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# Mechanism of the alkali-carbonate rock reaction

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# MECHANISM OF THE ALKALI - CARBONATE ROCK REACTION

BY

J. E. GILLOTT AND E. G. SWENSON

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OTTAWA

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#### MECANISMES DE REACTION DES ROCHES CARBONATEES EN PRESENCE DE BASES

#### SOMMAIRE

Le présent article fait le tour d'horizon des principales hypothèses proposées pour l'explication de la réaction des roches carbonatées en présence de bases et faitla démonstration du mécanisme proposé par le laboratoire des matériaux minéraux du Conseil. Ce laboratoire soutient que l'expansion causée par les bases dans certaines roches carbonatées contenant de la dolomite est due à l'absorption d'humidité, par les argiles qui auparavant étaient sèches. Cette humidification est rendue possible à cause de la réaction de dédolomitisation qui ménage des canaux d'accès à l'humidité.

Les faits nouveaux sont les suivants: (a) on n'observe aucun changement de volume des cristaux de dolomite pure immergés pendant 4 mois dans la soude caustique liquide à une concentration de 2 moles; (b) le taux d'expansion, mesuré à l'aide du dilatomètre, du mélange poudre de roc et soude caustique liquide à la concentration de 2 moles, diminue alors que l'on augmente la dimension des particules de dolomite pure; (c) l'observation par micrographie électronique à balayage des rocs réactifs ou non à la soude caustique révèle que la plupart des éléments de l'argile sont rassemblés autour des rhomboèdres de dolomite, expliquant ainsi beaucoup mieux l'idée que la dédolomitisation ouvre des canaux parlesquels l'humidité se rend jusqu'à l'argile, et (d) une étude détaillée de quelques 50 roches carbonatées allant de la plus calcaire à la plus dolomitique, effectuée principalement par des examens pétrographiques et par leurs relations avec les résultats des essais du comportement des matériaux.



# J. E. GILLOTT & E. G. SWENSON

#### SUMMARY

This paper reviews the main hypotheses proposed for the alkali-carbonate rock reaction, and presents evidence supporting the mechanism advanced by this laboratory. The latter postulates that the alkali-expansivity of certain carbonate rocks containing dolomite is due to a wetting of previously unwetted clay minerals; the wetting is made possible by the dedolomitization reaction which produces access channels for moisture.

The new evidence consists of (a) no volume change of pure dolomite crystals immersed in 2M NaOH for 4 months; (b) the decreasing expansion of solid plus liquid of rock powders in 2M NaOH with increasing particle size of pure dolomite, using a dilatometer technique; (c) the observation from scanning electron micrographs of alkali-reactive and non-reactive rocks that much of the clay constituent appears to be distributed close to the dolomite rhombs, thus accounting more readily for the idea that dedolomitization opens up channels for moisture to gain access to the clay; and (d) a detailed study of some 50 carbonate rocks from the highly calcitic to the highly dolomitic with special emphasis on petrographic examinations and their correlations with results of laboratory performance.

# 1. Introduction

LIMESTONES and dolomites are widely used as aggregates in concrete, and their record of service performance has been excellent. There are, however, a few argillaceous dolomitic limestones that produce excessive expansion and breakdown of concrete when present as coarse aggregate, and when a portland cement is used which contains a relatively high percentage of alkalis. This phenomenon is known as the alkali-carbonate rock reaction. The extensive studies of this problem since its discovery (Swenson 1957; Swenson & Gillott 1960; Hadley 1961) have been summarized in a symposium volume (Highway Research Board 1964).

Experimental studies and field observations have established practical remedial measures which are generally accepted (Swenson & Legget 1960). Where carbonate rock aggregates are known to be deleteriously reactive, excessive expansions of the concretes can be limited by use of a low alkali cement or by control of the main external influencing factors: moisture and temperature. Petrographic and other means of distinguishing expansive from non-expansive carbonate rocks have been established for practical use (Gillott 1963; Swenson & Gillott 1964).

Despite the extensive research carried out in several laboratories, there remains disagreement as to the mechanism of the expansion. The hypothesis of this laboratory, as developed in the earlier papers, has been supported by more recent experimental work (Swenson & Gillott 1967). In this paper the various theories are re-examined and some new data, including petrographic descriptions, are presented.

Q. Jl Engng Geol. Vol. 2, 1969, pp. 7-23, 1 fig., pls. 1-34. Printed in Great Britain.

# 2. Pertinent characteristics and reactions of alkali-expansive carbonate rocks

Expansively reactive carbonate rocks are fine-grained argillaceous dolomitic limestones, or argillaceous calcitic dolomites. Rhombic crystals of dolomite, commonly dusky with inclusions, and about 50  $\mu$  or less in cross-section, are set in a fine-grained matrix of calcite and clay. It is emphasized that all major studies of the alkali-carbonate rock reaction have shown that some considerable amount of acid-insoluble material was always present in alkali-expansive rocks. Clay and carbonate mineralogy have been described in detail for a large number of carbonate rocks by several researchers on this problem (references below). Illite is the dominant clay mineral with smaller amounts of chlorite. In rocks from Iowa and Indiana, mixed-layer clay composed of a random mixture of 10 Å and 14 Å material was found. Swelling clay minerals are absent. The dolomite crystals are generally disordered and frequently contain an excess of Ca above the ideal 50 mole per cent. It has not been possible, in spite of considerable effort, to relate expansivity to clay or carbonate mineralogy (Gillott 1963, 1964; Hadley 1961, 1964; Swenson & Gillott 1960; Newlon & Sherwood 1962; Highway Research Board 1964). The calcite phase in expansive rocks was invariably finely divided.

The physical and mechanical properties of many of the most alkali-expansive rocks satisfy the conventional test requirements for concrete aggregates (Swenson & Legget 1960).

Rate and degree of expansion of reactive rock immersed in alkali (or of concrete made with the rock as aggregate) increase with increase in available alkali, whether the alkali derives from the cement or is added as sodium or potassium hydroxide. A limited increase in temperature increases the rate of expansion, indicating some chemical action. Moisture, necessary for the expansive reaction, is taken up during the progress of the reaction (Swenson 1957; Swenson & Gillott 1960; Hadley 1961; Feldman & Sereda 1961; Gillott 1963, 1964). The dolomite constituent of the carbonate rock is attacked by the alkali with the formation of brucite, calcite and alkali carbonate (Swenson & Gillott 1960; Hadley 1961; Mather, Buck & Luke 1964). This reaction may be written in its simple form:

### $CaMg(CO_3)_2 + 2NaOH \rightarrow CaCO_3 + Na_2CO_3 + Mg(OH)_2.$

This is known as the dedolomitization reaction, the rate of which is directly affected by the size of the dolomite crystals, the temperature, and apparently by the particle size of the calcite. Despite several concerted attempts noted in the literature already cited, no quantitative relations have so far been demonstrated between expansivity and such variables as the state of crystalline order in the dolomite, porosity and permeability of the rock, and amount, type and distribution of clay minerals. Alkali concentration affects rate and probably also the nature of the reaction products (Swenson & Gillott 1964; Hadley 1964). Some workers have reported finding more complex salt products such as hydrotalcite-sjogrenite (Walker 1967) and gaylussite and buetschliite (Sherwood & Newlon 1964).

