

X-Ray Photoelectron Spectra of C_{1s} and O_{1s} in Carbonate Minerals

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Abstract

X-ray photoelectron spectra of C_{1s} and O_{1s} lines in various carbonate minerals illustrate that, as covalency increases, the O_{1s} binding energies also increase in calcite, magnesite, and otavite, but decrease in aragonite, strontianite, and witherite. No increase in binding energy could be detected for possible 2P-2P, pi bonding in aragonites and no increase in line-width was detected for O or C from the two sites in dolomite.

Introduction

X-ray photoelectron studies of O_{1s} and C_{1s} binding energies have been related to changes in the chemical environment of a large number of inorganic and organic compounds (e.g., Siegbahn *et al.*, 1967); however, relatively few naturally occurring solids or minerals have been studied. The shift in the O_{1s} line has been studied in silicates by Huntress and Wilson (1972) and by Yin, Ghose, and Adler (1971) in order to delineate the difference in binding energy between bridging and non-bridging oxygens. The corresponding X-ray emission line (O K α) has received much more attention and has been used for the characterization of surface oxides (e.g., Krause, Savanick, and White, 1970), and for bonding studies (e.g., Smith and O'Nions, 1972). Other studies have illustrated the functional value of utilizing the energy difference as related to X-ray emission wavelength shifts to compute Me-O distances (e.g., Wardle and Brindley, 1971). The recent structural refinements of aragonite, strontianite and witherite (DeVilliers, 1971) make possible a study of the behavior of their C and O binding energies relative to bond distance, structural type, and type of cation.

Methods

Well characterized, synthetic samples of calcite, CaCO₃; magnesite, MgCO₃; dolomite, CaMg(CO₃)₂; aragonite, CaCO₃; strontianite, SrCO₃; witherite, BaCO₃; and otavite, CdCO₃—as described by Sommer (1972)—were utilized together with an optical quality sample of Iceland spar. Samples were powdered and placed on double-sided cellophane tape

or pressed onto a copper grid. Portions of all samples were analyzed by X-ray diffraction after powdering to insure that no phase change had occurred. The photoelectron spectra were obtained using a Varian Associates IEE-5 electron spectrometer. The MgK α X-ray line (1253.6 eV) was used for photoelectron excitation. To compensate for charging effects, the sample spectra were referenced to the Au(4f_{7/2}) line at 83.0 eV, by vacuum depositing gold onto the samples. The correction was typically 3.0 eV. All spectra were recorded in triplicate and are reproducible to ± 0.1 eV. The binding energies reported are the average of three readings at the center of the peak at half maximum height plus the values of the first derivative of peak slope, *i.e.*, the average of six readings representing three measurements. An attempt was made to study variation in O K α X-ray emission band position with the 500 mm Rowland circle spectrometer and RAP crystal of a Cambridge MICROSCAN-5 microprobe. No significant differences could be detected, except for CdCO₃, in which the band was always at higher energies than for the other carbonates. However, data variability was too high, due to sample-beam interaction, to allow for interpretation.

Results and Discussion

The data in Table 1 show that the calcite-group carbonates—calcite, magnesite (dolomite), and otavite—have increasing O_{1s} binding energies that parallel increasing degrees of covalency as calculated from electronegativities, *i.e.*, Ca-O (79.4% ionic), Mg-O (71.2% ionic), and Cd-O (66.3% ionic) (Smith,

TABLE 1. X-Ray Photoelectron Spectra of C_{1s} and O_{1s} in Carbonate Minerals*

	Calcite	Magnesite	Dolomite	Otavite
O _{1s}	530.2	530.6	530.6	531.1
C _{1s}	282.5	282.8	282.9	282.7
	Aragonite	Strontianite	Witherite	
O _{1s}	530.0	530.5	531.1	
C _{1s}	282.4	282.4	283.8	

* (in eV).

1963). The C_{1s} energies increase slightly in that order as well. The aragonite-group carbonates—aragonite, strontianite, and witherite—increase in O_{1s} binding energy with decreasing calculated covalency, *i.e.*, Ca–O (79.4% ionic), Sr–O (81.9% ionic), and Ba–O (83.8% ionic). The C_{1s} binding energy is the same for aragonite and strontianite and higher for witherite. One would expect binding-energy values to increase with increasing amount of covalent character and decreasing bond length. However, the aragonite series increases in binding energy with increasing bond length and decreasing covalent character. Apparently the cation plays a major role in determining the binding energies. Similar effects have been reported for other materials (Yin *et al.*, 1971; Tossell, 1973). The aragonite structures are in various degrees of distortion because of the size range of the metals that occupy the 9-fold coordination polyhedron, the Ba²⁺ ion fitting best.

The triangular planar *sp*² CO₃²⁻ unit leaves a single 2*p* orbital perpendicular to the planar configuration and thus available for pi bonding with similarly directed 2*p* orbitals of adjacent oxygen atoms. Because the CO₃ units lie directly above (and below)

each other in aragonite but not in calcite, a higher probability for such pi bonding would be expected in aragonite. But no significant difference in binding energy was detected for O_{1s} or C_{1s} in Iceland spar or synthetic calcite as compared to aragonite. Also, no increase in line width over the average 2.5–3 eV was detected for dolomite where O_{1s} might be expected to exist as two types: Mg–O and Ca–O.

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