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EXPERIMENTAL EVIDENCE FOR THE EFFECT OF DEFECTS ON THE LUMINESCENCE OF SYNTHETIC CALCITE

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ABSTRACT

Synthetic calcite has been precipitated from $CaCl_2$ solution using four different reagents: (1) ammonium carbonate vapor, (2) ammonium carbonate solution, (3) sodium carbonate solution, and (4) sodium hydrogen carbonate. Crystals grew at room temperature over a period of 7 to 10 days using the first method and within 10 to 30 minutes at 6°C or below using methods (2) to (4). The calcite samples were heated hydrothermally and in CO_2 at 75° to 400°C and examined by SEM and powder X-ray diffraction to characterize the changes that take place during heating. Calcite synthesized by different methods has different initial sizes of crystals, widths of XRD reflections and intensity of cathodoluminescence (CL). On hydrothermal heating, crystal size increases and width of XRD reflections decreases. The magnitude of the changes in these parameters is greater at higher temperature and in longer experiments, and differs among the different types of calcite. Heating in CO_2 is relatively ineffective in changing grain size and width of XRD reflections. Differences in width and intensity of XRD reflections among different types of starting calcite are attributed to differing densities of defects acquired during crystal growth. The responses in width of XRD reflections and intensity of CL emission to heating are ascribed to the annihilation of defects.

Keywords: calcite, synthesis, recrystallization, luminescence, defects.

SOMMAIRE

La calcite synthétique a été précipitée à partir de solutions de $CaCl_2$ en ajoutant un de quatre réactifs: (1) vapeur de carbonate d'ammoniaque, (2) solution de carbonate d'ammoniaque, (3) solution de carbonate de sodium, et (4) bicarbonate de sodium. La croissance des cristaux à température ambiante s'est étalée sur une période de 7 à 10 jours avec la première méthode, et en dedans de 10 à 30 minutes à 6°C ou moins avec les méthodes (2) à (4). Les échantillons de calcite ont ensuite été chauffés en milieu hydrothermal ou en présence de CO_2 à une température entre 75° et 400°C et examinés par microscopie électronique à balayage et par diffraction X, méthode des poudres, afin de décrire les changements qui ont eu lieu au cours du traitement à température élevée. La calcite synthétisée selon les différentes méthodes avait une taille distincte de cristaux au départ, et se distinguait aussi par la largeur de réflexions en diffraction X et par l'intensité de la cathodoluminescence. Au cours du traitement hydrothermal, la taille des cristaux a augmenté, et la largeur des réflexions en diffraction X a diminué. L'importance des changements est d'autant plus grande qu'est la température, augmente avec le temps, et dépend aussi du type de calcite. Le chauffage en présence de CO_2 est relativement inefficace pour changer la granulométrie et la largeur des pics de diffraction. Les différences en largeurs des pics parmi les types de matériaux de départ résulterait de différences en densité de défauts acquis lors de la croissance des cristaux. L'influence du chauffage sur la largeur des pics de diffraction et l'intensité de la cathodoluminescence serait due à l'élimination des défauts structuraux.

(Traduit par la Rédaction)

Keywords: calcite, synthèse, recristallisation, luminescence, défauts.

INTRODUCTION

Luminescence involves the excitation to upper electronic states and relaxation to a lower energy state (usually the ground state) of electrons in a target substance. The available processes of relaxation include the emission of electromagnetic radiation, and it is this radiation that constitutes luminescence. Atoms that relax in this way are called activators; manganese is perhaps the most common example in minerals. Relaxation processes that do not involve radiative emission compete with activators to dissipate the excitation energy. Such relaxation processes are dominated by the production of phonons and are associated with elements (such as

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Fe) that are present, like the activators, in trace to minor quantities (Walker 1985). The intensity of luminescence emitted by a given substance is then normally interpreted in terms of the quantities of activator and quencher present (Marshall 1988).

Excitation and emission involve energy transfer between excitation source and activators, between individual activators, and from activators to quenchers (Marfunin 1979). Energy transfer depends critically on the nature of the matrix in which luminescence is being stimulated (*e.g.*, semiconductor *versus* insulator) and on its crystallinity (*i.e.*, level of crystal perfection). The quality and longevity of commercial phosphors are known to depend on crystal perfection (Ozawa 1990) because of its effect on the efficiency of energy transfer and because prolonged irradiation introduces defects.

Previous Work

Recently Mason (1994, 1998) has shown that 1) the intensity of cathodoluminescence (CL) from synthetic calcite depends on the method of synthesis (as well as on the concentration of the activator), and 2) heating causes an increase in the intensity of CL and may induce changes in the wavelength of emission. Calcite with an initially low intensity of CL was found to show the greatest increase in intensity on heating. The magnitude of the effect depends on temperature and is greater when heating is carried out in the presence of water. Preliminary evidence from scanning electron microscopy indicated that there is extensive coarsening of grain-size during hydrothermal treatment of synthetic calcite.

The intensity of CL, together with the wavelength and bandwidth of emission in natural calcite, can also be changed by heating. There is evidence of a temperature dependence of emission wavelength on the maximum paleotemperature attained by the host rock (Mason 1997).

Mason deduced that different methods of synthesis produce calcite with different degrees of crystallinity and that heating annihilates defects that interfere with the luminescence process, thus allowing increased efficiency of luminescence. A similar mechanism was inferred to operate in natural calcite. Mason (1998) showed that changes in the wavelength and bandwidth of luminescence induced by heating increase with increasing concentrations of Mn and Mg. It was inferred that these changes reflect redistribution of these elements with respect to the activator ions.

The present work explores the recrystallization process quantitatively, using scanning electron microscopy to study grain size, and powder X-ray diffraction to study degree of crystallinity. The results are discussed in terms of the luminescence data published previously (Mason 1998).

Experimental

Synthesis and heat treatment

Calcite was synthesized from aqueous chlorides of Ca, Mg and Mn prepared using BDH Analar and Merck Suprapur reagents with water purified in a Nanopure filtration system. The ratios of the chlorides were adjusted to produce calcite with the desired ratios of the cations. Four different methods of synthesis were used: (1) precipitation at approximately 22°C over 7 to 10 days using ammonium carbonate vapor as the titrant (ACV calcite), (2) precipitation from solution at 2.5 to 6°C by adding cooled Na_2CO_3 solution over a period of approximately 30 minutes (NC calcite), (3) precipitation at 2 to 3°C by adding cooled ammonium carbonate solution over a period of 10 minutes (AC calcite), (4) precipitation at approximately 22°C by adding $NaHCO_3$ powder over a period approximately 10 minutes (Glover & Sippel 1967) (NHC calcite). At the conclusion of each experiment, the precipitate and solutions were separated by washing with distilled water into a filtration system, then dried in air at room temperature. Chemical analyses were performed using atomic absorption and, for ACV calcite, electron-probe microanalysis. Further details are given in Mason (1998) and in Mason & Mariano (1990).

Two methods of heating were employed (1) at 1 atmosphere pressure of CO_2, and (2) in sealed tubes in the presence of water. The latter are referred to as hydrothermal experiments.

Experiments in the presence of CO_2 were carried out in a vertical tube furnace filled with the pure gas (to minimize decarbonation). Temperatures were monitored using a thermocouple suspended close to the samples. Recorded values are considered accurate to ±5°C. Quenching to room temperature took two to three minutes. Hydrothermal experiments were performed with the starting calcite sealed in Pt tubes with up to 4 wt% distilled water. Heating was carried out in standard cold-seal pressure vessels at 500 ± 40 bars. Recorded temperatures are considered accurate to ±5°C. At the end of each experiment, the pressure vessels were cooled in a stream of compressed air. Capsules that showed a weight change or in which the calcite was discolored after heating were deemed to have leaked and were discarded.

