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I am submitting herewith a thesis written by Michael Thomas DeAngelis entitled ”Experimental investigation of the breakdown of dolomite and isotope transport in rock cores at 100 MPa, 650–750 ℃” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

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We have read this thesis
and recommend its acceptance:

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Graduate Studies

(Original signatures are on file with official student records.)

EXPERIMENTAL INVESTIGATION OF THE BREAKDOWN OF DOLOMITE AND ISOTOPE TRANSPORT IN ROCK CORES AT 100 MPA, 650–750 °C

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Michael Thomas DeAngelis
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Dedication

This thesis is dedicated to all of my mentors. I would not have reached my goals if they had not been there teach and inspire me along the way. I want to especially dedicate this thesis to my father, Mark DeAngelis, who has taught me most of all.

Acknowledgments

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Abstract

The kinetics of the breakdown reaction dolomite = periclase + calcite + CO_2 were investigated using cores of dolomitic marble. Two samples of Reed Dolomite from southwestern Nevada were cut into cylinders approximately 4×6 mm in size. The cores were sealed in gold capsules with isotopically enriched water ($H_2{}^{18}O$ or $HD^{18}O_{0.5}{}^{16}O_{0.5}$). The samples were heated in a cold-seal hydrothermal apparatus to 650–750 °C at 100 MPa for durations ranging from 2–59 days. The cores were then sectioned and examined by EMP, XRD, and SIMS techniques. All experiments show some amount of reaction regardless of duration or temperature. Reaction products occur mainly along grain boundaries, fractures within grains, and along sample edges. Ion images and isotope-ratio analysis indicate that reaction products exchanged with infiltrating fluids. Reaction rates were calculated from measured extents of reaction, which were determined from modal analysis from optical point counting, automated EMP modal counts, and by CO_2 yield. At 700 °C, a range of reaction rates from 6.6×10^{-12} to 2.2×10^{-10} mols/cm^2/s was determined. The extent of reaction was found to have a log-linear relationship with the square root of time, suggesting a diffusion-controlled rate. Activation energies were 106.5 kJ/mol for coarse-grained samples and 202.0 kJ/mol for fine-grained samples. Initial reaction occurs relatively fast near the surface of dolomite grains, but continued diffusion through the reaction products ultimately controls the rate of dolomite breakdown.

Table of Contents

Part Page

List of Tables

List of Figures

PART I

Experimental investigation of the breakdown of dolomite in rock cores at 100 MPa, 650–750 °C

1. Introduction

Metamorphism of carbonate rock in contact-metamorphic aureoles is commonly the result of reaction between the minerals in the rock and an H_2O-rich fluid. The presence of periclase resulting from the breakdown of dolomite is an important indication of H_2O-rich fluid and implies fluid infiltration during pluton emplacement. Moore and Kerrick (1976), for example, recognized a sequence of isograds surrounding the Alta aureole, Utah, which includes the presence of a periclase zone near the contact of the Alta Stock. The stability of periclase at the temperatures (600–700 ℃) and pressures (100–200 MPa) of a contact metamorphic aureole requires low values of $x_{\mathrm{CO_2}}$ (<0.2) (Kerrick, 1970), despite of the large amount of CO_2 released by reaction.

Mass transfer during metamorphism commonly depends on both advection and diffusion to move fluids through country rock surrounding an intrusion (Ferry, 1991). Fluid flow is driven by a pressure gradient and results in flow along fractures and through the bulk rock along grain boundaries. Mass transport also occurs by diffusion along grain boundaries and through the fluid in fractures. Areas of reaction and fluid infiltration can be observed during detailed field mapping and petrographic analysis of rock samples. Overall reaction rates from field data, however, can be determined only with assumptions of heating rates and reaction mechanisms. Reaction rates and mechanisms must, therefore, be measured in the laboratory to complement field observations.

Experimental studies of reaction kinetics have been performed using mineral powders to approximate compositions of rock assemblages consistent with contact metamorphic reactions (Dachs and Metz, 1988; Heinrich et al., 1986, 1989; Kase and Metz, 1980; Kridelbaugh, 1973; Lüttge and Metz, 1991, 1993; Schramke et al., 1987; Tanner et al., 1985). Those studies were successful in describing the mechanisms and rates of reactions, but do not recreate the conditions found within actual rock. The large porosities of powders and the large surface areas of the mineral reactants in direct contact with an abundant fluid phase are conditions that differ considerably from the situation in rocks in natural systems (Lüttge and Metz, 1993). Rapid reaction rates and the presence of quench phases in powder experiments can make accurate measurement of the extent of reaction difficult.

This experimental study uses dolomitic marble cores to determine the rate of breakdown of dolomite as a function of both fluid transport and the rate of mineral reaction. Through use of samples of various grain size and texture, controlled pressure and temperature conditions, and use of isotopically and chemically characterized fluids, our experiments were effective in observing the areas of reaction and transport of fluids that occurred in natural rock samples. From these observations, we have been able to determine overall reaction rates and suggest mechanisms of reaction.

2. Methods

2.1. Experimental techniques

Two nonsiliceous dolomitic marble samples were selected from the Reed Dolomite, Tonopah, Nevada (Figure 1). The Reed Dolomite is a massive, brown to tan, medium- to coarse-grained dolomitic marble that contains rare thin layers of phyllite, quartzite, and calcitic marble (Richards et al., 1996). Sample LM57, from Lone Mountain, Nevada, is light-gray, homogeneous, and contains equant dolomite grains ranging in size from 0.25–0.50 mm in diameter. This sample is 95% dolomite, with minor amounts of quartz and opaque minerals, and has a slightly friable texture. Sample MR22-2, from Mineral Ridge, Nevada, is light-gray to yellow in color. Average dolomite grain size ranges from 0.5 to 1.0 mm in diameter and are irregular in shape. This sample also contains minor quartz veins and intergranular fractures.

Small cores, approximately 4 mm in diameter and 5–7 mm in length, were drilled from each marble sample. The cores were placed within thin-walled, 5 mm gold tubes, approximately 7.5 cm in length. An aliquot of $H_2{}^{18}O$ or $HD^{18}O_{0.5}{}^{16}O_{0.5}$ was added to each sample, and the capsules were purged with CO_2 gas and welded closed. The prepared capsules were placed in a vacuum oven for approximately 24 hours and then reweighed to ensure that there were no leaks. A capsule was positioned in a cold-seal hydrothermal apparatus and pressurized and heated for the desired experiment duration. Each experiment was heated to the desired temperature over a period of thirty to forty minutes. During the course of each experiment, both pressure and temperature were monitored and recorded. The experiment was isobarically quenched to ambient temperature over a period of fifteen to thirty minutes. The capsule was then removed from the hydrothermal apparatus, weighed to test for leakage, placed in a vacuum line, and punctured.

