

**SPECTROSCOPIC CHARACTERISATION OF TRAVERTINES BY EPR
TECHNIQUES: A MULTIFREQUENCY STUDY**

Di Benedetto, F.¹, Montegrossi, G.^{2,*}, Pardi, L.A.³, Bercu, V.³, Romanelli, M.⁴, Minissale, A.²
& Paladini, M.⁵

¹ Museo di Storia Naturale, Università di Firenze, via G. La Pira 4, I50121, Firenze (Italy)

² Istituto di Geoscienze e Georisorse - CNR, via G. La Pira 4, I50121, Firenze (Italy)

³ Istituto per i Processi Chimico- Fisici - CNR, via G. Moruzzi 1, I56124 Pisa (Italy)

⁴ Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, I50019 Sesto Fiorentino (Italy)

⁵ Dipartimento di Scienze della Terra, Università di Firenze, via G. La Pira 4, I50121, Firenze (Italy)

*e-mail: giordano@geo.unifi.it

The EPR characterisation of paramagnetic metal cations, *e.g.* Mn(II), Fe(III), in calcite-based materials has attracted many studies, because of the very informative experimental spectra and the peculiar crystal field of the Ca site in this mineral. Recently, EPR spectroscopy has been also applied to the travertine characterisation, appearing a promising tool for the understanding of the physico-chemical condition of its genesis.

Mn(II), occurring as an ubiquitous trace substituent of Ca, may be considered as an ideal tool for the systematic investigation of travertines of different localities and origins, because the EPR spectrum depends on the local ionic crystal field. Several parameters (zero-field and hyperfine structure, linewidth, isorientation) appear to be promising criteria to distinguish and classify different travertines. A significant variability of the EPR spectral parameters, in fact, can justify their use as minero-chemical and geochemical markers. Nevertheless, a very accurate knowledge of the dependence of the spectrum on all the Hamiltonian interactions is required. A multifrequency approach, therefore, has been undertaken, in order to refine and clarify the informations contained in the very complex X-band spectrum.

The study has been carried out on a sample, coming from Papigno (Terni, central Italy), a very recent deposit (60 ka), inactive nowadays. At present, a meteogene travertine is being deposited near the village of Marmore and the isotopic $\delta^{13}\text{C}$ composition of the two deposits is very similar (from -1.9 to 1.0 ‰ PDB at Papigno and from -0.8 to 0.5 ‰ PDB at Marmore). Room temperature 9.5, 95, 190 and 285 GHz EPR spectra were recorded at very low scan speed. While the 9.5 spectrum consists of the well-known sextet, characterised by a splitting of each major peak in positive and negative portions and by the forbidden lines, the high frequency spectra are simplified, being constituted only by the six $m_S -1/2 \Rightarrow +1/2$ allowed transitions. The multifrequency approach evidences a reduction of the linewidth passing from X band to 95 GHz and the presence of a field independent splitting of the transitions. The latter must be due to either fine or hyperfine structure or both. An interpretation of the multifrequency spectra in terms of the fine structure including third order perturbation terms is presented.