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EPR discrimination of microcrystalline calcite geomaterials

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Abstract

The EPR spectrum of Mn^{2+} in microcrystalline calcite geomaterials (e.g., marbles, travertines) possesses exceptional diagnostic characteristics, allowing to relate samples to their origin (natural/synthetic, inorganic, organogenic, …) and to evaluate the details of impurities clustering. This information, beyond their mineralogical and geochemical interest, is of paramount importance for environmental, palaeoclimatic, and cultural heritage studies.

Accessing the information hidden in the Mn^{2+} EPR spectrum relies on disentangling spurious self-correlation among spin Hamiltonian parameters in the powder spectrum. In the present study, this goal is achieved through a systematic comparison of the temperature dependencies of four different microcrystalline calcite geomaterials. Accordingly, an assessment of the internal correlation structure of the spin Hamiltonian parameters is provided and the most sensitive discriminating parameters, which are able to mark samples, are identified.

It has been found that the spin Hamiltonian parameters useful for discrimination purposes are those which are dependent on the ligand field interaction, whereas the Fermi contact interaction, as well as the spin-spin, spin-phonon, and spin-lattice interactions, are not able to "store" information related to formation processes, nor post-depositional events. This characteristic behavior is ascribed to the occurrence of mosaic structure and to the clustering among Mn^{2+} and other impurity ions, which are able to induce a strong and variable ligand field interaction.

In particular, the proposed method appears fully able to reveal the biogenic origin of microcrystalline calcites and to trace post-depositional events.

Keywords: EPR spectroscopy, microcrystalline calcite geomaterials, Mn^{2+}, internal correlation structure, compositional data analysis, ligand field interaction, clustering of impurities