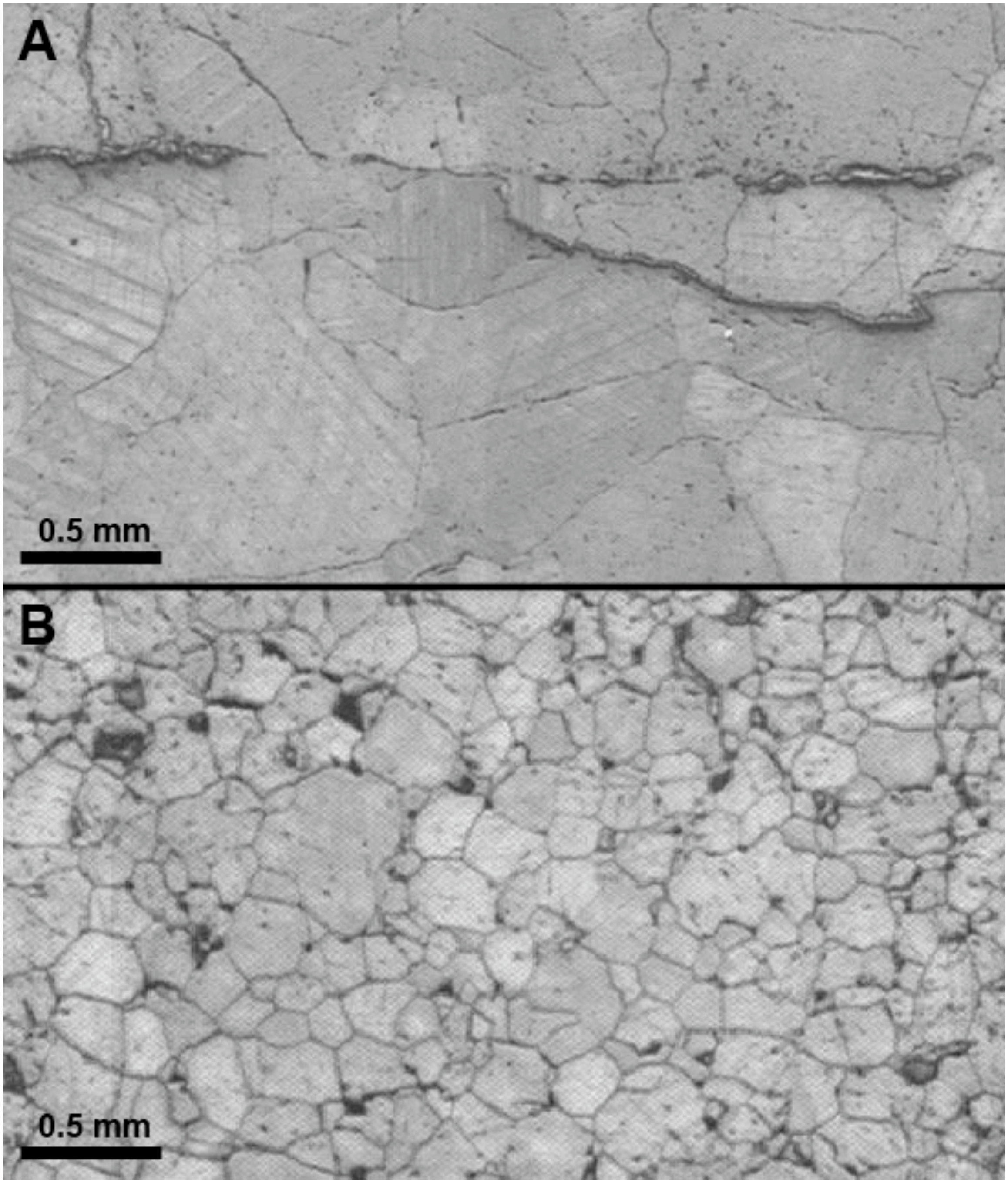

Figure 1. Thin sections of starting material. (A) Mineral Ridge dolomite sample MR22-2 with 0.5-1.0 mm average grain size. Note quartz vein in top half. (B) Lone Mountain dolomite samples LM57 with 0.25-0.5 mm average grain size.

Any CO_2 gas produced by reaction was measured by manometry. The sample was then removed from the gold tube, embedded in epoxy, and sectioned longitudinally.

Fifteen rock-core experiments were conducted at a pressure of 100 MPa and over a range in temperature from 650 to 750 °C, with the duration of experiments lasting from two days to two months. Table 1 contains a detailed list of all experiments.

2.2. Analytical techniques

In order to determine the extent of reaction, a transparent grid was laid over an enlarged photomicrograph (45x magnification) of each sample, and approximately 1000 grid points per photomicrograph at an interval of 2 mm were counted and classified as either dolomite or reaction products.

The extent of reaction was also obtained by electron microprobe (EMP) analysis using a fully automated Cameca SX-50 at the University of Tennessee. Over 50,000 analyses were collected using the the Oxford Instruments Energy Dispersive Spectrometer (EDS) FeatureScan option. Analyses were performed on a grid across the entire thin section, and the compositional value determined from each analysis was sorted into a predefined group.

The EMP was also used to observe mineral texture relationships by generating both back-scattered electron (BSE) and Ca, Mg, Si, and Fe X-ray images. For these analyses, the EMP had an accelerating voltage potential of 15 kV, a beam current of 4 nA, and a beam size of 1 µm. Images were generated by rastering over the area of interest, generally 256 x 256 µm using a 2 µm step with a counting

Table 1. Experimental Data

Experiment	Starting Material	Starting Fluid Composition	Temperature (°C)	Time (days)
MR1	MR22-2	$HD^{18}O_{0.5}{}^{16}O_{0.5}$	650	46
MR2	MR22-2	$HD^{18}O_{0.5}{}^{16}O_{0.6}$	700	2
MR6	MR22-2	$HD^{18}O_{0.5}{}^{16}O_{0.7}$	700	29
LM7	LM57	$HD^{18}O_{0.5}{}^{16}O_{0.8}$	700	29
MR8	MR22-2	$H_2{}^{18}O$	700	14
LM9	LM57	$H_2{}^{18}O$	700	59
MR10	MR22-2	$H_2{}^{18}O$	700	59
LM11	LM57	$H_2{}^{18}O$	700	43
MR12	MR22-2	$H_2{}^{18}O$	700	43
LM13	LM57	$H_2{}^{18}O$	700	14
LM15	LM57	$H_2{}^{18}O$	700	2
MR16	MR22-2	$H_2{}^{18}O$	650	29
LM17	LM57	$H_2{}^{18}O$	750	33
MR18	MR22-2	$H_2{}^{18}O$	750	29
LM19	MR22-2	$H_2{}^{18}O$	650	29

Table 1 continued

CO_2 yield*	Final X_{CO2}	Fluid Weight		Core Weight	
		Before	After**	Before	After
(mol)		(grams)	(grams)	(grams)	(grams)
-	-	0.04980	-	0.21897	0.21734
-	-	0.03739	-	0.25635	0.25181
1.83×10^{-4}	0.08	0.03805	0.03803	0.23775	0.22972
4.56×10^{-5}	0.02	0.03829	0.03317	0.23297	0.23608
4.43×10^{-5}	0.02	0.05252	0.04945	0.20438	0.2055
1.19×10^{-4}	0.05	0.04517	0.03965	0.15257	0.15286
3.49×10^{-4}	0.08	0.07011	0.06829	0.24581	0.23228
6.90×10^{-5}	0.02	0.05308	0.05910	0.32147	0.31242
2.61×10^{-4}	0.08	0.05168	0.05145	0.24101	0.22975
1.07×10^{-4}	0.04	0.05722	0.04781	0.28564	0.29036
3.79×10^{-5}	0.01	0.05730	0.05016	0.30933	0.3148
8.28×10^{-5}	0.03	0.05652	0.05475	0.26393	0.26206
-	-	0.05692	-	0.30273	0.28321
8.32×10^{-4}	0.23	0.05610	0.04924	0.22431	0.19456
3.45×10^{-5}	0.01	0.05642	0.05523	0.27804	0.27771

* MR1 & MR2 CO_2 not measured; LM17 capsule burst after experiment and CO_2 was lost

** Fluid Weight After calculated by weight difference time of 1 ms per step. Stage scanning was used for most images, though beam scanning was used for detailed images smaller than 128 x 128 µm.

Quantitative mineral analyses were also collected with the EMP (Table 2). For these analyses, the EMP had an accelerating voltage potential of 15kV, a beam current of 6 nA, a beam size of 1 µm, and a counting time of 40 seconds for most elements. Natural standards of calcite, dolomite, and periclase were used for calibration.

A Siemens D500 θ–θ X-ray powder diffractometer (XRD) was used to identify minerals present in experimental samples. Analyses were run using a Cu Kα X-ray tube at 40 kV and 30 mA, from 5 to 50° 2θ, with a 0.2° step, and with 30 s counting time per step.

Reaction produced CO_2 was cryogenically captured and measured by manometry across a calibrated volume with use of a vacuum line at Oak Ridge National Laboratory.

Ion imaging was performed with use of a Cameca 4f secondary ion mass spectrometer (SIMS) at Oak Ridge National Laboratory. Ion images were generated by rastering over a 250 x 250 µm area with a picoampere Cs^+ primary beam. A counting time of 30 s was used for ^{16}O images, and a counting time of 180 s was used for ^{18}O images.

Table 2. Selected electron microprobe analyses of carbonate minerals

	MR dolomite	LM dolomite	MR calcite	LM calcite
$Mg(CO_3)$	45.1	44.5	8.57	9.13
$Ca(CO_3)$	55.0	54.7	90.9	90.8
$Fe(CO_3)$	0.15	0.73	0	0.14
∑	100.3	99.9	99.5	100.1
Cation basis	6	6	3	3
Mg	0.99	0.98	0.10	0.11
Ca	1.01	1.01	0.90	0.89
Fe	0	0.01	0	0
∑	2	2	1	1

3. Results

Two series of experiments were performed. In the first series, experiments were carried out at constant T and P of 700 ℃ and 100 MPa, with durations ranging from 2 to 59 days. In the second series, experiments were carried out at 100 MPa for 30 days, with temperatures ranging from 650 to 750 ℃. All experiments contained an excess of either $H_2{}^{18}O$ or $HD^{18}O_{0.5}{}^{16}O_{0.5}$, ensuring x_{CO_2} conditions favorable for the formation of calcite and periclase.

All experiments, regardless of variation in time or temperature, show some degree of reaction. Areas of reaction generally began near the ends of the rock core and eventually reached the middle. Reaction products were located primarily along grain boundaries, fractures within grains, and along the outer edges of the rock core (Figure 2a, 2b). Ion images of ^{18}O indicate that reaction products exchanged with infiltrating isotopically enriched fluid (Figure 2c). In the MR samples, extensive reaction occurred along fractures and cleavage planes.

Despite grain-size differences in starting material, reaction textures resulting from experiments are similar. The initial reaction texture along grain boundaries has a symmetrical appearance, with a narrow (< 1 µm) center channel containing a Mg-rich phase surrounded on both sides by thicker (1–5 µm) bands of calcite (Figure 3a). Periclase, brucite [$Mg(OH)_2$], and magnesite [$MgCO_3$] were all located within these narrow channels. The release of CO_2 during reaction resulted in an overall reduction in the solid-rock core volume and an expansion of existing void space near the sites of reaction. Voids can be found between the calcite bands and the preexisting dolomite grains. As reaction continued, some dolomite grains were completely consumed, and reaction zones had a more mottled appearance (Figure 3b). Complete consumption of some dolomite grains, however, only occurred in the two experiments at 750 ℃.

