Infrared spectroscopic evaluation of iron contents and excess calcium in minerals of the dolomite–ankerite series

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Abstract

The proportion of dolomite end-member in minerals of the dolomite–ankerite series can be estimated from infrared spectra on the basis of either the position of an absorption band near 160 cm^{-1}, or the ratio of intensities of bands near 260 and 730 cm^{-1}. For the 10 minerals examined, the intensity ratio gave slightly more consistent results (± 2.5 percent dolomite) than the frequency measurement (± 4 percent dolomite). A high Ca/Mg ratio (1.23) in one dolomite did not appear to affect either measurement significantly.

Introduction

Evaluation of the dolomite content of carbonate deposits and the placing of a ferroan dolomite within the dolomite–ankerite series are of importance for the agricultural use of dolomite as a source of magnesium and as a soil pH regulator. Substitution of magnesium by iron in dolomites is also of industrial importance, since excessive iron contents are detrimental in many applications. Iron contents of carbonates can also be indicative of associated heavy-metal deposits, and can give information on depositional and diagenetic environments.

There is therefore a need for a convenient and rapid method for placing a mineral in the continuous isomorphous series, $Ca(Fe,Mg)(CO_3)_2$, that extends from dolomite through ferroan dolomite to ankerite, terminating for natural specimens at about 70 percent $CaFe(CO_3)_2$ (Deer *et al.*, 1962). Although X-ray diffraction (Howie and Broadhurst, 1958; Goldsmith *et al.*, 1962), refractive index (Howell and Dawson, 1958), differential thermal analysis (Kulp *et al.*, 1951) and differential staining (Warne, 1962; Evamy, 1963) have been applied, they all exhibit some limitations. In this paper, the value of infrared spectroscopy as a characterization tool is assessed. This technique has been used to determine the relative proportions of calcite and dolomite in mixtures (Chester and El-

derfield, 1967), but not to determine the composition of ankerites and ferroan dolomites.

Experimental

The spectra of ten samples of varying iron and manganese contents (Table 1) were examined in the region 4000–220 cm^{-1} on a Perkin Elmer 577 filter-grating spectrometer, using 0.5 mg samples in 12 mm KBr disks, and also in the region 400–50 cm^{-1} on a Beckman-RIIC Model 720 Fourier Transform Interferometer, using 1 mg and 0.5 mg samples in 12 mm polyethylene disks. Before preparing the pressed disks, samples were moistened with propanol in a mortar, and ground sufficiently finely to give spectra with symmetrical absorption bands, undistorted by the Christiansen effect (Russell, 1974).

Results and discussion

Typical spectra are shown in Figure 1. Comparison of ankerite (spectrum A) with dolomite (spectrum B) shows that iron substitution causes shifts in frequency of three bands, near 880 cm^{-1}, 730 cm^{-1}, and 150–160 cm^{-1}. Of these, the 150–160 cm^{-1} band shows the greatest frequency shift (about 9 cm^{-1}); moreover, its frequency could be measured with considerable precision (± 0.3 cm^{-1}), because of the intrinsic accuracy of frequency measurements by inter-
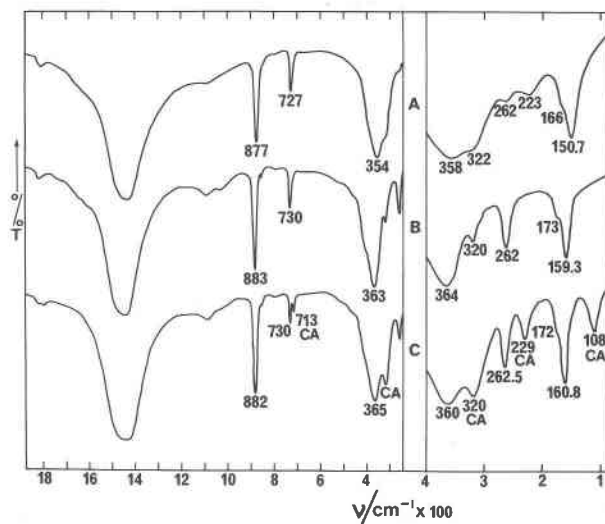
Fig. 1. Infrared spectra 1900–250 cm⁻¹ and 400–90 cm⁻¹, of A: ankerite (102), B: dolomite (366), and C: dolomite plus calcite (361). In spectrum C, calcite bands are labelled CA.
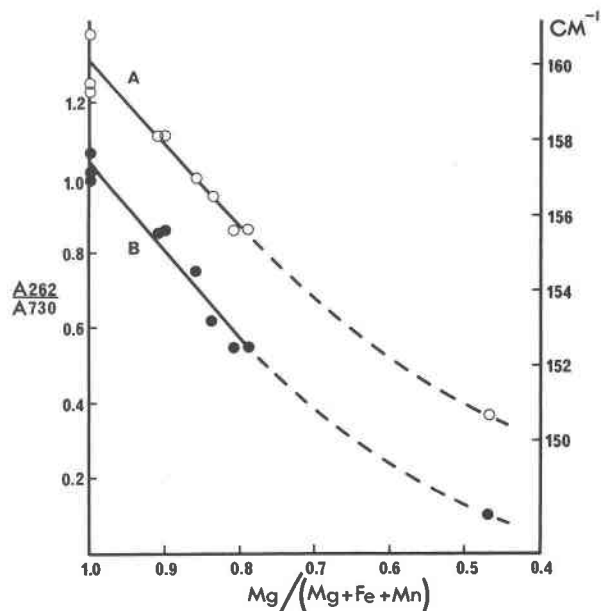