An experimental finding of Hadley (1961), which this laboratory was unable to reproduce, has formed the basis of one hypothesis. He obtained a large single crystal of dolomite which he immersed in a 3M NaOH solution. In 100 days the linear expansion was 0.15 per cent. This will be examined further.

It is important to note that, although a combination of certain compositional and textural characteristics must be present for a rock to show excessive expansion in the presence of a certain minimum alkali concentration, there are many carbonate rocks that do not expand excessively even though they possess most or even all these characteristics (Swenson & Gillott 1960, 1964, 1967). These features are dealt with in detail in this paper and in the literature already cited.

# 3. Hypotheses for observed expansion

The mechanisms which have been proposed can be divided into two categories: the direct mechanisms which attribute excessive expansion to the attack of the alkali upon the dolomite, and the indirect mechanisms which assign a trigger role to dedolomitization and invoke other factors as primary in producing the expansion.

In one mechanism it is postulated that the dedolomitization follows a different course from that expressed in the equation given earlier. Sherwood & Newlon (1964) suggested that complex hydrated double salts of large unit cell size caused the increase in solid volume. Hansen (1964, 1966, 1967), however, considered the details of the solution process and adapted ideas put forward by Frederickson (1951). Hansen proposed that the first step in dedolomitization involves penetration into the dolomite of  $OH^-$ , alkali metal ions and water. In his view this postulated invasion of the structure should enlarge the crystal and generate expansive forces regardless of the exact course followed by the subsequent reaction. Hence the calculation of volume changes from unit cell size data is regarded as an oversimplification, since net difference between cell size of reactants and products is largely irrelevant (Hansen 1962).

Where the dedolomitization reaction is not considered the direct cause of the expansion of certain carbonate rocks, the clay or clay-like materials have been held suspect.

Hadley (1961, p. 468) suggested that ion exchange or removal of organic coatings from the clay mineral surfaces might increase their water-sorptive characteristics. Later (Hadley 1964, p. 6) he postulated that expansion might result from osmotic forces. The alkali-carbonate solution at the reacting dolomite crystal may differ in concentration and nature from the solution in the pores. Differences in flow tendencies of the two solutions through interstitial clay may lead to the build-up of a swelling pressure.

The mechanism proposed by the authors (Gillott 1964; Swenson & Gillott 1964, 1967) suggests that the dedolomitization reaction exposes previously unwetted clay and other fine-grained materials by the development of access channels for moisture. Surface hydration and formation of hydrous double layers associated with clay minerals lead to moisture uptake and the development of swelling pressures which produce expansion. These clay minerals need not be the swelling clays recognized in soil science, e.g. mont-morillonite. Evidence has been developed to show that the so called non-swelling clays, e.g. illite, can produce sufficient expansion by uptake of water from a dry state, to account for the expansions observed in the alkali-carbonate rock reaction (Swenson & Gillott 1967). Envelopes of water surrounding the clay minerals at the time of deposition are believed to have been expelled by consolidation of the sediment and by other processes and conditions associated with rock formation. Once the rock is lithified, under some

conditions, water may not be able to rewet the clay minerals until some subsequent chemical or physical process opens up channels for moisture to enter. Dedolomitization is such a process.

# 4. Pure dolomite crystals in alkali

This laboratory repeated the experiment of Hadley on a single pure crystal of dolomite of about one inch cross-section obtained from the Federal Department of Energy, Mines and Resources in Ottawa. This was done because this single experiment has been cited in certain reviews, as prime evidence that the alkali expansivity of some dolomitic limestones is due directly to the dedolomitization reaction (Hansen 1966, 1967).

An x-ray diffraction powder photograph was taken on a Nonius Guinier quadruple focusing camera using  $As_2O_3$  as internal standard. This showed the dolomite had a composition of  $Ca_{50.87}Mg_{49.13} \pm 0.24$  (95 per cent confidence level); 'order' reflections were not noticeably weakened. The crystal therefore contains a slight excess of calcium above that found in 'ideal' dolomite. The amount of structural disorder, however, is only slight. This crystal was sliced by a special cutting procedure into three plates oriented parallel to the optical axis, and 0.050 to 0.075 in thick. Each of these was mounted in an optical extensometer and immersed continuously in 2M NaOH solution. Length changes after 154 days were +0.008 per cent, +0.004 per cent and -0.012 per cent.

This completely different result from that of Hadley could hardly be due to the difference in concentration (2M as against 3M) of the alkali employed in the two cases. It seems highly probable that if, as postulated by Hansen (1967), Na<sup>+</sup> and OH<sup>-</sup> ions enter the crystal, the rate at which they do so would be controlled and severely limited by ionic diffusion and re-arrangement in the solid as these processes are likely to be the rate-determining factors. The discrepancy in the results might be explained by suggesting that some pure dolomite crystals expand in alkali and some do not, depending on whether they are, or are not, disordered. This explanation is considered highly improbable because none of the essentially pure dolomite rocks studied in this laboratory gave evidence of alkali-expansivity, nor did numerous dolomitic limestones and calcitic dolomites in which the clay fraction was negligible (see data following). One would have expected at least some of these many rocks to contain dolomite which possessed some degree of disorder, and therefore to have shown response. Furthermore it has been demonstrated by x-ray diffraction methods that disordered dolomite is present in non-alkali expansive rocks (Hadley 1961; Gillott 1963, 1964). Hadley (1961) has suggested that the nonexpansivity of some dolomitic rocks might be due to restraint offered by interlocking dolomite crystals. In the present paper petrographic and other evidence is given which is in conflict with this view. Another possibility is that Hadley's crystal may have contained some inadvertent, artificial imperfection that resulted in the length change he observed.

After being soaked in alkali for 5 months the single crystal studied in this laboratory was analysed by powder x-ray diffraction. Photographs were taken with a Philips powder camera and with a Nonius Guinier quadruple focusing camera using monochromatic Cu-radiation. Separate photographs were taken of the powdered bulk crystal and of material scraped from the surface of one of the single crystal plates. Comparison between photographs of the sample prior to, and after, immersion in alkali showed that only a trace of dedolomitization had taken place.

