Eliminating closure in mineral formulae with specific application to amphiboles

E.D. Young, D. Virgo, and R.K. Popp

1Department of Earth Science, University of Oxford Parks Road, Oxford, OX1 3PR, U.K.
2Geophysical Laboratory, 5251 Broad Branch Road NW, Washington, DC 20015, U.S.A.
3Department of Geology and Geophysics, Texas A&M University, College Station, Texas 77843, U.S.A.

Abstract

Competition among atomic or molecular species for occupancy of crystallographic sites exaggerates correlations among chemical elements in suites of mineral chemical data, a phenomenon known as closure. Such exaggerated correlations can lead to incorrect conclusions about ionic substitution mechanisms and the petrological forces that drive them. Expressing mineral compositions in terms of a single additive component and molar concentrations of exchange components, eliminates the effects of closure. Statistical analysis of data so transformed can, in some instances, lead to conclusions distinct from analysis of the same data expressed in terms of ionic abundances. The chemical variability of fictive and naturally occurring amphiboles serves to illustrate the potential difficulties brought about by closure and the benefits of its elimination.

Introduction

In this paper we examine the petrological meaning of correlations among elemental concentrations in minerals. As a corollary, the distinction between ionic substitutions and proportions of exchange components is elucidated.

Spurious correlations that arise among geochemical variables where the variables represent portions of a single whole are well known (e.g., Chayes 1962). Their cause is straightforward: An increase in the proportion of one major component of the whole requires decreases in the proportions of the other major components. Identification of such correlations is often less straightforward. Known collectively as closure, they are considered spurious because they mask the more interesting interrelations that are products of geological phenomena, and it is demonstration of the latter that is a primary motivation for studying the chemistry of rocks and minerals. There has been considerable discussion of the effects of closure on whole-rock chemical data in recent years (e.g., Nicholls 1988; Russell and Nicholls 1988). The effects of closure on mineral chemical data have been largely ignored.

Bragg (1937) recognized that several conceptual pitfalls could be avoided by describing mineral structures and mineral compositions separately. He suggested that ideal formulae be used to convey crystal structure and that chemical variability, which is most often isomorphous or approximately so, be described by a set of independent operations that act on an ideal structural formula (Bragg 1937, p. 38). In this way crystal structure and chemical variations are decoupled. Stressing that the customary practice of using end-member formulae to describe mineral composition was inherently flawed, Bragg wrote that use of end-members "...implies the existence of a chemical 'molecule' in which a definite number of atoms form a characteristic subgroup in the structure."

He indicated that his scheme for confining structural information to a single formula and expressing compositions in terms of deviations from that formula should supplant the use of end-members; his scheme would eliminate the flawed concept of molecular mixing that end-members connote.

Thompson (1982) formalized Bragg's ideas (see also Burt 1976 and Burt 1988). In Thompson's approach, mineral chemical compositions are cast into a single ideal formula, or additive component, and a linearly independent set of operators, referred to as exchange components, that express deviations from the additive component. The purpose of the additive component is to characterize the structure of the mineral group. The exchange components depict changes in chemistry that leave the extensive amount of additive component unchanged.

A powerful yet commonly overlooked attribute of the Bragg-Thompson method for representing mineral compositions is that formulae so transformed are free from closure. In this paper we illustrate the utility of closure-free variables for elucidating the petrological significance of chemical variability in minerals that possess multiple crystallographic sites. The approach is used to investigate the important ionic substitutions in some natural amphiboles.

Closure in Mineral Formulae

Principles

Amphiboles are composed of numerous crystallographic sites that host a large variety of elements and are well-