Grain-size measurement

Very fine-grained calcite of the AC, NC and NHC series and products of their heating were gently crushed under acetone with sufficient force only to break up aggregates. Samples were mounted on aluminum stubs from suspension in alcohol. Scanning electron micrographs were collected and digitized. Image measurement was performed using Photoshop 4.0 with Image Processing Tool Kit plug-ins. Disaggregation of the samples was seldom complete, with the result that overlapping particles made automated measurement of grain size impossible. A manual method was adopted in which images of non-overlapped grains were excised for measurement. Typically 25 to 75 grains were measured from each sample.

Estimation of the grain size of ACV calcite was performed with a petrographic microscope equipped with a graticule.

Powder X-ray diffraction and measurements of resolution

Calcite from the AC, NC and NHC series was disaggregated in acetone and mounted on glass slides; crushing was unnecessary. ACV calcite and the coarser products of heating experiments were gently crushed in acetone before mounting. Care was taken not to exert excessive force during crushing because this is known to damage the structure (Cervelle *et al.* 1982). Data were collected by step-scanning with a Rigaku RU–200 diffractometer through the 2θ range 64 to 66.5°. This range includes the 300 and 00,12 reflections and provides a high signal-to-noise ratio and resolution of Cu$K\alpha_1$ and Cu$K\alpha_2$ peaks in well-crystallized calcite. The spectra were fitted to a model consisting of four Pearson VII peaks and a linear background; the widths (full-width-at-half-maximum-height, FWHM) were obtained from the fit coefficients.

RESULTS

Grain-size and FWHM data are listed in Tables 1 to 3. Grain size is recorded as the mean maximum dimension (length) with standard error, minimum and maximum dimension for each sample. FWHM data are best-fit values with uncertainties estimated in the fitting process. Duplicate measurements on starting calcite resulted in FWHM values within the quoted uncertainties. Experiments were conducted in the temperature range from 75 to 400°C and from approximately 6 to 663 hours.

Grain size of starting calcite

Grain-size measurements are given in Table 1. Calcite made by the NC, AC and NHC methods is aggregated in spheroidal masses consisting of individual crystals that average approximately 1 μm in length (Fig. 1) in AC and NC calcite and approximately 0.2 to 4 μm in NHC calcite. AC calcite is rhombic or acicular and arranged in parallel or radiating forms reminiscent of spherulites found in devitrified glass. Edges, corners and faces are well developed. In calcite of the NC series, the crystals are, on average, slightly smaller and have fewer perfect terminations than in AC calcite. Crystals of NHC calcite with the highest Mg and Mn concentrations average 0.2 to 0.3 μm across. Within the NHC series, grain size increases with decreasing concentration of magnesium (Table 1). The quality of the crystal terminations improves as the concentrations of Mn and Mg decrease.

The measurement of length presented problems in fine-grained calcite because of the difficulty of locating separated crystals for measurement and because of the inequant shapes in radiating structures. The problem was circumvented by focusing attention on disaggregated regions of the mount and by rotating the sample in the SEM to observe grain shape in three dimensions where possible. Nevertheless, the stereological arrangement imposes limitations on the quality of the data.

TABLE 1. COMPOSITION, GRAIN SIZE AND XRD FWHM OF STARTING CALCITE

Sample	Type	Ca	Mg	Mn	N*	Length (μm)				FWHM 300 (°2θ)	
		(a.p.f.u.)[+]	(a.p.f.u.)	(a.p.f.u.)		Mean	Std. error	Minimum	Maximum	Mean	Std. error
92020(c)	NC	n.a	n.a	0.00030	37	1.01	0.07	0.34	2.24	0.166	0.003
92020(b)	NC	n.a	n.a	0.00567	49	0.85	0.10	0.29	2.84	0.206	0.004
94007	AC	n.a	n.a	0.00072	20	1.46	0.11	0.69	2.53	0.129	0.003
94008	AC	n.a	n.a	0.00082	20	1.15	0.10	0.57	2.85	0.135	0.002
94009	AC	n.a	n.a	0.00147	25	1.30	0.09	0.40	1.76	0.168	0.003
90040	ACV	*0.898*	*<dl*	0.03560	10	100	-	50	120	0.124	0.008
94029	ACV	*0.943*	*0.007*	*0.00018*	10	875	-	500	1000	0.120	0.002
94030	ACV	*0.923*	*0.011*	*0.00011*	10	420	-	300	500	0.142	0.005
94031	ACV	*0.906*	*0.031*	*0.00018*	10	700	-	600	900	0.122	0.006
90043	ACV	n.a	n.a	0.00027	10	480	-	300	750	0.092	0.001
89029	ACV	*.981*	*<dl*	*0.00013*	10	325	-	200	400	0.101	0.003
94101	NHC	0.708	0.305	0.02952	33	0.34	0.04	0.12	0.76	-	-
94102	NHC	0.943	0.050	0.00648	67	2.09	0.20	0.29	5.20	0.157	0.004
94103	NHC	0.964	0.024	0.00747	30	2.75	0.35	0.75	5.66	0.160	0.002
94104	NHC	0.973	0	0	-	-	-	-	-	0.149	0.002
94105	NHC	0.983	0.006	0.00361	57	3.77	0.38	1.22	10.36	0.136	0.002
94110	NHC	0.688	0.247	0.09109	46	0.25	0.03	0.11	0.60	-	-
94111	NHC	0.964	0.028	0.00458	-	-	-	-	-	0.157	0.007
94112	NHC	0.972	0.016	0.00624	-	-	-	-	-	0.158	0.002
94113	NHC	0.981	0.006	0.00523	-	-	-	-	-	0.163	0.002
94114	NHC	0.985	<dl	0.00624	-	-	-	-	-	0.128	0.001

[+] Atoms per formula unit. Analyses by atomic absorption except for values in *italics*, obtained by electron 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. (2σ). n.a.: not analyzed. Details of analytical methods are given in Mason (1998). * Number of measured grains.

