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THE INFLUENCE OF HEATING ON CATHODOLUMINESCENCE EMISSION FROM NATURAL CALCITE

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ABSTRACT

Rocks from the Cambro-Ordovician carbonate platform of western Newfoundland were heated at 400°C for 18.8 to 336 hours. Cathodoluminescence (CL) emission spectra were collected from heated and unheated ("reference") calcite from these rocks. Three CL parameters were measured from the spectra: intensity, wavelength and bandwidth. On heating, CL intensity typically increases by up to 2.6 times, very similar to the behavior noted in synthetic calcite. Emission wavelength changes by –20 to +11 nm, and bandwidth changes by –6 to +12 nm. The natural calcite differs from synthetic calcite in displaying greater differences in emission wavelength and bandwidth between samples, and in experiencing greater changes in these parameters as a result of heating. The CL parameters and changes in them are compared with an indicator of thermal maturity, the Conodont Color Alteration Index (CAI). The majority of samples with a CAI of less than 3 have emission wavelength (reference) greater than 604 nm, change in wavelength less than 0 and change in bandwidth greater than 0. Most samples with CAI greater than 3 have emission wavelength (reference) less than 611 nm, change in wavelength greater than 0 and change in bandwidth less than 0. Twenty-eight (of 37) samples meet one or the other of the sets of criteria. Of these, 22 are correctly placed into the appropriate CAI group (a success rate of 79%). Six samples are placed into the wrong CAI group. The remaining nine samples meet neither set of criteria, and are thus "indeterminate". The potential of CL as a tool in geothermometry is confirmed, but substantial improvements in the precision and accuracy of the technique are required in order for it to be of practical utility.

Keywords: calcite, cathodoluminescence, geothermometry, carbonate platform, Newfoundland.

SOMMAIRE

Des échantillons de roches cambro-ordoviciennes de la plateforme de carbonates de l'ouest de Terre-Neuve ont été chauffés à 400°C de 18.8 à 336 heures. Le spectre d'émission en cathodoluminescence (CL) de la calcite de ces roches a été mesuré pour des échantillons chauffés et non chauffés (dits de référence). Trois paramètres ont été mesurés dans ces spectres CL: intensité, longueur d'onde et largeur de la bande d'émission. En chauffant, l'intensité de l'émission augmente, typiquement selon un facteur allant jusqu'à 2.6, comportement qui rappelle celui de la calcite synthétique. La longueur d'onde de l'émission est déplacée entre –20 et +11 nm, tandis que la largeur de la bande émise est modifiée, entre –6 et +12 nm. La calcite naturelle se distingue de la calcite synthétique par la plus grande dispersion de la longueur d'onde d'émission et de la largeur de la bande d'un échantillon à l'autre, et par la plus grande modification de ses paramètres suite au chauffage. Les paramètres CL et les changements décelés dans ces échantillons ont été comparés avec un indicateur indépendant de maturité thermique, l'indice de la couleur modifiée d'un conodonte (CAI). La majorité des échantillons ayant un indice CAI de moins de 3 ont une longueur d'onde d'émission (de référence) de plus de 604 nm, qui diminue et dont le pic s'élargit en chauffant. La plupart des échantillons ayant un indice CAI de plus de 3 possèdent une longueur d'onde d'émission (de référence) de moins de 611 nm, qui augmente et dont le pic se retrécie en chauffant. Vingt-huit des trente-sept échantillons satisfont à l'un ou l'autre de ces critères de comportement. De ceux-ci, 22 sont placés correctement dans le classement CAI approprié, pour un taux de réussite de 79%. Six échantillons ne sont pas placés dans le groupe CAI approprié. Les neuf autres échantillons ne satisfont à ni l'un ni l'autre des critères de comportement, et sont donc déclarés "indéterminés". Le potentiel de la cathodoluminescence en géothermométrie s'en trouve confirmé, mais des améliorations importantes dans la précision et la justesse de cette technique seront nécessaires pour en établir une utilité pratique.

(Traduit par la Rédaction)

Mots-clés: calcite, cathodoluminescence, géothermométrie, carbonates de plateforme, Terre-Neuve.

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INTRODUCTION

Spectra of Mn^{2+}-activated luminescence collected from material at room temperature contain broadened emission lines with lower intensity compared with spectra collected at, for example, 77 K (Imbusch 1978, Walker 1985). This effect is *reversible*: the spectral properties change with the temperature at which the data are collected. However, in calcite there is an *irreversible* increase in intensity of luminescence on heating calcite at up to 500°C for several hours (Medlin 1959, 1960, Borsi & Fornaca-Rinaldi 1968, Mason 1994). It has been suggested by Sommer (1972) and Nambi & Mitra (1978) that the temperature of crystal growth also influences the intensity of luminescence emission in natural calcite.

These studies indicate that the luminescence emission of calcite is sensitive to heating in the laboratory and suggest that a similar effect occurs naturally. The present work was undertaken to investigate the effects of heating on the intensity, wavelength and bandwidth of luminescence from natural calcite and to evaluate possible applications in geothermometry. To the latter end, the response to heating is compared with the Conodont Color Alteration Index (CAI; Epstein *et al.* 1977), a semiquantitative measure of the maximum temperature attained by a sedimentary rock.