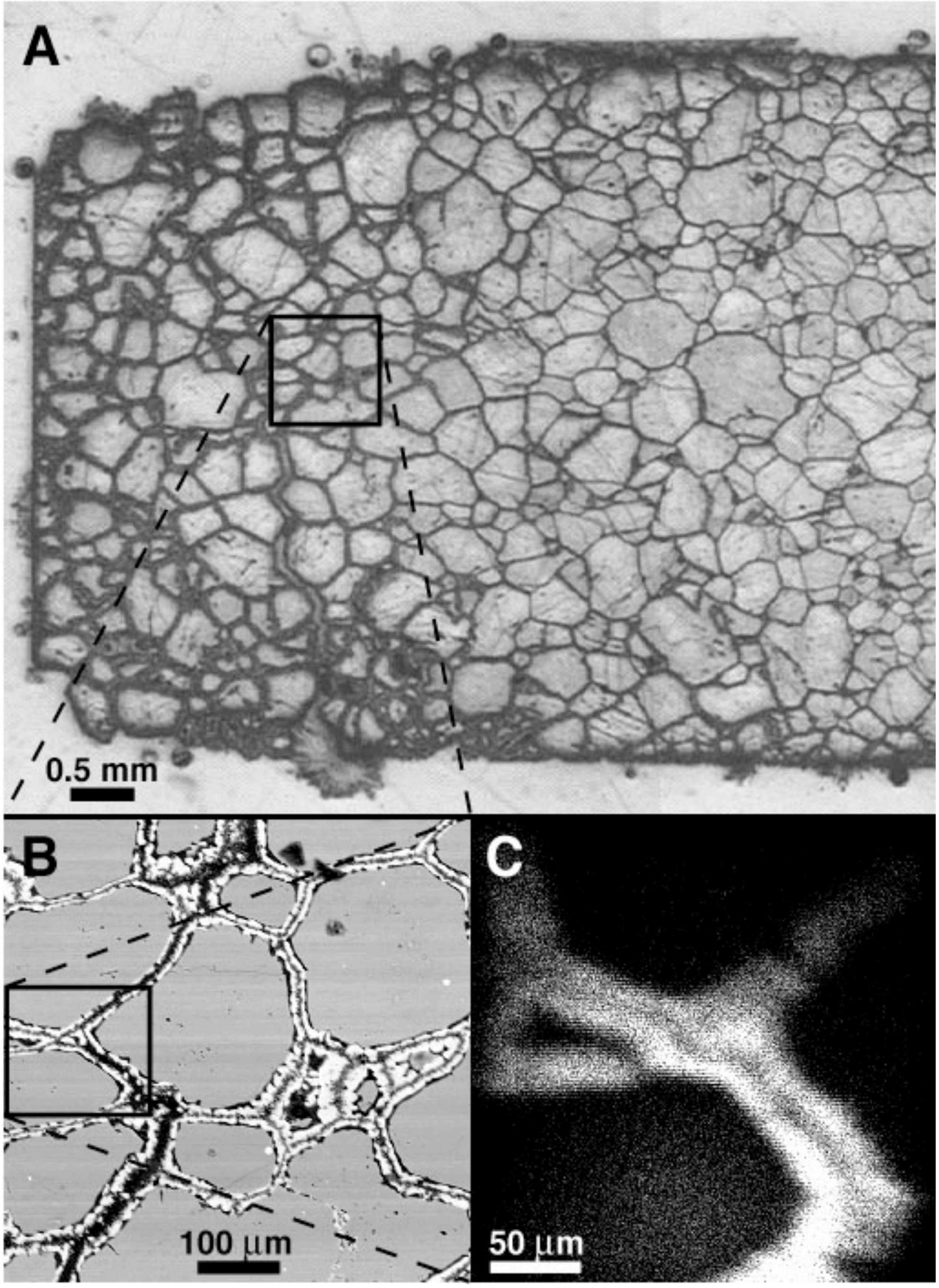

Figure 2. **(A)** Thin section photomicrograph of experiment LM7 (700 °C, 29 days). Areas of reaction are found primarily along grain boundaries, fractures within grains, and the outer edge of the sample. **(B)** LM7 BSE image showing distribution of reaction products along grain boundaries. **(C)** LM7 ^{18}O ion image showing an ^{18}O enrichment (white areas) in reaction products. Reaction products exchange with infiltrating isotopically enriched fluid during crystallization.

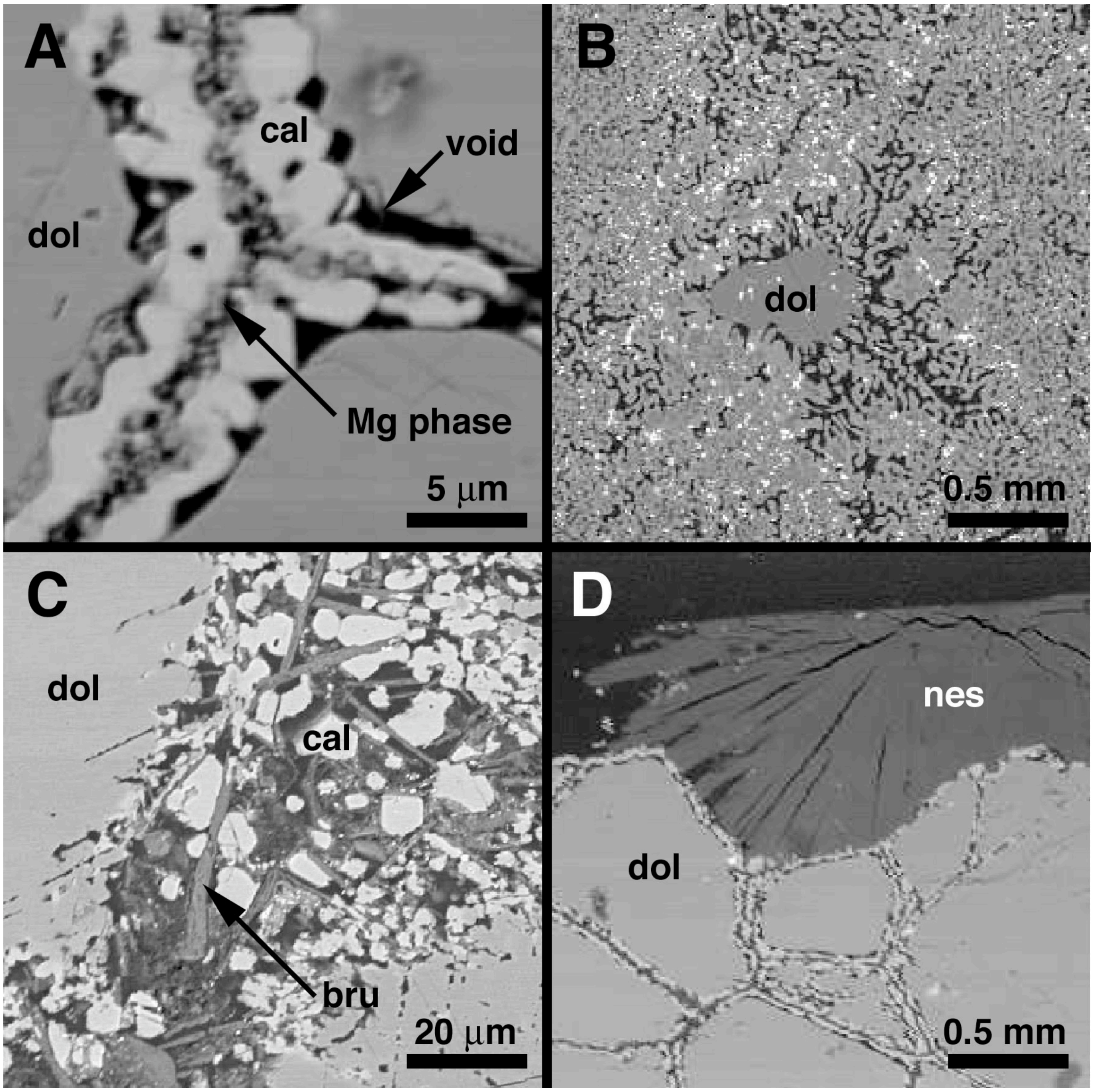

Figure 3. BSE images of reaction textures found in experimental samples. (**A**) Common grain boundary reaction textures from the LM9 (700 °C, 59 days) experiment show symmetrical bands of calcite split by narrow zone containing a Mg-rich phase. (**B**) Continued reaction in the MR18 (750 °C, 29 days) experiment shows complete consumption of most dolomite and resulting mottled reaction texture. (**C**) Long blades of brucite form in the MR1 (650 °C, 46 days) experiment. (**D**) Splays of nesquehonite ($MgCO_3 \cdot 3H_2O$) in the LM7 (700 °C, 29 days) experiment that form between the rock core and the gold capsule wall. Nesquehonite precipitates from solution during quench.

