Patterns in the compositions of oxysalt and sulfosalt minerals, and the paradoxical nature of quartz

L. BRUCE RAILSBACK*

Department of Geology, University of Georgia, Athens, Georgia 30602-2501, U.S.A.

ABSTRACT

Compositions of oxysalt, sulfosalt, seleniosalt, tellurisalt, and fluosalt minerals all follow the same generalizable patterns with regard to hardness or softness of cations, and with regard to ionic potential. For example, the hard F⁻ anion forms simple fluosalt minerals (fluoroborates and fluosilicates) with hard cations. The relatively hard O²⁻ anion forms simple oxysalts (e.g., sulfates and arsenates) largely with hard to intermediate cations. On the other hand, the softer S²⁻ anion forms sulfosalt minerals almost entirely with intermediate to soft cations, and the still softer anions Se²⁻ and Te²⁻ form seleniosalt and tellurisalt minerals with an even more predominately soft suite of cations. Thus, across all these classes of minerals, harder anions generally form minerals with harder cations, and softer anions form minerals with softer cations.

The compositions of simple oxysalt minerals of one inter-radical cation vary greatly, but they do not include minerals in which both the inter-radical cation and intra-radical cation (e.g., Ca²⁺ and S⁶⁺ in CaSO₄) have high ionic potential. Their compositions thus reach, but do not exceed, a limit on a plot of the ionic potential of cations in these minerals. The same general relationship, wherein no simple minerals contain both inter-radical and intra-radical cations of high ionic potential, also exists among sulfosalts, seleniosalts, tellurisalts, and fluosalts. These limits of ionic potential of cations are greatest in oxysalts and progressively less in fluosalts, sulfosalts, seleniosalts, and tellurisalts. The limits thus decrease, both through the 2– anions and across the hard anions, from more negative ionic potential of the anion to less so, seemingly because anions of less negative ionic potential have lesser capability to shield cations from each other and thereby preclude cation-cation repulsion.

Among the simple oxysalts of one inter-radical cation, three minerals near the oxysalt limit form less commonly, or with greater inhibition, than one might expect. For example, thermodynamic calculations indicate that magnesite should precipitate abundantly from seawater, but it does not instead, in low-temperature systems Mg²⁺ only forms simple carbonate minerals with a cation of lesser ionic potential (Ca²⁺). Similarly, the chemistry of Earth’s crust suggests that (Al,Fe³⁺)₂(SO₄)₃ would be a common mineral, but instead analogous hydrous minerals with additional cations of lesser ionic potential are common. Finally, SiO₂ minerals crystallize at distinctly low temperatures in magmatic systems, and they either fail to nucleate or precipitate as a hydrous disordered mineral in many low-temperature systems. In all three cases, cation-cation repulsion seemingly inhibits formation of what might otherwise be more common or more readily forming minerals.

Keywords: Geochemistry, systematic mineralogy, sulfosalts, quartz, magnesite, alunite, millosevichite, cations

INTRODUCTION

Oxysalts are minerals in which O²⁻ anions cluster around highly charged cations like S⁶⁺ to form anionic radical groups, such as SO₄²⁻ in sulfates like CaSO₄. Sulfosalts can be considered minerals with analogous chemical compositions in which S²⁻ replaces O²⁻; as in proustite (Ag₃AsS₃) and matildite (AgBiS₂) (Fig. 1). Seleniosalts, tellurisalts, and fluosalts are correspondingly minerals in which Se²⁻, Te²⁻, and F⁻ cluster around highly charged cations and take the place of O²⁻ in chemical formulae in minerals again stoichiometrically analogous to the more-familiar oxysalts (e.g., in minerals like bohdanowiczite (AgBiSe₂), volynskite (AgBiTe₂), and hieratite (K₂SiF₆) (Fig. 1).

Of the roughly 4100 minerals known at present (Mandarino and Back 2004), more than 2400 are oxysalts and more than 250 are sulfosalts. Seleniosalts, tellurisalts, and fluosalts are less numerous but chemically analogous mineral classes whose compositions provide insights into the chemistry of their more abundant cousins. Collectively, the various oxysalt, sulfosalt, seleniosalt, tellurisalt, and fluosalt anionic radical groups combine with most of the cations in the periodic table to make minerals (Fig. 2). There is thus great abundance and diversity of these minerals, and this paper reveals some patterns within their compositions. Those patterns allow an understanding of chemical principles controlling mineral compositions; they allow prediction of what new minerals might be discovered; and they provide a context in which to understand the seemingly paradoxical behavior of some common, or potentially common, minerals.