SAMPLE SELECTION, CAI DATA AND PETROGRAPHY

The samples were collected in western Newfoundland, from the Port-au-Port Peninsula in the south to Quirpon in the north. They range in age from Lower Cambrian to Lower Ordovician (Table 1). Dolostones were avoided, and the material removed from hand specimens for cathodoluminescence (CL) study was

TABLE 1. CAI AND LUMINESCENCE PARAMETERS, SAMPLES OF CARBONATE FROM WESTERN NEWFOUNDLAND

Sample	Formation or Group	CAI	Intensity ratio	Center (reference)	Center (heated)	FWHM (reference)	FWHM (heated)	$\Delta\lambda$	ΔFWHM
BP-1	Recent, Blue Pond		1.12 (0.16)	604.1 (1.7)	609.0 (0.7)	82.7 (1.0)	79.3 (1.4)	4.9 (1.8)	–3.4 (1.7)
WB-6	Black Cove Formation, Llanvirn	1	0.94 (0.07)	607.6 (1.8)	594.6 (1.5)	80.8 (1.2)	89.2 (0.9)	–13.1 (2.3)	8.4 (1.5)
WB-4	Black Cove Formation, Llanvirn	1	0.95 (0.06)	611.0 (0.1)	594.9 (1.7)	80.6 (0.3)	92.4 (1.0)	–16.1 (1.7)	11.7 (1.0)
WB-1	Table Cove Formation, Llanvirn	1	1.17 (0.15)	621.2 (0.5)	615.2 (2.8)	98.9 (3.4)	97.9 (2.4)	–6.0 (2.9)	–1.0 (4.1)
WB-10	Boat Harbour Formation, Tremadoc	1	1.28 (0.16)	609.1 (0.9)	589.4 (0.9)	85.5 (1.4)	93.7 (0.7)	–19.6 (1.3)	8.2 (1.6)
F88030	Table Point Formation, Arenig (?)	1	1.45 (0.08)	605.2 (0.3)	591.8 (0.7)	76.8 (0.6)	85.4 (0.5)	–13.4 (0.8)	8.6 (0.8)
WB-7	Port au Port Group (?), U. Cambrian	1	1.97 (0.16)	611.8 (0.4)	611.9 (0.2)	82.5 (0.9)	80.2 (0.2)	0.1 (0.5)	–2.3 (1.0)
WB-9	Cape Cormorant Formation, Llanvirn	1	2.28 (0.31)	614.4 (1.7)	612.5 (1.4)	87.3 (2.5)	94.5 (4.0)	–2.0 (2.2)	7.2 (4.7)
F88031	Catoche Formation, Arenig	1	2.64 (0.45)	614.6 (0.8)	612.7 (0.2)	83.6 (1.0)	81.4 (0.2)	–1.8 (0.9)	–2.2 (1.0)
F88027	Cow Head Group (?), Arenig	1.5	0.86 (0.10)	598.6 (1.8)	608.0 (0.6)	86.8 (1.0)	84.5 (1.3)	9.4 (1.9)	–2.2 (1.7)
F88029a	Green Point Formation, L. Cambrian (?)	1.5	1.18 (0.07)	612.8 (0.2)	612.9 (0.4)	81.7 (0.3)	81.4 (0.2)	0.1 (0.4)	–0.4 (0.3)
WB-3	Cow Head Group, U. Tremadoc	1.5	1.29 (0.05)	609.8 (0.1)	593.8 (2.0)	79.4 (0.2)	90.1 (1.1)	–16.0 (2.0)	10.7 (1.1)
F88028	Green Point Formation, L. Cambrian (?)	1.5	1.32 (0.16)	610.2 (0.3)	609.8 (0.5)	79.5 (0.8)	79.6 (0.4)	–0.5 (0.6)	0.2 (0.9)
F88022	Aguathuna Formation, Arenig	2	0.92 (0.05)	609.8 (0.4)	609.8 (0.5)	84.9 (0.5)	86.4 (0.5)	0.1 (0.7)	1.5 (0.7)
WB-2	Table Point Formation, Llanvirn	2	1.22 (0.06)	611.0 (0.3)	607.4 (1.3)	81.9 (0.6)	84.6 (0.8)	–3.6 (1.3)	2.7 (1.0)
WB-5	Catoche Formation, Hor. E, L. Arenig	2	1.31 (0.04)	612.5 (0.5)	611.7 (0.2)	80.5 (0.8)	81.7 (0.4)	–0.8 (0.5)	1.2 (0.9)
F88020	Table Head Group, Llanvirn	2	1.39 (0.11)	610.0 (0.5)	600.1 (1.9)	82.9 (0.6)	88.1 (1.0)	–9.9 (2.0)	5.3 (1.2)
F88019	Table Head Group, Llanvirn	2	1.51 (0.13)	609.4 (0.6)	603.9 (1.1)	81.3 (0.50	85.6 (0.8)	–5.5 (1.2)	4.3 (0.9)
F88001	Catoche Formation, L. Arenig	2	1.56 (0.19)	610.0 (0.3)	599.8 (2.6)	78.4 (0.7)	85.9 (2.2)	–10.2 (2.6)	7.5 (2.3)
F88007	Table Head Group, Llanvirn	3.5	1.03 (0.05)	611.5 (0.7)	612.7 (0.3)	81.3 (1.2)	80.2 (1.2)	1.2 (0.7)	–1.1 (1.7)
F88008	Table Head Group, Llanvirn	3.5	1.16 (0.09)	592.4 (0.8)	603.3 (0.7)	95.7 (0.5)	90.5 (0.9)	10.9 (1.1)	–5.2 (1.1)
F88013	Table Head Group, Llanvirn	3.5	1.21 (0.06)	610.2 (1.1)	610.3 (0.2)	81.4 (1.5)	79.6 (0.5)	0.1 (1.2)	–1.9 (1.6)
F88010	Table Head Group, Llanvirn	3.5	1.25 (0.10)	599.4 (2.3)	604.8 (1.1)	86.2 (0.9)	83.8 (0.8)	5.5 (2.5)	–2.4 (1.2)
F88009	Catoche Formation, Arenig	3.5	1.32 (0.16)	611.0 (0.1)	606.6 (1.4)	80.3 (0.3)	82.1 (0.7)	–4.4 (1.4)	1.8 (0.8)
F88018b	Table Head Group, Llanvirn	5	0.84 (0.06)	603.2 (0.3)	603.8 (0.4)	79.9 (0.6)	77.6 (0.4)	0.6 (0.5)	–2.3 (0.7)
F88015	Table Head Group, Llanvirn	5	0.85 (0.06)	598.1 (1.6)	606.5 (0.8)	88.1 (1.2)	81.9 (0.5)	8.4 (1.8)	–6.2 (1.3)
F88016d	Table Head Group, Llanvirn	5	0.90 (0.06)	593.3 (1.5)	596.9 (1.5)	90.3 (1.6)	88.4 (2.6)	3.6 (2.1)	–1.8 (3.1)
F88017b	Table Head Group, Llanvirn	5	1.11 (0.07)	604.5 (0.3)	603.1 (0.4)	76.4 (0.4)	77.8 (0.8)	–1.3 (0.5)	1.4 (0.9)
F88017a	Table Head Group, Llanvirn	5	1.13 (0.09)	590.8 (0.4)	593.7 (0.7)	90.6 (1.5)	86.7 (1.9)	2.9 (0.8)	–3.9 (2.4)
F88016a	Table Head Group, Llanvirn	5	1.16 (0.13)	590.8 (1.0)	593.9 (1.9)	90.8 (3.4)	87.5 (1.4)	3.2 (2.2)	–3.3 (3.6)
F88011	Table Head Group, Llanvirn	5	1.23 (0.10)	605.0 (0.3)	605.2 (0.5)	78.0 (0.5)	79.6 (1.0)	0.2 (0.6)	1.6 (1.1)
F88018a	Table Head Group, Llanvirn	5	1.24 (0.16)	606.3 (0.8)	606.7 (2.2)	83.6 (1.2)	80.9 (1.2)	0.4 (2.3)	–2.6 (1.7)
F88016b	Table Head Group, Llanvirn	5	1.33 (0.21)	591.3 (1.0)	594.3 (1.7)	89.3 (1.3)	89.0 (1.1)	3.0 (1.9)	–0.3 (1.7)
F88016c	Table Head Group, Llanvirn	5	1.37 (0.17)	600.5 (1.6)	592.1 (1.2)	82.6 (1.8)	89.8 (1.5)	–8.4 (2.0)	7.2 (2.3)
F88005	Catoche Formation (?), Arenig (?)	5	1.40 (0.25)	597.4 (2.1)	592.4 (1.6)	79.4 (2.8)	86.1 (1.8)	–5.0 (2.6)	6.6 (3.3)
WB-11	Forteau Formation, L. Cambrian	5	1.41 (0.09)	611.9 (0.2)	603.0 (1.7)	79.6 (0.2)	86.4 (1.1)	–8.9 (1.7)	6.8 (1.1)
F88012	Table Head Group, Llanvirn	5	1.53 (0.18)	608.8 (0.8)	604.3 (1.5)	79.8 (0.7)	82.3 (1.1)	–4.5 (1.7)	2.5 (1.3)