Although all the experiments were conducted within the stability range of periclase, Mg was soluble and formed crystals that precipitated on quench. Periclase, although detected by XRD analysis, was generally too small to optically identify or analyze with the electron microprobe. In the highest-temperature experiments, a few, very small (2–3 µm) nodules of periclase were identified. Long blades (10–20 µm) of brucite formed in large void spaces between dolomite grains in the MR1 experiment (Figure 3c).

Reaction products also crystallized on the outside of the dolomite rock cores. Calcite was sometimes observed as nodules attached to the outside of the cores, but usually only on the ends where the core was not in contact with the gold capsule during the experiment. Splays of nesquehonite [$MgCO_3 \cdot 3H_2O$] commonly crystallized between the outside of the rock core and the gold capsule during quench (Figure 3d).

While every attempt was made to select non-siliceous dolomite rocks, a few of the Mineral Ridge cores contain quartz veins. In those samples, dolomite reacted with the quartz to form forsterite and diopside.

Although most dolomite cores measured after experiment had an expected overall weight loss due to the release of CO_2 during reaction, a few had slight weight gains. It is possible that some of the cores were not completely dry before weighing and that the measured increase in weight was the result of liquid water on the dolomite core surface. More likely, however, the presence of hydrous quench phases, such as nesquehonite, on the exterior of the dolomite core contributed to an increase in overall core weight.

4. Discussion

4.1. Extent of reaction

We used three methods to determine the extent of reaction that occurred in each of our experiments (Table 3). The first method was to point count each sample, counting both areas containing reaction products and areas of preserved original dolomite. After each sample was sectioned, an enlarged photomicrograph (45x magnification) of the entire section was compiled. A grid was placed over the photomicrograph and approximately 1000 points were counted at a 2 mm interval. We found that an accurate measurement of the amount of dolomite versus non-dolomite could be achieved after the first 250 points were counted. Given the relatively small size of the cores (4mm x 6mm), we concluded that 1000 points exceeded the minimum number of necessary points to characterize the extent of reaction. A possible source of error with this method, however, is that the photomicrograph exposures may not reflect the true dimensions of the reaction products. Additionally, it was difficult to determine the difference between small void space and reaction products using this method.

The second method utilized automated modal analysis on the electron microprobe (Taylor et al., 1996). The concept of the EMP method is similar to the manual method, except that many more points (~50,000 points per section) were counted and voids were masked before counting. This method allows the user to specify mineral groupings on the basis of determined weight percent oxides. After the various groupings have been established, the EMP rasters over the entire thin section using a 10 µm step between each examined point. Every point is either classified as belonging to one of the previously established groupings or labeled as unclassified. Unclassified points generally composed less than 10% of the counted points. With further examination, these unclassified points were found to be ”mixed pixel”

Table 3. Measured extent of reaction from three different methods

Experiment	Extent by grid pointcount	Extent by EMP pointcount	Extent by measured CO2 yield*
MR2	17.5%	15.4%	-
MR6	30.0%	19.0%	3.5%
LM7	31.0%	15.6%	14.5%
MR8	42.2%	10.5%	4.0%
LM9	58.3%	43.4%	14.4%
MR10	56.1%	37.2%	26.2%
MR12	48.9%	41.2%	20.0%
LM13	23.1%	24.8%	6.9%
LM15	27.5%	22.0%	2.3%
MR16	23.0%	13.3%	5.8%
LM17	65.7%	51.2%	-
MR18	80.0%	62.8%	68.4%
LM19	2.2%	7.4%	2.3%

* MR2 CO_2 not measured; LM17 capsule burst after experiment and CO_2 was lost

points containing more than one mineral phase and were often found to lie within zones containing reaction products.

The final method was based on the amount of CO_2 generated by reaction. For every mole of dolomite that breaks down in this reaction, a corresponding mole of CO_2 is generated. The measured amount of CO_2, therefore, should correspond to the amount of dolomite converted. With the exception of a few experiments in which the gold capsules burst because of a high internal pressure after quench, we cryogenically captured and measured the produced CO_2.

As anticipated, each measurement method showed increasing extents of reaction with increasing temperature and time. The CO_2 measurements followed similar trends of increasing extent of reaction, but indicated overall lower amounts of total reaction. We attribute this difference to two possibilities. Fluid inclusion planes within the dolomite marble cores following experiment were sometimes present, and it may be that CO_2 generated by reaction was trapped as fluid inclusions. More likely, however, is that CO_2 was captured within mineral phases during quench. As noted earlier, minerals such as nesquehonite and magnesite were found as crystallized splays between the rock core and the gold capsule wall, and it may be minerals such as these trapped the missing CO_2.

4.2. Reaction rate and mechanism

To determine the overall rate for the dolomite breakdown reaction, we assumed that reaction progress could be calibrated by measuring the amount of preserved original dolomite and that there was no dolomite crystallized during quench. X-ray images confirm that dolomite did not crystallize during experiment. The assumption of spherical dolomite grains of equal size for each rock type, diameter of 0.3

mm for LM rock cores and diameter of 0.8 mm for MR rock cores, was necessary to approximate a total surface area in each sample. For the time-series experiments, a range of overall reaction rates from 6.6×10^{-12} to 2.2×10^{-10} mols/cm^2/s was calculated. Figure 4 shows the estimated reaction rates versus the duration of each experiment. The rate of reaction is fast in the short duration experiments for both the LM and MR time series experiments. With longer run durations, reaction rates are slower and more constant.

There are two possible explanations for the decrease in reaction rates. The first possibility is that CO_2 produced by reaction may be slowing dolomite breakdown. The final x_{CO_2} for each experiment was calculated by weight difference (Figure 5). As expected, the value of x_{CO_2} increased during reaction, thereby reducing the affinity (or Gibbs free energy of reaction (ΔG_r)) and slowing the reaction. All of the experiments, however, remain within the stability field for the formation of periclase and calcite. Although reaction may have slowed because of the increase of CO_2, it appears that it did not completely stop for any of the experiments.

The second possibility for the slowing of reaction may be a changing mechanism of reaction. Kinetic models of metamorphic reactions generally fall within three broad categories: heat flow controlled, surface controlled, or diffusion controlled (Fisher, 1978; Walther and Wood, 1984; Rubie and Thompson, 1985; Lasaga, 1986; Ridley and Thompson, 1986; Dachs and Metz, 1988; Lasaga, 1998). Since all our experiments were conducted at constant temperature, changes in heat flow were not a consideration. As described by Tanner et al. (1985), we can find the kinetic model that best describes this dolomite breakdown reaction by fitting our experimental data to an equation relating the fraction of remaining dolomite (F) to a function of time. A common approach to determine this relationship is to find a solution that best linearizes the F–t data (Kridelbaugh, 1973; Tanner et al., 1985). A plot of $-\ln(1-F)$ versus t is a fairly good fit, but the regression does not go through zero. We have found that plotting $-\ln(1-F)$ versus $\sqrt{t}$ produces a good fit

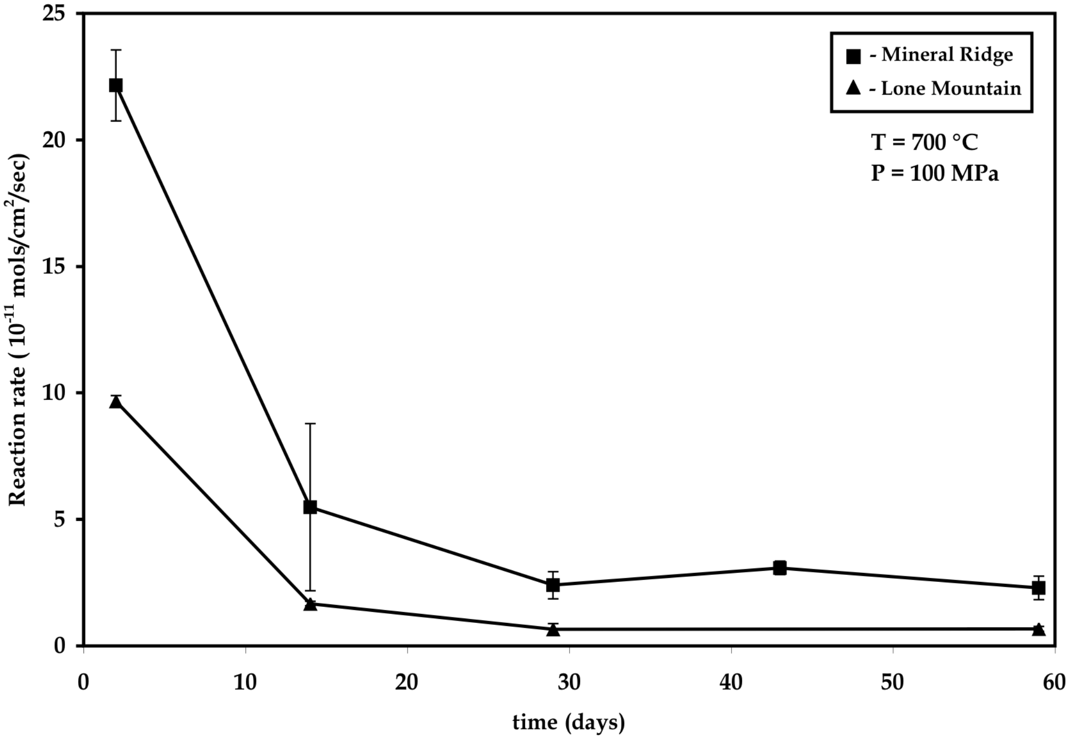

Figure 4. Reaction rate versus the duration for each LM and MR time series experiment. Error bars represent ranges in determined extent of reaction.