The reactivity in alkali of powdered samples of pure dolomites has been studied with two forms of dilatometer (Gillott 1964):

- (a) the 'simple dilatometer' in which volume changes in the whole system, solid plus liquid, are measured; and
- (b) the 'powder cell' in which volume changes in the solid are recorded independently of those in the liquid (Gillott 1963B, 1964).

In the 'powder cell', when dedolomitization takes place, no expansion is registered in pure dolomite powders. In the 'simple dilatometer' the same size fraction of pure dolomite does register expansion when dedolomitization takes place. This is considered as conclusive evidence that dedolomitization causes no increase in solid volume. The volume increase registered in the simple dilatometer, however, proves that dedolomitization is accompanied by an increase in the volume of the fluid phase. This volume increase registered may thus be used as a continuous and sensitive measure of the rate and degree of dedolomitization in 2M NaOH of powdered pure dolomite. The 'simple dilatometer' was used to follow the reactivity in 2M NaOH of pure dolomite. Three size fractions were used: 74 to 44  $\mu$ , 44 to 2  $\mu$ , and minus 2  $\mu$ . The volume changes, solid plus liquid, obtained are shown in Fig. 1. As may have been predicted, rate of reaction decreases

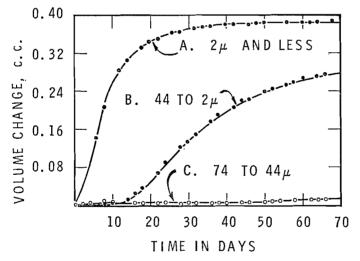


FIG. 1. Volume increase of solid plus liquid on dedolomitization of size-fractionated pure dolomite in 2M NaOH.

with increase in size of dolomite crystal, the coarsest 74 to  $44 \mu$  size showing very little expansion after 4 months. This agrees with previous studies (Highway Research Board 1964). Analyses of extracts of the solutions during test showed a decrease in alkali concentration with time, the amounts being dependent on the extent of the reaction. x-ray analyses of the reacted powders showed the presence of the expected products, brucite and calcite, and depletion of dolomite.

These experimental results support the contention of the authors that the dedolomitization reaction becomes negligibly slow when the crystals of dolomite exceed about the 75  $\mu$  size. It has been demonstrated in previously published work by this laboratory (Swenson & Gillott 1967), and further supported by additional evidence in this paper,

that dolomitic carbonate rocks with dolomite crystals above this size are not to be found among alkali-expansive rocks.

Hence the evidence does not support the contention that dedolomitization was responsible for the expansion of the single crystal.

# 5. Study of a suite of 51 carbonate rocks

#### (A) GENERAL

In a previous paper (Swenson & Gillott 1964) the authors describe briefly a study of some 50 carbonate rocks ranging in composition from essentially pure calcite to essentially pure dolomite. They were obtained from several countries in Europe and from North America. One of the original purposes of the investigation was to attempt to determine whether the acid-insoluble component was important to the expansion problem. In this paper, details not previously reported are presented because they are pertinent to an assessment of recent reviews of the alkali–carbonate rock reaction (Hansen 1966, 1967). These rocks are to be distinguished from another suite of some 50 carbonate rocks, studies of which are elsewhere described (Swenson & Gillott 1967).

Table 1 gives data on composition, length change performance of rock prisms and concrete beams, and other properties of 51 rocks, most of which were selected because of low or very low acid-insoluble content. The selection also included rocks of both coarse and fine texture and with some variability in porosity. There has been no attempt to give the geological ages of the samples in this table and geographical locations are given only in general terms under the petrographic description in the next section. It is considered that such data have no significant bearing on the behaviour of the rocks as concrete coarse aggregates.

Dolomite contents were calculated from chemical analyses on the assumption that all the magnesium was present in the form of dolomite. In some samples this was verified by a direct chemical method based on rates of carbon dioxide evolution on acid treatment (Skinner, Halstead & Brydon 1959) and by x-ray diffraction. The compositional groupings shown in the table are based on the scheme recommended by Pettijohn (1957). Porosities were calculated from vacuum saturation data, high values being checked with a mercury porosimeter.

Rock prisms measuring  $1 \times 1 \times 6$  in were cut parallel and normal to the bedding planes and immersed in 2M NaOH. Length changes were measured over a 2 to 3 yr period. Concrete prisms measuring  $3 \times 4 \times 16$  in were made with each rock as coarse aggregate, cured continuously in a moist room from 3 to  $7\frac{1}{2}$  yr, and measured for length change periodically. The proportions used were 3000 g normal portland cement, 6000 g unreactive concrete sand, and 9750 g of stone to  $\frac{3}{4}$  in maximum. Water-cement ratio was 0.475 and slump from 1 to 2 in. The high alkali cement had a soda equivalent of 1.1 and the low alkali cement 0.5. Those concrete prisms that were continued to  $7\frac{1}{2}$  years were cut to 3 by 3 by 4 in prisms and tested for compressive strength.

Microscopic thin sections were made from the untreated rock, from the rock after immersion in alkali solution, and from the concrete beams made with both high and low alkali cement. Etched fracture surfaces of selected samples were examined on the scanning electron microscope.

#### (B) COMPOSITION AND PHYSICAL PERFORMANCE

The concrete strengths shown in the table indicate that, with the possible exception of no. 38, the rocks were sound as aggregate. Even the concretes that expanded excessively were apparently able to accommodate the volume changes without producing deterioration—presumably because of the long-time factors of creep and autogenous healing. No. 27 is an example. These accommodation and healing processes probably minimize the worst effects of many varieties of slow deterioration. High porosities did appear to have the effect of lowering ultimate strengths: nos. 20, 33, 41, 48.

Length changes of rock prisms were considered excessive if they exceeded about 0.04 per cent, and of concrete prisms if they exceeded about 0.03 per cent. These are, of course arbitrary limits derived from much field and laboratory experience. The results from rock prisms correlated very closely with those of the concrete prisms and all were remarkably consistent over such a long period of time.

No cases of excessive expansion occurred for any rock with very low acid-insoluble content (therefore, also low in clay). It will be seen later that some of these had the other characteristics, textural and compositional, known to be favourable to the alkali– carbonate rock reaction.

The rocks showing excessive expansion were those with intermediate calcite-dolomite ratios, and containing significant amounts of acid-insoluble residue. Nos. 27 and 29 are very alkali-expansive, and nos. 20, 24, 30 and 32 mildly so. It is to be noted also that a high acid-insoluble content does not necessarily make for excessive expansion, e.g., no. 33. This is a well-established fact.