Standard errors are enclosed in brackets. Wavelength of emission λ and full width of peak at half-maximum height (FWHM) are quoted in nm.

chosen to minimize the amount of contaminant dolomite (in order simplify the CL spectra). Nevertheless, characterization of the powders used for the CL work by X-ray diffraction (XRD) shows that most contain some dolomite, and a few contain significant quantities. It was not possible to separate sparite from micrite, or porphyroclastic calcite from granoblastic calcite, nor was it possible to avoid veinlets in some samples.

The color alteration index (CAI) of conodonts was developed and calibrated by Epstein *et al.* (1977) as a means of assessing the paleotemperature of sediments in which there is insufficient material for measurements of vitrinite reflectance (Fig. 1). The index is a numerical scale running from 1 (approximately 50°C) to 5 (approximately 400°C). Changes in conodont color are progressive and irreversible: CAI thus records the maximum paleotemperature of the rocks.

The CAI data used in this study are taken from Nowlan & Barnes (1987). For limestone samples collected at the localities and stratigraphic horizons sampled by those authors, assignment of the CAI value was straightforward. In the absense of CAI data for a given location, equivalent horizons at immediately adjacent localities sampled by Nowlan & Barnes (1987) were used to make estimates. Recent calcite from various localities was examined, but only one sample had measurable luminescence (BP–1, Table 1). There are, of course, no CAI data for this locality.

Rocks with a CAI equal to 5 generally consist of a mosaic of sparite (*i.e.*, grains greater than 20 μm across). Micrite (*i.e.*, grains less than 5 μm across) is present in a minority of the rocks, with an abundance that is generally less than 10% by volume (one sample contains 70%), but fine sparite (*i.e.*, less than 20 μm across) is abundant in about half of the rocks. Where present, calcite porphyroclasts range from 100 μm to 3 mm in size. Porphyroblasts of dolomite are concentrated in specific horizons and range between 200 and 750 μm in size. Trace quantities of quartz were detected by XRD in many rocks, but it is rarely visible microscopically. Matrix sparite is infrequently twinned, the twins being thin (<3 μm) and straight [type I of Burkhard (1993)]. Porphyroclasts are ubiquitously twinned, the twins ranging from thin and straight to thick (greater than 30 μm), wedge-shaped and deformed [type III of Burkhard (1993)]. Deformation is indicated in the field by folds emphasized by dolomite-rich bands.

Rocks with a CAI less than 5 retain sedimentary textures and are more heterogeneous than those with a CAI of 5. They consist of 5 to 85% micrite in the form of peloids and carbonate mudstone, with sparite forming cement, infill to bioclasts and veins. Dolomite was detected by XRD in many samples. It is observed optically as rhombs up to 100 μm on a side in two samples, where it is associated with micrite. Sparite ranges up to 4 mm in size (in veins), but is typically 20 to 400 μm