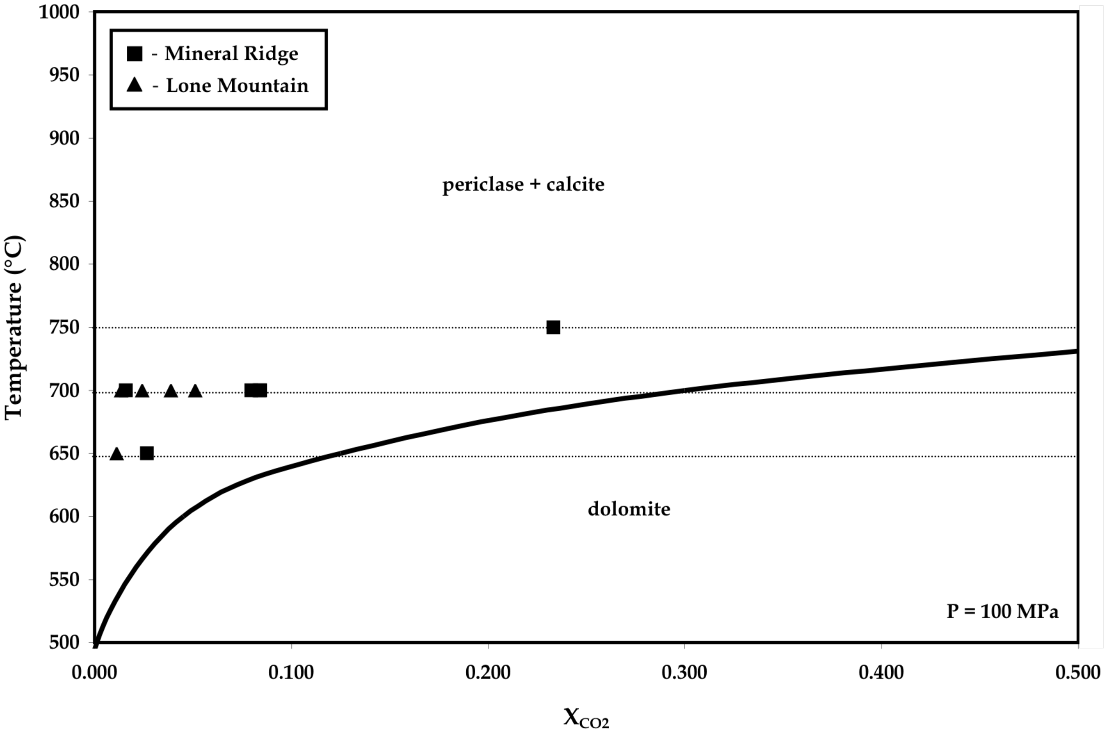

Figure 5. Final X(CO_2) values for each experiment. All experiments remain within the stability field of periclase + calcite during experiment.

for our data (Figure 6), and yields the equation:

$$-\ln(1-F) = 0.081\sqrt{t} \tag{1}$$

The form of this equation represents a one dimensional diffusion kinetic model (Hulbert, 1969; Brown et al., 1980; Rubie and Thompson, 1985; Tanner et al., 1985), in which the square of the extent of reaction is proportional to time. Although reaction textures indicate that reaction is initially surface controlled at the dolomite grain surface, the rate-limiting process involves diffusion along grain boundaries, fractures and through the products of reaction.

4.3. Activation energies

Since we have determined that the primary reaction mechanism for this dolomite breakdown reaction is diffusion, which is a thermally activated process (Tanner et al., 1995; Heinrich et al., 1989; Lasaga, 1998), we can calculate apparent activation energies using the Arrhenius equation:

$$k = Ae^{-E_\mathrm{a}/RT} \tag{2}$$

where A is the pre-exponentional factor and E_a is the apparent activation energy. The E_a can be determined directly from a plot of $\ln(k)$ versus $1/T$. Figure 7 shows an Arrhenius plot of the six temperature experiments performed. An $\mathrm{E_a}$ of 106.5 kJ/mol and an A of -11.1 mol/cm^2/s was obtained for the Mineral Ridge temperature series experiments and an $\mathrm{E_a}$ of 202.0 kJ/mol and an A of -1.05 mol/cm^2/s was obtained for the Lone Mountain temperature series experiments. The $\mathrm{E_a}$ for the Lone Mountain experiments was nearly double the $\mathrm{E_a}$ for the Mineral Ridge experiments, likely reflecting the difference in permeability between these two samples. These

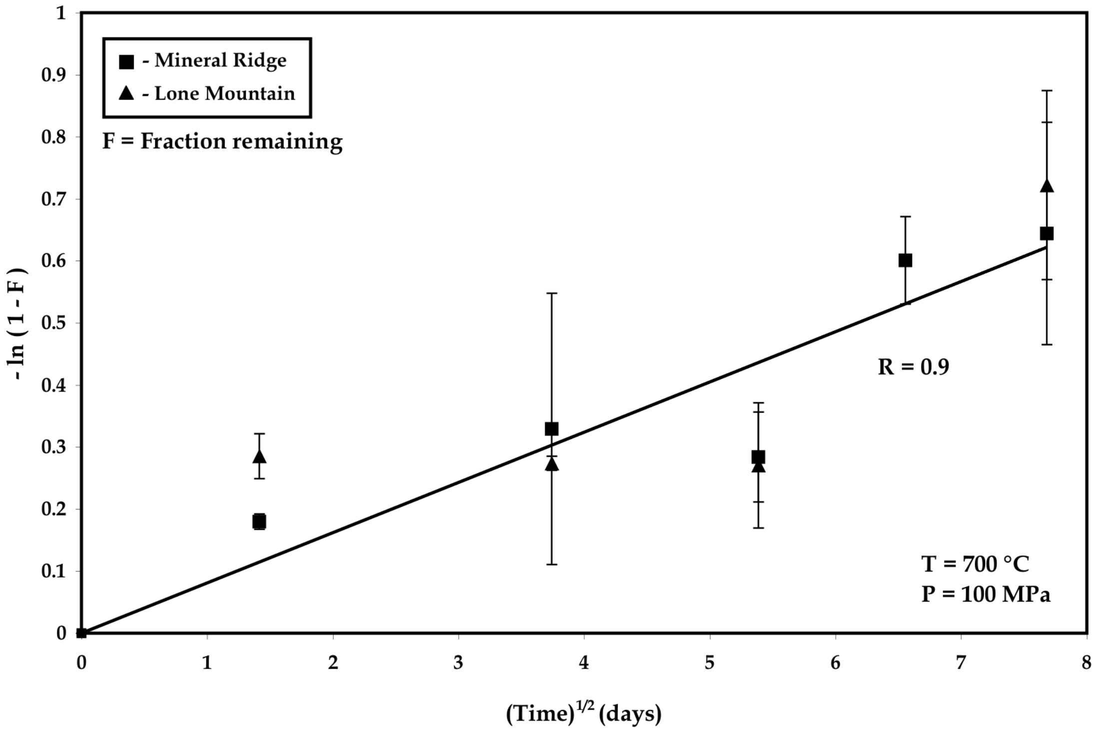

Figure 6. Plot of –ln(1-F) versus √t. This plot shows a log-linear relationship between the extent of reaction and the square root of time, and indicates that diffusion is the primary mechanism of reaction.

