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## FORMATION OF REPLACEMENT DOLOMITE IN THE LATEMAR CARBONATE BUILDUP, DOLOMITES, NORTHERN ITALY: PART 2. ORIGIN OF THE DOLOMITIZING FLUID AND THE AMOUNT AND DURATION OF FLUID FLOW

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**ABSTRACT.** Replacement dolomite in the Latemar carbonate buildup developed when limestone was infiltrated by reactive fluid. Minor-element, trace-element, and oxygen and carbon isotope compositions of dolomite and precursor limestone constrain the origin of the fluid and fundamental aspects of the flow. Inferred salinity (similar to seawater); temperature (45°–85°C);  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7076–0.7079); Ca/Mg (<1.4); and Fe, Mn, and Zn content of the dolomitizing fluid are consistent with a fluid similar to modern diffuse effluent. Modern diffuse effluent itself is approximately a mixture of seawater with up to ~25 percent high-temperature mid-ocean ridge hydrothermal vent fluid. Time-integrated fluid flux was in the range  $(2-4) \cdot 10^6$  mol fluid/cm<sup>2</sup> rock or  $(4-7) \cdot 10^7$  cm<sup>3</sup> fluid/cm<sup>2</sup> rock. Estimation of time-integrated flux leads to an internally consistent framework for the appropriate interpretation of the oxygen, strontium, and carbon isotope compositions of replacement dolomite. The oxygen and strontium isotope compositions reflect equilibration with dolomitizing fluid and provide a chemical fingerprint of the fluid. The carbon isotope composition of dolomite, however, was simply inherited directly from the precursor limestone in nearly all cases. A quantitative evaluation of the minor- and trace-element budget of dolomitization verifies that a fluid like modern diffuse effluent, but not unmodified seawater, could supply sufficient Fe, Mn, and Zn to enrich dolomite in these elements compared to limestone. If the flux of dolomitizing fluid was similar to that of modern diffuse effluent,  $\sim 0.02$  cm<sup>3</sup>/cm<sup>2</sup> · s, the duration of fluid flow and mineral-fluid reaction was short,  $\sim 100$  years. The total duration of dolomitization, however, could have been much longer if fluid flow was episodic, as in modern seafloor hydrothermal systems, depending on the time elapsed between episodes of flow. Conversion of limestone to dolomite likely occurred by a mechanism intermediate between the end-member cases of replacement at constant oxygen and carbon and replacement at constant volume.

### INTRODUCTION

The second in this two-part series examines the chemical and transport processes involved in the formation of replacement dolomite in the Triassic Latemar carbonate buildup. The study expands on the landmark investigation of Wilson and others (1990), both by consideration of a more extensive set of field measurements, minor- and trace-element data for carbonate minerals, and oxygen and carbon isotope compositions in both limestone and dolomite, and by interpreting the new data with simple analyses grounded in mass transport theory. Part 1 of the series (Carmichael and others, 2008) reviews the geologic setting of the Latemar carbonate buildup; describes the occurrence and geometry of replacement dolomite bodies; and presents

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modes, minor- and trace-element analyses, and oxygen and carbon isotope compositions of minerals in limestone and replacement dolomite. These data are used in Part 2 to address the following aspects of the formation of replacement dolomite: (1) the temperature of dolomitization, (2) the origin of the dolomitizing fluid, (3) the amount of fluid involved, as a time-integrated fluid flux, (4) the meaning of oxygen, carbon, and strontium isotope data for both replacement dolomite and limestone, (5) the duration of fluid-rock reaction during dolomitization, and (6) whether dolomite replaced calcite at constant carbon and oxygen, at constant volume, or something in between.

#### TEMPERATURE OF DOLOMITIZATION

##### *Oxygen Isotope Thermometry*

There is a general consensus that the fluid that drives the formation of replacement dolomite normally is either seawater or seawater-derived fluid (Land, 1985; Hardie, 1987; Budd, 1997). Based on the overlap in  $^{87}\text{Sr}/^{86}\text{Sr}$  between dolomite and Triassic seawater and on the seawater-like salinity of fluid inclusions in dolomite, Wilson and others (1990) concluded that heated seawater was the dolomitizing fluid specifically in the case of the Latemar carbonate buildup. Accordingly, the temperature of dolomitization can be estimated from measured  $\delta^{18}\text{O}$  of dolomite ( $\delta^{18}\text{O}_{\text{Dol}}$ ) using the temperature-dependence of the  $^{18}\text{O}$ - $^{16}\text{O}$  fractionation factor between dolomite and fluid ( $\alpha_{\text{Dol-fluid}}$ ), assuming  $\delta^{18}\text{O}$  of fluid ( $\delta^{18}\text{O}_{\text{fluid}}$ ) was 0 permil (VSMOW). Likewise, the temperature at which any limestone sample crystallized or recrystallized in the presence of seawater or seawater-derived fluid with  $\delta^{18}\text{O}_{\text{fluid}} = 0$  can be estimated from measured  $\delta^{18}\text{O}$  of calcite ( $\delta^{18}\text{O}_{\text{Cal}}$ ) and the temperature-dependence of  $\alpha_{\text{Cal-fluid}}$ . Although we demonstrate in the next section that the dolomitizing fluid was modified rather than pristine Triassic seawater, we will show that the assumption of  $\delta^{18}\text{O}_{\text{fluid}} = 0\text{‰}$  remains valid.

The calibration adopted for  $\alpha_{\text{Cal-fluid}}$  was  $1000\ln\alpha_{\text{Cal-H}_2\text{O}} = 2.78 \cdot 10^6/T^2(\text{K}) - 2.89$  (O'Neil and others, 1969, compiled in Friedman and O'Neil, 1977). The calibration adopted for  $\alpha_{\text{Dol-fluid}}$  was  $1000\ln\alpha_{\text{Dol-H}_2\text{O}} = 2.73 \cdot 10^6/T^2(\text{K}) + 0.26$  (Vasconcelos and others, 2005). The relationship between  $\delta^{18}\text{O}_{\text{Dol}}$  and  $\delta^{18}\text{O}_{\text{Cal}}$  and temperature can be illustrated on a single diagram if  $\delta^{18}\text{O}$  of either calcite or dolomite is adjusted for oxygen isotope fractionation between dolomite and calcite ( $\Delta^{18}\text{O}_{\text{Dol-Cal}}$ ). The choice is arbitrary, but analyses of calcite were adjusted because they are fewer in number. Values of  $\Delta^{18}\text{O}_{\text{Dol-Cal}}$  were computed from the expressions used for calibrations of  $\alpha_{\text{Dol-H}_2\text{O}}$  and  $\alpha_{\text{Cal-H}_2\text{O}}$ . Following correction of measured  $\delta^{18}\text{O}_{\text{Cal}}$  for dolomite-calcite oxygen isotope fractionation, analyses of calcite and dolomite fall into two almost separate groups (fig. 1). The range in temperature recorded by all analyzed dolomite is 45 to 85°C, and the range for all analyzed calcite in limestone is 27 to 54°C. The range of temperature recorded by replacement dolomite at individual outcrops is almost as large as that for all analyzed samples from the Latemar buildup (fig. 2). For example, 23 samples of dolomite from location 7 and 20 samples from location 8 record temperatures of 47 to 78°C and 47 to 75°C, respectively. The range of temperature recorded by 8 calcite samples in limestone from location 7 and by 12 calcite samples in limestone from location 8, 39 to 47°C and 29 to 44°C, respectively, also substantially overlap the range of temperature recorded by all analyzed calcite samples from the Latemar buildup.

Calculated values of temperature are not significantly different if other calibrations of  $\alpha_{\text{Cal-H}_2\text{O}}$  and  $\alpha_{\text{Dol-H}_2\text{O}}$  are considered. If the expression for  $\alpha_{\text{Cal-H}_2\text{O}}$  in Kim and O'Neil (1997) is used, the range of temperature recorded by all analyzed calcites is 25 to 52°C. If the calibrations of  $\alpha_{\text{Dol-H}_2\text{O}}$  by Northrup and Clayton (1966, compiled in Friedman and O'Neil, 1977) and Schmidt and others (2005) are used, the range in