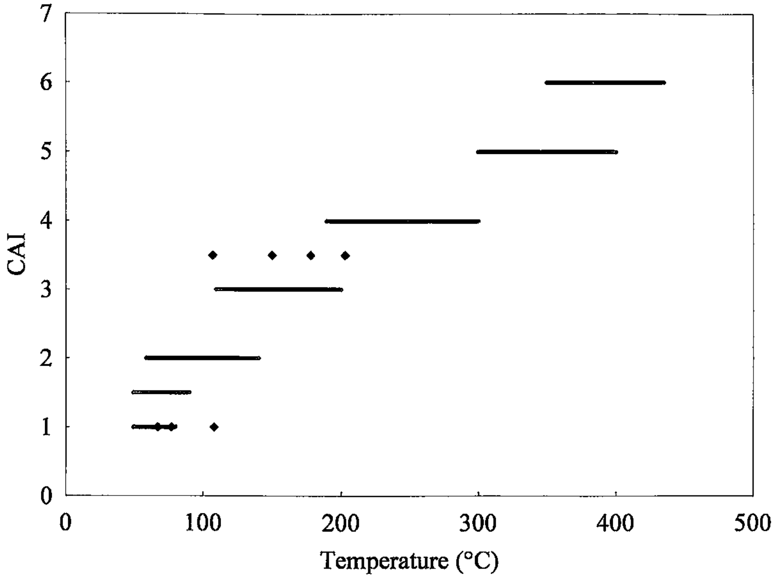

FIG. 1. The range of temperatures represented by each value of the CAI. The data (horizontal bars) are from Epstein *et al.* (1977). The filled diamonds represent fluid-inclusion homogenization temperatures (Saunders *et al.* 1992) from two localities sampled in this study and in Nowlan & Barnes (1987).

in cement and bioclasts. In a few bioclasts, finely fibrous calcite is present. Quartz was detected by XRD in trace to minor quantities, but is never observed microscopically. Twins are not always evident, even in sparite. Where found, they are of the straight, thin variety (Burkhard 1993, type I) except in one sample (with a CAI of 3.5) where some lensoid twins occur [type II of Burkhard (1993)].

EXPERIMENTAL METHODS

Samples were heated in the form of rock fragments crushed to approximately 1 mm on a side. The heating temperature and duration were 400 ± 5°C and 18.8 to 336 hrs, respectively. Heating was carried out in a vertical tube furnace under 1 atmosphere of CO_2 (in order to minimize decarbonation). Mason (1994) has shown that (in synthetic calcite) at this temperature, the exact duration of heating is unimportant within the range used. Following heating, the sample and an equivalent unheated reference sample were crushed (by hand under acetone) in an agate mortar and mounted for CL examination. Excessive grinding of calcite induces defects that modify the absorption spectra (Cervelle *et al.* 1982); consequently, great care was taken to minimize the loading used and the duration of crushing. Details of the sample preparation, mounting and heating procedures are given by Mason (1994).

Luminescence emission was excited using a modified JEOL JXA–50A electron microprobe operating at an accelerating voltage of 15 kV, with a beam diameter of approximately 50 μm and a beam current density of ~14 $\mu A/mm^2$.

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 any spectral overlap (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 ($y = a_o \exp[-x/a_1]$, with a_o the amplitude and a_1 the rate), and a peak function (the Haarhoff – Van der Linde function):

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

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 was chosen because it accommodates the observed assymetrical shape of the peak. The constants derived from the fitting procedure were used to calculate the center (*i.e.*, $dy/dx = 0$) and full-width at half-maximum height (FWHM).

Following the CL work, the powder was mounted for XRD estimation of the proportion of dolomite. This was carried out by direct comparison of the intensities of the (104) reflections of calcite and dolomite. No attempt was made to calibrate these intensities or to compensate for preferred orientation in the XRD mounts and, consequently, the results are only semiquantitative.

A Cameca CAMEBAX SX–50 microprobe equipped with a Link Analytical eXL energy-dispersion spectrometer (EDS) system was used to analyze calcite for Mg, Fe and Mn on polished thin sections of 27 samples and for Sr on ten samples. Ten to 25 analyses were made on each sample. The concentration of Ca was measured by EDS methods, and concentrations of Mg, Mn, Sr and Fe were measured by wavelength-dispersion methods. Calcite, dolomite, rhodochrosite, strontianite and siderite standards were used. The beam conditions were: accelerating voltage 15 kV, beam current 10 nA, and beam diameter 20 μm.

RESULTS

The wavelength and width of the CL emission band were monitored using the center and FWHM, respectively. The intensity was measured using the a_0 parameter obtained in the fitting procedure. These data were used to calculate the means and standard errors reported in Table 1. None of the measured or derived parameters described below shows any dependence on the duration of heating.

Cathodoluminescence spectra

A spectrum from 300 to 1000 nm is illustrated in Figure 2. The prominent emission band near 610 nm is typical of activation by Mn^{2+} incorporated in the Ca site of calcite. In several samples, this band overlaps with the long-wavelength "tail" of an emission band peaking at approximately 400 nm (Fig. 2). The overlap was approximated and removed by the exponential background function described above. This band originates from contaminant detrital or authigenic silicate grains, as indicated by the correlation of its intensity with the abundance of quartz detected by XRD.

Visual examination of polished thin sections by CL shows that dolomite is non-luminescent in these rocks, probably because the Mn^{2+} concentration is too low (electron-microprobe analyses on two samples showed that Mn is invariably below the detection limit of 0.02 wt%). Careful examination of the CL spectra failed to reveal any evidence of emission from dolomite in any of the powders, even where the calcite:dolomite ratio (estimated by XRD) is as low as 1. Such emission

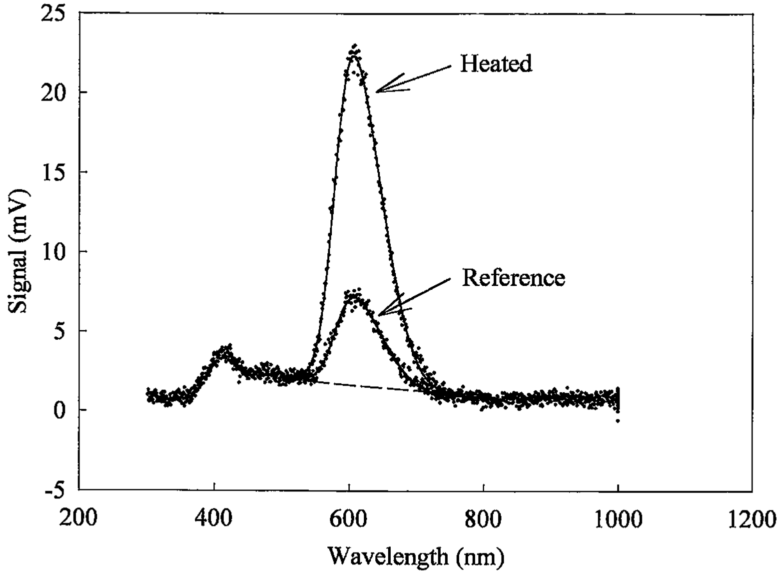

FIG. 2. CL emission spectrum showing broadband Mn^{2+}-activated luminescence at ~610 nm, together with a weaker band in the blue region, at ~400 nm. Data points are shown by solid squares, and fit lines, by solid lines in the region from 500 to 800 nm. The dashed line shows the exponential curve used to model the tail of the 400-nm band. The origin of the latter is discussed in the text. Sample F88031, Table 1.

