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# GEOCHEMISTRY AND ORIGIN OF REGIONAL DOLOMITES

## FINAL REPORT

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## INTRODUCTION

The main goal of our research on dolomites has been to better understand the composition of the fluids and processes of the fluid-rock interaction responsible for the formation of massive dolostones occurring over regional scales within sedimentary sequences. Understanding the timing of dolomitization, the fluids responsible for the dolomitization and the timing of the development of porosity has major economic ramifications in that dolomites are major oil reservoirs often having better reservoir properties than associated limestones. Our approach has been to apply trace element, major element, petrographic, crystallographic, stable isotope and radiogenic isotope systems to test models for the origins of dolomites and to give information that may allow us to develop new models. Fluid compositions and processes are evaluated through the use of numerical models which we have developed showing the simultaneous evolution of the trace element and isotope systems during dolomitization. Our research has included the application of B, O, C, Sr, Nd and Pb isotope systematics and the trace elements Mn, Fe, Sr, rare earth elements, Rb, Ba, U, Th, Pb, Zn, Na, Cl, F and $SO_4^{2-}$. Analyses are possible on individual cements or dolomite types using micro-sampling or microprobe techniques.

In some cases significant effort has been required for developing specific analytical techniques. Macro and micro-samples are analyzed at Stony Brook using: one of our three surface emission mass spectrometers for isotope dilution or isotope composition analysis, ion chromatography or DCP. Oxygen and carbon isotopes are analyzed at outside laboratories, mainly at the University of Michigan. The microprobe techniques used include synchrotron X-ray microprobe analysis at Brookhaven National Laboratory or electron microprobe at Stony Brook.

Lack of a modern analogue for ancient massive dolostones has limited the application of the uniformitarian concept to developing models for the ancient regional dolostones. In addition it has not been possible to synthesize dolomite in the laboratory under conditions similar to the sedimentary or diagenetic environments in which the dolomites must have formed. The result of this is the strong reliance of the carbonate research community on ancient examples for understanding regional dolostones. Recognizing this, we asked how we might better geochemically exploit ancient dolomites to better understand their origins. At the time of inception and development of our project, trace element and stable isotope geochemistry was widely applied to dolomites, however, our project was unusual in melding expertise in "hard rock" geochemistry (Hanson) with expertise in carbonate petrology (Meyers). Specifically, our philosophy was to apply geochemical approaches that had been highly successful in igneous and metamorphic petrology to carbonate diagenetic systems. We also recognized that successful application of geochemical approaches, especially new approaches, requires thorough petrographic and stratigraphic characterization of the diagenetic history of the studied unit. Our geochemical research on dolomites therefore had the goals of:

1) developing geochemical approaches new to diagenetic studies,
2) combining these new data with the existing trace element and isotope geochemical data in quantitative modelling of fluids and processes, and
3) producing Ph.D. students with expertise in both carbonate petrology and the application of isotope and trace element geochemistry to carbonate diagenesis.

Our project has achieved these goals as we show in the following discussion.

In the context of the impact of the project on dolomite studies in general, success of Banner's work and subsequent students' projects clearly showed the importance and usefulness of quantitative modelling of simultaneous variations of several geochemical parameters (rather than one or two) during water-rock interaction to constrain dolomitizing fluid chemistry and processes. Although, our group was not the first to apply water-rock modelling to carbonate diagenesis, the success and innovativeness of our studies have focussed attention of the carbonate community on its usefulness. One manifestation of this is the increasing number of publications on dolomites that apply water-rock interaction modelling to interpret trace element and stable isotope patterns, and the wide citing of Banner and Hanson's publications. In terms of new geochemical approaches, our group was one of the first to apply Sr isotopes to modeling diagenetic systems (others developed the seawater Sr isotope curve for stratigraphic and relative dating purposes, which we have subsequently used in our diagenesis studies); the first to apply the U-Th-Pb system to carbonate diagenesis studies and the dating of unconformities, and the first to develop and use B isotopes in carbonate formation and diagenesis.