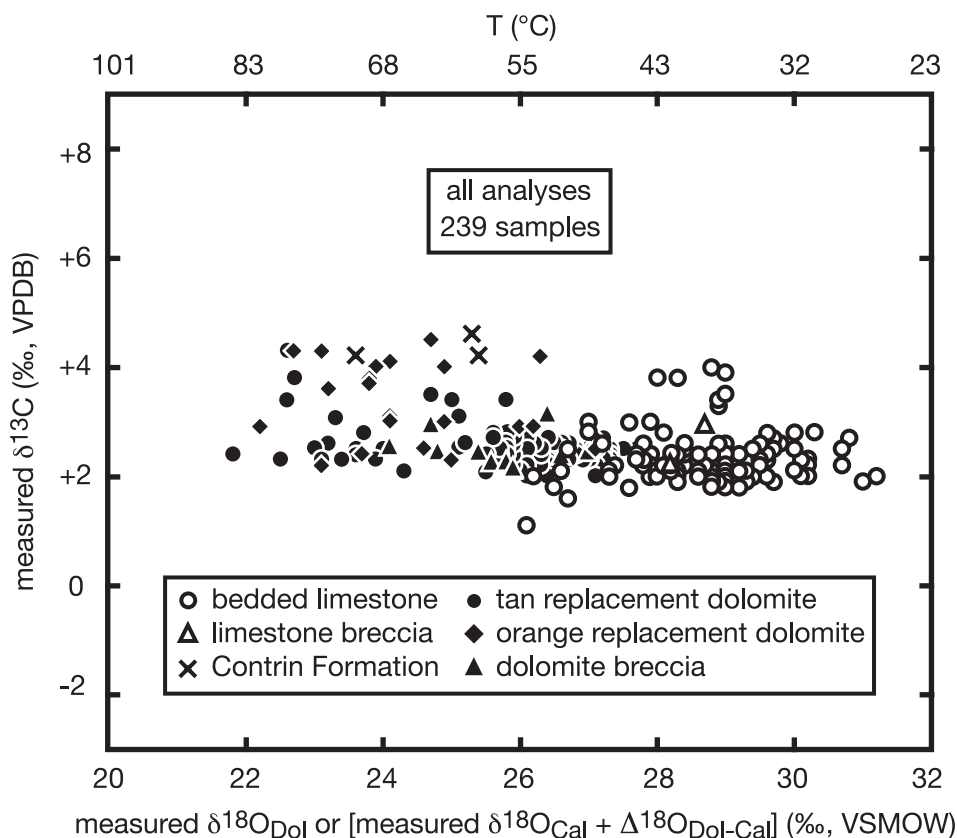


Fig. 1. Oxygen and carbon isotope compositions of all 239 analyzed samples of calcite and replacement dolomite from the Latemar buildup. Measured  $\delta^{18}\text{O}$  of calcite has been corrected for oxygen isotope fractionation between dolomite and calcite at the temperatures shown on the top horizontal axis, and is calculated assuming equilibrium between carbonate minerals and  $\text{H}_2\text{O}$  fluid with  $\delta^{18}\text{O} = 0$  ‰ VSMOW (see text). Data for dolomite and calcite fall into two almost separate groups with dolomite recording temperature in the range 45 to 85°C and with calcite recording temperature in the range 27 to 54°C. The data array indicates that  $\delta^{18}\text{O}$  of calcite and dolomite was set by equilibration with fluid at different temperatures while  $\delta^{13}\text{C}$  of dolomite in most cases was simply inherited from calcite in limestone precursor.

temperature recorded by all analyzed dolomites is 60 to 99°C and 57 to 105°C, respectively. The calibration of  $\alpha_{\text{Dol-H}_2\text{O}}$  by Northrup and Clayton (1966) in Friedman and O'Neil (1977), however, is probably less reliable because it represents the average of two consistently different expressions for different dolomites. The calibration by Schmidt and others (2005) is less appropriate than the others because it is based on experiments involving amorphous Ca-Mg carbonates.

The  $\delta^{18}\text{O}$  of seawater is not necessarily exactly 0; analyzed values can fall in the range -1 to +1 permil (Shanks and others, 1995). An uncertainty in  $\delta^{18}\text{O}_{\text{fluid}}$  of  $\pm 1$  permil translates into an uncertainty in temperature recorded by  $\delta^{18}\text{O}_{\text{Cal}}$  or  $\delta^{18}\text{O}_{\text{Dol}}$  of  $\pm 5$  to  $\pm 8^\circ\text{C}$ , depending on temperature.

The dolomitizing fluid was an aqueous salt solution rather than pure  $\text{H}_2\text{O}$ . The dependence of  $\alpha_{\text{Cal-H}_2\text{O}}$  on salinity, however, is not measurable in aqueous solutions with seawater-like salinity (Hu and Clayton, 2003). Values of  $\alpha_{\text{Dol-H}_2\text{O}}$  are probably independent of salinity as well.

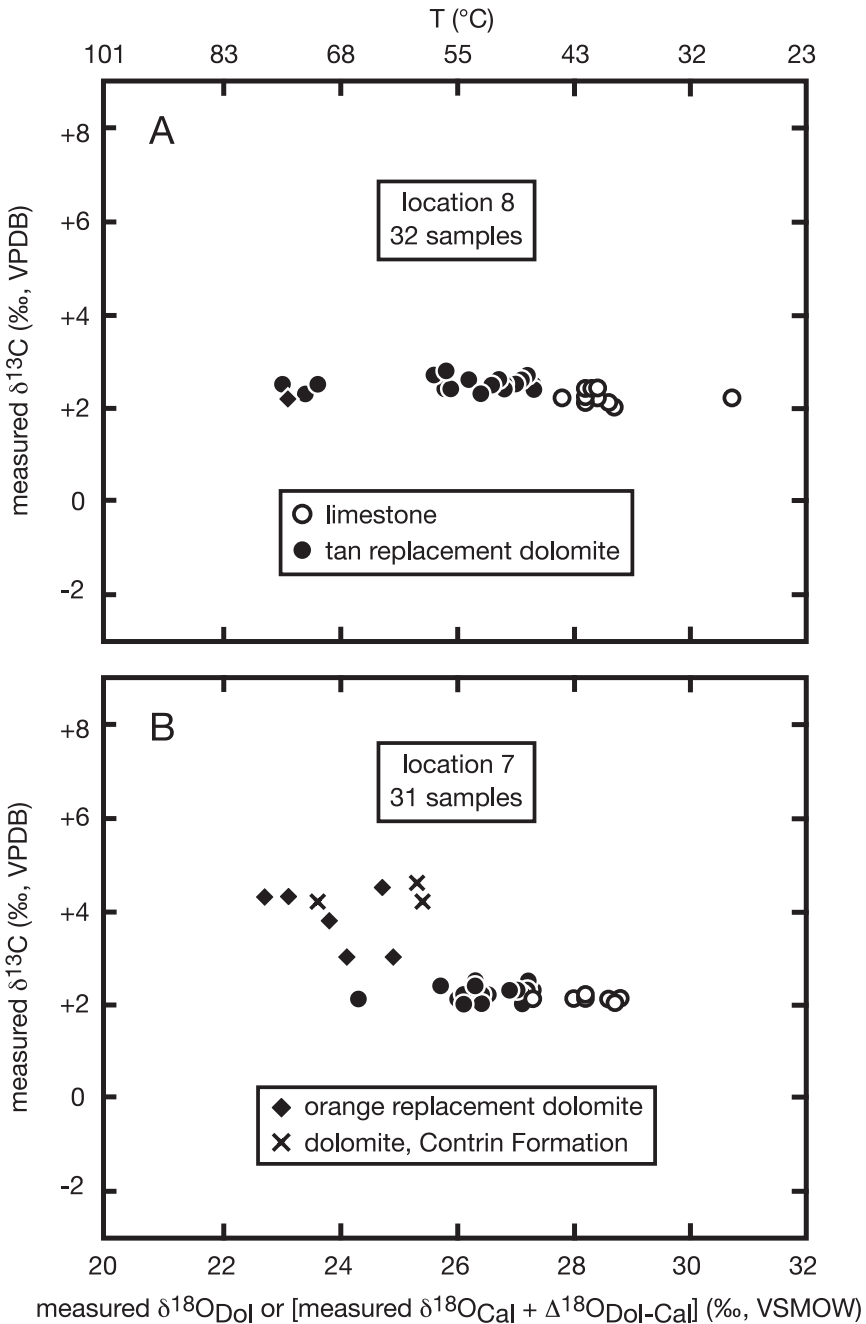


Fig. 2. Oxygen and carbon isotope compositions of all analyzed samples of calcite and replacement dolomite from locations 8 (A) and 7 (B). Measured  $\delta^{18}\text{O}$  of calcite has been corrected for oxygen isotope fractionation between dolomite and calcite as in figure 1. Data for dolomite and calcite fall into two separate groups with dolomite recording temperature in the range 47 to 75°C (location 8) and 47 to 78°C (location 7) and with calcite recording temperature in the range 29 to 44°C (location 8) and 39 to 47°C (location 7). The data array for all samples from location 8 and of limestone and tan replacement dolomite from location 7 confirms with greater precision than do data in figure 1 that the  $\delta^{18}\text{O}$  of calcite and dolomite were set by equilibration with fluid at different temperatures while  $\delta^{13}\text{C}$  of dolomite in most cases was simply inherited from calcite in limestone precursor. Orange replacement dolomite from location 7, however, is an example of the rare case of dolomite with  $\delta^{13}\text{C}$  significantly different from that of calcite in close proximity. The similarity in  $\delta^{13}\text{C}$  between orange dolomite and dolomite from the Contrin Formation suggests that carbon in orange dolomite could have been derived from the underlying Contrin Formation.