would be expected to reach a maximum in the range 640 to 670 nm (Marshall 1988, El Ali *et al.* 1993) and, if of sufficient intensity, to be partially resolved from the calcite:Mn emission band. The absence of interference due to dolomite simplifies considerably the interpretation of the spectra.

Cathodoluminescence parameters

The primary control on the intensity of the luminescence band at ~610 nm is the Mn content; a plot of CL intensity *versus* wt% Mn shows an excellent correlation where Mn concentration is above the detection limit of the electron microprobe. There is no evidence of concentration quenching (*i.e.*, reduction of luminescence intensity beyond a certain concentration of the activator; see Machel *et al.* 1991) within the range of Mn contents studied, a result in agreement with the data of Hemming *et al.* (1989). There is no correlation between the iron content and the CL intensity, suggesting that quenching by iron is not significant.

Changes in the Mn^{2+} CL intensity consequent on heating were measured using an "intensity ratio" I_H/I_R, in which I_H is the intensity from the heated material, and I_R is the intensity from the starting material or "reference" calcite (Mason 1994). If natural calcite has been heated after formation, those physical processes responsible for the change in luminescence intensity may have taken place. Heating of such a calcite in the laboratory should produce, at most, only a modest change in CL intensity. Conversely, calcite that has experienced only low temperatures should respond to laboratory heating with a significant increase in CL intensity, if the working hypothesis is correct. Thus, an intensity ratio greater than 1 should indicate a "low-temperature" calcite, and an intensity ratio near 1 should indicate a "high-temperature" calcite. Measured ratios of intensity range from 0.8 to 2.6, but most of the data lie in the range 0.9 to 1.6, with a mode near 1.2 to 1.3 (Table 1).

Figure 3 shows the intensity ratio plotted against CAI. Given that CAI increases with increasing temperature, and assuming the above hypothesis to be correct, there should be a negative relationship between the variables on this plot. This pattern is seen only in that I_H/I_R values for samples with CAI = 1 extend to 2.6, whereas there is almost complete overlap in the ranges of I_H/I_R for samples with CAI greater than 1. Grouping the samples by CAI and taking the mean intensity-ratio for each group emphasizes that the differences between adjacent CAI groups are insignificant in relation to the scatter of I_H/I_R within each group.

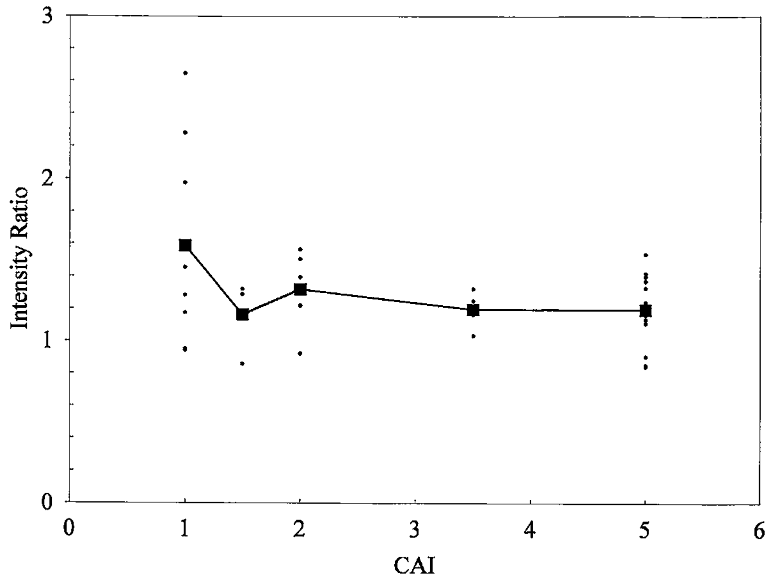

FIG. 3. Intensity ratio (I_H/I_R) plotted against CAI. The mean intensity ratio for each CAI group is shown as a large filled symbol.

The center of the Mn^{2+} emission band lies in the range 590 to 621 nm (standard error typically ±1 nm), with a mean of 606 nm in reference calcite and 603 nm in heated calcite (Table 1). There is no correlation between the emission wavelength of reference material and the calcite/dolomite ratio estimated from XRD data. Such a correlation would indicate spectral interference by Mn^{2+}-activated emission from dolomite. Likewise, there is no discernible relationship between chemical composition and wavelength.

The centers of emission bands from reference material are plotted against CAI in Figure 4. The data define a trend of decreasing wavelength of emission with increasing CAI, as emphasized by the mean values for each CAI group, although the scatter is such that measurement of the center of an individual sample does not allow accurate prediction of the CAI. Given the precision with which the position of the peak centers is known, the scatter within each CAI class must reflect real chemical or physical differences among the materials. For heated calcite, there is no relationship between emission wavelength and CAI.

