

PATTERNS IN THE COMPOSITIONS, PROPERTIES, AND GEOCHEMISTRY OF CARBONATE MINERALS

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ABSTRACT: The diversity of carbonate minerals is remarkable, if largely unappreciated. For example, 277 carbonate-bearing minerals have been recognized, and among them are 158 pure carbonates of cations with valences from 1+ to 6+. The other 119 minerals additionally contain chloride, fluoride, borate, sulfate, phosphate, arsenate, arsenite, antimonate, or silicate groups, or combinations of those anions. However, combinations of anions with cations are not uniformly distributed, so that there are no bicarbonates or simple carbonates of highly-charged cations, few hydrated or OH-bearing minerals of monovalent cations, and few U-bearing carbonates with anions other than CO_3^{2-} , OH, and O^{2-} . On the other hand, simple carbonates of divalent cations, OH-bearing Al carbonates, and fluoride-bearing carbonates of rare-earth elements are remarkably numerous. Many of these trends can be related to the coordination chemistry of cations in the solutions from which these minerals form.

Among nearly all the carbonate-bearing minerals, ionic potential of the cations is a major control on the extent of hydration. Degree of hydration is in turn a major control on hardness, density, and solubility.

Among the simple carbonates, hardness, density, and positions of spectroscopic peaks vary linearly with cation radius or mass, although such trends usually exist only within crystallographic groups or only within cation groups defined by the periodic table. In contrast, geochemical parameters, such as solubility and fractionation of oxygen isotopes, vary with degree of *cation fit* in the 6-fold or 9-fold site of the rhombohedral and orthorhombic simple carbonates, so that there is not a linear variation with cation size. The same is true for the distribution coefficients of cations in calcite and aragonite.

Patterns thus emerge among the compositions, properties, and geochemistry of the carbonate minerals, with cationic potential and type as a major influence on composition, with degree of hydration and cation radius or mass as a control on physical and spectroscopic properties, but with cation fit as the major control on geochemical parameters. These patterns allow qualitative prediction of mineral properties and help explain the origins of some of the major problems in carbonate petrology.

INTRODUCTION

Most geologists are familiar with at most about a dozen carbonate minerals (Hurlbut and Klein 1977), but mineralogists have recognized well over 250 distinct carbonate-bearing minerals. In addition, in the 1990s about 4 new carbonate-bearing minerals have been reported and their names confirmed each year by the International Mineralogical Association's Commission on New Minerals and Mineral Names. Carbonate minerals are of course found in the limestones, dolostones, marbles, and carbonatites with which most geologists are familiar, but they are increasingly found in a host of both natural and anthropogenic materials on Earth (e.g., Friedman and Schultz 1994; Signorelli et al. 1996), and we now think that they are present on Mars as well (Gooding et al. 1988; Romanek et al. 1994). As the scope of geological investigation increases in the coming years, the diversity of carbonate minerals that we encounter is likely to increase as well.

Previous papers and books have examined the structure and chemistry of the more common carbonate minerals (e.g., Tichelman 1973; Lippmann 1973; Reeder 1983, Speer 1983), or have dealt with one aspect of a larger proportion of the carbonates (e.g., White 1974; Zemmann 1981; Mandarino 1994), or have examined one subgroup of these minerals (e.g., Grice 1991, 1994). This paper, however, surveys the compositions, properties, and geochemistry of all the carbonate-bearing minerals. Such a survey shows that there is great mineralogical variability and seeming geochemical

complexity of which we should be aware, but within this diversity patterns emerge that are largely rooted in the cationic chemistry of the minerals involved.

COMPOSITIONS OF CARBONATE MINERALS

There are at least 277 carbonate-bearing minerals. (An updated appendix listing the names and chemical formulae of all these carbonate-bearing minerals is available on the World Wide Web at http://www.gly.uga.edu/CO3mins_intro.html). Of these, there are 65 in which CO_3^{2-} provides all the negative charge, and 88 minerals in which CO_3^{2-} combines with OH and/or O^{2-} to provide all the negative charge (Fig. 1). HCO_3^- provides all the negative charge in 3 minerals and joins CO_3^{2-} to provide it in 2 others. These 158 minerals can be considered "pure carbonates", whereas in the other 119 minerals, the aforementioned anions combine with chloride, fluoride, borate, sulfate, phosphate, arsenate, arsenite, antimonate, or silicate groups, or combinations of those anions, to provide the negative charge (Fig. 2). Many of the pure carbonates and the carbonates with other anions also contain structurally bound water. The imposing chemical formula for the skarn mineral harkerite, $\text{Ca}_{24}\text{Mg}_8\text{Al}_2\text{Si}_8(\text{O},\text{OH})_{32}(\text{BO}_3)_8(\text{CO}_3)_8(\text{H}_2\text{O},\text{Cl})$, provides a good example of the potential intricacy of these chemical combinations.

Pure Carbonates

Compositional trends.-- The 158 pure carbonates derive their positive charge from cations with valences ranging from 1+ to