

# NMR spectroscopic studies of the structure of organic and bicarbonate defects in calcite

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Calcite is a ubiquitous and reactive component of surficial environments. Many types of dissolved constituents such as metals, oxyanions, and organic molecules sorb strongly to the calcite surface and can be incorporated into growing crystals. We are using double-resonance NMR spectroscopic methods to determine the structure of defects that are incoherent with calcite structure. For example, <sup>13</sup>C{<sup>1</sup>H} cross-polarization (CP) allows detection of carbonate groups near H-bearing species and heteronuclear correlation (HetCor) gives spectra for the corresponding H. We have developed a simple correlation between the CP rate and C-H dipolar coupling that can be used to estimate distances in dilute systems such as calcite. From this correlation, we show that in calcite/citrate coprecipitates the distance between the citrate methylene protons and carbonate carbon is about 2.7 Å.

Although nominally anhydrous, most calcite samples yield <sup>13</sup>C{<sup>1</sup>H} CP/MAS spectra, which we show is due primarily to the presence of defects containing protonated carbonate groups (bicarbonate). The CP kinetics for a synthetic <sup>13</sup>C-enriched sample grown by the constant-addition method shows an oscillation characteristic of isolated C-H pairs separated by about 1.9 Å. The <sup>13</sup>C chemical shift for the protonated carbonate group, however, is indistinguishable from that for bulk mineral. HetCor spectra show that the associated hydrogens give a narrow <sup>1</sup>H NMR peak at +7.4 ppm. This chemical shift indicates a moderate hydrogen-bond interaction with d(OH...O) of about 1.85 Å, which indicates significant relaxation of the calcite structure near the defect. A small peak at this position can be detected in <sup>1</sup>H MAS/NMR spectra of calcite of biogenic and abiogenic origin. More intense <sup>1</sup>H signals from water and hydroxyl groups do not cross-polarize to the carbonate carbons, either because of motion or long C-H distances. Signal from bicarbonate groups is much stronger in calcite coprecipitates with organic molecules and phosphate, suggesting that protonation of carbonate groups is an important mechanism for accommodating defects in calcite.