In some samples, the wavelength of CL emission changed as a consequence of heating. The change is given by: $\Delta\lambda$ = center (heated) – center (reference). The value of $\Delta\lambda$ ranges from –20 to +11 nm, whereas the standard error is typically ±1.5 nm and never worse than ±3 nm. The change in wavelength is plotted as a function of CAI in Figure 5. For a given value of the CAI, there is considerable scatter in the magnitude of $\Delta\lambda$. However, the *sign* of $\Delta\lambda$ is moderately consistent. Of those samples with a CAI greater than 3, heating caused an increase in emission wavelength in a small majority. Of the samples with a CAI less than 3, the majority experienced a decrease in emission wavelength following heating. As with intensity ratios, the CAI could not be predicted with confidence from the behavior of a single sample.

The FWHM of the emission band varies from 76 to 99 nm in both heated and reference calcite (Table 1). The standard error of the measurements is typically ±1 nm, but rises to ±4 nm at the lowest intensity of emission. The FWHM of reference calcite is independent of CAI, but for heated material, there is a very weakly defined negative relationship between FWHM and CAI (Fig. 6). The change in the bandwidth of the Mn^{2+} emission line upon heating was monitored by defining ΔFWHM = FWHM (heated) – FWHM (reference). This parameter ranges from –6 to +12 nm, with a typical standard error of ±2 nm and a maximum of ±4.7 nm. The emission bands from samples with a CAI of less than 3 tend to get broader on heating, whereas both narrowing and broadening are observed for samples with a CAI between 3.5 and 5 (Fig. 7).

Chemical composition

The mean Mg content ranges between 0.07 and 0.50 wt%, with the highest and lowest individual determinations being 0.03 and 1.3 wt%, respectively. The

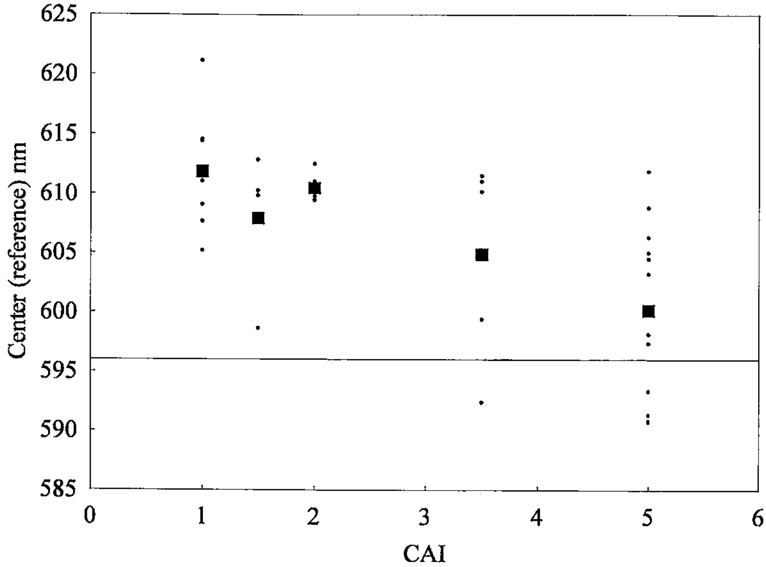

FIG. 4. Emission wavelength (center) of reference calcite as a function of CAI. The large filled symbols represent the mean for each CAI group. The line at 596 nm is the mean emission wavelength for synthetic calcite (Mason 1994; unpubl. data).

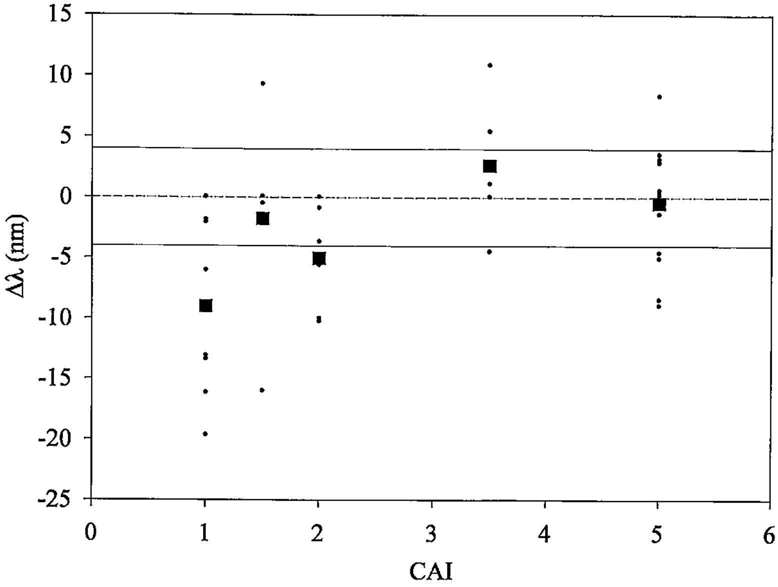

FIG. 5. Change in emission wavelength (Δλ) as a function of CAI. The mean for each CAI group is indicated by the large filled symbols. The lines at −4 and +4 nm enclose the range of Δλ observed for synthetic calcite (Mason 1994; unpubl. data).

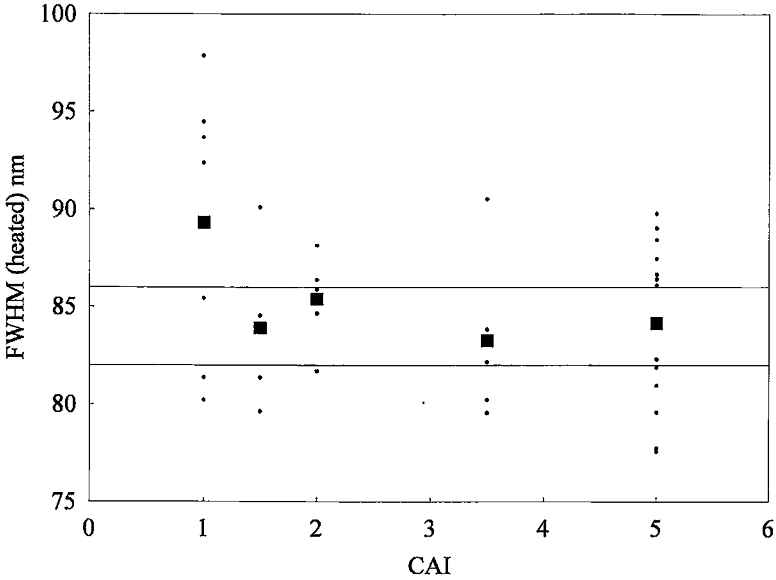

FIG. 6. Emission bandwidth (FWHM) of heated calcite *versus* CAI. Mean values for each CAI group are represented by large filled symbols. The lines at 82 and 86 nm enclose the data from synthetic calcite (Mason 1994; unpubl. data).

