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TECHNICAL PROGRESS REPORT
GEOCHEMISTRY AND ORIGIN OF REGIONAL DOLOMITES

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This grant supports the geochemical aspects of the research directed by Profs. W.J. Meyers and G.N. Hanson on the origins of regional dolomites. The field aspects and the stipend for most of the graduate students has been provided by donations from oil companies and by grants from NSF and ACS-PRF. Without the central DOE support for the geochemical studies the other support would be more difficult to obtain. As a result the DOE support is significantly leveraged. Eight graduate students are involved in research on dolomite allowing the diverse range of studies outlined below.

Gary Hemming for his Ph.D. thesis research has developed an analytical procedure for the negative ion analysis of boron isotopes, so that samples as small as a nannogram of boron can be analyzed on milligram size carbonate samples with a precision of about 0.5 per mil or better. The ultimate goal is to place constraints on the types of fluids responsible for dolomites. The results of the studies to date on modern marine carbonates are published in Hemming and Hanson, 1992. The major conclusion is that modern carbonates whether aragonite or calcite, biogenic or inorganic have the same isotope composition, within about 1 per mil two sigma, independent of temperature. In contrast to the small variations in isotopic composition, there are large differences in the B abundance (11 to 71 ppm).

Results on the boron isotope composition of Mississippian marine cements suggest that they have a much lower $^{11}B/^{10}B$ ratio than carbonates from modern seawater. Pristine Mississippian brachiopods, however, have $^{11}B/^{10}B$ ratios more similar to carbonates from modern seawater. These differences suggest that the fluids responsible for marine cements may have a complicated history (Hemming and Hanson, 1991).

In contrast to marine water and carbonates, freshwaters and freshwater carbonates have much lower B abundances. Groundwaters precipitating carbonate from Texas and Oklahoma have B abundances of less than 50 ppb. Their isotopic composition is similar to that for modern marine carbonates. These results are consistent with the B being derived from ancient marine carbonates.

Wilfried Stoudt has just passed his preliminary Ph.D. exam. He has developed an ion chromatographic technique for the analysis of Cl, SO_4, and F abundances in carbonates with an emphasis on dolomite. He finds that on scatter diagrams there are distinctly different fields for dolomites derived from burial brines, evaporitic brines and seawater/mixing brines (Staudt, Oswald and Schoonen, 1992). These results have prompted him to determine experimentally the distribution coefficients for Cl, F, Na and SO_4 in fluid-calcite and fluid-dolomite systems.

John Hoff has just finished his Ph.D. thesis on the Pb isotope chemistry of regional dolomites in the Mississippian Burlington-Keokuk Fms. and the Pennsylvanian Wahoo Fm. One of the most exciting aspects was his discovery that some samples of the Mississippian Burlington-Keokuk dolomites of Illinois, Iowa and Missouri had a large excess of recent

uranium. He concluded that this excess U was most likely due to recent weathering during which U was mobilized and transported to the dolomites, where the U was reduced and deposited. Jeremy Jameson of EXXON who was studying the diagenesis of hot dolomites (i.e. enriched in U) from the Pennsylvanian Wahoo Fm. on the North Slope in Alaska became interested in John's results and provided samples for John to analyzed. Presumably they had U added to them associated with a pre-upper Permian unconformity. The U-Pb and Pb-Pb ages showed that this was indeed the case.

John has just developed a new procedure for the separation of Sr and Pb from carbonates using Sr specific columns. This has made the Pb and Sr chemistry much simpler and lowered blank by factors of 5 to 10 compared to the older procedures.

Bruce Fouke's Ph.D. thesis research is on dolomitization of periplatform slope facies in the Seroe Domi (middle Miocence to Plio-Pleistocene), Curacao, Netherland Antilles. Petrography and geochemical characterization shows three distinct types of dolomite that exhibit a regional zonal stratigraphy based on cathodoluminescence. Based on the stratigraphy, petrography and geochemistry, he has developed a model involving two major episodes of dolomitizaton probably by brackish or seawater fluids. This work clearly establishes the time-stratigraphy of the Seroe Domi, absolute timing of dolomitization. Comparison with others research shows that dolomitization of the Seroe Domi has been accomplished by more than one process (reflux of evaporitic brines on Bonaire) on the several islands.