Use of expressions for  $\alpha_{\text{Cal-H}_2\text{O}}$  from Friedman and O'Neil (1977) and for  $\alpha_{\text{Dol-H}_2\text{O}}$  from Vasconcelos and others (2005) assumes  $^{18}\text{O}$ - $^{16}\text{O}$  exchange equilibrium was attained (or nearly so) between fluid with  $\delta^{18}\text{O} = 0$  and both dolomite and calcite. The assumption is justified by numerous oxygen isotope studies of coexisting carbonate minerals and natural fluids from both marine and terrestrial settings in the range of temperature inferred for dolomitization in the Latemar buildup (documented or reviewed by Hyeong and Capuano, 2001; Kelley and others, 2005; Vasconcelos and others, 2005). The assumption of  $^{18}\text{O}$ - $^{16}\text{O}$  exchange equilibrium between seawater and carbonate minerals has served as the foundation for paleothermometry of the oceans for >50 years (Emiliani and Edwards, 1953). The time ( $t$ ) needed for  $^{18}\text{O}$ - $^{18}\text{O}$  transport over a distance  $x = 1 \mu\text{m}$  by intracrystalline diffusion is  $x^2/D$ , where  $D$  is the diffusion coefficient. Using an estimated value of  $D$  for oxygen isotope diffusion in calcite at  $100^\circ\text{C}$  under "wet" conditions (Labotka and others, 2000),  $t = 7 \cdot 10^{14}$  y. Because this time is longer than the age of Earth, the mechanism by which mineral-fluid isotope exchange equilibrium was attained must have been solution-reprecipitation.

Temperatures in the range  $\sim 50$  to  $90^\circ\text{C}$  recorded by  $\delta^{18}\text{O}_{\text{Dol}}$  are interpreted as the temperature of dolomitization in the Latemar buildup. Formation of replacement dolomite at a similarly low temperature  $\sim 50$  to  $75^\circ\text{C}$  has been recently reported by Erel and others (2006). The low end of the range of temperature recorded by  $\delta^{18}\text{O}_{\text{Cal}}$ ,  $\sim 25^\circ\text{C}$ , is interpreted as the temperature at which primary carbonate precipitated from Triassic seawater. The upper end of the range of temperature recorded by  $\delta^{18}\text{O}_{\text{Cal}}$ ,  $\sim 50^\circ\text{C}$ , is above the limit that higher organisms can tolerate (Brock, 1985; Rothschild and Mancinelli, 2001), and is believed to represent recrystallization of calcite in the presence of heated fluids associated with dolomitization.

The vertical distributions of  $\delta^{18}\text{O}_{\text{Dol}}$  and  $\delta^{18}\text{O}_{\text{Cal}}$  and of the temperatures recorded by dolomite and calcite in the Latemar carbonate buildup are illustrated in figure 3A. Temperatures recorded by dolomite are scattered, but taken together over the 600 m of the Lower Edifice and Latemar Limestone sampled for this study, they suggest a geothermal gradient in the range 0 to  $100^\circ\text{C}/\text{km}$ .

#### *Fluid Inclusion Thermometry*

Wilson (ms, 1989) and Wilson and others (1990) proposed a higher temperature of dolomitization,  $\sim 70^\circ$  to  $220^\circ\text{C}$ , based on homogenization temperatures of two-phase liquid + vapor fluid inclusions in seven samples of replacement dolomite. The range in homogenization temperature for every sample for which >5 measurements were made, however, is large ( $\sim 100^\circ\text{C}$  or more) and likely indicates that many or all fluid inclusions have stretched and/or leaked (Prezbindowski and Larese, 1987). If the fluid inclusions leaked the liquid phase, their density would decrease, and they would record erroneously high entrapment temperature. For this reason, oxygen isotope thermometry is believed to provide a more accurate estimate of the temperature of dolomitization than do fluid inclusion homogenization temperatures. The densest, and hence likely least disturbed, fluid inclusions measured by Wilson (ms, 1989) and Wilson and others (1990) have homogenization temperatures  $\sim 70$  to  $90^\circ\text{C}$ , within the range of temperature recorded by oxygen isotope thermometry of dolomite.

#### ORIGIN OF THE DOLOMITIZING FLUID

##### *Chemical Constraints on the Dolomitizing Fluid*

*Salinity.*—Freezing temperatures of fluid inclusions in replacement dolomite (Wilson, ms, 1989; Wilson and others, 1990) correspond to salinities of 3.5 to 5.0 weight percent NaCl equivalent (seawater is 3.5 wt % NaCl equivalent). Measurements of freezing temperature should not be significantly affected by stretching or leakage of

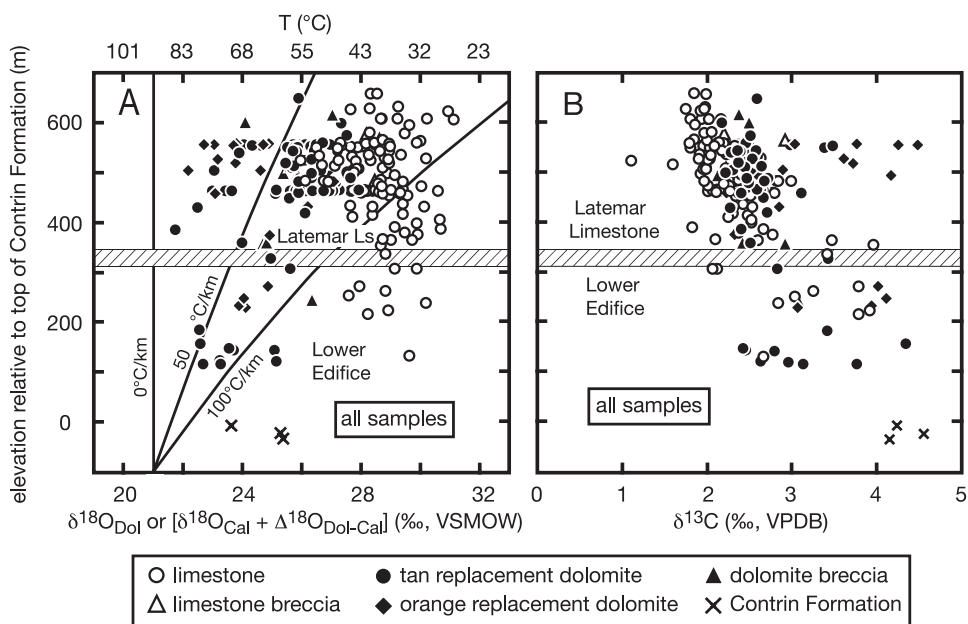


Fig. 3. Oxygen (A) and carbon (B) isotope compositions of all analyzed samples of calcite and replacement dolomite plotted against elevation above the stratigraphic contact between the Lower Edifice and the Contrin Formation (see fig. 12 and text in Carmichael and others, 2008). Measured  $\delta^{18}\text{O}$  of calcite has been corrected for oxygen isotope fractionation between dolomite and calcite as in figures 1 and 2. Fractionation-corrected values of  $\delta^{18}\text{O}$  of calcite are independent of elevation while  $\delta^{18}\text{O}$  of dolomite displays a weak positive trend consistent with a geothermal gradient during dolomitization in the range 0 to 100°C/km. Values of  $\delta^{13}\text{C}$  display a weak negative trend that could be explained by the kind of secular change in  $\delta^{13}\text{C}$  at the time of carbonate deposition in the Latemar buildup that was common during the Triassic (Korte and others, 2005). Unusually high values of  $\delta^{13}\text{C}$  in orange replacement dolomite at elevations of 500 to 600 m are like those illustrated in figure 2B.

the fluid inclusion following formation. The dolomitizing fluid therefore is expected to have had salinity like seawater or be slightly more saline.

*Sr isotope composition.*—Wilson (ms, 1989) and Wilson and others (1990) report measurements of  $^{87}\text{Sr}/^{86}\text{Sr}$  of four samples of replacement dolomite from the Latemar buildup in the range 0.7076 to 0.7079 and of one sample of limestone with 0.7076. These values are within the range of Triassic seawater, 0.7074 to 0.7079 (Burke and others, 1982), and  $^{87}\text{Sr}/^{86}\text{Sr}$  of the dolomitizing fluid is expected to have been similar.

*Ca/Mg.*—The Ca/Mg of dolomitizing fluid must be less than that of fluid coexisting with calcite and dolomite (Wilson and others, 1990). The Ca/Mg of aqueous fluid coexisting with calcite and dolomite at 50 to 90°C can be estimated from results of direct experiment (Rosenberg and Holland, 1964; Rosenberg and others, 1967), from calculations of mineral-fluid equilibrium using SUPCRT (Johnson and others, 1992), and from direct measurements of Ca/Mg in fluids coexisting with calcite and dolomite at depth in Texas Gulf Coast wells (Hyeong and Capuano, 2001). Application of the experimental data, however, involves relatively large extrapolations in temperature from 275°C (Rosenberg and Holland, 1964) or 295°C (Rosenberg and others, 1967) to the temperature of dolomitization in the Latemar buildup. In addition, calculation of Ca/Mg of fluid coexisting with calcite and dolomite using either the experimental data or the thermodynamic calculations is valid only to the extent that mineral-fluid equilibrium was attained or closely approached during dolomitization. The equation empirically relating Ca/Mg of fluid to temperature in

TABLE 1  
Comparison of the chemistry of the dolomitizing fluid in the Latemar buildup with that of possible analogs

	Target fluid	Triassic seawater*	Red Sea brine <sup>†</sup>	Salton Sea fluid <sup>§</sup>	Sea Oil field brine <sup>§</sup>	Creede ore fluid <sup>§</sup>	EPR vent fluid <sup>‡</sup>	Diffuse effluent**
Cl (mM)	≈546	546	4410	4260	4460	1312	490	570
Ca/Mg	<1.4	0.29	3.8	489	13	8	∞	0.33
<sup>87</sup> Sr/ <sup>86</sup> Sr	0.7076-0.7079	0.7074-0.7079	0.7070-0.7078	n.i. <sup>††</sup>	n.i. <sup>††</sup>	n.i. <sup>††</sup>	0.7074-0.7075	0.7076-0.7079
Fe (μM)	significant	1·10 <sup>-3</sup>	1500	27,900	5340	n.i. <sup>††</sup>	1660	710
Mn (μM)	significant	5·10 <sup>-4</sup>	1500	26,400	n.i. <sup>††</sup>	12,600	960	170
Zn (μM)	significant	6·10 <sup>-3</sup>	46	7920	4590	19,900	106	10

\*Hardie (1996), Stanley and Hardie (1998), Burke and others (1982), Millero and Sohn (1992).