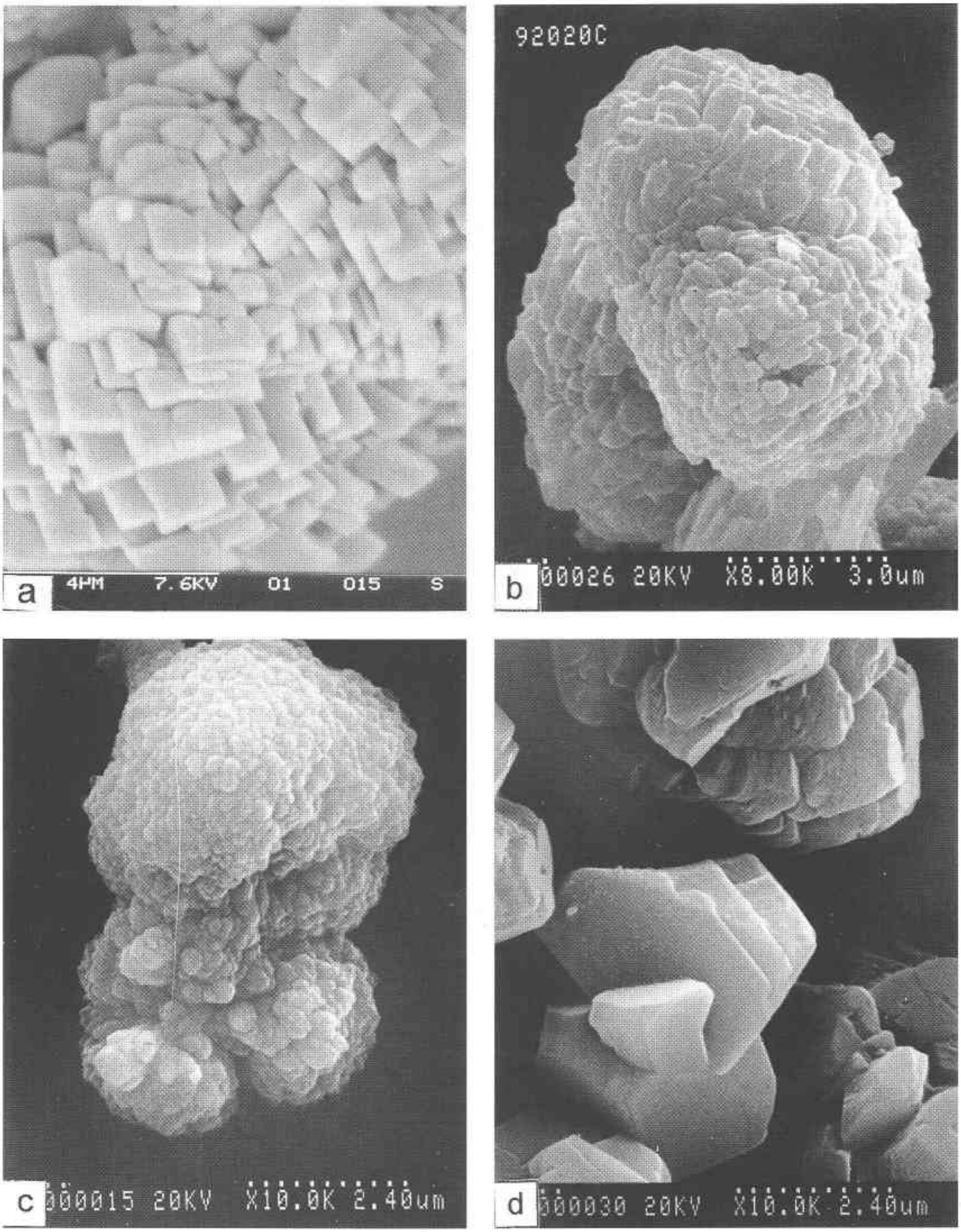

FIG. 1. Scanning electron micrographs of synthetic calcite. (a) AC, (b) NC, (c) NHC with high levels of Mn and Mg, and (d) NHC with low levels of Mn and Mg.

Calcite precipitated by the ACV method forms crystals (generally rhombs) that are approximately 100 μm to 1 or 2 mm in length. Calcite 90040 [ACV, 0.036 atoms per formula unit (*apfu*) Mn] is unusual in that cleavages are curved, giving an appearance reminiscent of saddle dolomite.

Grain size of heated calcite

Hydrothermal treatment induces recrystallization, with the magnitude of the change in grain size being dependent on the starting calcite, temperature and duration of the experiment. Heating in CO_2 causes modest or immeasurably small changes in grain size. The majority of the results were obtained for NC and AC calcite. Changes in the grain size of ACV calcite were not studied.

The largest grain-size was reached in the longest hydrothermal experiments on NC calcite at 300 and 400°C (Table 2). This calcite coarsened to 15 to 20 μm over 663 hours, an approximately 15- to 20-fold increase over the grain size at the start of the experiments (Fig. 2). At 300°C, NC calcite 92020(b) coarsened a little more rapidly than 92020(c). The most rapid coarsening occurred at 400°C. NC calcite did not coarsen measurably at 200°C and below, even in hydrothermal experiments lasting approximately 500 hours.

The AC calcite did not coarsen as rapidly or to the same extent as NC calcite (Fig. 2); it grew to approximately 5 μm in 100 hours at 400°C, compared with 10 to 11 μm for NC calcite heated under the same conditions. AC calcite heated at 300°C and below showed no measurable change in grain size in experiments lasting up to approximately 100 hours. In similar experiments, NC calcite coarsened to between 5 and 7 μm and failed to coarsen measurably only at temperatures of 200°C and below.

The NHC calcite with high concentrations of Mg and Mn coarsened very slightly at 200°C; however, the experiments were of short duration (94106 and 94108, Table 2). At 400°C, the same calcite experienced a modest increase in grain size and separated into two phases in an experiment lasting 15 hours (see Mason 1998). The NHC calcite with lower concentrations of

TABLE 2. GRAIN SIZE AND XRD FWHM OF HYDROTHERMALLY TREATED CALCITE

Sample	Starting calcite		Temperature	N	Time	Length (μm)				FWHM 300 (°2θ)	
	Number	Type	(°C)		(hours)	Mean	Std. error	Minimum	Maximum	Mean	Std. error
95087-1	94007	AC	300	57	21.7	1.32	0.12	0.50	3.10	0.172	0.002
95087-2	94007	AC	300	62	21.7	1.75	0.19	0.47	3.62	0.158	0.002
95079-1	94007	AC	300	101	119.8	1.62	0.21	0.29	8.67	0.166	0.002
95079-2	94007	AC	300	58	119.8	1.72	0.25	0.39	4.93	0.141	0.001
94085	94007	AC	400	34	21.8	5.41	0.34	2.93	8.64	-	-
94086	94007	AC	400	28	23.8	3.69	0.27	1.52	6.54	-	-
95019	94009	AC	75	20	24.8	1.30	0.09	0.71	2.08	-	-
95032-1	94009	AC	75	-	160.4	-	-	-	-	0.212	0.024
95032-2	94009	AC	75	-	160.4	-	-	-	-	0.176	0.017
95024-2	94009	AC	125	40	42.6	0.75	0.05	0.27	1.35	0.172	0.003
95017	94009	AC	200	20	31.0	0.81	0.06	0.48	1.54	0.173	0.003
95020	94009	AC	200	38	44.3	0.90	0.07	0.37	1.65	0.199	0.006
95016	94009	AC	400	20	29.0	5.14	0.24	3.64	7.99	-	-
94088	94009	AC	400	22	103.4	5.31	0.37	2.53	9.91	0.104	0.001
95034-2	92020(b)	NC	300	64	6.4	3.30	0.37	0.65	8.67	0.101	0.003
95034-1	92020(b)	NC	300	56	6.4	3.43	0.50	0.73	9.33	0.099	0.001
95035-1	92020(b)	NC	300	56	29.2	5.42	0.32	2.75	9.81	0.093	0.001
95035-2	92020(b)	NC	300	69	29.2	6.87	0.74	1.76	22.55	0.095	0.008
95047-1	92020(c)	NC	100	103	23.5	0.98	0.09	0.19	3.22	-	-
95040-2	92020(c)	NC	100	80	48.2	0.72	0.07	0.18	1.62	0.183	0.003
95040-1	92020(c)	NC	100	43	48.2	0.82	0.08	0.25	1.81	0.190	0.014
95045-2	92020(c)	NC	100	69	503.1	0.84	0.08	0.33	2.93	0.168	0.005
95045-1	92020(c)	NC	100	146	503.1	0.95	0.07	0.23	2.44	0.178	0.005
95041-2	92020(c)	NC	200	58	48.2	1.01	0.09	0.51	2.46	0.143	0.002
95041-1	92020(c)	NC	200	116	48.2	1.16	0.11	0.37	3.27	0.160	0.002
95046-1	92020(c)	NC	200	56	503.8	1.14	0.10	0.39	2.64	0.090	0.001
95046-2	92020(c)	NC	200	80	503.8	1.23	0.11	0.30	2.81	-	-
95043-2	92020(c)	NC	300	63	29.7	3.16	0.36	1.11	9.13	0.102	0.001
95042-1	92020(c)	NC	300	54	48.4	5.09	0.65	1.05	18.11	0.082	0.001
95042-2	92020(c)	NC	300	73	48.4	6.26	1.18	2.04	32.68	0.092	0.001
95038-2	92020(c)	NC	300	37	97.5	4.50	0.59	2.12	12.47	0.097	0.001
95038-1	92020(c)	NC	300	114	97.5	6.65	0.61	2.39	20.53	0.103	0.001
95077-1	92020(c)	NC	300	50	663.3	15.01	2.54	2.91	50.77	-	-
95077-2	92020(c)	NC	300	63	663.3	17.82	1.98	4.11	53.38	0.086	0.002
95050-2	92020(c)	NC	400	60	27.0	6.93	0.55	3.09	15.13	0.083	0.001
95044-2	92020(c)	NC	400	64	48.0	7.27	0.60	1.49	14.80	0.091	0.001
95039-2	92020(c)	NC	400	36	96.7	11.04	0.96	3.68	22.40	0.076	0.000
95039-1	92020(c)	NC	400	19	96.7	12.52	0.69	6.85	19.50	0.083	0.001
95076-2	92020(c)	NC	400	64	663.0	16.35	1.55	6.30	33.28	0.112	0.006
94106	94101	NHC	200	36	14.8	0.42	0.05	0.19	0.97	-	-
94108	94101	NHC	400	22	5.6	0.75	0.15	0.25	2.90	-	-
94115	94103	NHC	200	51	19.1	1.88	0.17	0.20	4.39	0.158	0.012
94109	94103	NHC	400	41	5.9	1.64	0.25	0.41	4.13	0.193	0.003