Many of the rock prisms undergo a considerable shrinkage during lengthy immersion in alkali. This phenomenon has been noted previously (Lemish & Moore 1964) and has never been explained satisfactorily. It does not appear to bear a direct relation to the alkali-carbonate rock reaction.

#### (C) PETROGRAPHY

As shown in Table 1, all the limestones, samples 1 to 7, and the magnesian limestones' samples 8 to 11, are non-expansive. Samples 1, from Quebec, 3 and 8, from Ontario, and 11, from Germany, are uniform fine-grained rocks which could be described as lithographic stones. Most of the calcite is in the 2 to 5  $\mu$  range though there are also some coarser crystals of about 10  $\mu$  diameter in the matrix of sample no. 1. They are illustrated in Pls. 1*a*, *b*, *c*. Samples 5, 6 and 7, from Ontario, have a matrix of micrite (micro-crystalline calcite of crystal size of about 2  $\mu$ ) and contain fossil fragments, intraclasts,<sup>1</sup> and pellets,<sup>2</sup> so that they are more heterogeneous. Samples 2, from Quebec, 4 and 9, from Georgia, and 10, from Oklahoma, are coarser grained rocks composed of anhedral interlocking crystals of calcite. A few well-formed euhedra of dolomite, 50 to 100  $\mu$  across, are present in sample 9. These rocks are illustrated in Pls. 1*d* and 1*e*.

The next group, nos. 12 to 29, are the dolomitic limestones, among which are found the alkali-expansive rocks which produce excessive expansion of concrete when they

<sup>&</sup>lt;sup>1</sup> "Fragments of penecontemporaneous, usually weakly consolidated carbonate sediments that have been eroded from adjoining parts of the sea-bottom and redeposited to form a new sediment" (Folk 1959, p. 4).

<sup>&</sup>lt;sup>2</sup> "Rounded, spherical to elliptical or ovoid aggregates of microcrystalline calcite ooze, devoid of any internal structure". The size range in different specimens is "between 0.03 mm and about 0.15 mm" (Folk 1959, pp. 6–7).

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	Percent	Percentage Composition	osition	Percentage porosity			Р	Percentage Expansion	Expansion				Comp streng	Compressive strengths on
	Calculated	llated			Rc	ock Prisms	Rock Prisms in 2M NaOH	НО	$3 \times 4 \times 16^{\circ}$	× 16″ Co Moist	% Concrete Moist Room	Prisms,	$3 \times 3 \times 4$ at $7\frac{1}{2}$	$3 \times 3 \times 4^{"}$ prisms at $7\frac{1}{2}$ years
			A cid	Voc Voc Cot	1 y	1 year	2 y	2 years	2 years	ars	3 <u>1</u> to	3 <sup>1</sup> / <sub>2</sub> to 10 years		
	Dolo- mite	Cal- insolubl cite	soluble	e MP-Mer. Pen.	Horiz.	Vert.	Horiz.	Vert.	High Alk.	Low Alk.	High Alk.	Low Alk.	High Alk.	Low Alk.
Limesto	Limestones; 0–5% Dolomite	% Dolom	ite 0.43	SV 4.0	0.002	000-0	00.0	0.00	0.01	000.0	0.010	0.010.021)		
- 0	<0.5	0.66<	0-59	2.3 VS	-0-011	-0.007	-0.023	0.014	0.008	0.008	0.012	0.012 (32) 0.012 (78)	11.060	10.920
<b>ω</b> ₹	<0.5	0.66<	0.46	1.9 VS	-0.018	0.005	-0.014	-0.011	0.011	0.011	0.011	$0.011(3\frac{1}{2})$		
t v	2.3	95.6	2.32	1.2 VS	710.0-	0.013	710.0-		0.010	010-0	010-0	(%) cI0-0 0-009 (3)	9,120	10,22U —
9	2.7	92.3	3.93	0.4 VS	-0.008	-0.012	-0.016	-0.010	0-008	600-0	900.0	$0.011(3\frac{1}{2})$	1	
	5.1	90.7	3.41	4·6 VS	Ι	-	Ι	Ι	0-021	0.013	0-033	0.021 (10)	10,810	12,720
Magnes	Magnesian Limestone;	tone; 5-1	5-10 % Dolomite	omite										
∞ 6	5.5 6.0	92•0 91•6	2·56 2·61	0-1 VS 0-4 VS		0.023	-0.017	-0-024	0.011 0.011	0.011 0.012	0.014 0.015	$0.015(7\frac{1}{2})$ $0.016(7\frac{1}{2})$	_	11,170 $10.420$
10	6·4 8·4	94-1 92-0	$0.84 \\ 1.51$	3·1 VS 4·6 VS	-0.005 0.008	-0.004 -0.002	-0-014 0-002	-0.010 -0.002	0-014 0-008	0-012 0-009	0-021 0-011	$0.021$ $(7\frac{1}{2})$ $0.013$ $(7\frac{1}{2})$	11,640 10,080	12,440 11,190
Dolomitic	ic Limest	Limestones: 10–15 % Dolomite	-15 % Do	lomite										
12	11.7	84.8	1.56	0-7 VS	-0.052	I	-0.059	I	607.0	0.013	0-014	0.018 (7 <sup>1</sup> / <sub>2</sub> )		10,830
13	13-6	85.6	1.60	0.5 VS	-0.012	-0.010	-0.005	600.0	0·012	0·008		$0.012(7\frac{1}{2})$	10,690	11,580
14	15.5	83.8	0.48	4.6	0.012	-0.012	-0.021	-0.028	0.00	0-010	0-015	$0.017(7_{\frac{1}{2}})$		10,330
16	17-4	78-0	0.40 4.46	0.4	-0.004	-0.002	0.010	0.005	0.012	cT0-0		$(\frac{4}{5})$ (4 $\frac{5}{13}$ ) (13 (7 $\frac{1}{3}$ )	10.110	11.280
17	17-9	79-3	2.13	2.2	-0.019	Ι	-0.026		0.013	0.015		0.015 (41)		
18	19.6	76-8	2.04	7.1	600-0-	-0.016	-0.010	-0.016	0.012	0.015		0.014 (41)		
20	22.7	70-8	6.18	11-6 VS	0.150		0.155		0-010	0-020	0-032	0-030 (7±)	10,190 100	9,920
21	22.9	71.3	4.42	1.1 VS	-0.016	0.024	-0.010	0.017	0.012	0.012		0.019 (7 <u>4</u> )	10,580	9,780
53	23-5	71.5	0·47 1·87	4·2 VS 0·3 VS	0.00-0	-0.016	-0.012 0.002	-0.017	$0.008 \\ 0.014$	0-009 0-012		0.006(3) $0.021(7\frac{1}{2})$		$\frac{-}{11,110}$
24	33-9	62.6	3.71		Ι		Ι		0.027	0.017	0.038	0.026 (7 <u>1</u> )	9,860	10,970