<sup>†</sup>Zierenberg (1990), Pierret and others (2001).

<sup>§</sup>Skinner (1997).

<sup>‡</sup>Sample OBS, 21N East Pacific Rise (Von Damm, 1990).

\*\*Sample HT20, site 2896-2, TAG 1995 site, Mid-Atlantic Ridge (James and Elderfield, 1996); Kelley and others (2005).

<sup>††</sup>no information.

Hyeong and Capuano (2001) has neither shortcoming. It is calibrated for the temperature range 40 to 150°C and is based on direct analyses of natural fluids coexisting with calcite and dolomite that were probably, but not necessarily, in equilibrium with the minerals. Additionally, the expression is appropriate for partially disordered dolomite like that in the Latemar buildup (Schubel, ms, 1997). The equation in Hyeong and Capuano (2001) gives molar Ca/Mg = 1.4 and 2.7 at 50 and 90°C, respectively, for fluid coexisting with calcite and dolomite. A value of Ca/Mg = 1.4 is greater than the minimum Ca/Mg estimated for 50 to 90°C from the experimental data of Rosenberg and Holland (1964) and Rosenberg and others (1967) (Ca/Mg = 0.8 and 0.4, respectively) and from thermodynamic calculations using SUPCRT (Ca/Mg = 0.8). The upper limit of Ca/Mg of the dolomitizing fluid therefore is considered to have been 1.4.

*Trace element composition.*—Replacement dolomite from the Latemar buildup is enriched in Fe, Mn, and Zn, as much as in Mg, with respect to precursor calcite but not in Cu, Ni, Co, Cr, Ba, or Pb (fig. 16 and table 3 of Carmichael and others, 2008). Formation of replacement dolomite must have involved transport of Fe, Mn, and Zn, as well as Mg, to the site of dolomitization but not transport of Cu, Ni, Co, Cr, Ba, or Pb. In addition, the Fe, Mn, and Zn contents of replacement dolomite vary in both space and time (the latter indicated by oscillatory growth zoning in dolomite illustrated in fig. 14 of Carmichael and others, 2008) with positive correlations in concentration. The dolomitizing fluid therefore must have had elevated concentrations of Fe, Mn, and Zn, as well as Mg, but not of Cu, Ni, Co, Cr, Ba, or Pb, and have displayed the analogous positive correlations among the concentrations of Fe, Mn, and Zn.

#### *Origin of the Dolomitizing Fluid*

Table 1 lists the required salinity, Ca/Mg, <sup>87</sup>Sr/<sup>86</sup>Sr, and Fe, Mn, and Zn contents of the dolomitizing fluid and the corresponding values for seven candidate fluids. Triassic seawater has appropriate salinity, Ca/Mg, and <sup>87</sup>Sr/<sup>86</sup>Sr, as recognized by Wilson and others (1990), but vanishingly small concentrations of Fe, Mn, and Zn. Red Sea and oil field brines, geothermal fluid from the Salton Sea, and Creede hydrothermal ore fluid all have suitably elevated concentrations of Fe, Mn, and Zn but are too saline and have too high Ca/Mg. Mid-ocean ridge hydrothermal vent fluid has

appropriate salinity and elevated concentrations of Fe, Mn, and Zn but is an impossible dolomitizing fluid because it contains no Mg. Modern diffuse effluent, on the other hand, matches the expected salinity; Ca/Mg;  $^{87}\text{Sr}/^{86}\text{Sr}$ ; and elevated Fe, Mn, and Zn contents of the target dolomitizing fluid.

Diffuse effluent is hydrothermal fluid that is emitted diffusively, rather than as focused flow at vents, within  $\sim 100$  km from mid-ocean ridges (James and Elderfield, 1996; Elderfield and others, 1999; Von Damm and Lilley, 2004; Kelley and others, 2005). Based on its Mg content, diffuse effluent can be considered approximately a mixture of seawater and up to  $\sim 25$  percent mid-ocean hydrothermal vent fluid (Von Damm and Lilley, 2004). In detail, however, diffuse effluent may deviate from this simple mixture to the extent that it is subsequently modified by mineral precipitation or dissolution, by subsurface biological activity, and by phase separation or “boiling” (common at the physical conditions of mid-ocean ridge hydrothermal systems, Von Damm and Lilley, 2004). Manganese is the element considered most likely conserved during mixing of seawater with hydrothermal vent fluid to form diffuse effluent (Von Damm and Lilley, 2004). Phase separation, either before or after mixing, can explain salinities of diffuse effluent that are somewhat greater than that of seawater, like those measured in fluid inclusions in replacement dolomite from the Latemar buildup (Wilson and others, 1990).

The properties of diffuse effluent additionally conform to other inferred characteristics of dolomitizing fluid. Direct measurements of diffuse effluent temperature range from 23 to 110°C (James and Elderfield, 1996; Von Damm and Lilley, 2004; Kelley and other, 2005), which overlaps the  $\sim 50$  to 90°C range inferred for dolomitization in the Latemar buildup. Measured concentrations of Fe, Mn, and Zn in diffuse effluent show positive correlations (fig. 4). The concentration of Cu, on the other hand, is negligible in comparison and exhibits no significant correlation with Mn (and hence with neither Fe nor Zn). As in analyzed dolomites from the Latemar buildup, the correlation between Fe and Mn concentrations in diffuse effluent is much better defined than the correlation between Zn and Mn concentrations. Concentrations of Fe and Mn in diffuse effluent from the Mid-Atlantic Ridge and from the East Pacific Rise are superimposed in figure 4A. The data in figure 4 from James and Elderfield (1996) refer to compositions of diffuse effluent sampled at different locations along the Mid-Atlantic Ridge collected over the relatively short time interval of 7 months. In contrast, the data in figure 4A from Von Damm and Lilley (2004) refer to compositions of diffuse effluent sampled at the same locations along the East Pacific Rise over a period of 10 years. Taken together, the two data sets demonstrate that, while Fe/Mn stays approximately the same, the concentrations of Fe and Mn in diffuse effluent vary in both time and space, as is inferred for the dolomitizing fluid in the Latemar buildup. The chemical variations in space and time are explained by spatial and temporal variations in the proportions of seawater and hydrothermal vent fluid that mix during formation of diffuse effluent.

Diffuse effluent further satisfies the requirement for a dolomitizing fluid that has sufficiently low S content that Fe is available for incorporation in dolomite rather than precipitated as iron sulfide. For example, a representative analysis of diffuse effluent reported by James and Elderfield (1996) contains  $3.26 \pm 0.12$  mM Fe and  $<0.04$  mM S as  $\text{H}_2\text{S}$ .

Hydrothermal vent fluid forms at mid-ocean ridges as seawater reacts with hot igneous rocks (review by German and Von Damm, 2004). Although the Latemar buildup developed in a marine basin, there was no mid-ocean ridge nearby during the Middle Triassic. There was, however, extension, strike-slip faulting, and related igneous activity of the Predazzo igneous complex that produced monzonite, granite, and a variety of mafic alkalic dikes at the time of dolomitization. Hydrothermal fluid, similar