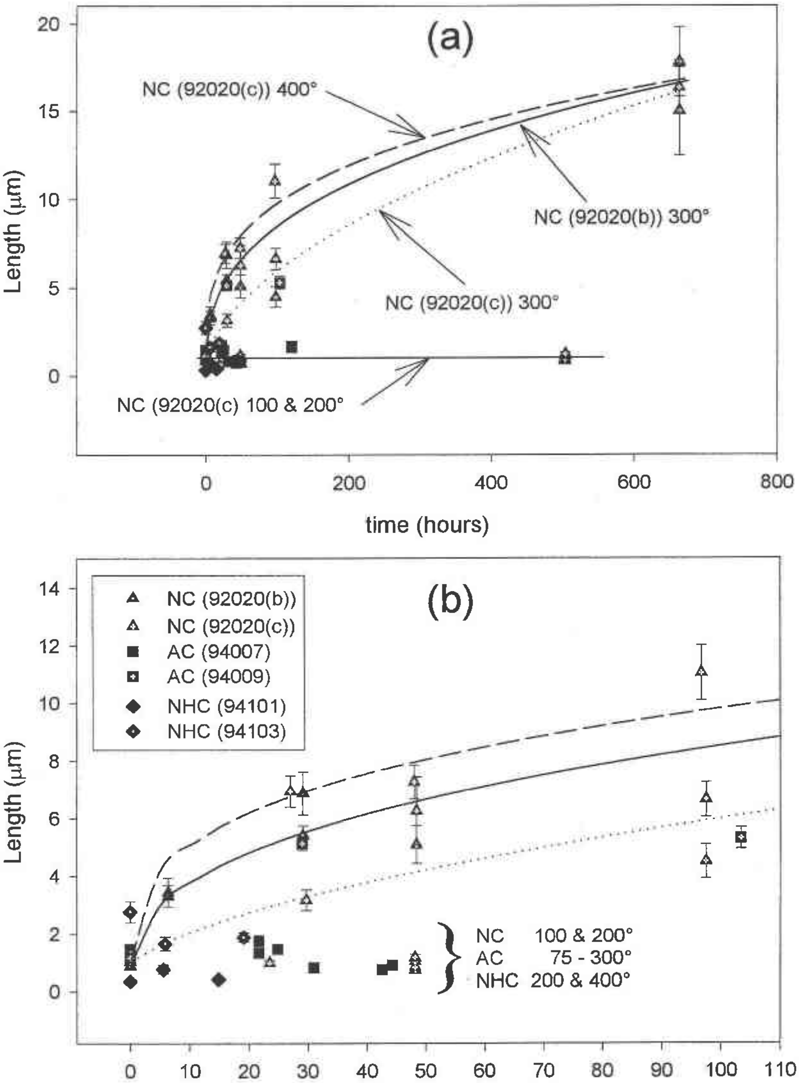

FIG. 2. Coarsening of synthetic calcite in hydrothermal experiments as a function of type of calcite, time and temperature. The curves are fits to the data of the equation $l = (l_on + kt - kt_o)^{1/n}$; see text for details. (a) The complete set of data, and (b) an expanded view of the data to 110 hours.

Mg, and Mn and greater initial grain-size did not coarsen significantly in hydrothermal experiments at 200 to 400°C (94109 and 94115, Table 2).

Heating in CO_2 has little effect on grain size (Table 3); only in a series of experiments on starting calcite 92020(b) is there any systematic coarsening as a function of time, from 0.8 to approximately 1.6 µm over approximately 30 hours at 400°C.

Figure 3 illustrates changes in grain shape as a function of time in NC calcite heated hydrothermally at 400°C. Compared with the starting calcite (Fig. 1b), the crystals have lost virtually all corners, edges and faces, and all vestiges of the spheroidal aggregates have vanished. Changes in grain shape were complete within less than 30 hours, and further heating served only to coarsen the crystals. Treatment at 300°C led to similar behavior, but the crystals better retained their faces and edges. When treated hydrothermally at 100° or 200°C, changes in grain shape were found to be slight, and the spheroidal aggregates present at the start

