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## DOLOMITE SOLUBILITY IN GROUND WATER

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*Abstract.*—The ion-activity product ( $IAP$ )<sub>d</sub> of dolomite has been computed for 87 samples of ground water from a variety of geologic environments. The upper limit of the ( $IAP$ )<sub>d</sub> for samples in or very near equilibrium with calcite agrees with the higher equilibrium constants reported in the literature.

Detailed studies of the composition of ground water have been undertaken in an effort to determine the thermodynamic state of reactions between minerals and water. The approach has been to obtain chemical analyses reflecting as closely as possible the composition of the water in its native state by determining alkalinity, pH, and temperature at the time of sampling (Barnes, 1964). Ion activities of the chemical constituents can be calculated from the laboratory data and the Debye-Hückel equation. From the activities, the ion-activity product ( $IAP$ ) can be calculated for a particular reaction, using the law of mass action. Departure from equilibrium is determined by comparing the  $IAP$  calculated from the chemical analyses of water with the equilibrium constant,  $K$  (Back, 1960). If the  $IAP$  is greater than the  $K$ , the water is supersaturated with respect to the mineral of interest. For calcite,

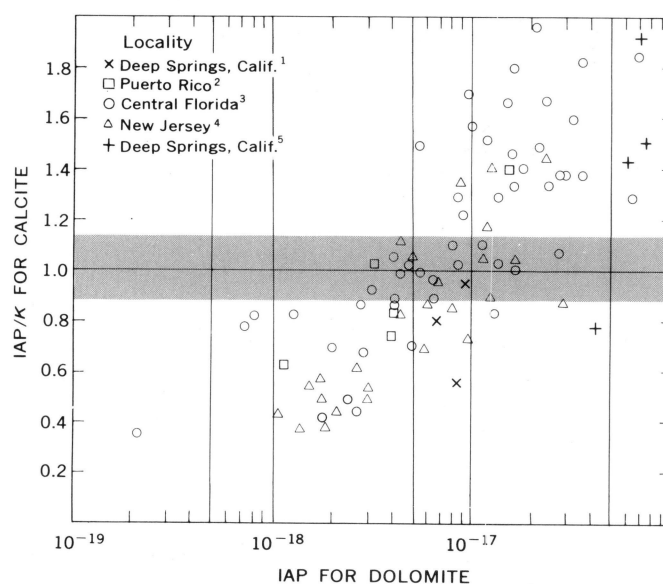
$$IAP_c = \alpha_{Ca^{+2}} \cdot \alpha_{CO_3^{-2}}, \quad (1)$$

and for dolomite,

$$IAP_d = \alpha_{Ca^{+2}} \cdot \alpha_{Mg^{+2}} (\alpha_{CO_3^{-2}})^2 \quad (2)$$

Figure 160.1 shows values of  $IAP_d$  and the ratio  $IAP/K$  for calcite. The pH, temperature, and bicarbonate concentrations for all these samples were determined in the field; the ionic strength of all samples plotted is less than 0.1 the limit for the Debye-Hückel equation.

For samples in equilibrium with calcite, that is, those with an  $IAP/K$  ratio of  $1.0 \pm$  about 0.12, the data show that the maximum  $IAP$  for dolomite is  $2.87 \times 10^{-17}$  (see shaded area in fig. 160.1). The data indicate that the



- <sup>1</sup> Barnes (unpublished analyses, 1962).
- <sup>2</sup> J. W. Crooks (oral communication, 1962).
- <sup>3</sup> Back (1963).
- <sup>4</sup> Seaber (1962).
- <sup>5</sup> Jones (1961).

FIGURE 160.1.—Graph showing relation of ion-activity product for dolomite and the  $IAP/K$  ratio for calcite. Shaded area represents samples in equilibrium with calcite.

upper limiting value for the  $IAP$  for dolomite in ground waters in equilibrium with calcite lies between approximately  $1.5 \times 10^{-17}$  and  $3 \times 10^{-17}$ . Owing to the sluggishness of the dolomite precipitation, water supersaturated with calcite probably is supersaturated also with dolomite.

These  $IAP$  data for dolomite may be compared with reported equilibrium constants for dolomite, as follows:

Holland others <sup>1</sup> .....	$1 \times 10^{-17}$
Kramer (1959).....	$1.5 \times 10^{-17}$
Hsu (1964).....	$2 \times 10^{-17}$
Van Tassel (cited by Halla, 1962).....	$2.5 \times 10^{-17}$

<sup>1</sup> Holland, H. D., Kirsipu, T. V., Huebner, J. S., and Oxbough, V. M., 1962, On some aspects of the chemical evolution of cave waters: Princeton Univ., technical report (duplicated).

Halla and Ritter (cited by Kramer, 1959).....	$3 \times 10^{-17}$
Robie (cited by Halla, 1962).....	$6.6 \times 10^{-19}$
Garrels and others (1960).....	$4.7 \times 10^{-20}$

If the lower solubilities of Garrels and Robie are accepted, all water samples used in this study are supersaturated with dolomite. On the other hand, if we postulate that dolomite reacts with aqueous solutions and tends toward an equilibrium, the equilibrium constant would appear to be on the order of 2 to  $3 \times 10^{-17}$ . In any event, the observed characteristics of the ground waters sampled are closer to the properties predicted at equilibrium with the higher solubilities reported than with the lower solubilities.

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