Fig. 2. Variations in (A) the wavenumber of the 160 cm⁻¹ band and (B) the intensity ratio of the 262 and 730 cm⁻¹ bands with the content of dolomite end-member in minerals of the dolomite-ankerite series, measured as the mole fraction $Mg/(Mg + Fe^{2+} + Mn^{2+})$.

ferometer where absorbance values are digitally calculated at 1.22 cm⁻¹ intervals, under the instrumental conditions used. A plot of this frequency against the mole fraction of the dolomite end-member [measured as $Mg/(Mg+Fe^{2+}+Mn^{2+})$] shows a consistent relationship, none of the dolomites or ferroan dolomites (100–79 percent dolomite) deviating from a straight line by more than 0.04 in mole fraction of dolomite (Fig. 2, curve A). No useful relationship could be established on the basis of the position of the 880 cm⁻¹ band, which could be estimated only to about ±0.5 cm⁻¹, and which lay within a range of only 1.5 cm⁻¹ for samples in the mole fraction range 1.00–0.79 dolomite. The 730 cm⁻¹ band was still less sensitive to substitution.

In addition to these frequency displacements, substitution of Mg by Fe^{2+} causes the 262 cm⁻¹ dolomite band to weaken rapidly and virtually to disappear when the mole fraction of dolomite drops to 0.47 (spectrum A, Fig. 1), where it begins to be replaced by a band at 223 cm⁻¹. To compensate for variations in absolute spectral intensities caused by impurities and other factors, the ratio of the intensities of the 260 cm⁻¹ and 730 cm⁻¹ bands in the grating spectra was used and found to give a good linear plot for the dolomites and ferroan dolomites, with deviations in

Table 1. Composition of dolomite–ankerite minerals as percent of total weight, mole fraction in total carbonates, and mole fraction of dolomite end-member measured as $Mg/(Mg + Fe^{2+} + Mn^{2+})$

Sample	CaCO₃ %	CaCO₃ Moles	MgCO₃ %	MgCO₃ Moles	FeCO₃ %	FeCO₃ Moles	MnCO₃ %	MnCO₃ Moles	Fe₂O₃ %	Al₂O₃ %	HCl Insoluble %	Mg / Mg+Fe+Mn
102	51.63	0.518	19.05	0.228	28.23	0.245	1.09	0.009	–	0.07	–	0.47
340	49.44	0.501	32.70	0.395	12.16	0.106	–	–	–	–	6.54	0.79
101	54.56	0.515	35.24	0.394	11.16	0.091	–	–	–	–	–	0.81
339	51.98	0.500	36.88	0.420	9.16	0.076	0.41	0.004	–	–	2.12	0.84
341	53.07	0.498	38.68	0.430	7.35	0.059	1.44	0.012	–	–	0.08	0.86
322	53.48	0.499	40.95	0.453	5.26	0.042	0.78	0.007	–	–	0.12	0.90
337	52.40	0.498	40.44	0.456	1.41	0.011	4.12	0.034	–	–	1.93	0.91
362	62.27	0.640	29.59	0.360	–	–	–	–	1.99	0.13	5.96	1.00
361	67.13	0.651	30.37	0.349	–	–	–	–	0.82	0.27	1.40	1.00
366	57.35	0.551	39.47	0.449	–	–	–	–	0.35	0.16	2.81	1.00

No entry indicates negligible contents.

mole fraction dolomite of only ±0.025 (Fig. 2, curve B). Judging from the slopes of curves A and B, Figure 2, this intensity ratio may be more sensitive to composition than the position of the 160 cm^{-1} band at high Fe contents. Moreover, the intensity of the 223 cm^{-1} band may prove useful when the Fe content increases beyond the level in the ankerites examined here.

Excess CaCO$_3$

In addition to defining composition in the dolomite–ankerite series, infrared spectra readily revealed the presence of calcite (bands labelled CA in Fig. 1C) or silicate impurities (bands around 1000–1100 cm^{-1}). All three iron-free dolomites examined contained excess calcium (Table 1), but two of these, samples 361 and 362, appeared to contain sufficient calcite to account for this excess. The third, sample 366, contained no detectable calcite (less than 2 percent), so its excess calcium must be in solid solution in the dolomite, giving it a Ca/Mg ratio of about 1.23. None of the ferroan dolomites or ankerites contained detectable calcite, and their calcium contents were close to the ideal (Table 1). The excess calcium in dolomite 366 does not appear to have caused significant deviations in either the ratio of intensities (1.07) or the band frequency (159.3 cm^{-1}), plotted in Figure 2.

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