

THE RESPONSE OF LUMINESCENCE IN SYNTHETIC CALCITE TO LABORATORY HEATING

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ABSTRACT

Synthetic calcite doped with Mn and Mg has been prepared from aqueous solutions of CaCl₂ using four different methods: (1) rapid precipitation using Na₂CO₃, (2) rapid precipitation using NaHCO₃, (3) rapid precipitation using ammonium carbonate, and (4) slow precipitation from solutions in contact with ammonium carbonate vapor. Calcite prepared using methods (1) to (3) forms rhombs 1 to 4 μm across and has relatively broad XRD peaks. Calcite prepared using method (4) forms rhombs up to 1 mm across and has relatively narrow XRD peak widths. Cathodoluminescence (CL) spectra were obtained to characterize the intensity, wavelength and bandwidth of emission. Calcite prepared using methods (1) and (2) generally has lower CL intensity than compositionally similar calcite prepared using methods (3) and (4). The wavelength of emission is independent of concentration where Mn and Mg total less than approximately 0.01 atoms per formula unit, but increases at higher concentrations of these elements. The bandwidth increases with the concentrations of Mn and Mg. Calcite prepared by methods (1) to (4) was heated in CO₂ and hydrothermally in the temperature range 75 to 400°C. Calcite prepared using methods (1) to (3) usually coarsens significantly, and XRD peak widths become smaller on heating, especially in the presence of water. Little change in grain size or XRD peak widths takes place on heating calcite prepared using method (4). The intensity of CL increases as a consequence of heating. Calcite made by methods (1) and (2) shows larger relative increases in CL intensity on heating than that made by methods (3) and (4). Hydrothermal treatment promotes a greater increase in CL intensity than does heating in CO₂. The wavelength of emission increases and bandwidth decreases on heating calcite that contains more than approximately 0.01 Mn and Mg *apfu*. Where the concentration of these elements is lower, changes in wavelength and bandwidth on heating are smaller and erratic in direction. The effects of heating on CL intensity and XRD peak width are attributed to the annihilation of defects during recrystallization. Changes in the wavelength and bandwidth of CL emission on heating are attributed to local redistribution of the activator ions.

Keywords: calcite, synthesis, luminescence, recrystallization.

SOMMAIRE

Ce travail porte sur la calcite synthétique dopée avec le Mn et le Mg, et préparée à partir de solutions aqueuses de CaCl₂ selon quatre protocoles différents: (1) précipitation rapide utilisant Na₂CO₃, (2) précipitation rapide utilisant NaHCO₃, (3) précipitation rapide utilisant le carbonate d'ammonium, et (4) précipitation lente à partir de solutions en contact avec des vapeurs de carbonate d'ammonium. La calcite préparée selon les méthodes (1) à (3) se présente sous forme de rhomboédres de 1 à 4 μm de taille, et fait preuve de réflexions relativement floues en diffraction X. La calcite préparée selon la méthode (4) se présente sous forme de rhomboédres atteignant 1 mm de taille; elle possède des raies relativement étroites. Les spectres de cathodoluminescence (CL) ont été mesurés pour en caractériser l'intensité, la longueur d'onde et la largeur de la bande d'émission. La calcite préparée selon les méthodes (1) et (2) montre en général une intensité CL plus faible que la calcite de composition semblable, mais préparée selon les méthodes (3) et (4). La longueur d'onde de l'émission est indépendante de la concentration dans les cas où les concentrations de Mn et Mg sont inférieures à environ 0.01 atomes par unité formulaire, mais elle augmente dans les cas où la concentration de ces éléments est plus élevée. La largeur de la bande d'émission augmente avec la teneur en Mn et Mg. La calcite préparée selon les méthodes (1) à (4) a été chauffée en présence de CO₂ et en milieu hydrothermal dans un intervalle de température entre 75 et 400°C. Les grains de calcite préparée selon les méthodes (1) à (3) deviennent en général plus grossiers, et les pics de diffraction X deviennent plus étroits suite au chauffage, surtout en présence d'eau. Il y a très peu de changement en granulométrie ou en largeur des pics de diffraction suite au chauffage de la calcite préparée selon la méthode (4). L'intensité de l'émission CL augmente avec le chauffage. La calcite préparée selon les méthodes (1) et (2) fait preuve d'augmentations relatives en intensité de CL par chauffage, par rapport à celle qui a été préparée selon les méthodes (3) et (4). Le traitement hydrothermal promouvait une plus grande augmentation en intensité d'émission CL qu'un traitement en présence de CO₂. La longueur d'émission augmente et la largeur de la bande diminue suite au chauffage de la calcite qui contient plus d'environ 0.01 Mn et Mg atomes par unité formulaire. Dans les cas où la concentration de ces éléments est plus faible, les changements en longueur d'onde et en largeur de la bande d'émission suite au chauffage sont minimes et erratiques en direction. Les effets du chauffage sur l'intensité d'émission CL et sur la largeur des réflexions en diffraction X seraient dus à l'annihilation des défauts par recristallisation. Les décalages en longueur d'onde de l'émission et en largeur de la bande suite au chauffage seraient attribuables à la redistribution locale des ions activateurs.

(Traduit par la Rédaction)

Mots-clés: calcite, synthèse, luminescence, recristallisation.

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INTRODUCTION

The major control on luminescence intensity in minerals is the presence and concentration of chemical activators (such as manganese and rare-earth elements, *REE*) and quenchers (such as iron) in the phase of interest. The minimum concentrations required to activate luminescence that is detectable by eye are known to be as low as ten to twenty parts per million (Marshall 1988, Machel *et al.* 1991), but the precise dependence of luminescence intensity on concentration of activators and quenchers is unknown. It is becoming clear, however, that trace-element abundances are not the sole control on luminescence intensity. Mason (1994, 1997) has shown that heating and radiation damage significantly influence the intensity of the cathodoluminescence (CL) signal from synthetic calcite, and that in natural calcite, heating causes changes in the wavelength and bandwidth of emission, as well as in its intensity.

These observations offer the prospect that thermally induced modifications to luminescence spectra could be used to estimate the paleotemperature of a carbonate-bearing rock. Such estimates would be valuable in the temperature region below 300°C, where phase equilibria are improbable because of kinetic constraints, and especially valuable below 200°C, where the maturation of organic matter takes place.

The prospect of a geothermometer based on CL is complicated by intersample variability in response to heating, which may be dependent on composition (Mason 1997) or on crystallinity (Mason 1994). The present study extends previous work by investigating how the luminescence signal and its response to heating depend on the crystallinity and composition of synthetic calcite with grain sizes spanning the range from micrite to sparite. In addition, the effect of heating in the presence of water (conditions similar to those that would apply during burial of sedimentary rocks) is compared with heating in the presence of CO₂.

EXPERIMENTAL METHODS

The methods of synthesis were designed to produce suites of synthetic calcite of widely differing chemistry and degree of crystal perfection (crystallinity) to be used as starting calcite in a series of heating experiments.

Synthesis

Calcite was precipitated from aqueous chlorides of Ca, Mg and Mn prepared from reagent-grade powders. The concentration of CaCl₂ was 0.1 mL, and those of MnCl₂ and MgCl₂ were adjusted to produce the desired composition of calcite.

Four different methods of precipitation were used: (1) Synthesis from manganese-bearing solutions over 7 to 10 days using ammonium carbonate vapor (ACV) as the titrant. In three experiments small quantities of Mg

were present in addition to Ca and Mn. The products of this method of synthesis are called ACV calcite; further details are given in Mason & Mariano (1990). (2) Synthesis from manganese-bearing solutions by adding Na₂CO₃ (NC) solution over a period of approximately 30 minutes (NC calcite). (3) Synthesis from manganese-bearing solutions by adding ammonium carbonate (AC) solution over a period of 10 minutes (AC calcite). (4) Synthesis from manganese- and magnesium-bearing solutions by adding sodium hydrogen carbonate (NHC) powder over a period of 10 minutes (Glover & Sippel 1967) (NHC calcite). The NC and AC syntheses were carried out at low temperature (2.5 to 6°C) to avoid coprecipitation of vaterite. The ACV and NHC syntheses were carried out at room temperature. At the conclusion of an experiment, the precipitates were washed with distilled water and dried in air.