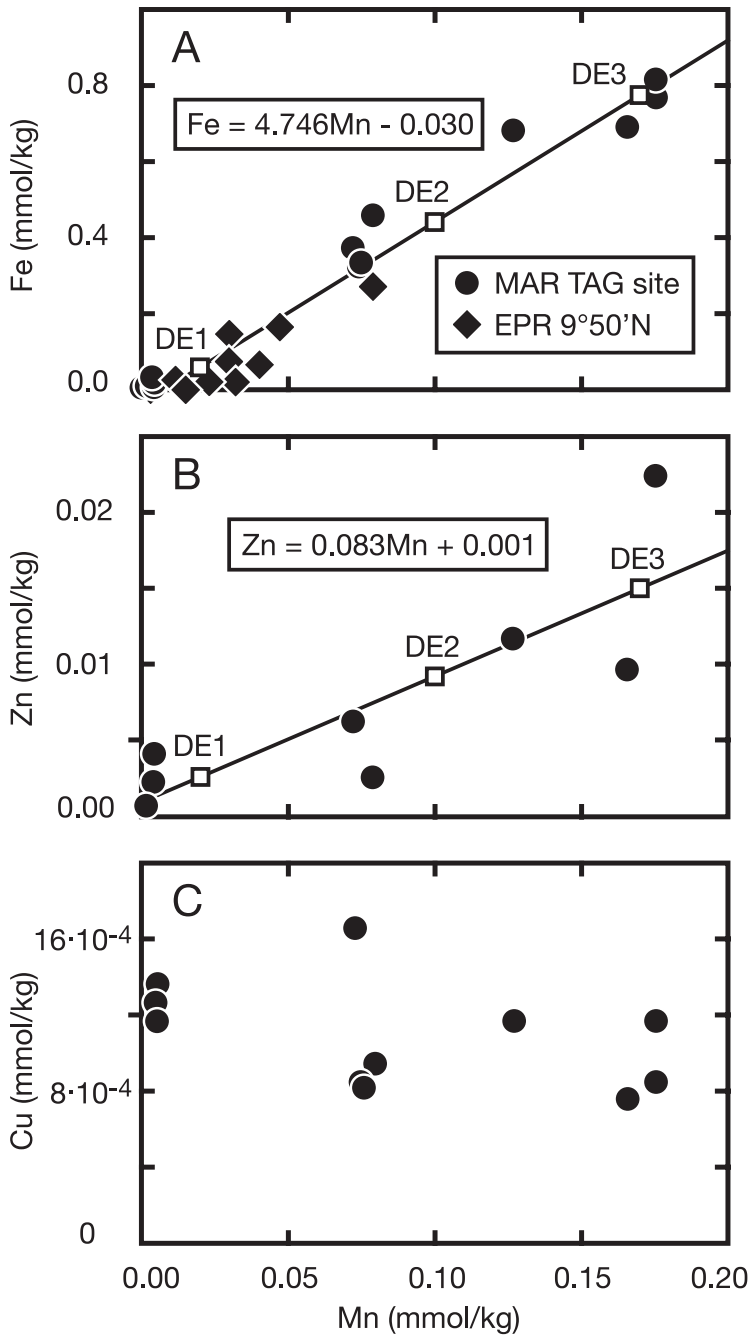


Fig. 4. Measured molalities of Fe (A), Zn (B), and Cu (C) as a function of the molality of Mn in modern diffuse effluent. Data from the TAG site, 26°N Mid-Atlantic Ridge (James and Elderfield, 1996) were collected at different locations at nearly the same time (August 1994 during the BRAVEX/94 cruise and March 1995 during cruise 132-02). Data from the 9°50'N site, East Pacific Rise (Von Damm and Lilley, 2004) were collected at the same locations over a 10 year period. Together, the data indicate variability in the composition of diffuse effluent in both space and time. Manganese molality was chosen as the abscissa because it is the element most likely conserved during mixing of seawater with mid-ocean ridge hydrothermal vent fluid to form diffuse effluent (Von Damm and Lilley, 2004). Lines and equations are linear fits to the data. Model compositions DE1-DE3 are used in calculations of the time-integrated flux of dolomitizing fluid and in the evaluation of the minor- and trace-element budget of dolomitization.

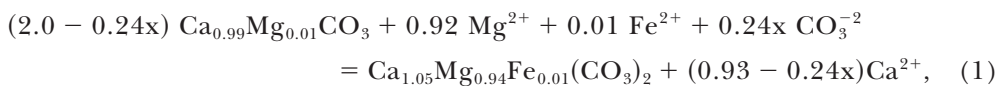
to vent fluid at mid-ocean ridges, likely formed as seawater reacted with hot igneous rocks of the Predazzo complex both adjacent to and beneath the Latemar buildup. A fluid like modern diffuse effluent could have formed by the mixing of this hydrothermal fluid with seawater in proportions that varied in space and time.

Mid-ocean ridge hydrothermal vent fluid normally has  $\delta^{18}\text{O} \sim 1$  permil greater than ambient seawater (Shanks and others, 1995). Because diffuse effluent usually is  $\sim 25$  percent or less hydrothermal vent fluid, the assumption of  $\delta^{18}\text{O}_{\text{fluid}} 0 \pm 1$  permil appears justified in calculations of the temperature of dolomitization from oxygen isotope thermometry.

#### AMOUNT OF DOLOMITIZING FLUID AS A TIME-INTEGRATED FLUX

##### Theory

Using representative measured compositions of tan replacement dolomite and of calcite from unreacted limestone and molar volumes of  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaMg}(\text{CO}_3)_2$ , and  $\text{CaFe}(\text{CO}_3)_2$  from Holland and Powell (1998), the reaction by which dolomite replaced calcite in the Latemar buildup is:



where  $x = 0$  corresponds to replacement at constant oxygen and carbon,  $x = 1$  to replacement at constant volume, and  $0 < x < 1$  to replacement at conditions in-between. Reaction (1) and other infiltration-driven reactions occur either when fluid flows along a gradient in pressure and/or temperature or when rocks are infiltrated by fluid that they are out of equilibrium with. The first, so-called gradient flow mechanism (Ferry and Gerdes, 1998), typically produces a substantial spatial interval along the flow path over which reactants and products coexist, separating a region in which the reaction has gone to completion upstream from a region in which the reaction has not occurred at all downstream. The second, so-called disequilibrium flow mechanism (Ferry and Gerdes, 1998), produces a reaction front along the flow path that is a sharp interface between completely reacted rock upstream and unreacted rock downstream. Individual sharp contacts between unreacted limestone and replacement dolomite in the Latemar buildup (fig. 6 of Carmichael and others, 2008) may be either reaction fronts or reaction sides (Yardley and Lloyd, 1995). It is unlikely that all contacts are reaction sides, and their sharpness points to a reaction (1) driven by the disequilibrium rather than by the gradient flow mechanism.

For reaction (1) driven by the disequilibrium flow mechanism, the relation between the amount of flow as a molar time-integrated flux of dolomitizing fluid ( $q_m$ ) and the distance ( $z$ ) along the flow path over which the reaction has occurred is:

$$q_m = -0.92\xi_{\text{max}} \int_0^{z_{\text{rf}}} [\text{X}_{\text{Mg}}^{\text{rf}}(z) - \text{X}_{\text{Mg}}^{\text{i}}]^{-1} dz, \quad (2)$$

where  $\xi_{\text{max}}$  is the progress of reaction (1) when it goes to completion and  $\text{X}_{\text{Mg}}$  is the mole fraction of Mg in fluid at the inlet to the flow system (superscript “i”) and at the reaction front (superscript “rf”), and  $z_{\text{rf}}$  is the distance between the inlet and the reaction front along the flow path. Equation (2) is derived following Ferry (1991) and simplified by recognizing that  $\text{X}_{\text{Mg}} \ll 0.92$ , the stoichiometric coefficient of  $\text{Mg}^{2+}$  in reaction (1).

##### Estimation of Time-integrated Fluid Flux

Equation (2) was applied after measuring or estimating values of  $\xi_{\text{max}}$ ,  $z_{\text{rf}}$ ,  $\text{X}_{\text{Mg}}^{\text{i}}$ , and  $\text{X}_{\text{Mg}}^{\text{rf}}(z)$ . For calcite limestone with 3 percent porosity converted to dolomite by

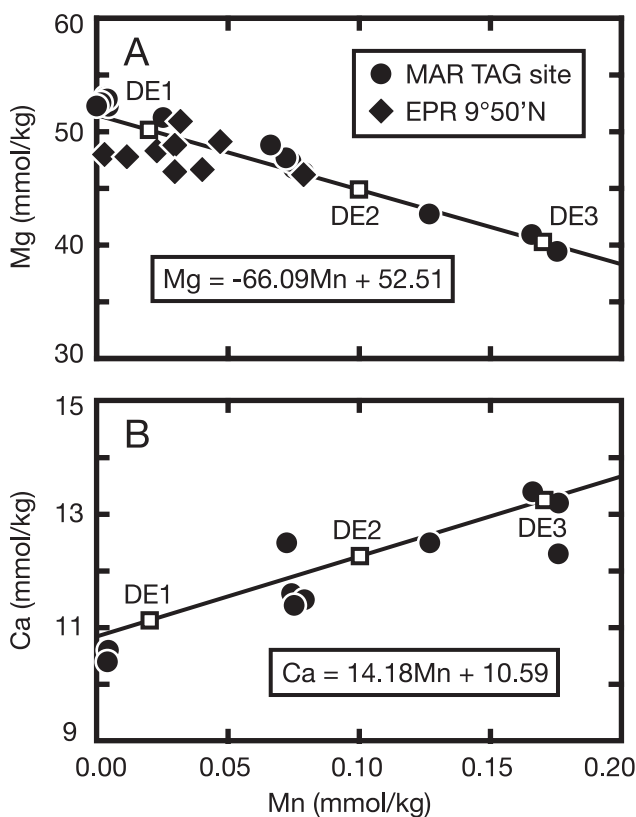


Fig. 5. Measured molalities of Mg (A) and Ca (B) as a function of the molality of Mn in modern diffuse effluent. Format and features are identical to those in figure 4.

reaction (1) at constant oxygen and carbon ( $x = 0$ ),  $\xi_{\max} = 0.0132 \text{ mol/cm}^3$ ; for replacement of the same limestone at constant volume ( $x = 1$ ),  $\xi_{\max} = 0.0150 \text{ mol/cm}^3$ . Replacement dolomite is exposed over 700 m in elevation in the Latemar buildup. The value of  $z_{\text{rf}}$  therefore is  $>0.7 \text{ km}$  but, given the size of the buildup, probably  $<2 \text{ km}$ . The value of  $X_{\text{Mg}}^{\text{rf}}$  was evaluated assuming the input dolomitizing fluid was the same chemically as modern diffuse effluent. Because the composition of diffuse effluent is variable, three estimates of input fluid composition were considered (DE1-DE3, figs. 4 and 5) based on Mn contents of 0.0205, 0.103, and 0.185 mM. Concentrations of Mg, Ca, Fe, and Zn were then computed from their measured correlations with the concentration of Mn (regression lines in figs. 4 and 5); results are listed in table 2. The value of  $X_{\text{Mg}}^{\text{rf}}(z)$  was computed assuming that Ca/Mg of fluid at the reaction front was defined by coexisting calcite and dolomite as specified by the expression in Hyeong and Capuano (2001). Starting with the input fluid, concentrations of Ca and Mg in the fluid were adjusted, subject to the constraints of the stoichiometry of reaction (1), to attain the Ca/Mg of fluid coexisting with calcite and dolomite. Calculations considered both the simplified case of dolomitization at constant T, in which case  $X_{\text{Mg}}^{\text{rf}}(z)$  was constant, and the more realistic case of dolomitization along a geothermal gradient, in which case  $X_{\text{Mg}}^{\text{rf}}(z)$  varied along the flow path. In the latter case, geothermal gradients in the range 0 to  $100^\circ\text{C}/\text{km}$  were considered (fig. 3), and equation (2) was solved numerically.