TABLE 3. GRAIN SIZE AND FWHM FOR CALCITE HEATED IN CO_2

Sample	Starting calcite		Temperature	N	Time	Length (μm)				FWHM 300 (°2θ)	
	Number	Type	(°C)		(hours)	Mean	Std. error	Minimum	Maximum	Mean	Std. error
95068	94007	AC	200	35	24.0	1.64	0.12	0.37	3.20	-	-
95065	94007	AC	300	29	26.0	1.30	0.08	0.46	2.15	0.163	0.002
95069	94009	AC	200	40	24.0	0.76	0.06	0.26	1.64	-	-
95013	92020(b)	NC	250	52	4.0	0.90	0.06	0.46	1.70	0.184	0.002
95014	92020(b)	NC	250	41	24.4	0.71	0.10	0.06	1.59	0.187	0.002
95010	92020(b)	NC	250	35	71.1	1.02	0.06	0.34	2.16	-	-
95011	92020(b)	NC	250	42	100.3	0.84	0.12	0.32	1.88	0.188	0.003
95015	92020(b)	NC	250	46	124.9	0.97	0.10	0.29	1.97	0.188	0.003
95012	92020(b)	NC	250	68	150.0	0.70	0.04	0.22	1.55	0.193	0.010
95001	92020(b)	NC	400	24	2.0	0.97	0.07	0.46	1.49	0.173	0.002
95002	92020(b)	NC	400	31	4.0	0.98	0.09	0.39	2.04	0.175	0.002
95003	92020(b)	NC	400	61	6.0	1.02	0.07	0.41	3.15	0.186	0.022
95004	92020(b)	NC	400	36	12.3	0.79	0.10	0.30	1.88	0.176	0.012
95005	92020(b)	NC	400	45	18.3	1.05	0.11	0.26	2.52	-	-
93012	92020(b)	NC	400	22	26.5	1.63	0.24	0.53	3.73	0.175	0.002
95006	92020(b)	NC	400	40	37.7	1.22	0.19	0.48	4.39	0.180	0.002
95070	92020(c)	NC	200	15	24.0	1.01	0.07	0.61	1.60	-	-
93013	92020(c)	NC	400	33	25.0	0.92	0.06	0.39	1.69	0.182	0.002
94122	94101	NHC	400	21	24.8	0.25	0.02	0.10	0.43	-	-
94118	94102	NHC	400	53	18.2	3.34	0.52	0.22	12.12	0.185	0.011
94119	94103	NHC	400	54	18.2	3.39	0.36	0.99	6.44	0.178	0.003
94120	94104	NHC	400	-	18.2	-	-	-	-	0.142	0.002
94121	94105	NHC	400	39	24.8	3.46	0.41	1.22	9.30	0.132	0.001
94126	94111	NHC	400	-	21.0	-	-	-	-	0.163	0.003
94127	94112	NHC	400	-	22.0	-	-	-	-	0.145	0.002
94128	94113	NHC	400	-	22.0	-	-	-	-	0.131	0.001
94129	94114	NHC	400	-	22.0	-	-	-	-	0.134	0.002

survived essentially intact, even in experiments lasting 504 hours.

Changes in grain shape upon heating in CO_2 were negligible. In AC calcite heated at 400°C, a slight loss of sharpness of edges and corners of the rhombs was discerned. No changes were detected in NC calcite, which began with less perfect terminations.

Width of XRD reflections in starting calcite

The width of reflections from the 300 planes is consistently greater than from 00,12 except in ACV calcite with low Mn and Mg, in which they have similar widths. The dependence of width on composition and heating is very similar for both reflections, and the discussion is therefore restricted to 300. Table 1 contains the data.

There are significant differences among types of calcite: representative XRD spectra are shown in Figure 4. ACV calcite has well-resolved peaks (*i.e.,* the FWHM is small), comparable with those of a sparry calcite. NC calcite has poorly resolved peaks (*i.e.,* the FWHM is large). In AC and (in most samples of) NHC calcite, the FWHM lies between these extremes. Within these generalizations there are some subtle differences in FWHM that depend on composition as well as method of preparation.

Figure 5 shows the measurements of FWHM for the 300 reflection as a function of Mn and Mg concentration. Width generally increases with Mn and Mg, but also depends on method of synthesis. The narrowest reflections are found in ACV calcite at all concentrations of Mn and Mg, ranging from 0.09 to 0.12°2θ. Calcite of the AC series has FWHM in the range 0.13 to 0.17°, and NHC calcite with combined Mn and Mg amounting to less than 0.06 *apfu* has reflection widths in the range 0.13 to 0.16°2θ. In NHC calcite with higher concentrations of Mn and Mg, the FWHM could not be measured because the 300 and 00,12 reflections are so wide as to be lost in the background. With these exceptions, NC calcite has the widest reflections (0.16 to 0.21°). The sequence of increasing width of XRD reflections, for samples having less than 0.06 *apfu* of Mn and Mg (combined), is seen to be: ACV < AC = NHC < NC (Fig. 5).

XRD resolution of heated calcite

The most complete study of the effects of temperature, time and heating method on the width of XRD reflections has been carried out on NC calcite, with a small number of results for the AC and NHC series. The effect of heating on the XRD spectra of ACV calcite was not studied. The data are contained in Tables 2 and 3.

Time and temperature control the magnitude of the change that takes place during hydrothermal heating. Figure 6 shows that at 100°C there is no change in the FWHM of NC calcite, even in long experiments. A decrease by approximately half, to a FWHM of approximately 0.1°2θ, occurs in progressively shorter times as temperature is increased to 400°C, at which temperature as little as 6 hours are sufficient to effect this change. At 200°C, the change takes place at some point between 50 and 500 hours. In contrast, heating in CO_2 is relatively ineffective, with no significant change in FWHM at 400°C in 100 hours.

The more limited results for AC calcite follow a similar pattern, but the temperature dependence is