Chemical analysis

The samples were analyzed by atomic absorption (AA) for Ca, Mn and Mg. ACV calcite was also analyzed using a Cameca Camebax SX-50 microprobe equipped with a Link Analytical eXL energy-dispersion spectrometer (EDS). The concentration of Ca was measured by EDS, and that of Mg, Fe and Mn was measured by wavelength-dispersion methods. Calcite, dolomite and rhodochrosite standards were used. The operating conditions were: accelerating voltage 15 kV, beam current 10 nA, and beam diameter 20 μm.

X-ray diffraction and scanning electron microscopy

An aliquot of each starting calcite and selected samples of heated calcite were prepared for powder X-ray diffraction (XRD) to identify crystalline phases. ACV calcite was crushed under acetone and spread on a glass slide. NC, AC and NHC calcite was of sufficiently small grain-size that only disaggregation was required for slide preparation. Selected samples were mounted with Si metal in order to measure unit-cell parameters. Data were acquired using either a Philips 1800 or a Rigaku RU-200 automated diffractometer. Samples were mounted on Al stubs and coated with gold before being examined with either a Cambridge Instruments Stereoscan 250 or a Hitachi S-570 scanning electron microscope.

Heating

Heating was carried out in the presence of CO₂ by filling a vertical ceramic-lined tube furnace with the pure gas. Temperatures were recorded every few minutes during the 15- to 20-minute warm-up period and thereafter, several times per day. Recorded temperatures did not vary by more than 3°C after warm-up and are believed to be accurate to ±5°C. Quenching to room temperature took 2 to 3 minutes.

The starting calcite was sealed in platinum tubes for experiments conducted in the presence of water (hydrothermal experiments). The amount of water added was from 0 to 8.6 wt%. The starting calcite was not dried before loading the tubes, so that adsorbed water was always present. Pressure was measured by a calibrated Bourdon gauge and transmitted by argon gas. Temperature was read every few minutes during the 20- to 40-minute warm-up time and thereafter several times per day. Recorded temperatures are accurate to within 5° and did not vary more than ± 2 to 4°C over the period of each experiment.

At the end of the experiment, the pressure vessel was cooled isobarically in a stream of compressed air. The tubes were cleaned and weighed. Those showing a weight change of more than ± 0.0005 g were considered to have leaked and were discarded.

Luminescence measurements

Luminescence was excited using a modified JEOL JXA-50A electron microprobe operating at an accelerating voltage of 10 kV with a beam diameter of approximately 50 μm and a beam-current density of approximately 14 $\mu\text{A}/\text{mm}^2$.

Spectra were collected on a Gamma Scientific NM-3H monochromator coupled to the microprobe optics by a fiber optic cable. All other instrumental details are as in Mason (1994). Seven to ten spectra were collected from each sample. Each spectrum was corrected for photomultiplier dark current and background (see below). Comparisons between samples are based on spectra collected in the same range of wavelengths (500 to 800 nm); consequently, corrections for photomultiplier response were not applied. The wavelength scale of the monochromator was calibrated in the range 300 to 1000 nm using the emission from a mercury vapor lamp.

Each spectrum was fitted using a background function ($y = b_0 \exp[-x/b_1]$), with b_0 the amplitude and b_1 the rate), and a peak function (the Haarrhoff - Van der Linde function):

$$y = \frac{a_0 a_2 \exp\left(-\frac{1}{2} z^2\right)}{a_1 a_3 \sqrt{2\pi} \left[\exp\left(\frac{a_1 a_2}{a_2^2}\right) - 1 \right]^{-1} + \frac{1}{2} \left[1 + \operatorname{erf}\left(\frac{z}{\sqrt{2}}\right) \right] } ,$$

in which a_0 is the area, a_1 the center of the undistorted peak, a_2 the width, a_3 the distortion, and $z = (x - a_1)/a_2$. This function accommodates asymmetrical peaks. The constants derived from the fitting procedure were averaged to derive values for the CL intensity, wavelength, bandwidth and standard errors in these parameters. Throughout this work, the quoted CL intensity refers to the peak area, emission wavelength is given as the peak center (position of the maximum calculated signal, denoted λ), and bandwidth is given as the full-width at half-maximum height (Γ). The area under the peak is a better measure of intensity than is peak height because

it takes account of differences in peak width among the samples.

Measurements on starting calcite were used as a reference against which spectra from heated calcite were compared. Changes in the CL parameters following heating are measured by the intensity ratio I_H/I_{Ref} (H: heated, Ref: reference), change in emission wavelength, $\Delta\lambda = \lambda_H - \lambda_{\text{Ref}}$, (nm) and change in bandwidth, $\Delta\Gamma (= \Gamma_H - \Gamma_{\text{Ref}}$, nm).

RESULTS

Nature of the starting calcite

ACV calcite forms transparent rhombs, typically 50 μm to 1 mm on a side, in some cases with irregular terminations. ACV calcite precipitated from Mg-bearing solutions has fewer well-developed faces than that precipitated from Mg-free solutions. Vaterite was found in the products of some (Mg-free) experiments, invariably aggregated into spheres and easily removed by hand-picking before the CL measurements and heating experiments were performed.

AC and NC calcite form rhombs and modified rhombs typically less than 1 μm across, usually aggregated into spheroidal masses (Fig. 1a) and, in some cases, with a spherulitic texture. NHC calcite with high Mn and Mg forms aggregates of modified rhombs that range from less than 1 to 4 μm across, the larger sizes

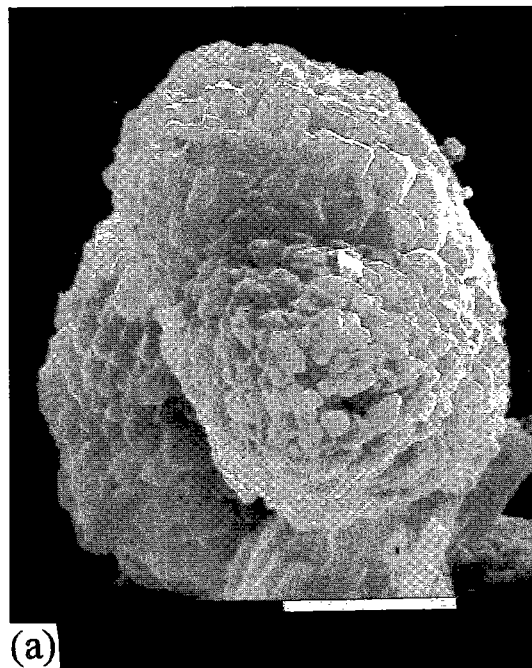


FIG. 1a. Physical appearance of NC calcite. Scale bar: 3 μm .

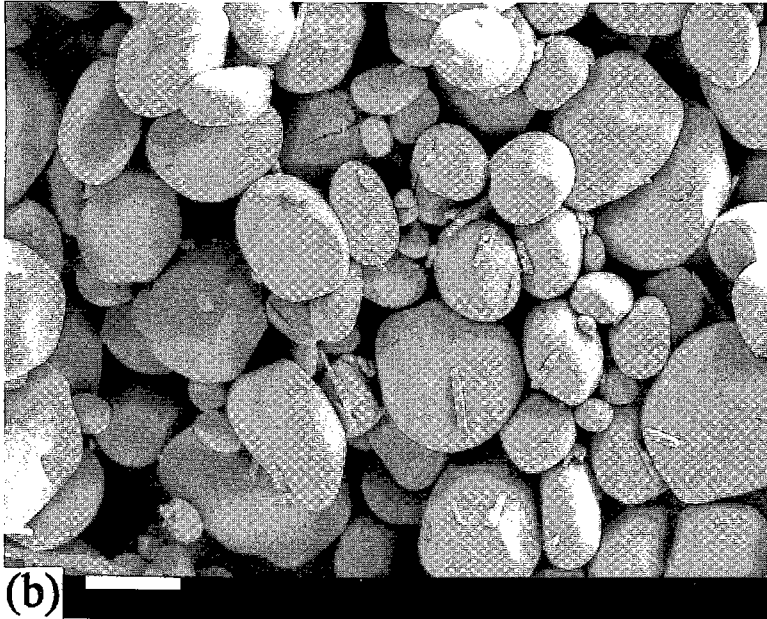


Fig. 1b. The same calcite as shown in Figure 1a after heating at 400°C for 96.7 hours in the presence of water. Note the increase in grain size and loss of edges and faces compared with (a). Scale bar: 10 μm .

being found in samples containing lower concentrations of Mn and Mg. Two samples of NHC calcite have compositions that lie inside the calcite – dolomite solvus. XRD spectra show that they are single-phase, though with broad reflections.