TABLE 2  
*Compositions of model diffuse effluent used to estimate the time-integrated flux of dolomitizing fluid and to evaluate the trace element budget of dolomitization\**

	DE1	DE2	DE3
Mg	$5.15 \cdot 10^{-5}$	$4.61 \cdot 10^{-5}$	$4.07 \cdot 10^{-5}$
Ca	$1.12 \cdot 10^{-5}$	$1.23 \cdot 10^{-5}$	$1.35 \cdot 10^{-5}$
Fe	$6.62 \cdot 10^{-8}$	$4.56 \cdot 10^{-7}$	$8.46 \cdot 10^{-7}$
Mn	$2.05 \cdot 10^{-8}$	$1.03 \cdot 10^{-7}$	$1.85 \cdot 10^{-7}$
Zn	$2.63 \cdot 10^{-9}$	$9.43 \cdot 10^{-9}$	$1.62 \cdot 10^{-8}$

\*Values (in mol/cm<sup>3</sup>) computed from specified Mn contents and equations in figures 1 and 2.

Results for a “baseline” calculation of  $q_m$  were obtained taking input parameters at their likeliest values. If limestone is replaced by dolomite at constant oxygen and carbon, porosity should be produced. Most replacement dolomite in the Latemar buildup indeed has greater porosity than the precursor limestone (table 1 of Carmichael and others, 2008). Dolomitization at constant oxygen and carbon therefore appears to be a better approximation than constant volume replacement (that is,  $\xi_{\max} = 0.0132$  mol/cm<sup>3</sup>). The input fluid was chosen as the intermediate composition of diffuse effluent, DE2 (table 2, figs. 4 and 5). The preferred choice for the distance of dolomitization along the flow path,  $z_{rf}$  is 1 km (inferred from Carmichael and others, 2008). An intermediate temperature gradient of  $-50^\circ\text{C}/\text{km}$  along the flow path was adopted (fig. 3). For  $z_{rf} = 1$  km and a temperature of  $50^\circ\text{C}$  at the reaction front (close to the lowest value computed from  $\delta^{18}\text{O}_{\text{Dol}}$ ), temperature at the inlet to the flow system was  $100^\circ\text{C}$ . Accordingly, calculated  $q_m = 2.5 \cdot 10^6$  mol fluid/cm<sup>2</sup> rock. The equivalent volumetric time-integrated flux  $q_v = 4.5 \cdot 10^7$  cm<sup>3</sup> fluid/cm<sup>2</sup> rock.

Table 3 summarizes the sensitivity of the preferred “baseline” value of  $q_m$  to plausible variations in the values of the input variables. If  $z_{rf}$  were 0.7 or 2, rather than 1 km,  $q_m$  would be 36 percent less or 76 percent greater, respectively. If compositions DE1 or DE3, rather than DE2 were taken as the input dolomitizing fluid,  $q_m$  would be 12 percent less or 20 percent greater, respectively. If temperature at the inlet of the flow system were 150 rather than  $100^\circ\text{C}$ ,  $q_m$  would be 24 percent less. If temperature along the flow path were a constant 50, 70, or  $90^\circ\text{C}$ ,  $q_m$  would be 24 percent greater, 4 percent greater, or 12 percent less, respectively. If dolomite replaced limestone at constant volume rather than constant oxygen and carbon, values of  $q_m$  increase by a factor of  $(0.0150/0.0132) = 1.14$ . For a broad range of values of input variables, the estimated time-integrated flux of dolomitizing fluid lies in the narrow range of  $(2-4) \cdot 10^6$  mol/cm<sup>2</sup> or  $q_v = (4-7) \cdot 10^7$  cm<sup>3</sup>/cm<sup>2</sup>.

Estimated values of the volumetric time-integrated fluid flux of dolomitization are fully consistent with a volumetric whole-system fluid-rock ratio  $\sim 500$  estimated by Wilson and others (1990) for their preferred model of dolomitization driven by seawater convection. Time-integrated fluid flux is related to a whole-system fluid-rock ratio as the product of the fluid-rock ratio and the distance of fluid-rock reaction along the flow path (Ferry, 1991). Taking the distance of fluid-rock reaction to be  $\sim 1$  km ( $10^5$  cm), the product of distance and fluid-rock ratio is  $5 \cdot 10^7$  cm =  $5 \cdot 10^7$  cm<sup>3</sup>/cm<sup>2</sup>, in the middle of the range of values computed from equation (2). Although Wilson and others (1990) did not explicitly consider time-integrated fluid fluxes, their work anticipated the enormous values inferred in this study.

TABLE 3  
*Evaluation of the dependence of time-integrated fluid flux on the value of selected input variables*

	$q_m$ (mol/cm <sup>2</sup> )
Baseline calculation in text	$2.5 \cdot 10^6$
$\Delta z = 0.7$ km*	$1.6 \cdot 10^6$
$\Delta z = 2.0$ km*	$4.4 \cdot 10^6$
$T(0) = 150^\circ\text{C}^\dagger$	$1.9 \cdot 10^6$
DE1 <sup>§</sup>	$2.2 \cdot 10^6$
DE3 <sup>§</sup>	$3.0 \cdot 10^6$
$(\partial T/\partial z) = 0$ , $T = 90^\circ\text{C}^\ddagger$	$2.2 \cdot 10^6$
$(\partial T/\partial z) = 0$ , $T = 70^\circ\text{C}^\ddagger$	$2.6 \cdot 10^6$
$(\partial T/\partial z) = 0$ , $T = 50^\circ\text{C}^\ddagger$	$3.1 \cdot 10^6$
Constant volume replacement <sup>#</sup>	$2.9 \cdot 10^6$

\* $\Delta z$  = distance of dolomitization along the fluid flow path.

<sup>†</sup>T of dolomitizing fluid at the inlet to the flow system.

<sup>§</sup>Input fluid has composition of either DE1 or DE3, table 2.

<sup>‡</sup>Constant T along the flow path of either 50, 70, or 90°C.

<sup>#</sup>Replacement of limestone by dolomite at constant volume.

A CONSISTENT FRAMEWORK FOR INTERPRETATION OF THE ISOTOPIC COMPOSITION OF  
 REPLACEMENT DOLOMITE AND PRECURSOR LIMESTONE

*Theory*

The infiltration of limestone by dolomitizing fluid in the Latemar buildup produced isotope reaction fronts as well as the mineral reaction front at which limestone was converted to dolomite by reaction (1). Rock upstream from each isotope reaction front approached or attained isotope exchange equilibrium with the dolomitizing fluid. Rock downstream from each front retained its original isotopic composition prior to dolomitization (that of precursor limestone). It is essential to know the position of each isotope reaction front in the Latemar buildup if a given measured isotopic composition is to be correctly interpreted either in terms of a chemical fingerprint of the dolomitizing fluid or in terms of direct inheritance from original limestone. Isotope exchange fronts in nature are broadened if there is significant isotope transport by diffusion and hydrodynamic dispersion and/or if the mineral-fluid isotope exchange reaction is kinetically limited (Bowman and others, 1994; Baumgartner and Valley, 2001). The sharpness of the interface between unreacted limestone and completely reacted replacement dolomite, however, argues for a close approach to mineral-fluid equilibrium at the site of dolomitization. The positions of isotope reaction fronts therefore were estimated assuming local mineral-fluid equilibrium:

$$\Delta z_i = q_m(N_f/V_r), \quad (3)$$

where  $\Delta z_i$  is the displacement of the isotope reaction front of element *i* from the inlet to the flow system during the flow event,  $N_f$  is the moles of the element of interest per mole fluid,  $V_r$  is the moles of the element of interest per unit volume of rock, and  $q_m$  is molar time-integrated fluid flux (Dipple and Ferry, 1992; Ferry and Gerdes, 1998).

*Predicted Location of Isotope Reaction Fronts*

Positions of the oxygen, strontium, and carbon isotope reaction fronts were computed relative to the position of the dolomite mineral reaction front at  $z_{\text{rf}} = 1$  km using the chemical compositions of limestone and replacement dolomite, the molar volumes of calcite and dolomite from Holland and Powell (1998), and the estimated time-integrated fluid flux of dolomitization.