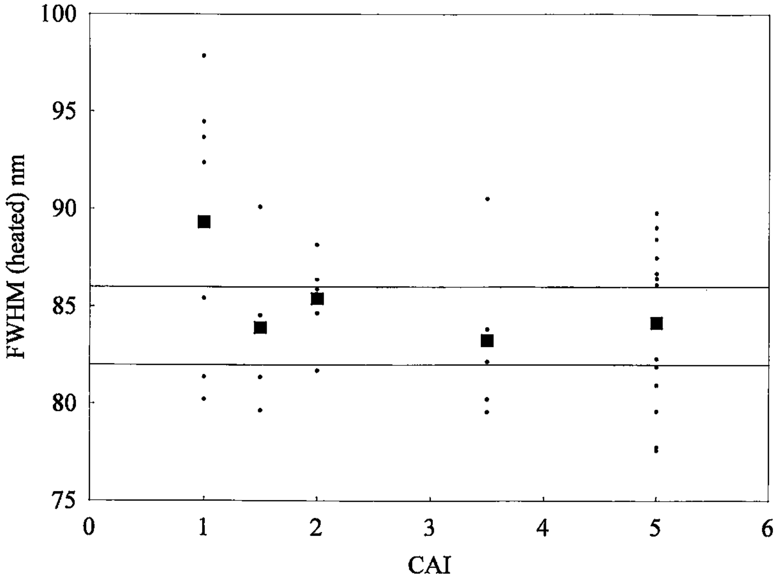

FIG. 7. Change in emission bandwidth (ΔFWHM) induced by heating plotted against CAI. Mean values for each CAI group are shown as large filled symbols. The lines at –2 and +3 nm enclose the data from synthetic calcite (Mason 1994; unpubl. data).

majority of the mean values for Fe lie close to the (1σ) detection limit (~0.02 wt%), with only four samples having mean concentrations of Fe equal to or greater than 0.1 wt% (maximum 0.21 wt%). The maximum concentration found in a single determination is 0.53 wt% Fe. In the majority of samples, the concentration of Mn is close to, or below, the detection limit of 0.02 wt%. Only one sample has a mean Mn content greater than 0.1 wt%, and the highest single determination was 0.13 wt% Mn. The low abundance of Mn is consistent with the observed relatively low intensity of CL. There is a weak positive correlation between concentrations of Mn and Fe. The calcite contains, on average, 0.04 to 0.14 wt% Sr, with individual determinations ranging from below the (1 σ) detection limit (0.03 wt%) to 0.22 wt%.

In a few samples, systematic differences in composition were detected between different textural types of calcite. Micrite tends to have higher Mg content than sparry calcite cement or vein calcite. This may reflect contamination from (unidentified) dolomite. In some of the more thoroughly recrystallized rocks (with CAI = 5), differences in Mg content were found between porphyroclasts and the surrounding granoblastic mosaic. However, these differences are not related to grain size in a consistent manner, perhaps because the porphyroclasts have diverse origins.

Analyses of both reference and heated calcite were made for six samples. The analyses were performed on polished chips a few millimeters in diameter, and care was taken to analyze texturally representative material (*e.g.*, micrite *versus* coarse calcite cement). Differences between the reference and heated material were found not to be statistically significant.

DISCUSSION

Use of CL as a geothermometer

The variability in intensity ratio from materials with the same CAI makes this parameter unreliable as an estimator of temperature. However, there are systematic relationships among emission wavelength (reference calcite), $\Delta\lambda$, ΔFWHM and CAI. Measurement of any one of the CL parameters alone cannot, however, provide a reliable estimate of the CAI, as is clear from perusal of Figures 4, 5 and 7. Nevertheless, by taking a suitable combination of the CL parameters, modestly successful discrimination into groupings with a CAI of less than 3 and greater than 3 is possible. Figures 4, 5 and 7 suggest that samples with a CAI of less than 3 should have emission wavelength (reference) greater than approximately 604 nm, a $\Delta\lambda$ less than 0, and a ΔFWHM greater than 0. The group with CAI greater than 3 is more diverse in terms of response to heating, but Figures 4, 5 and 7 suggest that the majority have an emission wavelength (reference) less than approximately 611 nm, a $\Delta\lambda$ greater than 0, and a ΔFWHM less than 0. Application of these two sets of criteria yields the following results. Twenty-eight (of 37) samples meet one or the other of the sets of criteria. Of these, 22 are correctly placed into the appropriate CAI group (a success rate of 79%). Six samples are placed into the wrong CAI group (including BP–1, which should belong to the "CAI less than 3" group). The remaining nine samples meet neither set of criteria, and are thus "indeterminate". If the properties identified with the "CAI less than 3" group were distributed randomly among the samples, the probability of correct assignment to this group is only 0.21. On a similar basis, the probability of correct assignment to the CAI greater than 3 group is 0.06. Relaxation of the criteria would decrease the number of indeterminate results, but at the cost of less reliable discrimination between groups.