TABLE 1: Compositional and performance properties of suite of 51 Carbonate rocks

# J. E. Gillott & E. G. Swenson

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34.7 35.6 37.4 42.8 48.5	Calcitic Dolomites; 50-90% Dol 30 55.0 31.9 11.05	56·2 59·4 69·0 70·1 71·1 62·1	79·6 80·3	81.7	82·9 83·8	88.5	Dolomites; 90–100% Dolomite 43 90-4 8-1 0-1	91.2 91.2 93.3	94-5 97-0	98•2 99•1	100-0
25 26 28 29 29 29	Calcitic 30	31 32 35 35 35 36	37 38	39	40 41	42	Dolomit 43	44 45 46	47 48	49 50	51

constitute the coarse aggregate. These have been extensively studied (Hadley 1961; Gillott 1963). Samples 12, 14, 15, 17, 18, 19 and 22, from Ohio, are non-expansive apart from a trace in 12. Petrographically they are fairly similar to one another although the dolomite content increases in the order shown in Table 1. Interlocking, anhedral calcite crystals,  $\frac{1}{2}$  to 2 mm across, a few fossil fragments, and euhedral dolomite rhombs (20 to 200  $\mu$  across) are enclosed in a fine calcite matrix of micrite and microspar (grain size 5 to 6  $\mu$  or greater). The proportions of coarse to fine calcite differ between samples. A typical example is illustrated in the optical micrograph, Pl. 1*f*. Comparison shows that apart from the low clay content this non-alkali-expansive rock is quite similar in appearance to the alkali-expansive rock shown in Pl. 2*c*. The fabric can be observed in more detail on the scanning electron micrograph, Pl. 1*g*, where contacts between dolomite crystals and matrix are displayed.

Samples 25, 26 and 28, from Alabama, Iowa and Ohio, which are not alkali-expansive, are similar rocks but the texture is coarser and the dolomite content higher (Pls. 2a and 3b). In the non-alkali-expansive sample 21, from New York, the dolomite crystals (50 to 200  $\mu$ ) occur in veins which cut through a fine matrix of micrite and intra-micrite. In sample 16, from Oklahoma, there are fine-grained intraclasts surrounded by a matrix of clear calcite and scattered subhedral rhombs of dolomite of about 100  $\mu$  cross-section.

Samples 20, 23, 24, 27 and 29 from Indiana, Virginia, Ontario, Georgia and Iowa, are fairly similar to the classical expansive rocks such as those from Kingston, Ontario, which have been described in detail elsewhere (Hadley 1961; Gillott 1963). All the samples show some alkali-expansivity apart from the Virginia sample which has quite a low acidinsoluble content. An optical micrograph of the alkali-expansive rock from Georgia, Pl. 2c, may be compared with a view of one of the expansive Kingston rocks in Pl. 2d. It is significant to the mechanism of expansion that the dolomite rhombs in the Kingston rock are quite close together and frequently interlock. Hadley's concept of restraint (Hadley 1964) is to be recalled. Scanning electron micrographs of this rock from Kingston, Pls. 2e and 2f show dolomite rhombs and matrix. The mica-type minerals have an open disposition which suggests the arrangement assumed on flocculation. This fabric would also result from accommodation to the growth of the carbonates, the clay minerals being excluded and 'pushed aside' into grain boundaries. Regardless of its origin, there is an intimate embrace between carbonates and layer structure silicates and the clay minerals are tightly enclosed within the fabric of the rock. Once moisture has been expelled by lithification it is unlikely that in rocks with this type of fabric the clay minerals would have been re-wetted in the absence of an external process such as dedolomitization. Many of the mica-type minerals occur at boundaries between dolomite crystals and matrix. In this regard the contact seems to be different from that illustrated previously for the non-expansive Alabama and Ohio rocks, Pls. 1g and 2b. There is apparently a tendency for mica-type minerals to be concentrated near the dolomite rhombs. This distribution of the clay minerals could arise either because they were expelled from within the growing crystal or because they acted as sites of dolomite nucleation (Kahle 1965). It is compatible with the hypothesis proposed by the authors that the concentration of clay near the dolomite crystals makes this fine material readily accessible to moisture after dedolomitization has provided the channels.

The next 13 samples, nos. 30 to 42, constitute the calcitic dolomites. Samples 30 and 33 are quite similar to those dolomitic limestones that are alkali-expansive, apart from the higher dolomite contents. Sample 30 does, indeed, show evidence of expansivity in alkali

but sample 33 does not (Table 1). This illustrates the previous conclusion that samples may be non-alkali-expansive even though they possess an adequate content of acidinsoluble material along with the other petrographic features of an alkali-expansive rock. There is no relationship between rate and degree of alkali-expansivity and the amount of acid-insoluble residue although it has been well established that some minimum quantity of clay or clay-like minerals is necessary to produce excessive expansion of the rock (Swenson & Gillott 1967). Samples 31, 32, 35, 36, 37, 38, 39 and 41, from Oklahoma, Ohio, Virginia, Alabama and Iowa, are quite similar to one another and are non-alkaliexpansive apart from no. 32 which shows a trace. Dolomite is present as euhedral crystals, sometimes containing inclusions, and ranging in size from 10 to 200  $\mu$  across. As the proportion of dolomite increases, calcite is more and more confined to an interstitial role where it occurs as anhedral crystals ranging from the micron to the millimetre size range in different rocks. Two typical examples are illustrated in Pls. 2g and 3a. The sample shown in Pl. 3a is finer grained and more porous than that shown in Pl. 2g. Sample 42, from England, is fairly similar to the calcitic dolomites just described but the dolomite occurs as 20 to 30  $\mu$  subhedral to anhedral crystals. In sample 40, from Alabama, (not alkali-expansive) there are patches of very fine calcite surrounded by subhedral dolomite crystals about 50  $\mu$  across. Sample 34, from Georgia, (not alkaliexpansive) contains dolomite euhedra ranging in size from 20 to  $150 \mu$  in interlocking aggregates which are in patches of 2 to 3 sq cm surrounded by areas of fine calcite (crystals of about 10  $\mu$  across).

