

LETTER

Observation of bicarbonate in calcite by NMR spectroscopy

JIAN FENG,¹ YOUNG J. LEE,² RICHARD J. REEDER,² AND BRIAN L. PHILLIPS^{2,*}

¹Center for Environmental Molecular Science, Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400, U.S.A.

²Center for Environmental Molecular Science, Department of Geosciences, State University of New York, Stony Brook, New York 11794-2100, U.S.A.

ABSTRACT

We show that the signal observed in $^{13}\text{C}\{^1\text{H}\}$ cross-polarization magic-angle-spinning (CP/MAS) NMR spectra of synthetic calcite precipitated at room temperature arises from bicarbonate ion. Although this peak occurs at the same chemical shift as for the bulk carbonate signal, its observation by CP/MAS indicates that it corresponds to carbonate associated with H. The variation in the CP/MAS intensity with contact time shows oscillations characteristic of C-H pairs separated by 1.9(1) Å and remote from other H, consistent with bicarbonate. $^{13}\text{C}\{^1\text{H}\}$ heteronuclear correlation spectra indicate that the hydrogen in the bicarbonate groups gives a relatively narrow ^1H NMR signal at +7.4 ppm. A peak at this chemical shift is also observed in direct-observe ^1H MAS NMR spectra of the synthetic sample, and also in natural biogenic and abiogenic calcite. This ^1H chemical shift indicates a moderate hydrogen bonding interaction $d(\text{OH}\dots\text{O}) \approx 1.85$ Å, which suggests significant structural relaxation occurs near the bicarbonate.

Keywords: Calcite, NMR spectroscopy, bicarbonate, trona, nahcolite, hydrogen bond