The rocks we initially selected for a detailed petrographic and geochemical case study were the Mississippian (Osagean) Burlington-Keokuk Fms. of Iowa, Illinois and Missouri. We chose this because of its well known stratigraphy, there are extensive dolomites in subtidal shelf limestones, there is well defined cement and dolomite zonal stratigraphy as determined from cathodoluminescence, and it is similar to other porous and permeable shelf dolomites that are hydrocarbon reservoirs. Our plan from the beginning was to first apply our geochemical techniques to this sequence of rocks to evaluate their diagenetic history; and to then apply the approaches to sequences that have quite different tectono-sedimentary settings, including those that are oil-producing reservoirs. As a result the Burlington-Keokuk Fms. became a valuable natural laboratory for developing new geochemical approaches because of the wealth of petrographic and geochemical background data we have amassed. We then extended our work to Devonian, other Mississippian carbonates, and to Neogene carbonates.

## RESULTS

Details of results of these studies are included in the theses and publications cited. Below are general summaries of some of our important results and conclusions:

1. The project has clearly demonstrated that carbonate petrologists need not be restricted to "traditional" geochemical approaches of stable isotopes and a few trace elements for diagenetic studies. Our project has applied and in some cases developed techniques for high precision analyses of microsamples (rather than solely whole rock) for Sr isotopes, REE, U, Pb, U and Pb isotopes, B and B isotopes, Na, Cl, F and sulfate.
2. The project has shown that high precision U-Pb dating can be accomplished on some U-enriched diagenetic phases, thus opening the door to the possibility of wider absolute dating of depositional ages and of diagenetic components in sedimentary rocks.
3. The quantitative modelling of simultaneous variations of isotopes and trace elements has proven extremely useful in constraining composition of dolomitizing fluids, differentiating mixing from water-rock interactions, identifying extraformational sources of chemical constituents and in some cases constraining their sources, in Sr isotope dating of Neogene strata and their diagenetic phases, and in assessing dolomite neomorphism.
4. Our case studies have confirmed that most massive dolomites involve several episodes of dolomitization, even in Neogene examples.
5. Our case studies have clearly shown that there is no single hydrologic/geochemical model that explains most massive dolomites. Instead they show that large relatively massive dolomite can be formed by subsurface brines (Burlington, Swan Hills Fms.), seawater evaporitic brines driven by sea surface circulation (Miocene of Spain), brackish groundwaters driven by mixing zone dynamics (Burlington, Seroe Domi Fms.), and relatively normal seawater driven by mixing zone circulation below the base of a fresh water lens (Devonian, W. Australia). This is important because there is a strong sentiment in the carbonate community that most massive dolomites are seawater dolomites.
6. Our case studies have shown that the scale and effects of dolomite recrystallization can be assessed through combined petrographic and geochemical approaches (e.g. Swan Hills, Burlington, Devonian of W. Australia). They have shown that many dolomites have not been neomorphosed, and in some cases, pristine and neomorphosed dolomites can easily be differentiated, one of the clearest examples being the Burlington dolomites. This is important because there is a sentiment in the carbonate community that

most ancient dolomites have been recrystallized and therefore their geochemistry cannot be used to determine their origin.

Our geochemical approaches have been and are applied to rock suites that have been studied in great detail stratigraphically and petrographically, and have been well characterized by conventional geochemical parameters. We have studied carbonate strata of academic and economic interest. Our earlier efforts were dominantly in Devonian and Mississippian carbonates, while more recent efforts have included Neogene carbonates. A listing of the areas of study can be deduced from the titles of the MS and Ph.D. theses and publications at the end of this report.

That our research provided "fundamental knowledge and understanding in the Geosciences to support National Energy Policy goals" is reflected in the interest that the oil industry has had in our research and their willingness to help support the research once DOE provided the initial base funding. When we first began discussions with members of the DOE Geosciences Research Program regarding the proposed studies on the geochemistry and origins of regional dolomites we were strongly encouraged to approach the oil industry to help supplement the DOE funding for our studies. We did approach members of the oil industry with our DOE proposal and received a warm welcome both in terms of financial support and willingness of their personnel to attend our short courses. As a result field and petrographic research on some of our studies has been supported by funding from the Petroleum Research Fund of ACS, Texaco, Amoco, Arco, Champlin, Marathon, Chevron, Unocal and Exxon. The support from DOE was essential, because it has been used to develop the geochemical approaches and maintain geochemical facilities. The funds from the other sources have been only adequate to pay student stipends or support field work. Typically the funding from any one oil company has been $5,000 to $15,000 per year. It has been made quite clear by representatives of some of the oil companies that without the support of DOE to maintain the geochemical studies, their companies would be reluctant to offer any support, because significant results would be unlikely. Without the support from agencies other than DOE we would not have had as many studies going on simultaneously. Having a number of studies of dolomite under different conditions and by different approaches occurring simultaneously has been of great advantage to the individual researchers because there is significant feedback and a lively, but healthy, questioning of the various investigators' results and interpretations. As a result we have attracted a relatively large number of high quality, productive graduate students interested in carbonate diagenesis to Stony Brook.