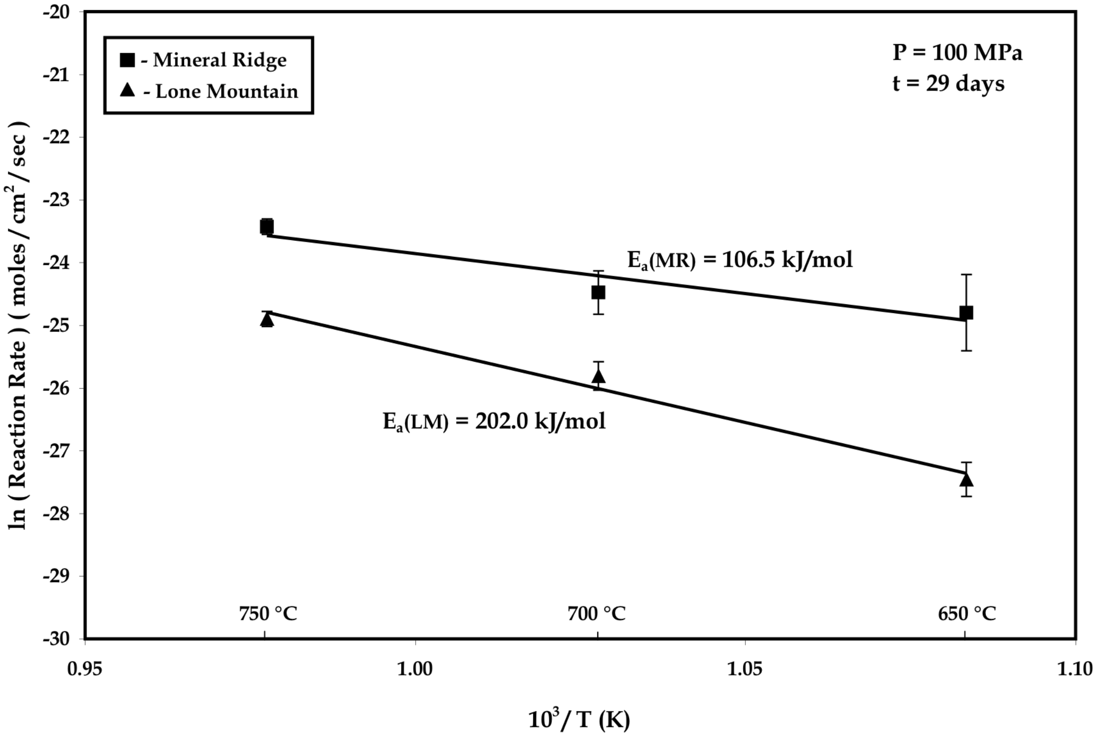

Figure 7. An Arrhenius plot of the six temperature experiments performed. E_a = 106.5 kJ/mol for the Mineral Ridge temperature series experiments and E_a = 202.0 kJ/mol for the Lone Mountain temperature experiments.

values are similar to other experimentally determined values for activation energies of dehydration and decarbonation reactions (Tanner et al., 1985; Schramke et al., 1987; Heinrich et al., 1988). Tanner et al. (1985), for example, looked at the decarbonation reaction calcite + quartz = wollastonite + CO_2 and determined an E_a of 225 (±78) kJ/mol.

4.4. Implications

Fluid transport in contact metamorphic aureoles is regulated by three primary processes. The first process is the transport of fluids through fractures. This process is driven by a pressure gradient and is responsible for moving large amounts of fluids to zones of reaction. The second method of moving fluids through rock is bulk transport along grain boundaries. This type of transport is similar to fracture transport in that overall transport direction is unidirectional along a pressure gradient, but here transport paths along grain boundaries are more tortuous. The final type of transport in contact metamorphism is diffusion along grain boundaries, in which transport is controlled by chemical potential gradients and can occur in many directions simultaneously.

Our experiments were most effective in observing diffusion along dolomite grain boundaries and fractures and through products of reaction along grain boundaries. Because of the closed system design of our rock core experiments, there were no major concerns about temperature or pressure gradients effecting fluid transport. An important difference between our experiments and natural systems, therefore, is that there is no continual resupply of H_2O near the site of reaction. This lack of continual movement of H_2O to the site of reaction and CO_2 away from the site of reaction results in local x_{CO_2} increases that effectively reduce the ΔG_r and slow reaction. These local increases in x_{CO_2} may explain the presence of magnesite in our reaction products, although magnesite must be metastable since our experiment temperatures are higher and $x_{\mathrm{CO_2}}$ is lower than is required for the stable formation of magnesite.

Many experimental studies of reaction kinetics have used mineral powders to determine reaction rates (Dachs and Metz, 1988; Heinrich et al., 1986, 1989; Kase and Metz, 1980; Kridelbaugh, 1973; Lüttge and Metz, 1991, 1993; Schramke et al., 1987; Tanner et al., 1985). An inherent concern with those kinds of experiments is that mineral powder reactants have, in general, much larger surface areas and porosities resulting in fast rates of conversion (Lüttge and Metz, 1993). The amount of time required for complete conversion of dolomite powders can be calculated using the reaction rates determined in this study. For example, if the powder experiment contained an amount of 50 µm diameter dolomite powder equivalent to the volume of a typical rock core (~250 mg), we would expect complete conversion of the dolomite powder in as little as 18 hours. This simple calculation, however, considers only differences in the surface area of reactants. If the larger porosities and fluid flow paths within mineral powder experiments were also included, even faster rates of conversion should be expected since CO_2 residence times at sites of reaction would be diminished. Rock core experiments, therefore, are closer to natural processes than are mineral powders experiments, giving reaction rates that are more representative of rocks in nature.

PART II

Experimental investigation of isotope transport in dolomitic marble cores at 100 MPa, 650–750 °C

1. Introduction

Metamorphism of country rock surrounding a pluton results from reaction controlled by both heat and the presence of fluids. While heat flow is generally considered to be the principal driving force for reaction, fluids are equally important when contact metamorphism occurs in H_2O reactive rocks such as carbonates (Ferry, 1991). The presence of periclase and calcite resulting from the decarbonation breakdown of dolomite, for example, indicates infiltration of an H_2O-rich fluid. For continued decarbonation reaction to occur at the temperatures and pressures found within most contact-metamorphic environments, CO_2 generated by reaction must be removed. Fluid infiltration, therefore, is necessary to move H_2O to the site of reaction and CO_2 away from the site of reaction.

Fluid transport in contact metamorphic aureoles is regulated by three primary processes: transport through fractures, transport along grain boundaries, and grain boundary diffusion. The transport of fluids though fractures and along grain boundaries is driven by a pressure gradient and is responsible for moving large amounts of fluids to zones of reaction. Grain boundary diffusion is controlled by chemical potential gradients and can occur in many directions simultaneously.

Stable isotopes of light elements such as oxygen, carbon, and hydrogen are useful as tracers of fluid transport, because they are common components of minerals and fluids found in contact metamorphic environments (Nabelek, 1991; Valley et al., 1986; Valley and Cole, 2001). Stable isotope ratios of these elements, therefore, are extremely sensitive to physical and chemical changes during contact metamorphism (Nabelek, 1991). Exchange kinetics of stable isotopes can be fast for the temperatures associated with contact metamorphism. In a study of the Alta contact aureole, Utah, Bowman et al. (1994) saw an increase in the heterogeneity of δ^{18}O values, ranging from 9‰ to 22‰ (SMOW), of rocks collected from within the periclase zone. This heterogeneity was originally interpreted as being due to the infiltration of H_2O-rich fluids through rocks with heterogeneous permeabilities. Detailed laser fluorination analysis of samples from within the periclase zone suggest that incorrect assumptions of local equilibrium during exchange may also be an important factor in the heterogeneities δ^{18}O values reported at Alta (Bowman and Valley, 1999). Laboratory measurements of isotope transport and exchange can be useful, therefore, to complement observations from field studies.

This experimental study uses isotopically and chemically characterized fluids as tracers to monitor isotope exchange resulting from diffusion during dolomite breakdown. Through the use of dolomitic marble cores of various grain size and texture and by controlling pressure and temperature conditions, our experiments were effective in observing the transport of fluids and exchange of isotopes that occurred in natural rocks.

2. Methods

2.1. Experimental techniques

Two nonsiliceous dolomitic marble samples were selected from the Reed Dolomite, Tonopah, Nevada (see Figure 1). The Reed Dolomite is a massive, brown to tan, medium- to coarse-grained dolomitic marble that contains rare thin layers of phyllite, quartzite, and calcitic marble (Richards et al., 1996). Sample LM57, from Lone Mountain, Nevada, is light-gray, homogeneous, and contains equant dolomite grains ranging in size from 0.25–0.50 mm in diameter. This sample is 95% dolomite, with minor amounts of quartz and opaque minerals, and has a slightly friable texture. Sample MR22-2, from Mineral Ridge, Nevada, is light-gray to yellow in color. Average dolomite grain size ranges from 0.5 to 1.0 mm in diameter and are irregular in shape. This sample also contains minor quartz veins and intergranular fractures.

Small cores, approximately 4 mm in diameter and 5–7 mm in length, were drilled from each marble sample. The cores were placed within thin-walled, 5 mm gold tubes, approximately 7.5 cm in length. An aliquot of $H_2{}^{18}O$ or $HD^{18}O_{0.5}{}^{16}O_{0.5}$ was added to each sample, and the capsules were purged with CO_2 gas and welded closed. The prepared capsules were placed in a vacuum oven for approximately 24 hours and then reweighed to ensure that there were no leaks. A capsule was positioned in a cold-seal hydrothermal apparatus and pressurized and heated for the desired experiment duration. Each experiment was heated to the desired temperature over a period of thirty to forty minutes. During the course of each experiment, both pressure and temperature were monitored and recorded. The experiment was isobarically quenched to ambient temperature over a period of fifteen to thirty minutes. The capsule was then removed from the hydrothermal apparatus, weighed to test for leakage, placed in a vacuum line, and punctured.

Any CO_2 gas produced by reaction was measured by manometry. The sample was then removed from the gold tube, embedded in epoxy, and sectioned longitudinally.

Fifteen rock-core experiments were conducted at a pressure of 100 MPa and over a range in temperature from 650 to 750 ℃, with the duration of experiments lasting from two days to two months. See Table 1 contains a detailed list of all experiments.

