

## THE ISOTOPIC AND TRACE ELEMENT GEOCHEMISTRY OF DOLOMITE: THE STATE OF THE ART

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### ABSTRACT

Large variations in the perfection of order and in substitution of calcium for magnesium occur in sedimentary dolomite, and complicate the trace element and isotopic chemistry of this complex mineral. The stabilization of metastable disordered and/or Ca-rich phases is as important in forming ancient dolomitic rocks as is the stabilization of aragonite and Mg-calcite in forming ancient limestones.

The equilibrium value of  $\Delta^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{calcite}}$ ) is most likely  $3 \pm 1\%$  at 25° C. Redetermination of phosphoric acid fractionation factors ( $\alpha = (^{18}\text{O}/^{16}\text{O}_{\text{CO}_2}) / (^{18}\text{O}/^{16}\text{O}_{\text{carbonate}})$ ) yields values of  $10^3$  in  $\alpha$  between 11.4 and 11.9 for most sedimentary dolomite. The redetermined value for calcite is 10.5. Holocene dolomite from two localities yields values of about 12.5. Most ancient dolomite is very depleted in  $^{18}\text{O}$  relative to presumed Holocene analogs.

Mathematical modeling of the diagenetic behavior of the trace element Sr in conjunction with oxygen isotopic changes during the diagenesis of limestone substantiates recent suggestions that experimentally determined distribution coefficients for calcite do not apply under actual diagenetic conditions. An analogous situation probably exists with respect to dolomite. Most ancient dolomite is trace-element-depleted relative to Holocene analogs.

At present, quantitative interpretation of absolute isotopic or trace element values of dolomite is tenuous, not only due to problems in assigning distribution coefficients and fractionation factors, but also in coping with multiple recrystallizations in partly closed chemical systems. Because recrystallization is neither completely open nor completely closed-system, chemical information from early events is incompletely erased by later ones. Qualitative interpretation of regional or stratigraphic variations in chemical or crystallographic parameters appears to be quite useful, however, given our present state of ignorance.

### INTRODUCTION

The essence of the "dolomite problem" is still being debated. We have not yet fully answered the question: Under what geologic conditions or sequence of conditions do thick sequences of bedded dolomite form? This is true despite all the data which have emerged since Fairbridge (1957), Ingerson (1962) and Friedman and Sanders (1967) reviewed the subject. Most geologists agree that the dolomite in this type of deposit is largely secondary in the sense that some sort of carbonate sediment precursor existed prior to replacement (and often cementation) by dolomite. "Primary" dolomite, formed by direct nucleation from solution and resulting in the accumulation of sediment, is thought to be quite rare. Nobody has yet synthesized dolomite either by replacement or by direct nucleation under conditions typical of sedimentary depositional environments (but see Mansfield, in press), yet many examples of Holocene dolomite have been described. Syntheses of dolomite at elevated temperatures (greater than about 150° C) are numerous, rapid and relatively uncomplicated.

Before turning to the purpose of this paper, namely to review the clarification and/or confusion that isotopic and trace element analyses have contributed to the understanding of the origin of

bedded sedimentary dolomite, I would like to stress two facts which are often overlooked.

First, there is no unique environment of dolomitization. Aside from the very basic chemical constraint that a solution must be oversaturated with dolomite in order to crystallize it, dolomite clearly forms in a variety of chemical environments. Within the last few thousand years, dolomite has formed from subtidal hypersaline water of marine derivation (Illing and others, 1965; Behrens and Land, 1972), from hypersaline water of continental derivation (Clayton, Jones, and Berner, 1968; Clayton and others, 1968; Von der Borch and others, 1975; Muir and others, this volume) and as supratidal caliche-like crusts and concretions with marine affinities (Shinn and others, 1965; Lucia, 1968; Shinn, 1968; Cook, 1973).

At the other end of the salinity spectrum and on the same time scale, dolomite has also formed in hyposaline shallow groundwater lenses where mixing between potable groundwater and seawater occurs (Land, 1973a). All these examples (only one paper has been cited for each locality) are documented cases of the dolomite precipitation within the late Holocene. There can be no argument that dolomite does form in a variety of chemical environments. The question is: under