## PROJECT OUTPUT

Below we summarize the results of some of the more recent studies.

### Trace element and isotope systematics during Water-Rock Interaction

A valid criticism of trace element and isotopic geochemical studies is that the analytical data are often used quite indiscriminantly as fingerprints. Using the fingerprint approach does not take into consideration that during diagenesis the fluid and rock are both evolving. We would suggest that it is more appropriate to describe how a given element changes concentration or isotopic composition in the fluid and rock as a function of initial concentration, physical process of diagenesis (e.g. water-rock interaction, dissolution-reprecipitation, etc.), magnitude of the distribution coefficient, porosity, etc. We have made progress in understanding the factors controlling the rate of change of trace element abundances and radiogenic and stable isotope ratios during equilibrium water-rock interaction. Oxygen isotope ratios in a carbonate will be reset to the equilibrium value with water at a water-to-rock ratio (mass) of 2.5 for a rock with negligible porosity, and a water-to-rock ratio of 5.6 for a rock with 75% porosity. The water-to-rock ratio is dependent on the abundance of oxygen in the fluid and rock and porosity. Because the oxygen content in water and rock have only a limited variability, the water-to-rock ratio varies only with the porosity. The rate at which delta $^{13}C$ varies during water-rock interaction is a function only of the total dissolved carbon in the water. The rate at which cations vary in a limestone or dolomite is a function of the Ca and/or Mg ion concentration in the water and the cation/Ca and/or cation/Mg distribution coefficient and to a lesser extent the porosity. For example, the Sr isotope ratio of a limestone with 50% porosity interacting with brine a with 20,000 ppm Ca will attain the fluid's Sr isotope ratio in about 5 water-to-rock ratios similar to the rate at which oxygen is re-equilibrated. However, if the water has 40 ppm Ca in solution, a water-to-rock ratio greater than 2000 is required to equilibrate the fluid. Thus, on a plot of delta $^{18}O$ vs $^{87}Sr/^{86}Sr$ the effects of a Ca-rich brine can easily be distinguished from freshwater even though the end-member compositions are identical. While the value of the Sr/Ca distribution coefficient will affect the water-to-rock ratio required to re-equilibrate the system, because of the very large differences in the Ca concentrations between freshwater and brine, the nature of the interaction is not very sensitive to the exact value of the distribution coefficient.

### U-Pb systematics at an unconformity

The Wahoo Fm. is a 60 to 90 meter thick sequence of limestones and dolostones deposited in an interior platform setting as a mosaic of lagoonal and shoal facies. At Prudhoe Bay the Wahoo Fm. is buried to more than 3000 m and forms a giant hydrocarbon reservoir of the Lisburne Field. The sequence is overlain unconformably by the Kavik Shale (Upper Permian). The age of the Kavik Shale broadly constrains this bounding unconformity to be pre-Upper Permian and therefore this feature is commonly referred to as the PUPU.

A zone of extensively dolomitized rocks occurs just beneath the PUPU. These rocks have been termed "hot" dolostones because they are enriched in U (up to 55 ppm). Based on spatial relationships and trace element gradients away from the PUPU, dolomitization is thought to post-date formation of the unconformity. The Pb in the dolostones exhibits a considerable spread in uranogenic Pb , but little spread in thorogenic Pb implying enrichment of U relative to Th. Induced fission track analysis (P. Swart, Univ. Miami) indicates that U is enriched in minor, non-carbonate phases (most likely authigenic clays). The relative enrichment of U is undoubtedly related to the greater mobility of U compared to Th at near-surface conditions. A regression of the Pb data yields an age of $263 \pm 40$ Ma. The age and the uncertainty are comparable with the estimated time and duration of exposure of the PUPU. The lack of evidence for resetting of the Pb isotope system during burial dolomitization in the Permo-Triassic and development of an extensive unconformity in the Lower Cretaceous indicates that the Pb isotope system in carbonates is relatively robust to subsequent diagenesis.