Table 1 gives the bulk compositions. The bulk Mn concentration for ACV calcite ranges from 1×10^{-4} to approximately 0.04 atoms per formula unit (*apfu*). Magnesium is present in three samples, attaining 0.03 *apfu*. Manganese concentrations in AC calcite range from 7×10^{-4} to 1.4×10^{-3} *apfu*. Manganese concentrations in NC calcite lie between 3×10^{-4} and approximately 0.01 *apfu*. In NHC calcite, Mn concentrations are between 0.004 and 0.09 *apfu*, and Mg reaches 0.3 *apfu*. NHC calcite with a high concentration of Mn also has high Mg. These elements total 0.33 *apfu* in two samples.

ACV calcite is zoned in Mn and, where present in the starting solution, Mg. Both sector and concentric patterns of zonation are observed. Manganese concentrations in individual CL zones range from below the limit of detection of the microprobe (6.6×10^{-4} *apfu*, 2σ) to a high of 0.07 *apfu*. Magnesium concentrations in individual zones attain 0.05 *apfu*. Calcite crystals made by the AC, NC and NHC methods are too small for microprobe analysis and for zoning to be detected.

With the exception of NHC calcite with high concentrations of Mn and Mg, the unit-cell dimensions are

very close to the values for calcite given by Reeder (1983). There are no systematic differences attributable to method of synthesis, but both *a* and *c* become shorter with increasing replacement of Ca by Mn and Mg.

Luminescence of starting calcite

The luminescence measurements are given in Table 1. Figure 2 shows the CL intensity as a function of Mn content. The data shown were collected in a single day, and great care was taken to ensure stability of the microprobe during data collection.

Intensity increases with Mn concentration to a maximum for ACV calcite containing approximately 0.04 Mn *apfu*. NHC calcite, in contrast, shows systematically declining intensity of emission between 0.004 and 0.09 *apfu* Mn. Within the composition range from approximately 0.005 to 0.04 Mn *apfu*, therefore, two different trends of concentration dependence are observed. Calcite synthesized by the NC method generally has slightly lower intensity of luminescence than compositionally similar AC and ACV calcite.

Starting calcite has emission wavelength (λ) in the range 598 to 618 nm (Table 1). There is no evidence of any dependence of λ on method of synthesis. In ACV and NHC calcite, there is a positive dependence of wavelength on the combined concentrations of Mn and Mg that becomes apparent when these elements total

TABLE 1. CHEMISTRY AND LUMINESCENCE DATA FOR STARTING CALCITE

Run	Type	Ca ⁺	Mg	Mn	Γ^{\dagger}	λ^{\ddagger} (nm)	Γ^{\S} (nm)
94007	AC			0.00072	10.6 (0.3)	600.1 (0.2)	78.3 (0.1)
94008	AC			0.00082	27.4 (0.3)	599.9 (0.0)	79.5 (0.0)
94009	AC			0.00147	13.8 (0.3)	600.1 (0.1)	78.7 (0.1)
88001	AC			0.00003	0.4 (0.0)	602.4 (2.6)	77.0 (3.3)
88020	AC			0.00006	2.2 (0.2)	600.0 (0.8)	78.7 (0.8)
89029	ACV	0.981	<dl	0.00013	7.4 (0.9)	599.8 (0.3)	79.0 (0.2)
89030	ACV	0.951	<dl	0.00032	5.6 (0.6)	600.6 (0.3)	78.2 (0.3)
90040	ACV	0.898	<dl	0.03560	38.9 (2.0)	605.3 (0.2)	79.4 (0.2)
90043	ACV			0.00027	6.0 (0.6)	601.5 (0.8)	81.2 (0.7)
92014	ACV			0.00892	31.4 (0.4)	600.3 (0.1)	79.2 (0.1)
92015	ACV			0.00792	26.7 (1.0)	599.3 (0.3)	79.7 (0.2)
94029	ACV	0.943	0.007	0.00018	4.6 (0.1)	602.7 (0.9)	80.6 (0.6)
94030	ACV	0.923	0.011	0.00011	6.7 (0.3)	601.6 (0.3)	81.0 (0.3)
94031	ACV	0.906	0.031	0.00018		606.5 (0.2)	81.3 (0.6)
92019(a)	NC			0.00059	4.8 (0.7)	600.7 (0.2)	79.6 (0.3)
92019(b)	NC			0.00049	1.9 (0.1)	602.1 (0.3)	76.2 (0.4)
92020(a)	NC			0.00992	27.9 (0.5)	599.9 (0.2)	80.8 (0.2)
92020(b)	NC			0.00567	16.6 (0.3)	600.2 (0.6)	78.6 (0.1)
92020(c)	NC			0.00030	3.1 (0.1)	600.5 (0.3)	78.0 (0.1)
94101	NHC	0.708	0.305	0.02952	6.9 (0.1)	610.8 (0.5)	92.4 (0.3)
94102	NHC	0.943	0.050	0.00648	15.5 (0.6)	605.4 (0.3)	81.7 (0.1)
94103	NHC	0.964	0.024	0.00747		600.6 (0.1)	81.2 (0.0)
94104	NHC	0.973	0.017	0.00431		600.3 (0.1)	80.6 (0.1)
94105	NHC	0.983	0.006	0.00361	31.2 (1.4)	602.0 (0.2)	80.6 (0.7)
94110	NHC	0.688	0.247	0.09109	2.8 (0.1)	618.0 (0.4)	92.0 (0.5)
94111	NHC	0.964	0.028	0.00458		597.8 (0.2)	84.1 (0.1)
94112	NHC	0.972	0.016	0.00624		598.5 (0.1)	81.9 (0.1)
94113	NHC	0.981	0.006	0.00523		599.5 (0.1)	79.4 (0.1)
94114	NHC	0.985	<dl	0.00624		599.6 (0.1)	79.2 (0.2)

[†] Atoms per formula unit. Analyses by atomic absorption except values in italics by microprobe, for which limits of detection are: Mg 5.3×10^{-4} atoms p. f. u.; Mn 6.6×10^{-4} atoms p. f. u. (2 σ).

[‡] Standard error in brackets

[§] Wavelength.

[¶] Full-width-at-half-maximum-height

more than approximately 0.01 *apfu* (Fig. 3). There is no discernible dependence of wavelength on composition at lower concentrations for any of the different types of starting calcite. (See the Discussion regarding the choice of total Mn and Mg as the independent variable in this and other figures.)

The range of bandwidths (Γ) observed for the synthesis products is 76 to 92 nm, but only two samples of

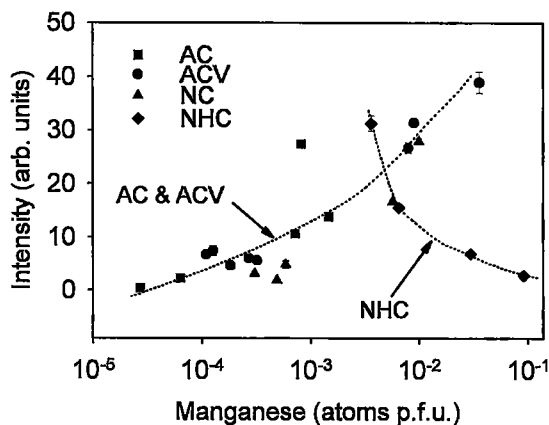


FIG. 2. Relationship between CL intensity and Mn concentration for starting calcite. The dotted lines highlight trends described in the text. Concentration is plotted on a logarithmic scale. Error bars are less than the symbol size, except where shown.

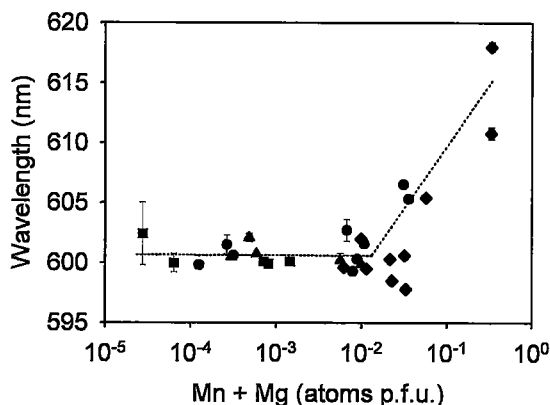


FIG. 3. Dependence of the wavelength (λ) on the combined concentration of Mn and Mg. Concentration is plotted on a logarithmic scale. Symbols as Figure 2.

starting calcite have Γ greater than 82 nm (Table 1). Bandwidth increases with the combined concentrations of Mn and Mg (Fig. 4). There is no evidence of any systematic dependence of Γ on method of synthesis.