2.2. Analytical techniques

Reaction products, reaction textures, and extent of reaction were determined by petrographic, electron microprobe (EMP), and X-ray diffraction (XRD) analysis. For generation of back-scattered electron (BSE) and Ca, Mg, Si, and Fe X-ray images, the EMP had an accelerating voltage potential of 15 kV, a beam current of 4 nA, and a beam size of 1 µm. Images were generated by rastering over the area of interest, generally 256 x 256 µm using a 2 µm step with a counting time of 1 ms per step. Stage scanning was used for most images, though beam scanning was used for detailed images smaller than 128 x 128 µm. Quantitative mineral analyses were also collected with the EMP (Table 2). For these analyses, the EMP had an accelerating voltage potential of 15kV, a beam current of 6 nA, a beam size of 1 µm, and a counting time of 40 seconds for most elements. Natural standards of calcite, dolomite, and periclase were used for calibration. A Siemens D500 θ–θ X-ray powder diffractometer was used to identify minerals present in experimental samples. Analyses were run using a Cu Kα tube at 40 kV and 30 mA, from 5 to 50° 2θ, with a 0.2° step, and with 30 s counting time per step.

Isotope transport was observed by both ion imaging and isotope-ratio analysis. Ion imaging and isotope-ratio analysis was performed with use of a Cameca 4f secondary ion mass spectrometer (SIMS) at Oak Ridge National Laboratory. Ion images were generated by rastering over a 250 x 250 µm area with a picoampere Cs^+ primary beam. A counting time of 30 s was used for ^{16}O images, and a counting time of 180 s was used for ^{18}O images. Isotope-ratio analyses were collected with the use of a picoampere Cs^+ primary beam, with spot sizes generally about 10–15 µm and with no energy offset.

Co-registered X-ray and ion images were generated with use of RSI ENVI 4.0 software by selecting corresponding ground control points and warping the ion image to match X-ray image dimensions.

3. Results and Discussion

3.1 Isotope transport and exchange

Two series of experiments were performed. In the first series, experiments were carried out at constant T and P of 700 ℃ and 100 MPa, with durations ranging from 2 to 59 days. In the second series, experiments were carried out at 100 MPa for 30 days, with temperatures ranging from 650 to 750 ℃. All experiments contained an excess of either $H_2{}^{18}O$ or $HD^{18}O_{0.5}{}^{16}O_{0.5}$, ensuring x_{CO_2} conditions favorable for the formation of calcite and periclase.

Average δ^{18}O values from dolomitic marbles of the Reed Dolomite have been measured by Richards et al. (1996) and range from 11.1‰ to 21.5‰ (SMOW). Since all of our experiments contain either $H_2{}^{18}O$ or $HD^{18}O_{0.5}{}^{16}O_{0.5}$, the amount of ^{18}O in the introduced water far exceeds the amount in the original dolomitic marble. Any measured increase in the ^{18}O of our experiment cores, therefore, can be assumed to result from exchange with the fluid.

All experiments, regardless of duration or temperature, show some degree of reaction. Areas of reaction generally began near the ends of the core and eventually reached the middle. Figure 8 contains a Mg and Ca X-ray map with an ion image inset from the middle of the MR2 (700 ℃, 2 days) rock core. Although there are no visible reaction products near the center of this sample, the ion image inset in Figure 8 indicates that fluids infiltrated the sample along grain boundaries after only two days.

Reaction products were found primarily along grain boundaries, fractures within grains, and along the outer edge of the rock core. Figure 9 contains a Mg and Ca X-ray map with an ion image inset from MR6 (700 ℃, 29 days) that shows reaction products that formed along a grain boundary. The ion image inset in Figure 9

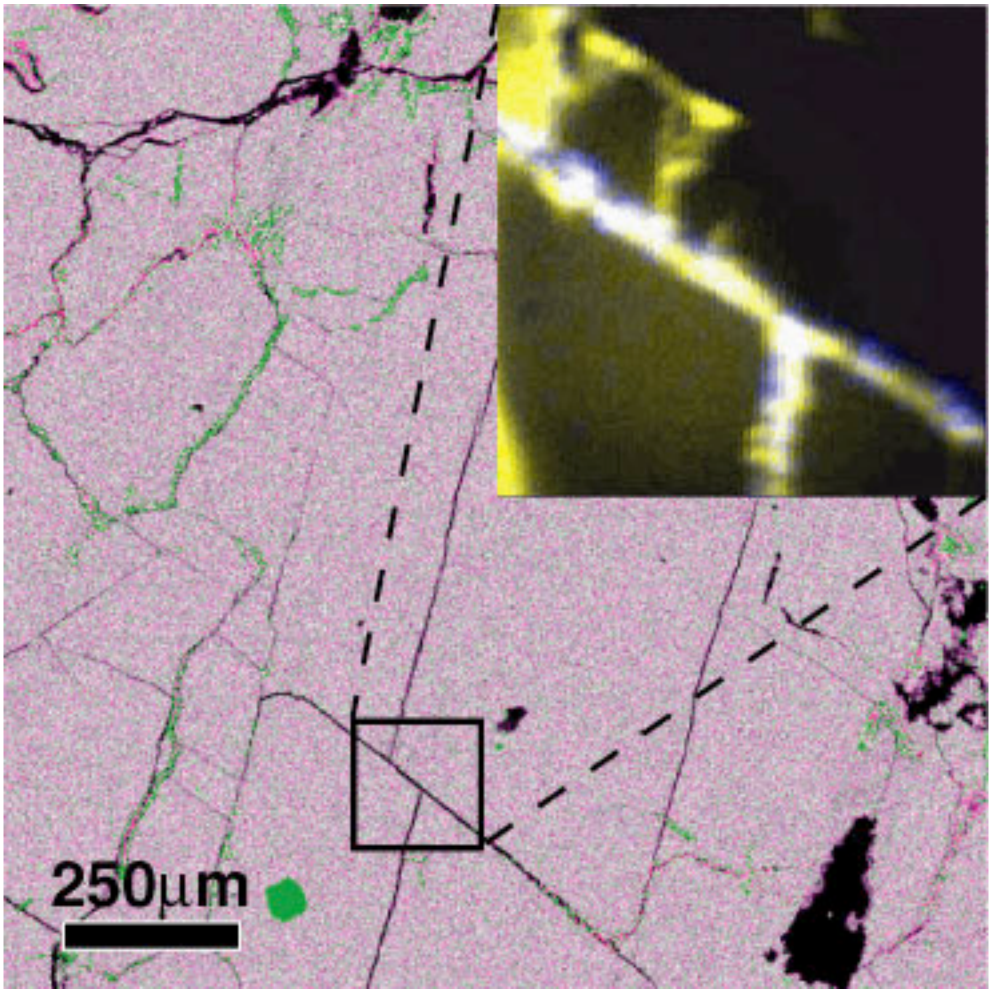

Figure 8. MR2 (700 °C, 2 days) X-ray image (Mg – dark pink, Ca – green, dolomite – green/dark pink mix) with ion image inset (^{16}O – yellow, ^{18}O – blue, ^{16}O & ^{18}O – white). Ion image show enrichment of ^{18}O despite the lack of reaction products indicating fluid infiltration occurs quickly.