A more detailed summary of Pb isotope studies in dolomitic rocks is appended.

### Boron Isotopes in Carbonates

We have developed procedures for analysis so that reproducibility is better than $\pm 0.75‰$ ($2\sigma$) for less than 1 ng of B. We predict that the wide range of boron isotope compositions and boron abundances of various waters will allow boron isotope systematics in carbonates to characterize the fluids responsible for their precepitation. Seawater has consistent boron isotope composition $\delta^{11}B$ of +40 (relative to NBS 951) and abundances (4.5 ppm) independent of latitude or water depth. The first part of these studies was to evaluate the boron isotope composition of marine carbonates of diverse locations and types. It was found that marine carbonates independent of temperature, host organism or mineralogy have a small range in $\delta^{11}B$ +19 to +25 whereas they have a rather large range in abundances, 1 to 100 ppm. It is suggested that the boron isotope composition of carbonates is controlled by pH and the isotopic compostion of the fluid. pH determines the relative abundances of the $B(OH)_3$ and $B(OH)_4^{1-}$ species. For seawater there is a fractionation factor of 1.0194 between $B(OH)_3$ and $B(OH)_4^{1-}$ at 25°C with only a small variation with temperature. It is concluded that only the $B(OH)_4^{1-}$ species is incorporated in the carbonate. Thus, boron isotopes have the capability of determining the pH of waters. Recently begun collaborative research with Wally Broecker shows that modern planktonic foraminifera based on their boron isotope ratio give a pH of 8.2 and benthonic foraminifera give a pH of 7.8. Both of these results are consistent with the known pH of the seawater in which they grew. Further studies are planned to determine seawater pH at various times during the Quaternary which will allow an evaluation of paleo-atmospheric $CO_2$ abundances.

Mississippian (Waulsortian) marine cements were chosen for study because they are pristine based on oxygen and strontium isotopes (Douthit *et al*, in press). The boron isotopic composition of all samples fall within a relatively narrow range (0 to +2.5‰) whereas modern marine carbonates have values of +19 to 25‰. Boron abundances range from 32 to 65 ppm, similar to that found in modern marine carbonates. Pristine Mississippian brachiopods, however, have boron isotope compositions of +17‰ with 20 to 40 ppm B which would suggest that B isotope composition of Mississippian seawater is lighter than modern seawater (+34 and +40‰ respectively), but not as different as the marine cements might suggest. If this is the case, the isotopic composition of boron may be an important criterion for establishing whether a carbonate phase is pristine.

A more detailed summary of recent experimental studies of Mineral/fluid partitioning and isotopic fractionation of boron in laboratory grown calcite is appended.

### Dolomitization of Late Miocene Reef Complexes

An important component of our investigations into massive dolomites has been the study of diagenesis in late Miocene reef complexes in Mallorca. Continuation of this work at Nijar, mainland Spain, is being continued in order to test the regional applicability of the evaporitic seawater dolomitization model derived from the Mallorca study. The study of Mallorcan reefs (Ph.D. research of Erik Oswald) has shown that young Tertiary rocks are particularly attractive laboratories for diagenetic work because of the generally excellent timing constraints provided by Sr isotopes, accurate knowledge of precursor mineralogies, detailed eustatic sea-level curves. These Upper Miocene reefs are well preserved and well exposed, and their stratigraphy and facies have received detailed study, their paleotopographic setting is well known, and the lack of deeper-burial diagenesis reduces the number of applicable dolomitization models, and because they (along with other late Miocene reefs around the western Mediterranean) provide the most modern example of a large-scale, reef- rimmed evaporite basin, a common setting for ancient reefs.