Effects of heating on CL spectra

Heating experiments were carried out at temperatures in the range 75 to 400°C for up to 1921 hrs, with the majority of experiments in the range 15 to 50 hrs. Pressure in the hydrothermal experiments was 500 ± 40 bars except in a series of experiments on AC calcite at 300°C, in which pressures of 930, 1660 and 2146 bars were used. Pressure in the CO₂ experiments was approximately 1 bar. Results of luminescence measurements on heated calcite are presented in Table 2.

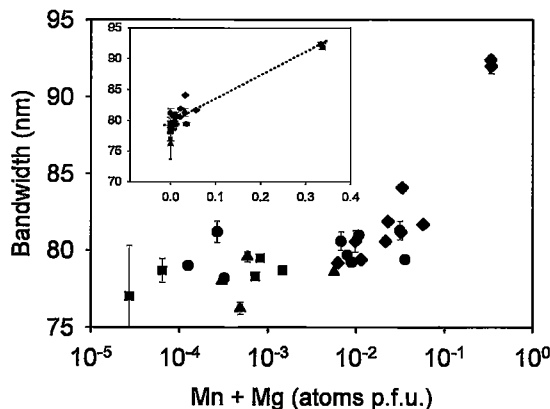


FIG. 4. Dependence of bandwidth (Γ) on the combined concentration of Mn and Mg. The apparent change in slope near 0.06 *apfu* is an artifact of the logarithmic scale used for concentration. Symbols as Figure 2.

Run	Starting calcite	Temp. (°C)	Time (hours)	I_H/I_{Ref}^1	$\Delta\lambda$ (nm)	$\Delta\Gamma$ (nm)
AC 75 - 400 °C						
95033-2	94008	76	27.3	1.08 (0.02)	-0.52 (0.25)	0.26 (0.50)
95031-2	94008	76	184	1.01 (0.03)	1.35 (0.22)	-1.01 (0.43)
95026-2	94008	102	27.3	0.97 (0.02)	1.77 (0.20)	-1.21 (0.53)
95060-2	94008	99	1920.4	1.32 (0.04)	0.15 (0.38)	-0.32 (0.41)
95025-2	94008	123	28.2	1.15 (0.03)	0.99 (0.23)	-1.01 (0.49)
95061-2	94008	128	1920.8	1.23 (0.07)	1.52 (0.45)	-1.11 (0.44)
95027-2	94008	196	28	1.21 (0.08)	1.30 (0.27)	-0.61 (0.53)
94087	94008	399	23.8	1.73 (0.03)	-0.28 (0.25)	-0.37 (0.49)
AC 75 - 400 °C						
95019	94009	74	24.8	1.29 (0.02)	-2.46 (0.49)	1.76 (0.46)
95032-2	94009	70	160.4	1.18 (0.02)	-0.29 (0.10)	0.12 (0.36)
95018	94009	94	25.2	1.14 (0.01)	0.39 (0.08)	-0.25 (0.30)
95023-2	94009	94	42.7	1.19 (0.04)	-1.20 (0.23)	-0.37 (0.49)
95024-2	94009	117	42.6	1.15 (0.08)	-3.13 (0.51)	2.90 (0.34)
95017	94009	201	31	1.39 (0.03)	-0.55 (0.14)	0.56 (0.32)
95086 ²	94009	300	161.5	1.58 (0.05)	0.22 (0.11)	-0.86 (0.39)
95088 ³	94009	301	24.3	1.58 (0.04)	-0.86 (0.12)	0.24 (0.40)
95089 ⁴	94009	299	23.1	1.69 (0.04)	-0.14 (0.13)	-0.92 (0.40)
95016	94009	400	29	1.78 (0.01)	0.37 (0.07)	0.04 (0.29)
94088	94009	399	103.4	1.74 (0.04)	0.41 (0.10)	-0.57 (0.32)
ACV 400 °C						
94082	94029	400	20.4	2.63 (0.28)	0.01 (0.97)	-1.33 (0.65)
94083	94030	403	23.8	1.39 (0.07)	2.12 (0.37)	-1.59 (0.46)
94084	94031	401	21.8	3.15 (0.34)	-4.07 (0.49)	0.43 (0.78)

¹ Standard errors in brackets. ² Pressure = 930 bars. ³ Pressure = 1660 bars.
⁴ Pressure = 2146 bars

X-ray-diffraction spectra show that NHC calcite with compositions inside the calcite - dolomite solvus breaks down into two phases on heating. The XRD reflections from the exsolved phases are very wide, but the patterns match a dolomite-like phase (without superstructure reflections) and calcite. Compositions estimated from the (calibrated) positions of the 104 reflections indicate that the combined concentration of Mn and Mg in the Ca-rich phase is less than approximately 0.015 *apfu*. The relative intensities of the 104 reflections suggest that the dolomite-like phase is quantitatively dominant in all the two-phase mixtures. Other samples of NHC calcite and all samples of AC, NC and ACV calcite remain single-phase on heating.

The factors that influence the value of I_H/I_{Ref} obtained in a given experiment are temperature, method of heating and method of preparation of the starting calcite. There are also consistent differences among samples prepared by the same method. There is no evidence of a pressure effect in the hydrothermal experiments within the range 500 to 2146 bars. Changes in CL intensity are accomplished within 2 to 5 hours at 100°C and above. The few data available suggest that at a lower temperature, longer experiments are required for the changes in CL intensity to be completed. The quantity of water present in the hydrothermal experiments has no influence on the value of I_H/I_{Ref} attained at any temperature or on the rate at which changes in CL intensity take place.

Heating causes an increase in luminescence intensity, with the majority of I_H/I_{Ref} in the range 1 to 7. The full range of I_H/I_{Ref} is 0.65 to 16.5, with five experiments yielding I_H/I_{Ref} less than 1 and six giving values greater than 7. The highest I_H/I_{Ref} came from an NHC starting calcite containing 0.03 Mn and 0.3 Mg *apfu* that recrystallized hydrothermally to two phases at 400°C (Table 2).

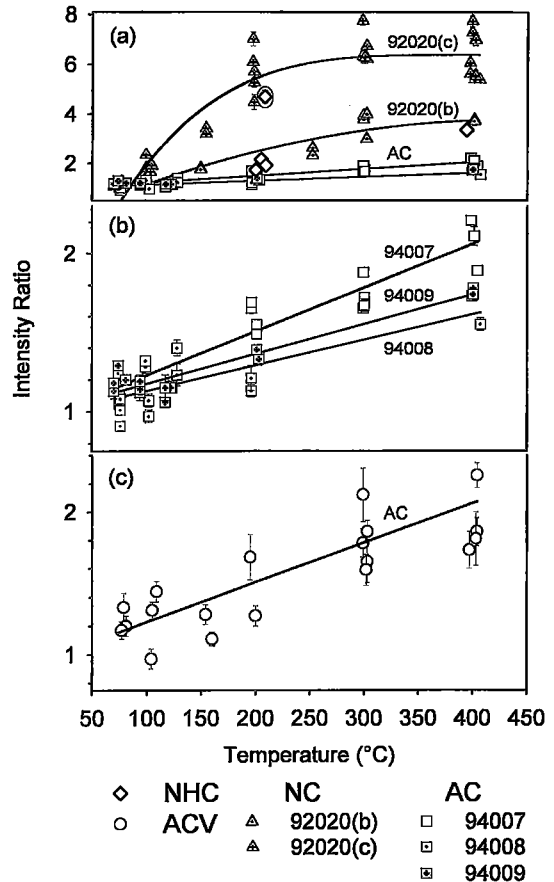


Fig. 5. I_H/I_{Ref} as a function of temperature and starting calcite for the hydrothermal experiments. Note the difference in scale of the abscissa in (a), (b) and (c). The curves and lines have no theoretical significance. The line in (c) is that for the 94007 data from (b). The circled datum on (a) is from a sample that broke down to two phases on heating. One datum for NHC calcite ($I_H/I_{Ref} = 16.5$ at 400°C) is not shown. Error bars are less than the symbol size except where shown.