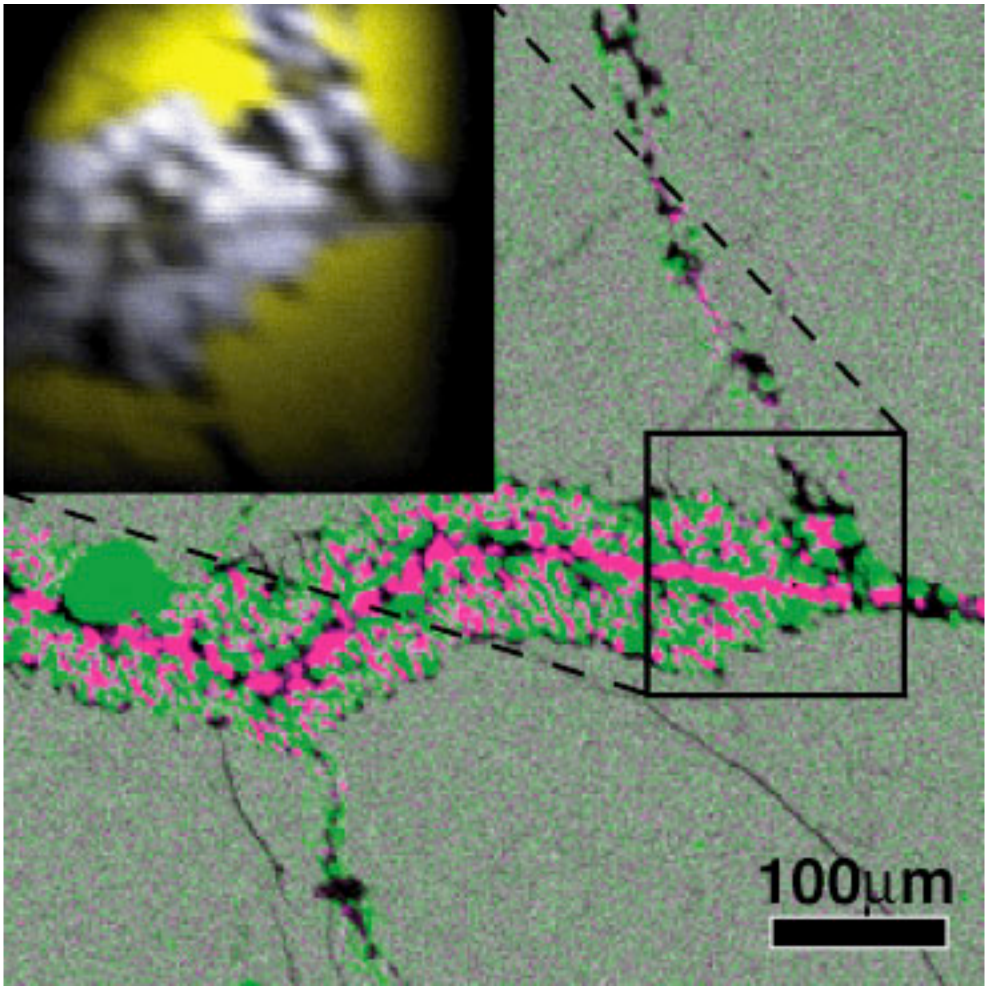

Figure 9. MR6 (700 °C, 29 days) X-ray image (Mg – dark pink, Ca – green, dolomite – green/pink mix) with ion image inset (^{16}O – yellow, ^{18}O – blue, ^{16}O & ^{18}O – white). X-ray image shows formation of reaction products within grain boundaries. Ion image shows that reaction products are enriched in ^{18}O indicating that they formed by exchanging with infiltrating fluids.

shows elevated ^{18}O within the reaction products indicating that they exchanged with the infiltrating fluid.

Elevated levels of ^{18}O were also apparent from ion imaging along the edges of unreacted dolomite grains. Figure 10 is a co-registered image of an area of LM7 (700 ℃, 29 days) composed of a Mg X-ray image, a Ca X-ray image, and an ^{18}O ion image. Areas of red are Mg-rich, blue are Ca-rich, and purple are dolomite. Other colors represent areas of ^{18}O enrichment. Green areas along the rims of dolomite grains show a marked increase in ^{18}O. To quantify the extent of isotope exchange through the dolomite grains, isotope ratio analyses were collected along traverses from the rim to the core of the dolomite grains. The traverses verify the enrichment qualitatively seen in the ion image, with values of 4783‰ relative to the grain core in grain G1 and a value of 865‰ relative to grain core G2.

3.2 Implications

The transport of isotopes within our experiments primarily occurred along grain boundaries. Shorter duration experiments showed elevated levels of ^{18}O in the center of rock cores despite the lack of reaction products. This indicates that initial transport of fluid though the cores occurred quickly. No reaction products were found without elevated values of ^{18}O, thereby confirming the necessity of fluid present during reaction.

Enrichment of ^{18}O along the edges of unreacted dolomite grains suggest that either recrystallization of dolomite or exchange through the dolomite crystal lattice may have taken place. It is equally plausible, however, that dolomite grains contain microfractures that is allowing diffusion of ^{18}O. Bowman et al. (1984), for example, describe thin, interconnected networks of calcite within the periclase zone marbles

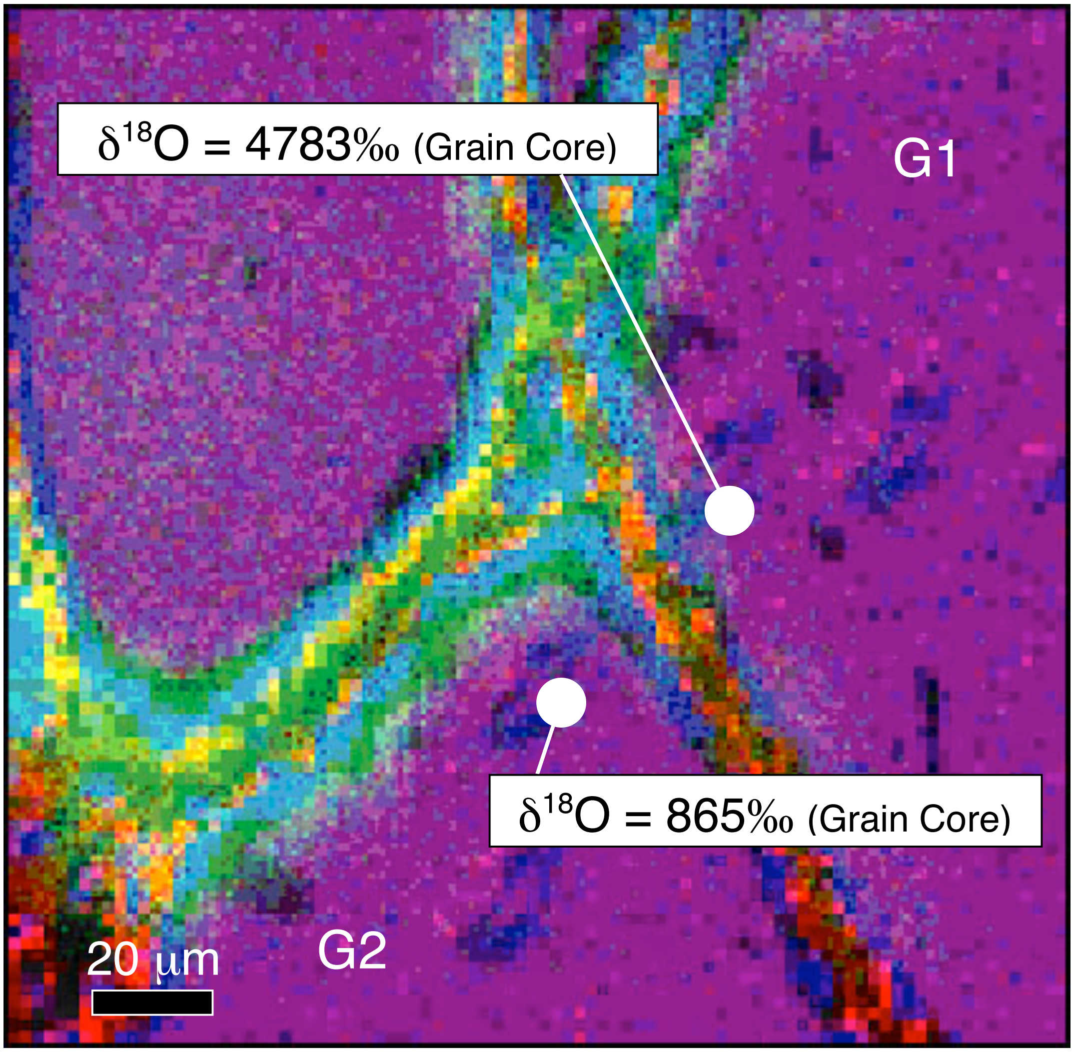

Figure 10. A co-registered image of an area of LM7 (700 °C, 29 days) composed of a Mg X-ray image, a Ca X-ray image, and an ^{18}O ion image. Areas of red are Mg-rich, blue are Ca-rich, and purple are dolomite. Other colors represent areas of ^{18}O enrichment. Green areas along dolomite grain boundaries represent ^{18}O enrichment near dolomite grain rims. Additional isotope-ratio spot analyses are labeled and show significant enrichment in rims relative to unaltered grain cores.

in the Alta contact aureole that they interpreted as healed microfractures formed by infiltrating fluids that altered the isotopic composition of the calcite. While microfractures might explain the elevated levels of ^{18}O within dolomite grains, additional experiments using luminescent tracers such as manganese or dysprosium oxide need to be performed in order to view possible microfractures by cathodoluminescence.

The introduction of fluids containing at least 50% ^{18}O have proven effective as tracers within our rock core experiments. Although these amounts of ^{18}O do not occur naturally in contact metamorphic environments, the processes of grain boundary diffusion and isotope exchange and transport that they highlight are common in natural settings.

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Vita

Michael Thomas DeAngelis was born on September 21, 1975, in Milwaukee, Wisconsin. He was raised in Waukesha, Wisconsin, where he attended Hadfield Elementary School and Central Middle School. It was in elementary school that Michael first became interested in the study of geology, having worked on an independent project to build a ”glacier-in-a-box” and spending countless hours exploring the glacially sculpted landscape of the Kettle Moraine areas of southeastern Wisconsin. He graduated from Waukesha South High School in the spring of 1993.

After graduating from high school, Michael attended the University of Wisconsin – Madison where he majored in geology with an emphasis in metamorphic petrology. His senior thesis project focused on skarn formation within calc-silicate rocks related to the Morin Anorthosite Massif, Quebec.

After completion of his undergraduate degree in the spring of 1998, Michael worked as a computer programmer for the next four years. He returned to the study of geology in the fall of 2002, attending the Department of Earth and Planetary Sciences at the University of Tennessee in Knoxville under the advising of Dr. Theodore C. Labotka. There his research focused on determining the kinetics of dolomite breakdown commonly associated with metamorphism within contact metamorphic aureoles. He is planning on pursuing a doctorate degree in geology.