*Position of the oxygen isotope alteration front.*—For oxygen in diffuse effluent (or any other aqueous fluid),  $N_f = 1$  mol O/mol fluid. Limestone is considered pure calcite with  $V_r = 0.0813$  mol O/cm<sup>3</sup> rock. Taking  $q_m = 2.5 \cdot 10^6$  mol/cm<sup>2</sup>,  $\Delta z_O = 3.1 \cdot 10^7$  cm = 310 km. The oxygen isotope alteration front traveled  $\sim 310$  times faster and farther than the dolomitization front ( $z_{\text{rf}}$ ). Results are not significantly different if other plausible values of  $q_m$  are considered. Calcite therefore was appropriate to evaluate  $V_r$  in the calculation because the oxygen isotope alteration front traveled exclusively in limestone.

Regardless of the value of  $q_m$ ,  $\Delta z_O \approx 310z_{\text{rf}}$  (eq. 3). Because  $\Delta z_O \gg z_{\text{rf}}$ , values of  $\delta^{18}\text{O}_{\text{Dol}}$  represent  $^{18}\text{O}$ - $^{16}\text{O}$  exchange equilibrium or approach to isotope exchange equilibrium with the dolomitizing fluid. The calculation therefore justifies the interpretation of the oxygen isotope temperature recorded by dolomite as representing the temperature of dolomitization. Because of the slow rate of intracrystalline oxygen isotope diffusion in calcite below 100°C, equilibration of oxygen isotopes between calcite and fluid could only have occurred by mineral solution and reprecipitation. Interpretation of  $\delta^{18}\text{O}_{\text{Cal}}$  in terms of temperatures attained during dolomitization therefore is appropriate only to the extent that calcite recrystallized during dolomitization. The degree to which most individual samples of limestone recrystallized downstream from the calcite-dolomite reaction front is difficult to assess, and the significance of  $\delta^{18}\text{O}_{\text{Cal}}$  in terms of temperature is accordingly less certain than for replacement dolomite. Nevertheless, the greater predicted spatial extent of oxygen isotope alteration relative to the extent of dolomitization explains why some limestone samples have  $\delta^{18}\text{O}$  corresponding to temperatures up to 54°C but remain undolomitized. Temperatures recorded by calcite above  $\sim 38^\circ\text{C}$  are greater than those that higher organisms can tolerate (Brock, 1985; Rothschild and Mancinelli, 2001), and they may be interpreted as the temperature at which warm fluids infiltrated and drove recrystallization of calcite in limestone after they passed beyond the dolomite reaction front where they lost their dolomitizing potential.

*Position of the strontium isotope alteration front.*—The strontium content of the dolomitizing fluid was taken as that of modern seawater,  $\sim 90$   $\mu\text{M}$  (Millero and Sohn, 1992; James and Elderfield, 1996). Accordingly,  $N_f = 1.6 \cdot 10^{-6}$  mol Sr/mol fluid. Representative calcite in limestone from the Latemar buildup contains  $\sim 175$  ppm Sr (table 2 of Carmichael and others, 2008). The value of  $V_r$  then is  $6.5 \cdot 10^{-6}$  mol Sr/cm<sup>3</sup> rock. Taking  $q_m = 2.5 \cdot 10^6$  mol/cm<sup>2</sup>,  $\Delta z_{\text{Sr}} = 7.4 \cdot 10^5$  cm = 7.4 km. The strontium isotope alteration front traveled  $\sim 7$  times faster and farther than the dolomitization front. Calcite therefore was also appropriate to evaluate  $V_r$  in the calculation because the strontium isotope alteration front traveled exclusively in limestone.

Regardless of the value of  $q_m$ ,  $\Delta z_{\text{Sr}} \approx 7z_{\text{rf}}$ . Because  $\Delta z_{\text{Sr}} > z_{\text{rf}}$ , values of  $^{87}\text{Sr}/^{86}\text{Sr}$  of dolomite represent  $^{87}\text{Sr}$ - $^{86}\text{Sr}$  exchange equilibrium or approach to isotope exchange equilibrium with the dolomitizing fluid. The calculation of  $\Delta z_{\text{Sr}}$  justifies the interpretation of  $^{87}\text{Sr}/^{86}\text{Sr}$  of dolomite as a direct proxy for  $^{87}\text{Sr}/^{86}\text{Sr}$  of the dolomitizing fluid.

*Position of the carbon isotope alteration front.*—The carbon content of diffuse effluent is  $\sim 5$  to 10 mM (Van Damm and Lilley, 2004). Accordingly,  $N_f = (0.9\text{--}1.8) \cdot 10^{-4}$  mol C/mol fluid. Dolomite has  $V_r = 0.031$  mol C/cm<sup>3</sup> rock. Taking  $q_m = 2.5 \cdot 10^6$  mol/cm<sup>2</sup>,  $\Delta z_C = (0.73\text{--}1.5) \cdot 10^4$  cm = 73–150 m. Unlike the case of oxygen and strontium, the carbon isotope alteration front traveled  $\sim 10$  times slower than and only

TABLE 4

Summary of input parameters and results in the evaluation of the minor- and trace-element budget of dolomitization

	Concentration in limestone (ppm)	Concentration in tan dolomite (ppm)	Addition during dolomitization (mol/km <sup>2</sup> ·cm <sup>2</sup> )	Amount in 2.5·10 <sup>6</sup> mol fluid DE2 (mol)	Amount in 1.1·10 <sup>6</sup> mol seawater (mol)
Fe	250	3000	12	21	2.0·10 <sup>-5</sup>
Mn	10	100	3.9·10 <sup>-1</sup>	4.6	1.0·10 <sup>-5</sup>
Zn	1	4	1.1·10 <sup>-2</sup>	0.42	1.2·10 <sup>-4</sup>

~10 percent as far as the dolomitization front. Dolomite therefore was appropriate to evaluate  $V_r$  in the calculation because the carbon isotope alteration front traveled in replacement dolomite.

Regardless of the value of  $q_m$ ,  $\Delta z_c = (0.07-0.15)z_{rf}$ . Because  $\Delta z_c \approx 0.1z_{rf}$ , the  $\delta^{13}C$  of most replacement dolomite near limestone-dolomite contacts would have been unaffected by  $^{13}C$ - $^{12}C$  exchange with the dolomitizing fluids. Values of  $\delta^{13}C_{Dol}$  were simply inherited from precursor calcite, as was argued by Carmichael and others (2008) on the basis of horizontal data arrays on  $\delta^{18}O$ - $\delta^{13}C$  plots (figs. 1 and 2). The exceptions are some samples of orange dolomite, such as those from location 7 (figs. 2B and 3B), that have  $\delta^{13}C$  unlike calcite in proximal limestone but similar to  $\delta^{13}C$  of dolomite in the underlying Contrin Formation. The Contrin Formation lies ~555 m below location 7. Equilibration of carbon isotopes in orange dolomite at location 7 with carbon from the Contrin Formation could have occurred if unusual local factors allowed a carbon isotope reaction front to rise 555 m from the contact between Contrin Formation and the Lower Edifice. Equation (3) identifies two possible factors. Either the dolomitizing fluid that drove formation of orange dolomite at location 7 contained carbon concentrations ~4 to 8 times higher than expected (~40 mM) or the time-integrated fluid flux involved in formation of the orange dolomite locally was ~4 to 8 times larger than the baseline value [that is,  $q_m \cdot (1-2) \cdot 10^7$  mol/cm<sup>2</sup>].

#### THE MINOR- AND TRACE-ELEMENT BUDGET OF DOLOMITIZATION

Triassic seawater was dismissed as a dolomitizing fluid because of its small Fe, Mn, and Zn contents. An evaluation of the minor- and trace-element budget of dolomitization allows for quantitative assessment both of whether seawater, in fact, has insufficient amounts of Fe, Mn, and Zn to account for the enrichment of replacement dolomite in these elements over calcite and of whether a preferred dolomitizing fluid, such as DE2, does have sufficient amounts. The evaluation is based on representative Fe, Mn, and Zn contents of calcite in limestone, of tan replacement dolomite (the most abundant kind of dolomite in the Latemar buildup), and model diffuse effluent DE2 (tables 2 and 4). The molar amounts of Fe, Mn, and Zn per cm<sup>2</sup> in 1 km of unaltered limestone with 3 percent porosity and in that quantity of rock after it is converted to tan replacement dolomite at constant oxygen and carbon are listed in table 4. Comparing dolomite with limestone, 12 mol/cm<sup>2</sup> Fe,  $3.9 \cdot 10^{-1}$  mol/cm<sup>2</sup> Mn, and  $1.1 \cdot 10^{-2}$  mol/cm<sup>2</sup> Zn were added to each km of tan replacement dolomite (table 4). An amount of fluid corresponding to the baseline calculation of  $q_m$ ,  $2.5 \cdot 10^6$  mol/cm<sup>2</sup>, with the composition of DE2 (table 2) contains more than enough Fe, Mn, and Zn to explain the enrichment of these elements in tan replacement dolomite even allowing for <100 percent efficiency in the extraction of Fe, Mn, and Zn from fluid during dolomitization (table 4). The same conclusion is reached if other plausible values of  $q_m$  are consid-

ered (table 3) and if fluid with composition DE3, table 2, is taken as the dolomitizing fluid. A time-integrated flux of  $2.2 \cdot 10^6$  mol/cm<sup>2</sup> (table 3) of fluid with composition DE1 can account for the Mn and Zn budget of the representative tan dolomite in table 4 but not, however, for its Fe budget.