The last group of 9 samples, nos. 43 to 51, classed as dolomites show no alkali-expansivity. They were obtained from Virginia, South Carolina, Iowa, Colorado, England and Wales. The rocks consist chiefly of interlocking anhedral dolomite crystals, but with some euhedra also present. The crystals range in size from 10  $\mu$  up to 1 mm or more in some rocks. The rocks differ in porosity, samples 43, 46, 48 and 50 being the most porous. Optical micrographs of three of these rocks are shown in Pls. 3b, c and d.

Sample 49 in Pl. 4b shows a close-textured rock of low porosity made up of small subhedral to anhedral crystals of dolomite. Sample 46 in Pl. 3c is coarser grained and of intermediate porosity, while sample 50 (Pl. 3d) is the coarsest example with the highest porosity of the rocks in this group (Table 1). The appearance of the dolomite crystals and the nature of the intercrystal contacts as seen on etched fracture surfaces in the scanning electron microscope, are shown in Pls. 3e and 3f. Cleavage is more apparent in the crystals shown in Pl. 3e than in those of Pl. 3f. It should be particularly noticed in considering the direct mechanisms of alkali expansion that some of these rocks (especially nos. 49, 44, 47) display low porosity and are composed of quite small crystals of dolomite. Crystals are fine enough to react with alkali yet very little pore space is available to accommodate an increase of volume internally. However, no expansion was registered.

#### (D) GENERAL CORRELATION

The above results from petrographic analyses and from the studies of composition and performance confirm previous work and interpretations of this laboratory (Swenson & Gillott 1960, 1964, 1967; Gillott 1964).

Both clay minerals and dolomite are necessary to the alkali-expansivity of carbonate rock, and therefore both have a role in the mechanism. The proportion of clay need not

be large (Swenson & Gillott 1967) and there appears to be a tendency for it to be more concentrated around dolomite rhombs. The dolomite crystals must be small in size and distributed in a fine-grained matrix of calcite and some clay.

It is most important to note, however, that even if these special requirements are met, the rock is not necessarily alkali-expansive.

# 6. Discussion of hypotheses

The experimental evidence makes untenable any of the proposals in which dedolomitization is held to be directly responsible for the alkali-expansion observed in some carbonate rocks.

If the Na<sub>2</sub>CO<sub>3</sub> product of dedolomitization crystallized fully as the solid hydrate  $Na_2CO_3$ . 10H<sub>2</sub>O, or if hydrated double salts formed, there would result a net increase in solid volume which could account for observed alkali-expansion. There is, however, little experimental evidence that hydrates or hydrated double salts form in the dolomite crystal or in the matrix under conditions known to be optimum for expansion. Available phase data (Bury & Redd 1933) indicate that crystallization of gaylussite, for example, takes place only at quite high concentrations of  $Na_2CO_3$ . In concrete made with a dolomitic limestone and a high alkali cement the proportion of the dolomite which undergoes dedolomitization is very small even after many months. The reaction itself appears to be slow and the alkali reactant is limited in quantity. Hence, it would be highly unlikely that significant amounts of either Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O or other complex hydrates could crystallize out even if the 'juices' became fairly concentrated through loss of water to the hydrating cement or to the atmosphere. The amounts of such potential products of dedolomitization observed on reacted specimens, whether in concrete (Mather et al. 1964) or in rock prisms subjected to immersion in 1M or 2M alkali (Sherwood & Newlon 1964, Walker 1967), have been small and do not constitute good evidence that they are directly responsible for the excessive expansions in question. In rock prisms immersed continuously in 2M alkali the juices will not become more concentrated as is possible in concrete. Hence the environment should be less favourable to crystallization of reaction products, and therefore rock prisms should suffer less expansion. Experimental results do not bear this out.

Maximum rate and degree of expansion of concretes containing high-alkali cement and reactive dolomitic limestones occur under conditions of maximum moisture availability, and thus optimum for dissolution of sodium carbonate. In an early experiment (Swenson & Gillott 1960) it was found that concrete prisms which expanded excessively at 100 per cent R.H., did not expand at 50 per cent R.H. If, however, the latter were again placed in water or in 100 per cent R.H. conditions, expansion was resumed. Partial drying, as at 50 per cent R.H., should have favoured expansion by aiding crystallization of hydrates or complex salts.

A large number and variety of carbonate rocks investigated by this laboratory contained dolomite in the form of small crystals. If dedolomitization was directly responsible for the expansion of the rock, one would expect that the proportion of alkali-expansive rocks among the dolomite-containing limestones would be much greater than is the case. Indeed all dolomite rocks would then be capable of producing excessive expansion of concretes, which is fortunately contrary to fact.

If some dolomite crystals could expand excessively in alkali because of some instability or disorder in the lattice, one would again expect response from at least some of the many dolomite-containing carbonate rocks tested, even though they contain little or no clay. This did not occur. The dolomite in most expansive rocks has been found to be of the disordered type but this kind of disordered dolomite is also present in many non-alkali expansive rocks (Hadley 1961, p. 467; Gillot 1963, p. 764; Gillot 1964, pp. 123, 130).

If the Na<sup>+</sup> and OH<sup>-</sup> ions and water penetrate the dolomite crystal (Hansen 1967), they must do so through the surface of the crystal. The effects they produce must then increase as the crystal size decreases for a given quantity of dolomite. Results obtained in this laboratory on powdered carbonate rocks immersed in 2M NaOH solution show that the finer the particle size the smaller the expansion of the solids (Gillott 1964; Swenson & Gillott 1964). This is taken as strong evidence that dedolomitization, which was shown to have occurred in significant amounts in these experiments, does not produce measurable expansion of the dolomite crystals. Furthermore, results obtained in this laboratory failed to confirm the observation (Hadley 1961) of expansion when a single dolomite crystal is immersed in alkali.

The suggestion that a close framework of interconnected dolomite crystals may be sufficiently strong to resist the expansive forces of the alkali-carbonate rock reaction (Hadley 1961, 1964) is not borne out by observation. Interlocking can be found in expansive rocks (Pl. 2d) and there are many non-expansive rocks in which the dolomite rhombs are essentially independent of each other (Pl. 1f).

If it is assumed that the relative accommodation of the solid reaction products in the void system would account for most dolomitic limestones being non-alkali-expansive, the experimental evidence is not supportive. No relation has been found between porosity and expansivity (Swenson & Gillott 1967). In the presence of moisture the  $Na_2CO_3$  product of dedolomitization could readily migrate in solution to voids, thus relieving the system of any pressures due to over-all volume increase. Any initial pressure created just prior to dissolution would tend to increase solution pressure.