The major conclusion is that Mediterranean Messinian evaporitic seawater was the dolomitizing solution of Messinian reefs in Mallorca, the evaporitic brines forming during evaporitic drawdown, and dolomitization of reefs rimming the Western Mediterranean occurring during the subsequent re-filling of the basin(s) by seawater. Evidence for this model is the Messinian age of dolomites as constrained by stratigraphy and by Sr isotope ages, dolomite distribution, dolomite geochemistry ("heavy" O isotopes, elevated Na, Cl, sulphate contents), quantitative modelling of covariation of geochemical parameters, spacial trends in geochemical parameters, and petrography (distinctive spheroidal fabrics). The model is also supported by thermodynamic modelling of dolomite replacement of limestone by hypersaline brines.

### Analysis of $SO_4^{2-}$, $F^{1-}$ and $Cl^{1-}$ in Dolomitic Rocks

Although there has been a fair amount of work on Na as a paleosalinity indicator of dolomitizing fluids, there has been very little use of anions. In combination with cation abundances and stable isotope data, the abundances of $SO_4^{2-}$, $Cl^{1-}$ and $F^{1-}$ can be used to distinguish freshwater from seawater-derived brine origin of the potentially dolomitizing fluid. Although this information can also be obtained from fluid inclusion work, the direct analysis of these anions has several advantages. First, the analysis can be carried out on any type of dolomite crystals and dolomite cements, and second, it is possible to evaluate whether these anions are mostly present in fluid inclusions or incorporated in the dolomite crystals.

Willie Staudt has developed a high precision technique for the analysis of these anions using Ion Chromatography. Miocene dolomites from Spain interpreted to have formed from seawater evaporitic brines, generally have greater concentrations of Cl, and sulfate than "non- evaporitic" dolomites. A plot of Na abundances in the dolomites versus Cl concentrations shows good covariation with the regression line having a slope much less than one, the slope that would prevail if all Na and Cl were in halite or evaporitic brine inclusions. Thus most of the Na is probably incorporated in the dolomite lattice. Increasing concentrations of Na may reflect increasing sodium relative to calcium and magnesium in the dolomitizing solution.

Sulfate is an abundant anion in most proposed dolomitizing solutions. Sulfate concentrations in dolomites may be related to the relative abundance of sulfate relative to total dissolved carbon in dolomitizing solutions. The positive covariation of Na and sulfate in the Mallorcan samples suggests that sulfate is not derived from solid inclusions of gypsum and that both sodium and sulfate are related to their relative concentrations in the dolomitizing solution.

### Dolomitization of the Seroe Domi Formation Cuaracao, Netherlands Antilles

The Ph.D. thesis research of Bruce Fouke shows that the Seroe Domi Formation is a partially dolomitized 350m thick sequence of mixed carbonates and siliciclastics deposited on the flanks of the Cuaracao horst in deep forereef to reef environments. Biostratigraphy and Sr isotope stratigraphy on shell material has established that the age ranges from Middle Miocene to Early Pleistocene. Three petrographically and geochemically distinct dolomites have been mapped in the Seroe Domi, Dolomites I, I' and II. Petrographic relationships with calcite cements and and shell molds, stable isotopes, Na, Cl, sulphate, Sr and other trace elements plus quantitative modelling of their co-variations indicates that these dolomites were precipitated from fluids derived from mixing of normal seawater with freshwater that took place soon after subaerial exposure and stabilization of the host limestone. They clearly are not evaporitic dolomites as has been proposed for the Seroe Domi on other Antillean islands. Stratigraphic distribution and Sr isotope chronology suggests that Dolomite I was precipitated during late Middle Miocene to early Late Miocene, Dolomite I' was precipitated during Late Miocene to Early Pliocene. Dolomite II is distinctive in having some Sr isotope values less radiogenic than host limestone and in having elevated concentrations of Zn and Cu (compared to Dolomites I and I"). Dolomite II, therefore, precipitated from mixed fresh water and seawater that interacted with the basement or basement-derived clastics during Late Pliocene to Early Pleistocene. Each of these successive events of deposition, meteoric stabilization and dolomitization correlate with significant third-order sealevel lowstands and their ensuing sealevel rises.

## PH.D. AND MS STUDENTS

Eight MS students and nine Ph.D. students associated with this project have completed their studies at Stony Brook.

### MS. Theses

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