The intensity ratio increases with temperature for any given starting calcite and method of heating. When heated hydrothermally, NC calcite has higher I_H/I_{Ref} at a given temperature than AC and ACV calcite (Fig. 5). The intensity ratio of heated NC calcite increases non-linearly with temperature, apparently reaching a plateau at 300 to 400°C (Fig. 5a). Intensity ratios for heated calcite 92020(b) are consistently lower than for heated calcite 92020(c). Data for hydrothermally treated NHC calcite are few, but I_H/I_{Ref} are similar to those for NC calcite (Fig. 5a). NHC calcite with compositions inside the calcite - dolomite solvus invariably broke down into two phases on heating. In general, I_H/I_{Ref} is greater for

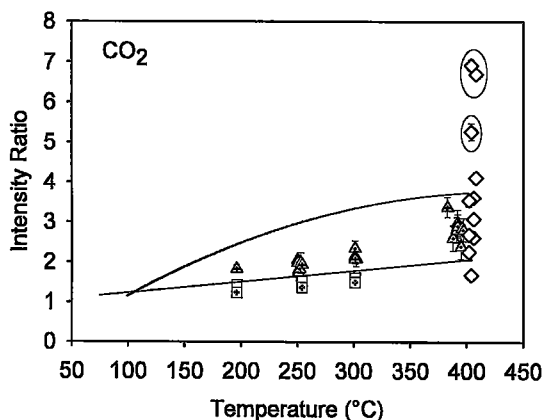


FIG. 6. Intensity ratio (I_H/I_{Ref}) as a function of temperature and starting calcite for the CO_2 experiments. The curved line is for NC calcite 92020(b) (from Fig. 5a), and the straight line is for AC calcite 94007 (from Fig. 5b). Symbols as Fig. 5. The circled data are from samples that broke down to two phases on heating.

these samples compared with NHC calcite that remains single-phase. Intensity ratios for hydrothermally heated AC calcite increase with temperature, but there is no indication that a plateau is reached over the temperature range studied. AC calcite 94007 has the highest, 94009 has intermediate, and 94008 has the lowest I_H/I_{Ref} at any temperature (Fig. 5b). Hydrothermally heated ACV calcite has intensity ratios similar to those of AC calcite heated under the same conditions; there is, however, considerable scatter in the data (Fig. 5c). There is no compelling evidence of systematic differences in I_H/I_{Ref} among samples of ACV calcite.

Heating in CO_2 generally yields lower intensity ratios than heating under hydrothermal conditions (Fig. 6). In NC calcite, the difference between the two methods of heating is relatively large, whereas in AC calcite it is small. The few data available for hydrothermal treatment of NHC calcite make clear that their I_H/I_{Ref} extend to higher values than for heating in CO_2 . There are systematic differences among the types of starting calcite, with NC calcite and NHC calcite having higher I_H/I_{Ref} than AC and ACV calcite heated under similar conditions. This behavior is similar to that observed when heating is carried out in the presence of water.

There is no significant difference in I_H/I_{Ref} between the two samples of NC calcite when heated in CO_2 . This is in contrast to hydrothermal treatment. Two samples of AC calcite heated in CO_2 differ in I_H/I_{Ref} , with calcite 94007 having consistently higher values than calcite 94009. This difference is in the same sense as observed in the hydrothermal experiments. Intensity ratios for ACV calcite heated in CO_2 (Mason 1994) are essentially the same as for hydrothermal treatment.

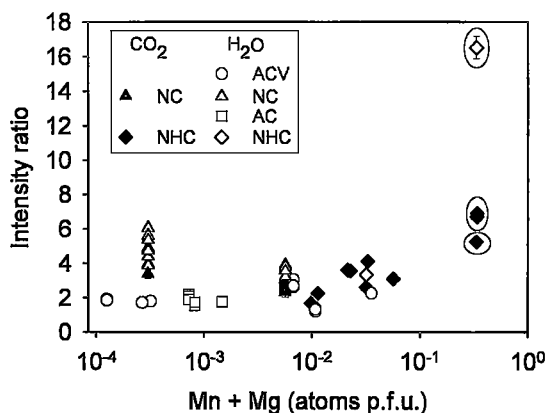


FIG. 7. Intensity ratio (I_H/I_{Ref}) as a function of the combined concentration of Mn and Mg for hydrothermal and CO_2 experiments conducted at $400^\circ C$. Concentration is plotted on a logarithmic scale. The circled data are from calcite that broke down to two phases on heating.

In heated NHC calcite, I_H/I_{Ref} increases systematically as the combined concentration of Mn and Mg increases from approximately 0.01 to 0.33 *apfu*. This trend is most clearly shown by the data for heating in CO_2 , although similar behavior is suggested by the more limited data for hydrothermal treatment (Fig. 7). The largest I_H/I_{Ref} are found for starting calcite that broke down to two phases on heating. Among heated AC, ACV and NC calcite, there is no evidence of any systematic dependence of I_H/I_{Ref} on composition, although, as described above, individual samples of NC and AC calcite attain different intensity ratios when heated under the same conditions.

An attempt was made to ascertain if I_H/I_{Ref} is a reversible function of temperature. The NC calcite 92020(c) was heated hydrothermally at $400^\circ C$ for 71 hours, resulting in an I_H/I_{Ref} of 5.4 ± 0.2 . Two portions of this heated calcite were then separated and heated hydrothermally for 164 hours at 480 bars, one portion at 100° and one at $150^\circ C$. At $100^\circ C$ there was, statistically, no change in the intensity ratio ($I_H/I_{Ref} = 5.6 \pm 0.2$), whereas at $150^\circ C$ the intensity ratio increased to 6.8 ± 0.2 . The latter value lies within the range of I_H/I_{Ref} observed for hydrothermal heating of this starting calcite at $400^\circ C$. These results show that the change in intensity induced by heating is irreversible.

Heating induced changes in the wavelength of CL emission in some experiments. The changes ($\Delta\lambda$) range from -7 to 13 nm for calcite heated in CO_2 and -4.6 to 9 nm for calcite heated hydrothermally (Table 2). In general, only changes in wavelength greater than approximately ± 1 nm are statistically significant. There was no significant change in wavelength for either of the reversal experiments.

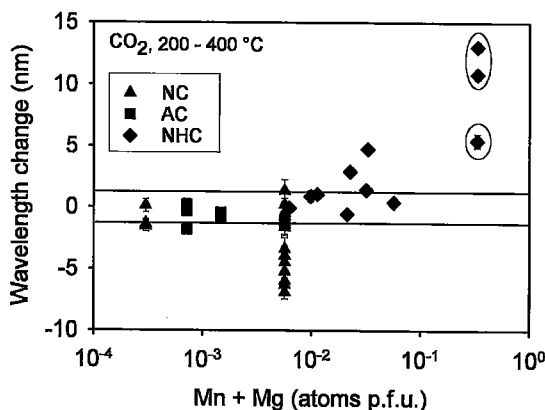


FIG. 8. Change in wavelength ($\Delta\lambda$) as a function of the combined concentration of Mn and Mg for samples heated in CO_2 at 200 to 400°C. The horizontal lines represent the approximate limits of significant change in wavelength (± 1 nm). Concentration is plotted on a logarithmic scale. The circled data are from calcite that broke down to two phases on heating.

Changes in wavelength are erratic for hydrothermally heated calcite, with no evidence that $\Delta\lambda$ is temperature-dependent. The largest $\Delta\lambda$ was recorded for heated NHC calcite (with Mn and Mg totaling 0.33 *apfu*) that separated into two phases on heating. There is no evidence of a systematic dependence of $\Delta\lambda$ on composition for the remaining samples.

Wavelength became shorter in 15 out of 19 experiments in which NC calcite was heated in CO_2 ($\Delta\lambda$ was insignificant for the remainder). There is a systematic decrease in the magnitude of $\Delta\lambda$ (from an average of -4 to -0.4 nm) with increasing temperature between 250 and 400°C. Among heated samples of NHC calcite, $\Delta\lambda$ is dominantly positive (*i.e.*, wavelength increases on heating) and increases as total Mn and Mg increases from 0.01 to 0.33 *apfu* (Fig. 8). At the latter composition, two phases formed during heating. Changes in wavelength for heated AC calcite were invariably very small.

Changes in the bandwidth ($\Delta\Gamma$) of the CL emission peak are generally small (ranging from -6 to 3.5 nm) and typically less than ± 2 nm. In hydrothermally heated NHC calcite, $\Delta\Gamma$ is consistently negative (*i.e.*, the bandwidth decreases on heating), but in AC, ACV and NC calcite, it is erratic in sign. There is no evidence of any dependence of $\Delta\Gamma$ on composition or temperature. The greatest changes in bandwidth were found in NHC calcite heated in CO_2 (Fig. 9) and, as with the hydrothermal data for this type of calcite, $\Delta\Gamma$ is consistently negative. There is no evidence of any dependence of $\Delta\Gamma$ on temperature for any of the different types of starting calcite, but Figure 9 suggests that in calcite containing more than approximately 0.01 Mn and Mg *apfu*, the CL emission band becomes narrower on heating.