On imbibition of water by the clay minerals there would be no such ready migration, particularly in moderate-to-low porosity carbonate rocks, among which are found the deleteriously alkali-expansive ones. This explanation for the mechanism of expansion is thus compatible with the experimentally observed facts whereas the  $Na_2CO_3$  theory is not.

As explanations of alkali-carbonate rock reactivity based directly on dedolomitization are inadequate to account for the observed facts, one is forced to consider alternative indirect mechanisms. The extensive experimental studies of this laboratory, taken in conjunction with published studies of others, support the idea that the clay component in dolomitic limestones is responsible for alkali-expansivity. Without a known exception, in all the rocks studied, including well over 100 investigated by this laboratory, all alkali-expansive rocks contain significant amounts of clay or clay-like minerals. All rocks studied in this laboratory which had a zero or extremely small content of such clay minerals were non-alkali-expansive, despite the presence of some or all those characteristics which have been established to be associated with the phenomenon, including small dolomite rhombs in adequate amount, and distributed in a matrix of finely divided calcite.

Hadley's early proposal (Hadley 1964) of an osmotic mechanism involving the clay is not compatible with experimental facts. He suggested that "expansion of carbonate rocks might be largely attributable to osmotic forces centered at the reacting dolomite crystals

and operating through the interstitial clay-carbonate matrix". In this laboratory powder mixtures of the same composition as alkali-expansive rocks failed to register expansion in the powder cell even though significant dedolomitization had taken place (Gillott 1964). The clay was in a position to function as a semi-permeable membrane in this case. It is possible, however, that the original fabric of the rock is in some way vital to the mechanism.

It is to be noted in the scanning electron-micrograph in Pl. 2e that there seems to be a tendency for the clay minerals to be preferentially distributed in the vicinity of the dolomite crystals. This again suggests involvement of the clay. The open stacking of the clay minerals and their arrangement along grain boundaries appear incompatible, however, with the idea that they function as a semi-permeable membrane surrounding the dolomite crystals.

The mechanism advanced by this laboratory, first postulated by Gillott (1964) and supported by further studies (Swenson & Gillott 1967), has already been described. It is based on the direct role of the clay or clay-like constituents of the rock in producing expansion through moisture uptake. It requires that the alkali-expansive rocks be those in which the clay has remained unwetted until exposed to wetting by dedolomitization. This is a chemical reaction but it is the physical effect of providing access routes for water to the clay and other fine-grained minerals which is significant to the expansion mechanism. A physical process was demonstrated in this laboratory and reported in a previous paper (Swenson & Gillott 1967). It consisted of heating the reactive rock to 490°c for 3 hours and then cooling it. This temperature was selected because it was just low enough to avoid altering the composition of the rock but high enough to produce some microcracking due to thermal volume changes. These microcracks should, in this theory, provide access routes for moisture to the previously unwetted clay. This idea was apparently confirmed since, as predicted, the rock expanded when moisture alone was made available. As alkali was absent no dedolomitization could occur, so all direct mechanisms based on this reaction are excluded. Likewise the postulated osmotic mechanism could not operate. Conversely, once moisture had gained access to the clay the original alkali expansivity of the rock was eliminated. It has also beeen shown (Swenson & Gillott 1967) that relatively small amounts of illite, which is the major clay constituent occurring in expansive rocks, can produce sufficient expansion to account for the observed expansions of rocks. It is recognized, of course, that the comparatively large irreversible expansion of the rock resulting from the heating process described could have precipitated, or triggered, the very expansion that normally accompanied the alkali immersion. Non-alkali-expansive rocks exhibited irreversible expansions, in this heating and cooling treatment, of equal and even greater magnitudes than was the case for the alkali-expansive rocks, however.

Quantitative petrographic studies in this laboratory show a correlation between the specific surface of the dolomite constituent in argillaceous carbonate rocks and their expansive reaction in alkali (Swenson & Gillott 1967). Thus the initiation of the expansive reaction is controlled by the dedolomitization reaction.

## 7. Conclusions

The major findings from a review of previous studies and from the additional work described in this paper are as follows:

(1) Moisture uptake by previously unwetted clay minerals is responsible for the expansion in alkali of certain argillaceous dolomitic limestones.

(2) The wetting is made possible by the dedolomitization reaction which opens access routes for moisture.

(3) The dolomite crystals must be less than about 75  $\mu$  since dedolomitization, necessary to trigger expansion, becomes very slow when the crystals exceed this size.

(4) Observations on the scanning electron microscope suggest that much of the clay constituent is distributed close to the dolomite rhombs where dedolomitization is likely to open up channelways.

(5) Potentially expansive rocks cannot be identified with certainty by petrographic means if the analysis is restricted to light optical microscopy. This follows as the clay minerals may be at sites within the fabric which do not become exposed and accessible to moisture following dedolomitization. There appears to be no technique currently available to distinguish dry clay from clay that has been prewetted.

(6) Rate of expansion affects extent of distress in concrete. If expansion of the aggregate is sufficiently slow the concrete may not deteriorate presumably because of long time factors of creep and autogenous healing.

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#### plates 1-3

PLATE 1(a). Scanning electron micrograph of fine-grained limestone, Ontario, Canada. Sub-equant anhedral calcite crystals about  $2 \mu$  across with edge and tilted plate surfaces of mica-type minerals disposed in edge-to-edge and edge-to-face orientation along grain boundaries. Non-expansive in alkali.

PLATE 1(b). Scanning electron micrograph of fine-grained magnesian limestone, Germany. Sub-equant anhedral calcite crystals about  $2 \mu$  across. Mica-type minerals absent. Nonexpansive in alkali.

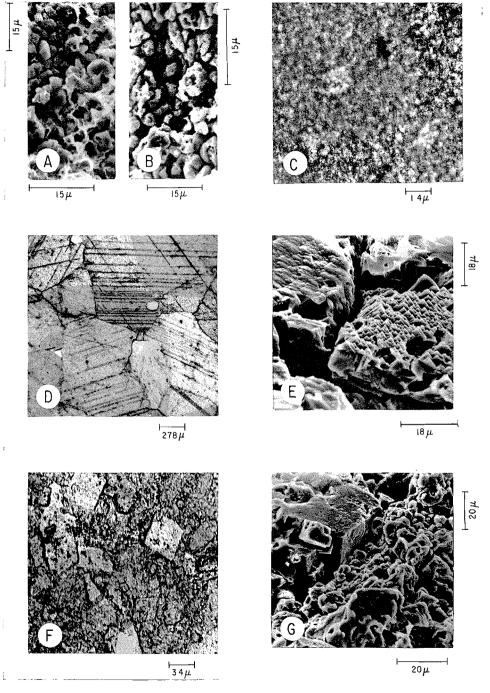
PLATE 1(c). Optical micrograph of magnesian limestone, Ontario, Canada (ordinary light). Fine calcite crystals ( $\sim 2 \mu$ ) with poorly defined rhombs of nascent dolomite. Non-expansive in alkali.