Replacement dolomite can be considerably more enriched in Fe, Mn, and Zn than the representative composition of tan dolomite listed in table 4, up to ~30,000 ppm Fe, up to ~750 ppm Mn, and up to ~18 ppm Zn (fig. 16 of Carmichael and others, 2008). By the same analysis, either a time-integrated flux of  $2.5 \cdot 10^6$  mol/cm<sup>2</sup> of fluid with composition DE2 or a time-integrated flux of  $3.0 \cdot 10^6$  mol/cm<sup>2</sup> (table 3) of fluid with composition DE3 can account for the Mn and Zn budget of the most Mn- and Zn-enriched dolomite but not for the most Fe-enriched. The most Fe-rich replacement dolomite therefore requires local infiltration of unusually Fe-rich fluid or locally focused fluid flow that results in time-integrated fluid flux greater than the values in table 3. Samples that have elevated Fe concentrations also have  $\delta^{13}\text{C}$  values consistent with derivation of carbon from the underlying Contrin Formation. Both chemical characteristics can be explained by locally elevated time-integrated fluid flux.

The efficacy of seawater as an agent for enriching typical tan dolomite in Fe, Mn, and Zn was analyzed in the same fashion. First, a value of  $q_m$  required to replace a 1 km x 1cm<sup>2</sup> column of limestone with tan dolomite was computed, as described earlier, using the Ca and Mg contents inferred for Middle Triassic seawater (Hardie, 1996; Stanley and Hardie, 1998). The result is  $q_m = 1.1 \cdot 10^6$  mol/cm<sup>2</sup> ( $q_v = 2.0 \cdot 10^7$  cm<sup>3</sup>/cm<sup>2</sup>). Triassic seawater is a more potent agent of dolomitization than fluid with composition DE2 because it has lower Ca/Mg. Using the Fe, Mn, and Zn contents of modern seawater (1 nM, 0.5 nM, and 6 nM, respectively, from Millero and Sohn, 1992) as proxies for the composition of Triassic seawater, the molar amounts of the elements in  $1.1 \cdot 10^6$  moles fluid were computed (table 4). Seawater is a hopelessly inadequate source for Fe, Mn, and Zn in tan replacement dolomite with deficits ranging between 2 (Zn) and >5 (Fe) orders of magnitude. The calculations formally confirm that pristine Triassic seawater could not have been the fluid that drove formation of replacement dolomite in the Latemar buildup.

#### FORMATION OF REPLACEMENT DOLomite AT CONSTANT OXYGEN AND CARBON OR AT CONSTANT VOLUME

Many investigations and reviews of the formation of replacement dolomite consider that the reaction (1) proceeds at constant oxygen and carbon (for example, Land, 1985; Wilson and others, 1990; Budd, 1997). Others, however, have argued that the replacement occurs at constant volume (for example, Merino, 2003). One criterion for evaluating the mechanism of replacement is porosity. Replacement at constant oxygen and carbon should produce ~13 percent porosity; replacement at constant volume should produce dolomite with porosity the same as the precursor limestone. Limestone in the Latemar buildup typically has ~3 percent porosity (Carmichael, ms, 2006; Carmichael and others, 2008). One analyzed sample of dolomite from the Latemar buildup has 16 percent porosity and meets the criterion for replacement at constant oxygen and carbon. Another has 3 percent porosity and meets the criterion for replacement at constant volume. The porosity of most replacement dolomite, however, is in the range 5 to 10 percent and is inconclusive. An additional complication is that replacement dolomite may have had larger porosity when it initially formed but that some porosity was eliminated by later compaction or cementation.

An unrecognized aspect of the debate is that formation of replacement dolomite at constant volume has consequences in terms of mass transport. Specifically, if reaction (1) proceeds with  $x = 1$ , the dolomitizing fluid must contain sufficient carbon to introduce 0.24 moles carbon for every mole dolomite produced. This chemical criterion can be quantitatively evaluated for replacement dolomite from the Latemar



buildup. Formation of 1 km of dolomite from limestone with 3 percent porosity at constant volume requires introduction of 480 mol C/cm<sup>2</sup>. Diffuse effluent contains a maximum of ~5 to 10 mM carbon (Von Damm and Lilley, 2004). A time-integrated flux of  $(4-7) \cdot 10^7$  cm<sup>3</sup>/cm<sup>2</sup> of fluid like diffuse effluent (table 3) then contains no more than ~200 to 700 mol carbon. Strictly constant volume replacement of calcite by dolomite in the Latemar buildup was possible only if the uptake of carbon by dolomite from the fluid was very efficient, if time-integrated fluxes were larger than those estimated in table 3, and/or if the dolomitizing fluid had unusually high carbon contents >10 mM. Nevertheless, the amounts and carbon contents of the dolomitizing fluid are not greatly inadequate to account for constant volume replacement. Measured porosities of dolomite in the range 5 to 10 percent therefore are perhaps best interpreted in terms of formation of dolomite by a mechanism intermediate between the end-member cases of constant oxygen and carbon and of constant volume [ $0 < x < 1$  in reaction (1)].

#### DURATION OF FLUID-ROCK REACTION DURING DOLOMITIZATION

Mottl and others (1998) report a direct measurement of the flux of modern diffuse effluent of 0.02 cm<sup>3</sup>/cm<sup>2</sup> · s. If fluid fluxes were similar during dolomitization in the Latemar buildup, the duration of fluid flow and mineral-fluid reaction may be estimated by dividing the volumetric time-integrated fluid flux by the volumetric fluid flux. The duration is surprisingly short,  $[(4-7) \cdot 10^7 \text{ cm}^3/\text{cm}^2 / 0.02 \text{ cm}^3/\text{cm}^2 \cdot \text{s}] = (2-4) \cdot 10^9 \text{ s} = 60-120 \text{ y}$ .

The inferred duration of fluid flow and reaction is much less than the duration of fluid flow of ~10<sup>6</sup> y, predicted by Wilson and others (1990) from a heuristic hydrologic model of the Latemar buildup. The hydrologic model, however, predicts smooth and regular variations in temperature at the km scale during fluid flow that are inconsistent with observed variations in temperature at the outcrop scale that are almost as large as those over the entire buildup (figs. 1, 2 and 3). The applicability of the model to the Latemar buildup therefore is unclear. Nevertheless, the difference between the two estimates of duration is not as great as it appears and, in part, may be reconciled by the episodic and spatially variable fluid flow characteristic of seafloor hydrothermal systems (Corliss and others, 1979; Mottl, 1983). Fluid flow during dolomitization in the Latemar buildup may have been widespread at any one time but occurred in a few hundred episodes with a few hundred or thousand years' duration between pulses. Alternatively, episodes of fluid flow may have occurred more often, but flow at any one time was spatially restricted to a small portion of the buildup. In either case, the total duration of the dolomitization process would have been much longer than ~100 y.

#### SIMILAR OCCURRENCES OF REPLACEMENT DOLOMITE

Zempolich (ms, 1995) and Zempolich and Hardie (1997) describe bodies of replacement dolomite in the Venetian Alps, Italy, with similar sizes and shapes. Columns of dolomite breccia in the Venetian Alps, in particular, are like those in the Latemar buildup (compare, fig. 7 of Carmichael and others, 2008, with fig. 14 of Zempolich and Hardie, 1997). Flow of dolomitizing fluid likewise was focused by preexisting structures such as breccias, faults, fractures, and lithologic contacts. Oxygen isotope thermometry indicates that some of the dolomite developed at low temperature (<100°C) similar to the Latemar buildup.

Cenozoic replacement dolomite on Enewetak and Niue Atolls in the South Pacific formed in a geologic setting similar to the Latemar buildup during the Triassic (Saller, 1984; Aharon and others, 1987). The increasing abundance of dolomite with depth in drill cores in the atolls points to upward directed flow of dolomitizing fluid similar to that in the Latemar buildup. Replacement dolomite on Niue likewise is enriched in Fe, Mn, and Zn relative to limestone precursors (Aharon and others, 1987). The metals

are believed to have been leached from underlying mafic volcanic rocks by the dolomitizing fluids. Unlike that in the Latemar buildup, replacement dolomite on Niue is enriched in Cu as well as in Fe, Mn, and Zn.

Tertiary replacement dolomite in the Negev desert, Israel, is similar in many ways to that in the Latemar buildup despite its non-marine geologic setting (Erel and others, 2006). Dolomitization occurred at temperatures of ~50 to 75°C. The spatial distribution of replacement dolomite demonstrates that flow of dolomitizing fluid was focused by faults and lithologic contacts. Dolomite in the Negev is enriched in an even wider range of elements than is dolomite in the Latemar buildup, including Cu, Ni, V, and U, as well as Fe, Mn, and Zn. The metals are believed to have been leached from igneous basement rocks along the flow path of dolomitizing fluid. The dolomitizing fluid in the Negev, however, is considered heated and chemically modified groundwater rather than seawater-derived fluid.

The similarities of these occurrences with the Latemar buildup suggest that multifaceted studies involving field mapping; major-, minor-, and trace-element analysis; measurement of stable isotope compositions; and interpretation of data with simple concepts grounded in transport theory have potential to provide a more complete understanding of the formation of replacement dolomite worldwide.

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