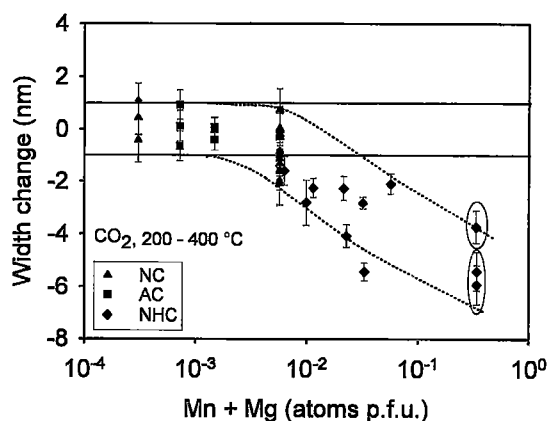


FIG. 9. Change in bandwidth ($\Delta\Gamma$) as a function of the combined concentration of Mn and Mg for samples heated in CO_2 at 200 to 400°C. The horizontal lines represent the approximate limits of significant change in bandwidth (± 1 nm). Concentration is plotted on a logarithmic scale. The circled data are from calcite that broke down to two phases on heating.

Other effects of heating

XRD peaks become narrower as a result of heating, especially under hydrothermal conditions at 300°C and above and for NC and NHC calcite. Figure 10 illustrates, for NC calcite, the spectral region containing reflections from lattice planes 214, 208 and 119. After hydrothermal treatment at 300°C or above, the width of the peaks is comparable to that of natural calcite. In contrast, heating hydrothermally at 100°C, or at any temperature in CO_2 , has little effect on XRD peak widths. AC calcite has substantially narrower XRD peaks, and heating causes only a slight reduction. In ACV calcite (Fig. 11), peak width is comparable to that of natural calcite, and heating causes no change. Notably, any decrease in the width of XRD peaks is greatest where I_H/I_{Ref} is relatively large. Unit-cell parameters did not change as a result of heating except where the starting calcite broke down into two phases.

SEM examination of heated calcite shows that there are systematic changes in grain size and morphology during heating. These are most apparent in hydrothermally heated calcite. Figure 1b illustrates an example from the NC series. After being heated hydrothermally at 400°C for 100 hours, the crystals have coarsened to 5–20 μm and have lost any faces and edges present in the starting calcite (Fig. 1a). Similar changes take place in calcite of the AC and NHC series, though coarsening of AC calcite is less extensive than that of NC calcite. Hydrothermal treatment of ACV calcite leaves the crystals essentially intact, but with a little recrystallization at the margins.

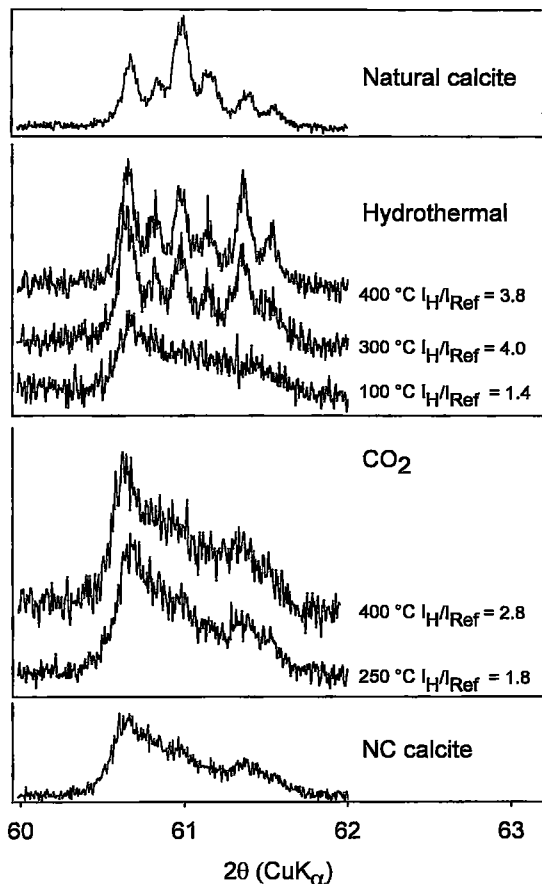


FIG. 10. XRD spectra for the 2θ region 60 to 62° for natural calcite and for AC calcite before and after heating hydrothermally and in CO₂.

DISCUSSION

This discussion will first deal with hypotheses that may explain the data before going on to consider how the results apply to natural calcite. Finally, some comments will be presented regarding prospects for use of CL as a geothermometer.

Controls on CL intensity

The principal observations to be explained are (a) that heating of synthetic calcite causes an increase in the CL intensity, (b) that different methods of synthesis produce calcite that differs in its response to heating, and (c) that individual samples of calcite prepared by the same method differ in their response to heating. There are two hypotheses that can, in principle, explain the effect of heating on CL intensity. Both hypotheses involve changing the concentration dependence of

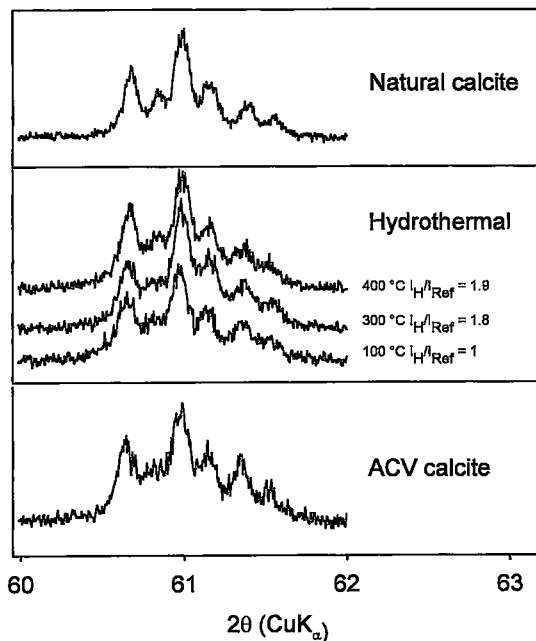


FIG. 11. XRD spectra for the 2θ region 60 to 62° for natural calcite and for ACV calcite before and after heating hydrothermally.

luminescence. A brief review of that dependence is presented below, and further details are given in Walker (1985) and Imbusch (1978). A quantitative treatment is given by Johnson and Williams (1950a, b).

As the concentration of activator ions in a matrix increases, the intensity of luminescence increases to a concentration beyond which the addition of activator ions causes it to diminish. This phenomenon (concentration quenching) arises because there is a finite probability that an activator in an excited electronic state will transfer the excitation energy to an adjacent activator that is sufficiently close. This process can continue until the excitation energy is released radiatively (*i.e.*, with the production of luminescence) or non-radiatively (*i.e.*, with the production of phonons only). Non-radiative release is more probable if the excitation energy is passed to an activator that is close to a defect (*e.g.*, a vacancy, an impurity, *etc.*) (Imbusch 1978). The more times the excitation energy is passed among adjacent activators, the greater the chance that it will eventually encounter an activator on which non-radiative decay is probable. Thus as the number of activator ions in close proximity increases, so too does the probability of non-radiative release of excitation energy.

If the distribution of activator ions on the available sites is random, then as the activator concentration is increased, the number of isolated activators will increase. So too, however, will the probability of find-

ing activators on adjacent sites in clusters of different sizes. At a high concentration of the activator, there are relatively few isolated activator ions, resulting in relatively low intensity of luminescence. The distribution of the activators on the available sites (in clusters, in random occupancy, in patterns of order, *etc.*) and the nature and concentration of defects that encourage non-radiative release of excitation energy will therefore play important roles in controlling CL intensity. The hypotheses to be considered deal with these effects; they will be stated, then compared with the evidence presented above.

The hypothesis of defects: Defects of unknown type are present at different concentrations in calcite made by different methods. Heating causes destruction of these defects, thus allowing increased CL emission without change in the bulk composition of the calcite.

The hypothesis of clusters: Calcite synthesized by different methods has differently distributed activator ions (*e.g.*, different numbers and sizes of clusters), leading to different extents of concentration quenching at a given (bulk) concentration of activator. Heating disperses the clusters, leading to enhanced efficiency of CL.