This analysis of the results shows that the CL technique has some potential for discriminating calcite into two groups that differ in CAI, and, by implication, temperature. Based on the calibration by Epstein *et al.* (1977), the samples studied have experienced maximum temperatures between 50 and 400°C, *i.e.*, from the diagenetic regime to the greenschist metamorphic facies (Fig. 1). Each CAI represents a considerable range of temperature, with significant overlaps in the ranges assigned to adjacent CAI values, especially for a CAI below 3. Some confidence in the *general* interval of temperature represented by the CAI can be obtained from comparison with the fluid-inclusion data of Saunders *et al.* (1992) for replacement and vein-filling sphalerite from two localities close to those studied in this work and in Nowlan & Barnes (1987) (Fig. 1). These data provide estimates of the minimum temperature experienced by the host rock. A pessimistic interpretation of Figure 1 is that all CAI values below 3 should be assigned to a temperature range of 50 to 140°C, without subdivision. For higher CAI values, there is a more nearly monotonic relationship with temperature, but each CAI value spans at least 90°C. On the basis of this analysis, the combination of the CL parameters used above is capable of assigning a sample to the temperature range less than 50 to 140°C (CAI less than 3) or 110 to 400°C (CAI greater than 3) with a probability of success of approximately 0.8.

Comparison with synthetic calcite

Results for natural calcite are compared with those for synthetic calcite heated in CO_2 at 390°C for 1.2 to 288.5 hours (Mason 1994, Table 2). To facilitate comparisons, the calcite:Mn spectra of Mason (1994) were reprocessed using the fitting methods of the present work. The reprocessed data are quoted here and include a complete set of measurements for the FWHM (*cf.* Mason 1994, Table 2). Differences between emission wavelength, FWHM, I_H/I_R, $\Delta\lambda$ and ΔFWHM values obtained from the published and from the reprocessed data sets are within statistical uncertainties. Comparisons of emission wavelength are made in terms of the *center* of the emission band rather than the *centroid* values quoted by Mason (1994). The center lies 6 to 9 nm lower in wavelength than the centroid.

The range of I_H/I_R in natural calcite (0.8 to 2.6) is close to that found in synthetic calcite (0.6 to 2.2) heated under similar conditions. However, there are differences between synthetic and natural calcite in the emission wavelength and FWHM and in the responses of these parameters to heating in the laboratory. The range of emission wavelengths from natural (reference) calcite (591 to 621 nm; Fig. 4) is significantly greater than is obtained on synthetic (reference) calcite (594 to 598 nm), and the mean lies at 606 nm compared with 596 nm. The range of emission bandwidths from Mn^{2+} in natural (reference) calcite (76 to 99 nm; Fig. 6) is greater than is observed for synthetic (reference) calcite (82 to 86 nm), but the mean differs insignificantly, at 83 nm compared with 85 nm in synthetic calcite. Changes in emission wavelength induced by heating natural calcite (range –20 to +11 nm; Fig. 5) are generally larger than in synthetic calcite (–4 to +4 nm). The emission bandwidth from natural calcite may change by –6 to +12 nm on heating (Fig. 7), whereas in synthetic calcite, the change ranges from –2 to +3 nm, with no change recorded from the majority of experiments.

Explanations for differences in wavelength, bandwidth, $\Delta\lambda$ and ΔFWHM, between synthetic and natural calcite may lie their respective phase-assemblages and chemical composition, and in the possible effects of deformation. The synthetic calcite of Mason (1994) contains Mg and Fe at concentrations less than 0.01 wt%, and Sr less than 0.03 wt%, compared with up to 0.5 wt%, 0.21 wt% and 0.14 wt%, respectively, in the natural calcite. The range of Mn contents of the natural calcite (<0.02 to 0.13 wt%) lies within that of the synthetic calcite (0.001 to 1.96 wt%). The natural calcite differs from the synthetic material in that both calcite *and* dolomite are detectable by XRD in the majority of samples (detection limit approximately 1%) and in the evidence of deformation, afforded by the presence of twinning.

The wavelength of CL emission for an activator depends on its average coordination environment, a function of host composition and, in a solid solution, mixing properties. Smith (1953) argued that emission wavelength from a given activator should be linearly related to composition within a solid solution if mixing is random. For a set of spectra recorded at one temperature, the bandwidth should also depend on the composition and the manner in which the impurities mix (Smith 1953). Neither the wavelength nor bandwidth of emision of either reference or heated calcite displays any correlation with concentration of minor elements; consequently, differences in these parameters between samples must be caused by other factors. One possibility is that Mg, Fe, Mn and Sr mix nonrandomly with Ca, and that there are significant differences between samples in the coordination environment of Mn. Certainly, the calcite–dolomite solvus and experimental data on the metastable high-magnesium calcite solid solution (Morse & MacKenzie 1990, Wenk *et al.* 1993, Tsipursky & Buseck 1993) suggest that Ca–Mg mixing is nonrandom, but this possibility cannot be tested with the present data.

The presence of dolomite in these rocks allows the possibility of Ca–Mg exchange with calcite during heating in the laboratory. This could, in principle, explain the shifts in wavelength between heated and reference calcite. However, the observed shifts in wavelength require changes by several wt% in the concentration of Mg; a comparative study of the composition of heated *versus* reference calcite rules out significant exchange. Mason (1994) found no evidence (in the zoning patterns) for significant transport of Mn within heated single crystals of synthetic calcite.

The presence of twinning in the natural calcite, together with field evidence noted above, suggest that the host rocks have experienced deformation. With the exception of porphyroclasts that are present in some of the samples with CAI = 5, the styles of twinning suggest relatively mild deformation at temperatures below 200°C (Burkhard 1993, W.R. Jamison, pers. comm.). Careful examination of the results for samples with CAI = 5 has failed to produce evidence of a relationship between style of twinning and the response of CL to heating. Consequently, it is concluded that any effects of deformation are minor. It should also be noted that the samples were crushed only to rather coarse size before an aliquot was subjected to heating. This method was chosen to eliminate the possibility of inducing deformation effects (Cervelle *et al.* 1982) that could be relaxed in the heated calcite, but not in the reference calcite.

This study demonstrates that the thermal history of calcite has an influence on the response of its CL emission behavior to laboratory heating, although the mechanism of the effect remains unclear. Development of the technique as an independent, reliable geothermometer requires that the causes of variability in the response to heating be identified, and methods found to compensate for them. This will involve calibration against a better scale of temperature than is provided by the CAI, and consideration of the mechanism(s) by which changes in the CL parameters are accomplished.

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