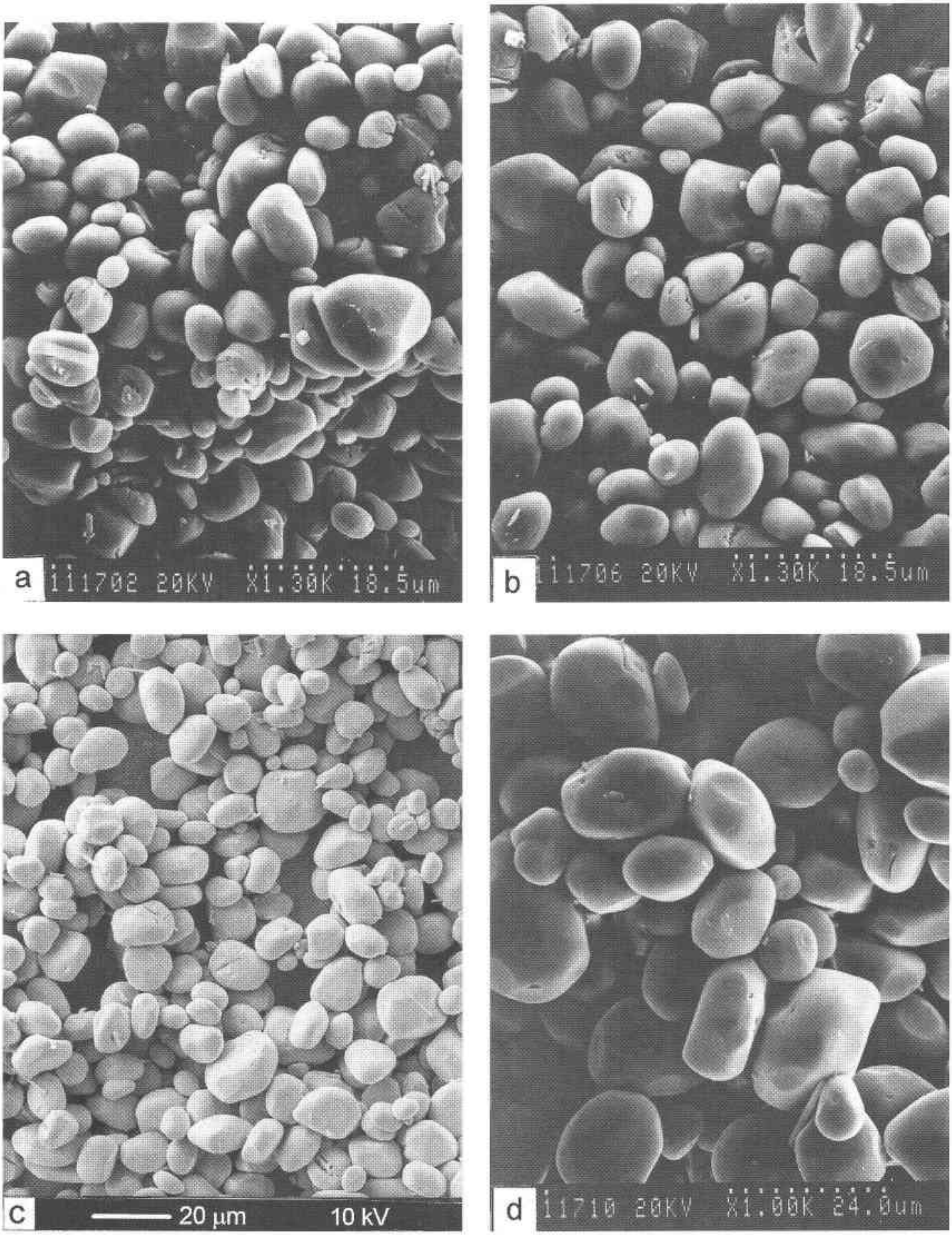

FIG. 3. Scanning electron photomicrographs of NC calcite hydrothermally heated at 400°C for (a) 27 hours, (b) 48 hours, (c) 98 hours, and (d) 663 hours.

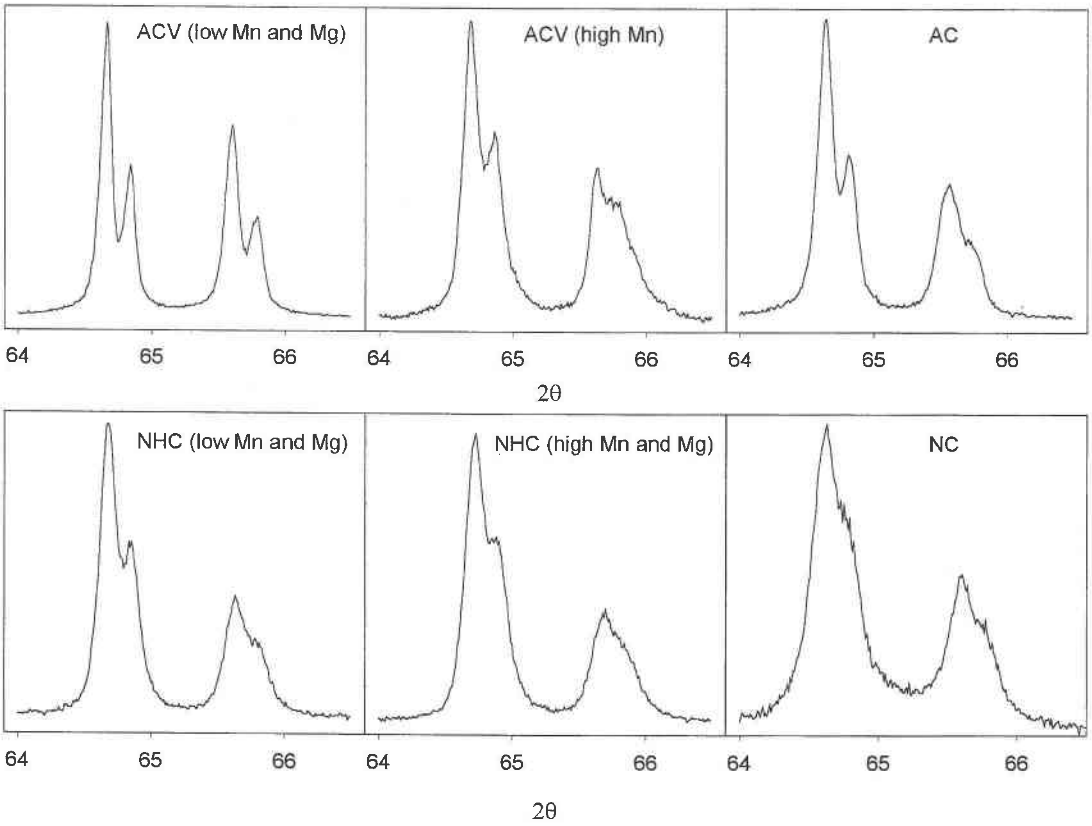

FIG. 4. Representative XRD spectra for each of the different types of calcite studied. The peak at a lower angle (2θ) is 300, whereas the peak at a higher angle is 00,12.

different. On hydrothermal heating, significant reduction in FWHM is observed only at 400°C, which, in AC calcite 94009, decreases to approximately 0.1° in 100 hours. In AC calcite 94007, FWHM increased slightly after in 119 hours at 300°C. Results from hydrothermal experiments on calcite of the ACV and NHC series are not available.

NHC calcite heated in CO_2 displays a positive dependence of FWHM on Mn and Mg concentration (Fig. 7). At a combined concentration of Mn and Mg below 0.03 *apfu*, heating generally causes narrowing of the XRD reflections. Significant widening took place in NHC calcite in which Mn and Mg total more than 0.03 *apfu*.

DISCUSSION

Grain size and recrystallization

Grain growth is the normal response to heating in a wide range of materials, the driving force being the lowering of free energy by reduction of total surface-area for a fixed volume of reactant. At constant temperature, coarsening generally follows a rate law of the form: $d = (d_o n + kt - kt_o)^{1/n}$, in which d is the mean diameter of the grains at time t, d_o is the mean diameter at time t_o, k is the rate constant, and n is a constant that normally lies between 2 and 5. In principle, the value of n can be used to infer the mechanism of recrystallization (Joesten 1991). The recrystallization of calcite has been studied experimentally by a number of investigators, and the data have been summarized by Joesten (1991).

Among the present data, only the hydrothermal results for NC calcite at 300°C and 400°C provide sufficient measurements to constrain the parameters of the equation given above. The fitted curves are presented in Figure 2. The exponent (n) ranges between 1.88 and 3.52, suggesting that different mechanisms dominate the coarsening process in different series of experiments. However, the uncertainties in n are large because of the relatively small number of experiments at each temperature. Determination of a reaction mechanism and esti-

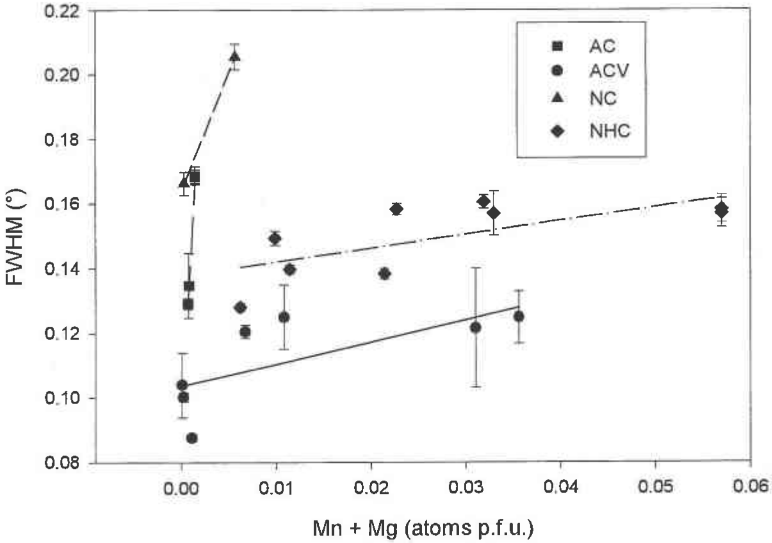

FIG. 5. Width (FWHM) of the 300 reflection for starting calcite as a function of the sum of the concentrations of Mn and Mg.