Both hypotheses explain the observations on CL intensity and its change on heating. If the hypothesis of defects is correct, then NC and NHC calcite have greater concentrations of defects than AC and ACV calcite. If the hypothesis of clusters is correct, then NC and NHC calcite have a greater portion of their Mn concentration contained in clusters than do AC and ACV calcite. The evidence from XRD spectra and from changes in the wavelength of CL emission on heating, together with indirect evidence concerning the local distribution of Mn that can be inferred from phase equilibria, are important in testing these hypotheses and will be discussed below.

XRD spectra and crystal size

As described above, both NC and NHC calcite have relatively wide XRD reflections that become significantly narrower on (hydrothermal) heating. The width of XRD reflections depends on the degree of perfection (crystallinity) of the structure and on the size of the crystals, being greater where the crystallinity is poor and crystals are small (Klug & Alexander 1974). The difference in width of XRD peaks among types of starting calcite cannot be attributed to grain-size effects because AC calcite, with relatively narrow XRD peaks, has similar grain-size to NC calcite, with wide XRD peaks. It is unlikely that the cluster hypothesis can explain differences in XRD spectra among NC, AC and ACV calcite because Mn concentrations are generally too low to cause significant structural distortion. The evidence from XRD spectra of NC, AC and ACV calcite thus favors the hypothesis of defects. The width of XRD peaks from NHC calcite with high Mn and Mg could be

explained by the distribution of these elements, by defects, or a combination of both factors.

Wavelength

The wavelength of emission depends on the number and identity of cations in the second coordination shell about an activator, because they exert an influence on the *M*-O distance of the activator. This changes the energy difference between the lowest excited state and the lower level state involved in emission (usually the electronic ground state) (Walker 1985, Imbush 1978). Where an activator is in dilute solution in the host, it is dominantly the host cations (Ca in the present case) that occupy the second coordination shell. As these are replaced by other substituents (Mn or Mg in the present case), the wavelength of emission should shift systematically in a direction controlled by the characteristic *M*-O distance of the substituent, together with any changes in distance brought about by relaxation of the structural strain associated with substitution of a differently sized ion (Waychunas 1988). Sommer (1972) demonstrated that in the rhombohedral carbonates, the wavelength of emission from Mn²⁺ increases with increasing Mg content. This is consistent with the shorter *M*-O distances observed in Mg-O polyhedra in dolomite and magnesite (Reeder 1983).

The present data do not permit the effects of Mn and Mg unambiguously to be separated because the majority of samples with substantial Mg also have a high concentration of Mn. Starting calcite lacking Mg has Mn concentrations in the range 3×10^{-5} to 0.036 *apfu* (Table 1). The starting calcite with the highest concentration of Mn in this group has the longest emission wavelength (605 nm), suggesting that wavelength increases with Mn concentration. The behavior of wavelength as a function of Mn can also be inferred from crystal-chemical arguments. In rhodochrosite, the *M*-O distance is 0.219 nm (Reeder 1983, Table 2a), compared with 0.210 nm for magnesite and 0.236 nm for calcite. It is expected, therefore, that the effects of Mn and Mg on λ will be complementary, substitution of both causing an increase in the wavelength of emission. This explains the systematic increase in λ that is observed for combined Mn and Mg concentrations greater than approximately 0.01 *apfu*. (This expected similarity in the effect of Mn and Mg substitution on wavelength is the reason that the total of these ions per formula unit is used as the independent variable in plots of λ and $\Delta\lambda$ as a function of composition.)

Given that local coordination controls the wavelength of emission, then changes therein must reflect changes in the coordination of the activator induced by heating. A simple interpretation based on the relations between wavelength and composition discussed above is that shifts to shorter wavelength (negative $\Delta\lambda$) reflect decreasing abundances of Mn or Mg or both around any one activator, and a positive $\Delta\lambda$ reflects an increase. In

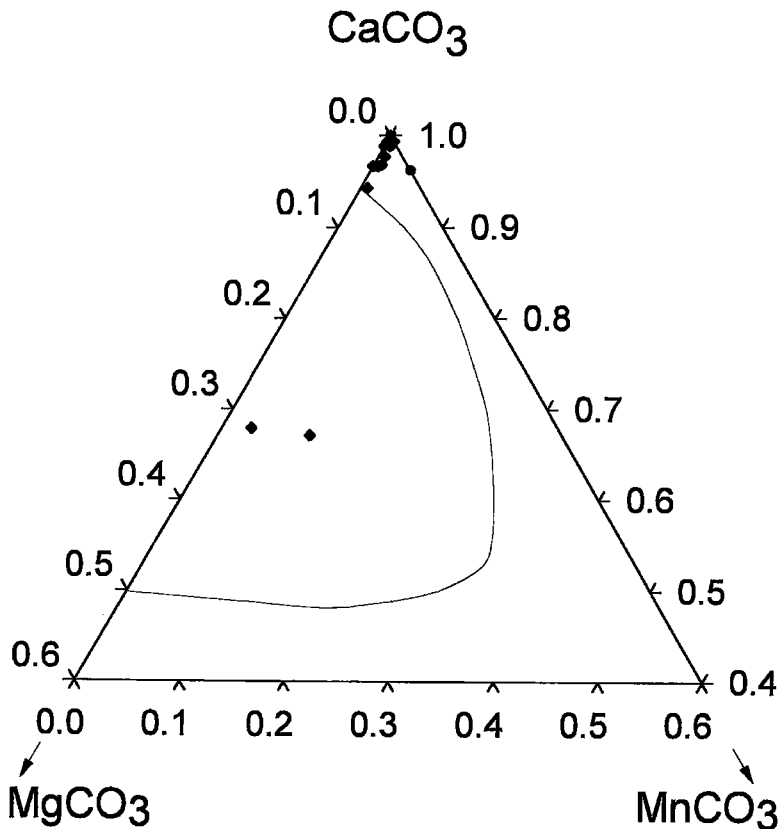


FIG. 12. A portion of the system $\text{CaCO}_3 - \text{MnCO}_3 - \text{MgCO}_3$ at 500°C , 10 kbar (after Goldsmith & Graf 1957). The solid symbols indicate the compositions of starting calcite. Symbols as Figure 2.

terms of the cluster hypothesis, negative $\Delta\lambda$ represents dispersal of clusters, and positive $\Delta\lambda$ represents the formation of clusters. Inferences regarding the likelihood of the formation or dispersal of clusters can be drawn from consideration of phase relations in the system $\text{CaCO}_3 - \text{MgCO}_3 - \text{MnCO}_3$, together with $\Delta\lambda$.

The $\text{CaCO}_3 - \text{MgCO}_3 - \text{MnCO}_3$ system was studied by Goldsmith & Graf (1960). Their phase boundaries for the Ca-rich portion of the system at 500°C and 10 kbar (the closest approach to the heating temperatures used in the present study) are shown in Figure 12, along with the phase compositions of starting calcite used in the present work. In the temperature range of the present study, the ternary solvus should be slightly wider. Low pressures should also serve to widen the solvus if the data of Goldsmith & Newton (1969) on the $\text{CaCO}_3 - \text{MgCO}_3$ binary join extend to the ternary system. There is some uncertainty in phase relations on the join $\text{CaCO}_3 - \text{CaMn}(\text{CO}_3)_2$, the compositional region occupied by NC, AC and all but three samples of ACV calcite. Data from phase-equilibrium studies (Goldsmith

& Graf 1957, de Capitani & Peters 1981) indicate the presence of a solid solution from calcite to a composition close to $\text{Ca}:\text{Mn} = 50:50$, even at low temperature. However, reaction rates in this system are low, and Goldsmith (1983) and Peacor *et al.* (1987) have discussed evidence from natural assemblages suggesting that under equilibrium conditions a solvus exists between a Ca-rich solid solution and kutnohorite. If these interpretations are correct, then Ca-Ca and Mn-Mn clusters in Mg-poor calcite should be stable relative to random distributions, even for samples with compositions that lie outside the two-phase region.