Bruce Fouke has found sector zoning in some dolomite rhombs. Sector zoning of this type has previously been recorded for dolomites only from the Mississippian Burlington Formation of Iowa (Reeder and Prosky, 1986). Systematic trace and major element differences occur between synchronously precipitated nonequivalent growth sectors in individual rhombs based on electron microprobe analysis in the ESS Department at Stony Brook and with Synchrotron X-ray Flouresence Micro-Analysis (SXRFMA) at the National Synchrotron Light Source facilities at Brookhaven National Laboratories. These results have been submitted for publication (Fouke and Reeder, submitted)

Erik Oswald, who is presently working for EXXON, will defend his Ph.D. thesis in June, 1992. His study is on dolomitization in Miocene reef complexes, Mallorca, Spain. He has developed a model for massive dolomitization by evaporitic Messinian Mediterranean seawater, that promises to be widely applicable. A paper describing geochemical modelling of the evolution of this dolomitizing fluid has been reviewed and is being revised (Oswald and Schoonen, submitted).

Beatrix Packmoor is preparing her proposal for her Ph.D. thesis which is a continuation of the studies on dolomitization in Miocene reefs. She will focus on a reef complex in southern mainland Spain. The goal of this will be to compare the age, stratigraphy, and dolomitization history with that on Mallorca to test the general applicability of the "Oswald model" to late Miocene reefs of Spain.

Bibek Ghosh finished his M.S. thesis in August, 1991 on the diagenesis of crinoids in the Burlington-Keokuk Formation. Crinoids contain the earliest cements, and show consistent regional variations in stable isotopes compositions. His study focused on the regional distribution of the microdolomite contents of crinoids, and their trace element contents.

Bruce Ward will complete his Ph.D. thesis this summer on regional limestone diagenesis and dolomitization of Devonian reef complex carbonates, Napier Range, Canning Basin, Western Australia. His work has added significantly to the understanding of platform evolution, calcite cementation in meteoric and marine environments, and to dolomitization.

Fluid inclusion studies by Ann Cox in the Burlington-Keokuk dolomites has shown that most (about 3/4) of the fluid inclusions in Dolomite I are single phase, and therefore are likely to be unaltered primary inclusions. The fluid inclusions are dominantly more saline than seawater suggesting that hypersaline (evaporitic?) fluids not mixing-zone fluids are responsible for the formation of Dolomite I. This work is continuing with additional studies of Dolomites I and II.

Publications

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Fouke, B.W. and Reeder, R.J., Surface structural controls on dolomite composition: Evidence from sector zoning, Geochim. Cosmochim, Acta (submitted)

Hemming, N.G. and Hanson, G.N., 1991, Boron isotopic composition of Osagean (Miss.) marine cements and brachiopods:Implications for marine cement fluids and secular variation of B isotopes, G.S.A. Abstracts, 23, A149.

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Kaufman, J., Meyers, W.J., Hanson, G.N., 1991, Dolomitization of the Devonian Swan Hills Formation, Rosevear Field, Alberta, Canada: Sedimentology, 38, 41-66.

Meyers, W.J., 1991, Carbonate cement stratigraphy: an overview: in Barker and Kopp, eds., SEPM Shortcourse Volume on Luminescence, Annual SEPM Meeting, p. 133-148.

Oswald, E., and Schoonen, M., in review, Dolomitizing seas in evaporitic basins: a model for pervasive dolomitization of platform carbonates: Jour. Sed. Petrology.

Staudt, W., Oswald, E.J. and Schoonen, M.A.A., 1992, Determination of trace ion concentrations (Cl, F. SO_4) in dolomites: A new analytical procedure to constrain the composition of dolomitizing fluids. Abst. AAPG Annual Convention,

Plans for Next Year

The plans for the coming year are essentially as presented in the proposal submitted in January, 1990 and as modified in the revised budget in April, 1990. We estimate that there will be no unspent funds.

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