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. 1Xs 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 décélés dans ces échantillons ont été comparés avec un indicateur indépendant de maturité thermique, l’indice de la couleur modifiée d’un conodont (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 retrécit 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.

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

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INTRODUCTION

Spectra of Mn⁴⁺-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...
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 porphyroelastic 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 absence 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)]. Porphyroblasts 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 across.

![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).](image-url)
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 CO₂ (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 approximately 14 µA/mm².

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 \( y = a_0 \exp \left[ -\frac{1}{2} \xi^2 \right] \), with \( a_0 \) the amplitude and \( a_1 \) the rate, and a peak function (the Haarhoff – Van der Linde function):

\[
y = \frac{a_0 a_2}{a_1 a_3 \sqrt{2\pi}} \exp \left\{ -\frac{1}{2} \left( \frac{\xi - 1}{a_3} \right)^2 \right\} \frac{1}{\sqrt{\pi}} \exp \left\{ -\frac{1}{2} \left( \frac{\xi - 1}{a_3} \right)^2 \right\} \text{erf} \left( \frac{\xi - 1}{a_3} \right)
\]

in which \( a_0 \) is the area, \( a_1 \) the center of the undistorted peak, \( a_2 \) the width, \( a_3 \) the distortion, and \( \xi = (x - a_1)/a_2 \). This function was chosen because it accommodates the observed asymmetrical 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 Mn²⁺ 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 Mn²⁺ 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
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.
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: Δλ = center (heated) − center (reference). The value of Δλ 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 Δλ. However, the sign of Δλ 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 (FWHM) 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 concentra-
tion 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 determina-
tion 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 determi-
nations ranging from below the (1σ) detection limit
(0.03 wt%) to 0.22 wt%.

In a few samples, systematic differences in composi-
tion 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 porphy-
roclasts and the surrounding granoblastic mosaic.
However, these differences are not related to grain size
in a consistent manner, perhaps because the porphy-
roclasts 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 system-
atic relationships among emission wavelength (refer-
cence calcite), Δλ, 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 Δλ 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 approxi-
mately 611 nm, a Δλ 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 assign-
ment 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 tech-
nique 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 maxi-
imum 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
dolomite from two localities close to those studied in
this work and in Nowlan & Barnes (1987) (Fig. 1).
These data provide estimates of the minimum tempera-
ture experienced by the host rock. A pessimistic inter-
pretation 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 CO₂ at 390°C for 1.2 to
288.5 hours (Mason 1994, Table 2). To facilitate com-
parisons, 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, Iᵣ/Iᵣᵣ, Δλ and ΔFWHM values
obtained from the published and from the reprocessed
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 emission 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, Tsuchiyama & 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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