Only the two samples of NHC calcite containing the greatest abundances of Mn and Mg have $\Delta\lambda$ that are large and consistent in direction between hydrothermal and CO_2 heating experiments. Manganese partitions into the Mg-rich phase in their unmixed products. This result is consistent with the observations of Lloyd *et al.* (1993) and El Ali *et al.* (1993), who have shown that in dolomite, Mn partitions into the Mg site in preference to the Ca site. The positive $\Delta\lambda$ recorded for these materials

are thus consistent with the changed coordination of Mn implied by phase separation. Partitioning of Mn into the Mg-rich phase requires slight enrichment of Mn relative to the starting calcite. This effect must lead, on average, to closer proximity of the Mn ions than in the starting calcite, and should lead to enhanced concentration quenching and a reduction in CL intensity. Instead, heating of these two samples of calcite invariably caused an increase in CL intensity. Indeed, the largest values of I_H/I_{Ref} encountered in this study came from calcite that unmixed into two phases during hydrothermal treatment. This shows that the cluster hypothesis does not explain the changes in CL intensity, at least within this range of composition.

There is no evidence of phase separation during heating of the remaining samples of NHC calcite. Although their compositions lie outside the ternary solvus (Fig. 12), at low temperature Ca-rich and Mg-rich clusters should be stable relative to a random distribution of cations, their compositions being determined by mixing properties in the Ca–Mg–Mn carbonate system. Both dispersal and growth of clusters are possible, depending on the initial distribution of cations, which is unknown. The preference of Mn for Mg-enriched carbonates (Lloyd *et al.* 1993, El Ali *et al.* 1993) makes it likely that any Mg-rich clusters will partition Mn preferentially relative to Ca-rich clusters. The predominantly positive $\Delta\lambda$ observed for these samples (when heated in CO₂) suggests that such (Mg,Mn)-enriched clusters either form or grow larger during heating. Formation or growth of Mn-enriched clusters should enhance the operation of concentration quenching and cause a reduction in CL intensity on heating. This is not the behavior observed: heating invariably causes an increase in CL intensity.

The erratic nature of wavelength changes for AC, ACV and NC calcite, which lie on the CaCO₃–CaMn(CO₃)₂ join (Fig. 12), and uncertainties regarding phase relations in this part of the system, make evaluation of the cluster hypothesis difficult for these compositions. However, if dispersal of any Mn clusters formed during crystal growth is a major cause of increased CL intensity with heat treatment, then there should be a negative relation between $\Delta\lambda$ and I_H/I_{Ref} for these materials. Such a relationship does not exist. Within the composition range of AC, ACV and NC calcite, the cluster hypothesis is unlikely to explain changes in CL intensity on heating.

Bandwidth

The bandwidth of CL depends on the extent of vibrational interaction between the activator and the ions to which it is coordinated (Walker 1985). The slight increase in bandwidth of luminescence emission with increasing concentration of Mn and Mg could be interpreted as arising solely from changes in this interaction as ions of different mass and electronic structure pro-

gressively replace Ca. If this hypothesis is correct, then the bandwidth of emission from Mn²⁺ in magnesite should differ from that in calcite. This is not the case: the bandwidth (Γ) of CL emission from magnesite is typically 77 to 85 nm (Mason, unpubl. data), a range enclosed by that of calcite in the present study.

An alternative explanation of the effect of composition on bandwidth is that increasing replacement of Ca by Mn and Mg increases the range of coordination environments of the activator. Both random substitution and chemical zoning could cause this effect (Smith 1953, Walker *et al.* 1989). If substitution of Mn and Mg is random, then simple statistics suggest that the greatest range of coordination environments of the activator should arise when Mn and Mg total 0.5 *apfu*. The present measurements are consistent with this interpretation in that Γ increases continuously up to a total Mn and Mg concentration of 0.33 *apfu*, the maximum available in this study. The critical test, to observe if Γ decreases as the total of Mn and Mg approaches 1 *apfu*, cannot be performed with the presently available data. In the absence of evidence to the contrary, it is assumed that the statistical hypothesis is correct.

Heating of NHC calcite caused the emission band to become narrower (*i.e.*, $\Delta\Gamma$ is negative). Taking the statistical hypothesis to be correct, this observation suggests that heating causes a reduction in the range of coordination environments of the activator. This interpretation is consistent with preferential partitioning of the Mn into one phase for those samples that break down into two phases on heating. It is inferred from their negative $\Delta\Gamma$ that in NHC calcite containing lesser amounts of Mn + Mg, there is an increase in clustering of these elements, but without phase separation. This inference agrees with the deductions made on the basis of changes in wavelength.

If the cluster hypothesis is correct, then dispersal of Mn-rich clusters on heating causes the CL intensity to increase. The evidence from changes in wavelength and bandwidth, together with behavior inferred from phase relations in the system CaCO₃–MgCO₃–MnCO₃, is that clusters are more likely to form or enlarge than to disperse during heating. This should lead to reduction in CL intensity, contrary to the observations. The cluster hypothesis is thus considered to be false.

Recrystallization

Morphological study by SEM shows that hydrothermal conditions are optimum for recrystallization, probably because a process of dissolution and reprecipitation can operate, whereas in CO₂ it cannot. The modest recrystallization and improvement in crystallinity that occur when calcite is heated in CO₂ suggest that the correspondingly modest increase in I_H/I_{Ref} under these conditions is a kinetic effect. Where a driving force for recrystallization exists (*e.g.*, phase separation) and a mechanism is available (*e.g.*, solution – reprecipitation),

large changes in CL intensity result from heating. Conversely, when the driving force for recrystallization is smaller, changes in CL intensity are relatively modest. It is concluded that extensive recrystallization under hydrothermal conditions aids the annihilation of defects, causing a reduction in the widths of XRD peaks and a large increase in CL intensity.

Comparison with natural calcite

Among the four methods of synthesis used in the present work, the ACV method produces calcite that is most comparable with natural calcite in terms of crystallinity (as manifested in width of XRD peaks) and of the relatively modest response of CL intensity to heating. The ACV method of synthesis is thus most appropriate if a chemically simple analogue of natural calcite is required for a study of CL. There are, nevertheless, some differences between ACV and natural calcite. The latter exhibits greater variability in the wavelength and width of the CL emission band activated by Mn^{2+} , and in the response of this band to heating (in CO_2), than does ACV calcite. Mason (1997) attributed this variability to the presence of Mg, which extends to 0.02 *apfu* compared with up to 0.03 *apfu* in ACV calcite, in addition to Mn. The present results show that the presence of Mg within this range of concentration does not explain these differences. As discussed above, the wavelength and bandwidth of CL emission, and changes in these parameters, most probably depend on the local distribution of Mn and Mg. If this interpretation is correct, differences between natural and ACV calcite may reflect greater variability in their distributions in the former. Alternatively, the presence of both Fe and Sr in natural calcite might play a role, although their low concentrations [0.004 and 0.0003 *apfu*, respectively; Mason (1997)] make this unlikely.

The existence of a temperature effect on CL intensity raises the possibility that it could be used as a geothermometer. Mason (1997) showed that whereas CL intensity in natural calcite can be modified by heating, any systematic effects are overwhelmed by variability in the response of individual samples. The present results confirm that different samples of calcite respond differently to heating. The results of attempted reversals show also that CL intensity responds in a complex way to heating at a sequence of temperatures, as might be encountered during exhumation of a sedimentary succession. The origin of these effects must be understood if the goal of using CL as a geothermometer is to be realized.

CONCLUSIONS

(1) The intensity of luminescence from synthetic calcite doped with Mn^{2+} depends on the method of preparation. Differences in CL intensity are ascribed to

differences in the density of defects acquired during crystal growth.

(2) The wavelength and bandwidth of CL of emission from calcite increase as Ca atoms are replaced by Mn and Mg.

(3) There are significant differences in the width of XRD peaks among batches of calcite synthesized by different methods. These differences are attributed to differences in the density of defects.

(4) The intensity of luminescence from Mn^{2+} -activated calcite is increased by heating, especially in the presence of H_2O . The increase is greater at higher temperatures.

(5) The magnitude of the increase in CL intensity induced by heating depends on the method by which calcite is synthesized. Differences among batches of calcite prepared by different methods are attributed to systematic differences in density of defects.

(6) Wavelength and bandwidth of CL emission may change during heating. These changes are attributed to redistribution of Mn and Mg at the available sites.

(7) XRD peaks become narrower when synthetic calcite is heated in the presence of water. The change is greatest at higher temperature and in calcite showing the largest concomitant increase in CL intensity.

(8) Individual samples prepared by the same method differ in the magnitude of their response to heating. Composition contributes to this effect, but sample-to-sample differences in density of defects also may be important.

(9) Changes in the CL intensity and reduction in XRD peak width induced by heating are attributed to annihilation of defects.

(10) Calcite precipitated from $CaCl_2$ solution by contact with ammonium carbonate vapor provides the best synthetic analogue of natural calcite in terms of its response to heating.

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