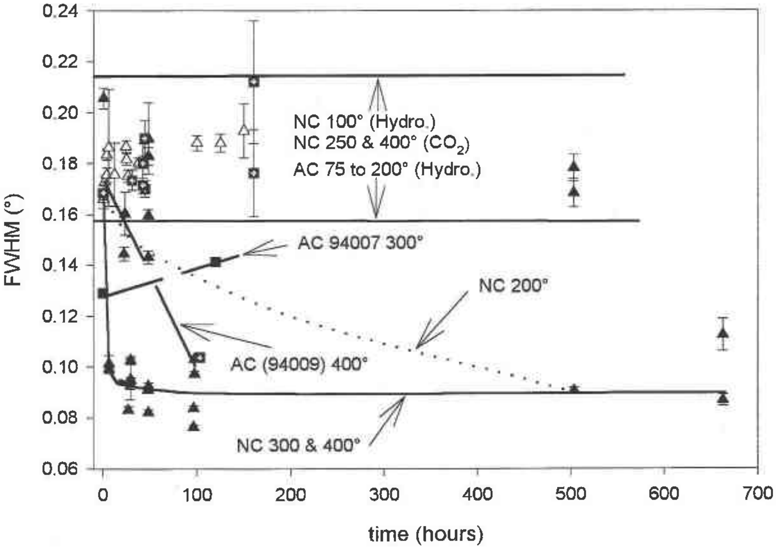

FIG. 6. Changes in FWHM as a result of heating. The upper pair of lines encloses the results from hydrothermal heating of NC and AC calcite at 200°C and below, together with the results from heating NC calcite in CO_2 at 250° and 400°C. Open symbols: CO_2, filled symbols: hydrothermal, triangles: NC, squares: AC.

mation of an activation energy from these data are unwarranted. The data are good enough to show, however, that rates of recrystallization are substantially lower than for the data collected in Joesten (1991, Table 1), as may be expected from the much lower temperatures used in the present investigation.

Differences in rate of coarsening among samples of calcite synthesized by different methods show that they

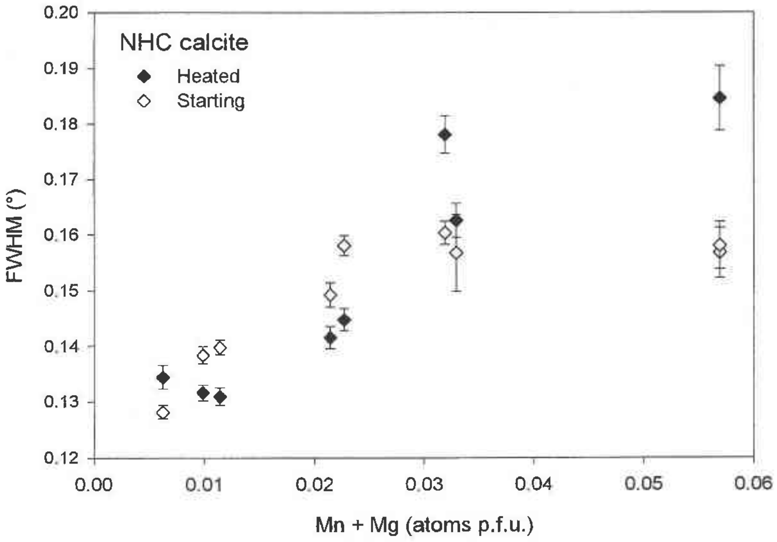

FIG. 7. FWHM of NHC calcite before and after heating in CO_2 at 400°C for 18 to 24 hours as a function of the total concentration of Mn and Mg.

differ in some physical or chemical property. In the case of NHC calcite having initial grain-size less than 1 μm, the large surface-area may be a control on rate of coarsening, because these are the only samples in which measurable coarsening took place below 300°C (in hydrothermal experiments). Initial grain-size cannot explain the faster coarsening in NC calcite compared with AC calcite, because both have lengths of approximately 1 μm. The difference in rate of coarsening correlates with differences in the width of their XRD reflections: calcite with broader reflections (NC) coarsens more rapidly. This finding suggests that rate of coarsening depends on the "crystallinity" of the calcite, as discussed below.

Width of XRD reflections and recrystallization

Both size and strain may contribute to the width of powder XRD reflections. Assuming for the moment that the strain contribution is zero, an estimate of the probable contribution of grain size to the measured widths of reflections can be obtained using the Scherrer formula: $L = (k\lambda)/(\Gamma \cos\theta)$, in which L is the grain size, k is a constant close to 1, λ is the wavelength of the X-rays, Γ is the FWHM, and θ is the diffraction angle (Klug & Alexander 1974). In this equation, Γ is the *extra* width contributed by grain size that would be added to (strictly, convolved with) the intrinsic linewidth of the incident radiation and the width arising from the instrumental parameters. The latter two effects can be eliminated; being constants, they cannot account for differences among results obtained using a single instrument under standardized conditions.

If measured grain-sizes are inserted into the Scherrer formula, estimates of the contributions that they should make to the FWHM are obtained. At the observed mean grain-size of NC and AC calcite (~1 μm), only approximately 0.01° of the FWHM arises from grain-size effects. The (very small) difference in size between calcite of the AC and NC series would contribute only approximately 0.005° to the observed difference in FWHM between them, which amount to 0.03 to 0.07°. Measurements of width of XRD peaks were not possible on the 0.2 to 0.3 μm grains of NHC calcite with the highest concentrations of Mn and Mg. The range of mean grain-size for the remaining NHC calcite is 2 to 4 μm, corresponding to a range of approximately 0.003° in FWHM. The measured difference, approximately 0.03°, is ten times greater. Again, the observed grain-sizes do not explain widths of XRD reflections. Note that preparation for XRD measurements of the NC, AC and NHC starting calcite did not involve any *grinding* that would reduce particle size; only gentle disaggregation was performed. Thus, the grain size measured in the SEM reflects the grain size on which the XRD measurements were made.

Calcite showing the greatest coarsening (NC calcite heated hydrothermally at 300° and 400°C) also shows the greatest reduction in the width of XRD reflections during heating. As stated above, the grain size of NC calcite should contribute approximately 0.01°2θ to the FWHM. This provides an upper limit on the amount by which the FWHM could be reduced by heating, if coarsening is solely responsible for the change in FWHM. The measured change is *at least 6 times larger*. Observed differences in grain size among types of calcite and members of individual series thus cannot account for the range in FWHM among them. Nor can changes in observed grain-size explain the effects of heating on the FWHM.

Grain size measured from SEM photographs reflects the size of individual crystals. Examination in a SEM may not, however, reveal the subgrain structure possessed by all real (*i.e.*, imperfect) crystals. Such subgrains could be present in the form of twins, misoriented slabs of structure, compositional heterogeneities, or as all three. In the absence of strain, the width of XRD reflections measures an *effective* size of particles, *i.e.*, the distance over which scattering is coherent. Thus, the widths of XRD reflections could be determined by an effective particle-size much smaller than the grains *observed* using the SEM, with each observed grain being, effectively, a polycrystalline aggregate.

