and marl-limestone from the Lower and Middle Jurassic (Cunha et al, 2020). The Cerâmica Cave is a shallow, longitudinal, well-ventilated cave with five main chambers. The cave sediments and the sedimentary cover correspond to clayey to silty materials inherited from the weathering of the host carbonates and organic matter, the so-called Terra Rossa. The stalagmites contain reddish ("dirty"), and off-white (light-yellow) carbonate lamina interspersed with some whitish layers.

Methodology

Magnetic measurements were conducted at the laboratory of paleomagnetism of the Department of Earth Sciences of the University of Coimbra and in the laboratory of Archaeomagnetism of the CENIEH (Centro Nacional de Investigación sobre la Evolución Humana), Burgos. Measurements consisted of stepwise alternating field (AF) demagnetization of the natural remanent magnetization (NRM), acquisition of anhysteretic remanence (ARM) and isothermal remanent magnetization (IRM) curves, measurement of mass normalized magnetic susceptibility, hysteresis, and first-order reversal curve (FORC) diagrams. AF demagnetization and NRM measurements were conducted using a 2G long core SQUID magnetometer. Stepwise IRM acquisition curves were obtained by applying a field with an impulse magnetizer (ASC Scientific) over 35 steps up to 1.1T for stalagmites samples, and over 45 steps up to 1.1T approximately for the cave sediments and sedimentary cover samples. IRM was then measured with a JR6 (AGICO) magnetometer. IRM curves were analyzed using a cumulative Log-Gaussian function (CLG) using the Kruiver et al. (2021) Excel file and a Skewed Generalized Function (SGG) using the MaxUnmix software (Maxbauer et al., 2016). ARM acquisition curves were obtained using a unidirectional DC field (H_{DC}) of 0.1 mT in 16 steps up to 100 mT for soil and sediment samples and an H_{DC} of 0.05 mT in 20 steps up to 100 mT for stalagmites samples. Hysteresis curves and FORC diagrams were performed with a Micromag (Princeton) and processed with FORCinel software (Harrison and Feinberg, 2008). Carbon and oxygen isotope composition of the stalagmite samples were measured at the University of Lausanne, Switzerland, and calibrated with the VPDB standard.

Results

The samples exhibited well-defined and well-clustered magnetic directions after AF cleaning. The values of the NRM are between $6x10^{-5}$ – $5.5x10^{-3}$ A/m. The orthogonal plot from paleomagnetic measurements shows the presence of two components. The first component, probably corresponding to a viscous remanent magnetization is removed by AF of ~40 to 60 mT. The mean declination and inclination values of the second component are ~333º and 68.7º, respectively, which is consistent with the values of the recent Earth's geomagnetic field at this location which is ~358º and 54º.
IRM acquisition curves from stalagmites samples contain two main coercivity components. Component 1 has saturation isothermal remanent magnetization (SIRM) values of 0.13 – 0.92 A/m, with a mean coercivity ($B_{1/2}$) of 21.9 – 26.9 mT, typical of magnetite (Egli, 2004), and a dispersion parameter (DP) of 0.19 – 0.24 mT. Component 2 has SIRM values of 0.17 – 0.19 A/m approximately, with $B_{1/2}$ around 100 – 316.23 mT, typical of hematite, and DP values of 0.35 – 0.45 mT. Component 1 contributes to 43.1 - 80.2% of the total SIRM. The calculated S-ratio ($(1-IRM_{-0.3T}/IRM_{1T})/2$) shows constant values comprised between 0.898 to 1, indicating a major contribution of low coercivity magnetic minerals. IRM curves of the cave sediments and sedimentary cover appear to contain a single coercivity component with 32.8 – 124 A/m SIRM, $B_{1/2}$ values of 21.9 - 26.9 mT, and DP values of 0.22 - 0.25 mT.
ARM acquisition curves show SARM values of 0.058 - 0.094 A/m for the stalagmite, 3.715 - 3.99 A/m for cave sediments, and 5.07 - 6.37 A/m for the sedimentary cover. Median demagnetization field values (MDF) are 15.3 - 16.1 mT for the stalagmite samples and 11.56 - 12.52 mT for cave sediments and sedimentary cover suggesting that fine-grained magnetite is being preferentially captured by the speleothems.
After slope correction of the paramagnetic contribution, hysteresis loops from stalagmites samples, show H_{cr}/H_c and M_{rs}/M_s values vary from 2.14 - 2.69 and 0.29 - 0.30. Hysteresis loops show a wasp-wasted shape, with H_{cr}/H_c and Mrs/Ms of 1.96 - 2.59 and 0.31 - 0.33 respectively, indicating a mixture of a single domain (SD) and superparamagnetic magnetite, or a mixture of low and high coercivity particles. The presence of high coercivity particles is indicated by the loop opening in higher fields (Roberts et al., 1995; Dunlop and Özdemir, 1997). Hysteresis ratio is plotted close to the PSD domain (vortex states) in the diagram of Day (Day, 1977).
FORC signatures of stalagmite samples are dominated by a low-coercivity component associated with well-dispersed particles in the SP/SD range. Additional low-amplitude contributions from SD clusters and/or single vortex (SV) particles whose nature needs to be further investigated, e.g., by comparison with the source material. All samples are located near the pedogenic zone in a scatter plot of k_{ARM}/IRM vs. MDF of ARM (Egli, 2004). Stalagmites show slightly higher MDF values and higher k_{ARM}/IRM than Terra Rossa sediments, by the fact that the karst system acts like a filter, allowing smaller (preferentially SD) particles to be deposited onto the surface of the stalagmite. Because k_{ARM}/IRM is highly selective towards non-interacting SD particles, it is mainly controlled by the relative proportion of the central ridge and low-amplitude contributions with broad vertical distribution in the FORC diagram.
Oxygen isotope compositions ($d^{18}O$) are comprised between -4.6 and -3.7‰ VPDB, while the carbon isotopic ($d^{13}C$) values vary between -12.3 and -10.7‰ VPDB. These values differ from the values of other Portuguese speleothems (Font et al., 2014) probably due to different local conditions and/or different ages.
A weak to moderate negative correlation is observed between carbon ($d^{13}C$) and oxygen ($d^{18}O$) composition, magnetic susceptibility (R^2 = 0.323 and 0.311), and ARM (R^2 = 0.1592 and 0.1499) data from stalagmites samples.

Conclusions

Magnetic mineralogy of the speleothem of Cerâmica Cave provided the following information:
Stalagmites from Cerâmica Cave are good recorders of the Earth's magnetic field, showing stable and coherent magnetic directions, consistent with the direction of the present-day Earth's magnetic field.
Analysis of the IRM curves, hysteresis curves, and FORC diagrams show that stalagmites contain magnetite particles, mainly in the SP to SD grain size range, and hematite, while the sedimentary cover and cave sediments are dominated primarily by magnetite.
k_{ARM}/IRM ratio versus MDF point to a low coercivity, pedogenic, origin for the magnetite contained in the soil, the cave sediment, and the stalagmite.
The presence of hematite in the stalagmites can be explained by hematite filtered from overlaying sediments or the occurrence of chemical alteration during or soon after the precipitation of the calcite layers.
Weak to moderate correlation between isotopic composition and magnetite concentration suggests that precipitation and soil erosion may partially control the transport of magnetite into the cave.

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