PLATE 1(d). Optical micrograph of recrystallized limestone (marble), Georgia, U.S.A. (ordinary light). Interlocking crystals of calcite showing cleavage with clear rounded quartz grains. Non-expansive in alkali.

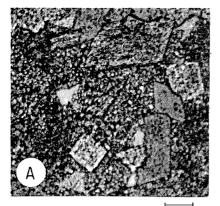
PLATE 1(e). Scanning electron micrograph of recrystallized limestone, Georgia, U.S.A. Grain boundaries between calcite crystals showing cleavage on etched fracture surface. Non-expansive in alkali.

PLATE 1(f). Optical micrograph of dolomitic limestone, Ohio, U.S.A. (ordinary light). Rhombic crystals of dolomite ( $\sim 20$  to 60  $\mu$ ) 'floating' in matrix of fine calcite. Non-expansive inalkali.

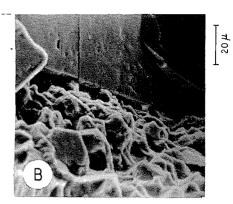
PLATE 1(g). Scanning electron micrograph of dolomitic limestone, Ohio, U.S.A. Contact relations between dolomite rhombs and matrix calcite crystals. Mica-type minerals absent. Non-expansive in alkali.



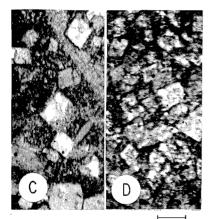
[Full explanation on p. 22]



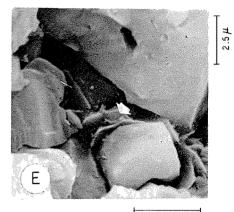
86.4 μ



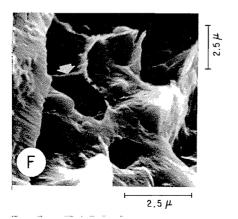
20 µ

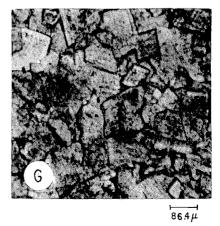


35.4 µ



2.5 JL





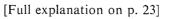
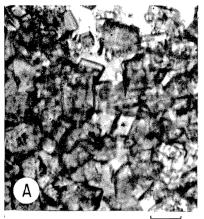
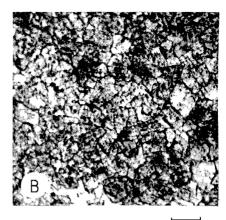


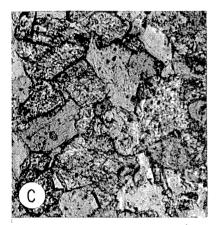
plate 2



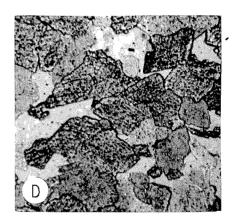
35.4 µ



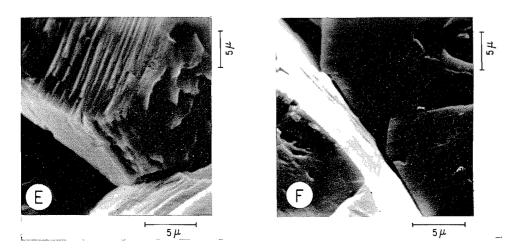
86.4 µ



35.4µ



86.4µ



[Full explanation on p. 23]

PLATE 2(a). Optical micrograph of dolomitic limestone, Alabama, U.S.A. (ordinary light). Rhombic crystals of dolomite (~50 to 300  $\mu$ ) in calcite matrix. (~10  $\mu$ ). Non-expansive in alkali.

PLATE 2(b). Scanning electron micrograph of dolomitic limestone, Alabama, U.S.A. Contacts between coarse dolomite crystals and fine calcite crystals of the matrix. Mica-type minerals absent. Non-expansive in alkali.

PLATE 2(c). Optical micrograph of dolomitic limestone, Georgia, U.S.A. (ordinary light) Rhombic crystals of dolomite (~10 to 100  $\mu$ ) in matrix of fine clacite and clay. Expansive in alkali.

PLATE 2(d). Optical micrograph of dolomitic limestone, Kingston, Ontario, Canada (ordinary light). Rhombic crystals of dolomite ( $\sim 15$  to 80  $\mu$ ) in matrix of fine calcite and clay. Expansive in alkali.

PLATE 2(e). Scanning electron micrograph of dolomitic limestone, Kingston, Ontario, Canada. Layer silicate minerals (arrows) at grain-boundaries of carbonate crystals. Expansive in alkali.

PLATE 2(f). Scanning electron micrograph of dolomitic limestone, Kingston, Ontario, Canada. Contact between dolomite rhomb (on left) and layer silicate minerals (arrows) and matrix. Expansive in alkali.

PLATE 2(g). Optical micrograph of calcite dolomite, Ohio, U.S.A. (Ordinary light) Interlocking dolomite rhombs ( $\sim 20$  to  $200 \mu$ ) with interstitial calcite. Non-expansive in alkali.

PLATE 3(a). Optical micrograph of calcite dolomite, Alabama, U.S.A. (ordinary light). Euhedral rhombs of dolomite ( $\sim 10$  to 70  $\mu$ ) in porous rock. Non-expansive in alkali.

PLATE 3(b). Optical micrograph of dolomite, Wales, United Kingdom (ordinary light). Interlocking crystals of dolomite (~20 to 100  $\mu$ ) in rock of low porosity. Non-expansive in alkali.

PLATE 3(c). Optical micrograph of Iowa, U.S.A. (ordinary light). Subhedral crystal of dolomite ( $\sim 15$  to 80  $\mu$ ) in moderately porous rock. Non-expansive in alkali.

PLATE 3(d). Optical micrograph of dolomite, Nottinghamshire, England (ordinary light). Subhedral and anhedral crystals of dolomite. (15 to 200  $\mu$ ) in porous rock. Non-expansive in alkali.

PLATE 3(e). Scanning electron micrograph of dolomite, Wales, United Kingdom. Contact between dolomite crystals showing cleavage on etched fracture surface. Non-expansive in alkali.

PLATE 3(f). Scanning electron micrograph of dolomite, Nottinghamshire, England. Contacts between subhedral dolomite crystals on etched fracture surface. Non-expansive in alkali.

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