In the analysis presented above, it was assumed that grain size alone contributes to the width of XRD reflections. However, strain also can cause broadening of X-ray reflections (Klug & Alexander 1974, Snyder 1995, Delhez *et al.* 1995). One possible cause of strain is the incorporation of "foreign" elements. The dependence of FWHM on the concentration of Mn and Mg could be a manifestation of this effect. The present data do not allow the separation of the strain and grain-size contributions to the FWHM, and neither can be eliminated.

Differences in the widths of XRD reflections from different types of calcite are considered to be controlled by either differences in the effective size of particles, or by strain, or both. If particle size is important, one can infer that the size range must be much smaller than the sizes of the discrete grains measured using the SEM and must differ among the types of calcite studied. Similarly, if strain is responsible for the observed widths of reflections, it must differ among the different types of calcite. These physical differences among types of calcite are a function of the different methods used in their synthesis. The change in width of XRD reflections induced by heating is attributed to coarsening of the effective particle-size, release of strain, or both.

Defects, luminescence and recrystallization

Subgrains and strain in solids (particularly those like calcite that are brittle at low temperature) involve defects that accommodate deformation and misorientation effects (Putnis 1992, Kretz 1994, Tsipursky & Buseck 1993). Materials with small subgrains possess a greater density of defects (number of defects per unit volume) than those with large subgrains because they contain a greater area of subgrain boundaries per unit volume. The presence of subgrains and strain raises the energy of a crystal; the extra energy provides a driving force for recrystallization in addition to that provided by surface energy. In the presence of water, extended arrays of defects that intersect crystal surfaces can also be expected to allow ingress of fluid, thus enhancing the reaction rate. The difference in rate of coarsening between the hydrothermal and CO_2 experiments is rationalized by the solubility of calcite in water, providing a mechanism for recrystallization (solution–reprecipitation) in the former but not in the latter.

NC calcite has wider XRD reflections than AC calcite and is inferred to have a higher density of defects (and possibly greater strain) than AC calcite. It follows that NC calcite should exhibit greater susceptibility to recrystallization and coarsening than AC calcite, as observed. The interpretation of results for NHC calcite is complicated because of the compositional dependence of the widths of XRD reflections and by phase separation. However, NHC calcite with modest levels of Mn and Mg has XRD reflections of approximately the same width as AC calcite and, if the conclusion regarding the influence of defects and strain on recrystallization is valid, would be expected to coarsen at a similar rate. This is the behavior observed. Differences in the rate of coarsening of the different types of calcite and changes in width of their XRD reflections thus seem to be controlled by differences in the density of defects (or states of strain).

Mason (1994, 1997, 1998) has proposed that the intensity of luminescence in calcite is partially controlled by the abundance of defects, with a high density of defects leading to lower emission for a given Mn content. Thus, calcite with wide XRD reflections should have a lower intensity of CL emission than a sample of calcite of similar Mn content with narrow XRD reflections. This is the pattern observed; for example, NC calcite (with wide XRD maxima) exhibits slightly lower intensity of CL emission than AC and ACV calcite of similar composition (Mason 1998). Similarly, NHC calcite with a high concentration of Mn has wide XRD reflections and lower intensity of CL emission than ACV calcite, with narrower XRD reflections and comparable Mn content (Mason 1998). The defect hypothesis of Mason (1998) is strongly supported by the present data.

The term "recrystallization" includes a number of processes, including the coarsening observed in this work. Recrystallization also typically involves the annihilation of defects and the recovery of strain. On the basis of a discussion of the causes of widening of XRD peaks, changes in FWHM induced by heating are thought to reflect these processes. The inferred loss of defects is considered to cause increased intensity of luminescence from calcite on heating (Mason 1994, 1997, 1998).

The magnitude of the heating effect on CL intensity, and the change in FWHM of XRD reflections, depend on method of heating, temperature attained, and starting calcite (Mason 1998). Hydrothermal heating is more effective than CO_2 in promoting an increase in CL emission at any given temperature, and the magnitude of the increase is greater at high than at low temperature. Given that changes in CL intensity are accelerated in the presence of H_2O, a link between the CL and data on coarsening is indicated. This link is further supported by the relative magnitude of the response of CL to heating among the types of calcite studied (NC > AC ≈ ACV), which is the same as that for coarsening rate and change in width of XRD reflections in the present study. The relative increase in CL intensity for hydrothermal experiments depends on the type of starting calcite in the following sequence: NC > AC ≈ ACV. (Too few experiments were performed on NHC calcite to draw firm conclusions as to its position in this sequence; note that there are complications arising from phase separation in some members of the series.)

The coarsening and CL data differ significantly in one important respect: in NC calcite, the increase in CL intensity takes place rapidly, within less than 10 hours, whereas coarsening is still taking place at an appreciable rate after hydrothermal heating for 100 hours at 300 to 400°C. In contrast, the decrease in FWHM in NC calcite is comparatively rapid at these temperatures, also being essentially complete after less than 10 hours. The different time-scales of *visible* coarsening and increase in CL emission intensity suggest that there is no direct causative link between them. The time-scale of the change in FWHM, however, is fully consistent with that of the increase in CL intensity, suggesting that the common cause for both of these responses to heating is the annihilation of defects (or relaxation of strain).

Natural calcite

The suggested presence of subgrains and associated strain and defects in synthetic calcite receives support from studies of natural calcite, in which a number of different kinds of microstructure are known to exist. These include a modulation on $(10\bar{1}4)$ (Gunderson & Wenk 1981), small spherical domains (Wenk *et al.* 1991) and a mosaic microstructure consisting of slightly misoriented domains (Tsipursky & Buseck 1993). These microstructures have been described from low-temperature parageneses, but examples from carbonatite may be their high-temperature analogues (Barber & Wenk 1984). Low-temperature microstructures have been found in calcite ranging from Recent echinoderm spines (Tsipursky & Buseck 1993) to Lower Jurrassic cement (Wenk *et al.* 1991). There are no reports of microstructures in metamorphic calcite (other than those associated with deformation: Wenk *et al.* 1983).

The origins of the microstructures remain unclear, but conditions of growth and the presence of cation order have been invoked to explain them (Tsipursky & Buseck 1993, Reksten 1990). It is not clear how microstructures formed during crystal growth evolve during diagenesis and any subsequent recrystallization, but the fact that they exist in ancient as well as modern calcite attests to their persistence, at least under some conditions. Their apparent absence in metamorphic rocks may indicate that they are destroyed by prolonged heating; it is tempting to draw an analogy with the recrystallization of synthetic calcite documented here.

Carbonate sediments are commonly rather heterogeneous, consisting of micrite and sparite that may be partially or completely recrystallized from original aragonite or high-magnesium calcite during diagenesis or burial. If the hypothesis outlined above is correct, the presence or absence (or exact nature of) surviving microstructures in the calcite of ancient sedimentary rocks may influence its luminescence behavior. The response to heating in the laboratory may thus be very dependent on the nature of the material sampled for study. If this is so, the variation in the sensitivity to heating in the suite of calcite studied by Mason (1997) may be explained.

CONCLUSIONS

(1) Samples of synthetic calcite that differ in composition also differ in their density of defects, state of strain or both.

(2) Different methods of synthesis produce calcite samples that differ in their density of defects, state of strain or both.

(3) Recrystallization, especially in hydrothermal conditions, causes annihilation of defects (or relaxation of strain), leading to a reduction in the width of XRD reflections and an increase in CL intensity.

(4) The microstructure of calcite is a significant control on its CL emission.

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