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THE CRYSTAL CHEMISTRY OF THE AMPHIBOLES

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ABSTRACT

Much experimental work on the crystallography and crystal chemistry of the amphiboles has appeared since the studies of Warren (1929, 1930) and Warren & Modell (1930b). Crystal-structure refinement and absorption spectroscopy have played a major role, particularly in the past twenty years. Over 70 crystal structures have been refined, and ~120 amphiboles have been characterized by Mössbauer spectroscopy. There has been considerable work in infrared-absorption spectroscopy, and electronic-absorption spectroscopy is becoming increasingly important. Scattered through the scientific literature is much miscellaneous experimental work on amphiboles: X-ray photoelectron spectroscopy, diffuse-reflectance spectroscopy, Raman spectroscopy, nuclear magnetic-resonance spectroscopy, electron-spin-resonance spectroscopy, neutron inelastic-scattering spectroscopy, oxidation-dehydroxylation studies, measurement of elastic, magnetic and electrical properties, characterization of deformational behavior. This information has been assembled here, and all derivative data have been recalculated to remove (numerous) misprints and errors in the original publications. In addition, these data have been critically assessed as to quality and significance. The result is a consistent data-set that may form the basis for further studies.

Amphiboles belong to five principal structure-types, with space groups *C2/m*, *P2/a*, *P2₁/m*, *Pnma*, and *Pnmn*, but the *C2/m* and *Pnma* structures are by far the most common. The M(4) site is of major importance in amphibole crystal chemistry. The large X cation that occupies M(4) is the primary feature on which the current nomenclature of the amphiboles is based; amphiboles with differing M(4) occupancies are generally immiscible, and thus the resulting classification is natural and convenient. Compositional variation in the amphiboles can generally be correlated with structural variations; such correlations are useful to derive crystallochemical information where the experimental data give ambiguous results.

Keywords: amphiboles, crystal chemistry, review, structure, spectroscopy.

SOMMAIRE

La cristallographie et la cristallochimie des amphiboles ont fait l'objet de nombreux travaux expérimentaux depuis les découvertes de Warren (1929, 1930) et de Warren & Modell (1930b). Parmi ceux-ci, l'affinement de la structure cristalline et l'étude du spectre d'absorption ont joué un rôle important, surtout au cours des vingt dernières années. Plus de 70 affinements ont été réalisés, et environ 120 échantillons d'amphibole ont été caractérisés par spectroscopie Mössbauer. On note de grands progrès en spectroscopie par absorption infrarouge et, de plus en plus, par absorption électronique. On trouve aussi, éparpillés dans la littérature scientifique, nombre de résultats expérimentaux sur les amphiboles: d'une part, études spectroscopiques de divers types (photoélectrons rayons X, réflectance diffuse, Raman, résonance nucléaire magnétique, résonance de spin électronique, dispersion inélastique des neutrons) et, d'autre part: études d'oxydation et de déshydroxylation, mensuration des propriétés élastiques, magnétiques et électriques, comportement sous contrainte. On présente ici toutes ces données rassemblées, tous calculs vérifiés pour éliminer de nombreuses fautes d'impression et erreurs des mémoires originaux. De plus, on a évalué de façon critique la qualité et la portée de ces données. Il en résulte une collection cohérente de données qui peut servir de point de départ aux travaux futurs.

Les amphiboles se répartissent en cinq types de structure principaux, de groupes spatiaux *C2/m*, *P2/a*, *P2₁/m*, *Pnma* et *Pnmn*, parmi lesquels *C2/m* et *Pnma* prédominent. La position M(4) possède une grande importance dans la cristallochimie des amphiboles: le cation X (de grande taille) qui en occupe les sites détermine largement, en fait, la nomenclature actuelle. Deux amphiboles qui diffèrent par la composition cationique des sites M(4) sont généralement immiscibles; la classification fondée sur M(4) est donc naturelle et commode. En général, on parvient à établir une corrélation entre variations de composition et variations structurelles. Ces corrélations peuvent fournir de l'information cristallochimique pour lever l'ambiguïté des résultats d'expériences.

(Traduit par la Rédaction)

Mots-clés: amphiboles, cristallochimie, revue, structure, spectroscopie.

INTRODUCTION

The amphiboles are the most complex group of rock-forming minerals, exhibiting wide chemical variation and a bewildering variety of parageneses. They are common constituents across the complete range of igneous rocks, from acid (Borley 1963, Lyons 1976) to ultrabasic (Onuki 1964). In sedimentary rocks, amphiboles occur both as detrital (Blatt *et al.* 1972, Pettijohn 1975) and authigenic phases (Milton & Eugster 1959, Milton *et al.* 1974). In metamorphic rocks, amphiboles are important constituents from very low grade to high grade and over a wide variety of rock compositions. Changes in amphibole composition with increasing grade of metamorphism in specific areas are well documented (Compton 1958, Engel & Engel 1962, Binns 1965, Fabries 1968, Hietanen 1974) but the effects of bulk-rock composition are not well understood. The occurrence of amphibole in mafic and ultramafic nodules in calc-alkaline and basaltic rocks led to the suggestion that amphibole is a mantle phase (Green & Ringwood 1963), and the principal source of K_2O (Oxburgh 1964, Hart & Aldrich 1967). Although not common, amphiboles are also found in meteorites; these are usually fluor-richterite (Olsen 1967, Olsen *et al.* 1973, Graham *et al.* 1976), but hydroxy-amphiboles (kaersutite) have recently been found (Floran *et al.* 1978). The discovery of amphiboles in lunar rock (Gay *et al.* 1970, Dence *et al.* 1971) completes the list of parageneses of these minerals. The occurrence of fluor-richterite parallels its fairly common occurrence in meteorites, but the discovery of tschermakite as a possible hydroxyl-bearing lunar phase is intriguing.

The amphibole structure is one of great chemical compliance (Ernst 1968), and the wide chemical variations within this group may be seen as arising from the general geometry of the structure. In each structure-type, several crystallographically unique sites occur; these sites may accommodate cations of formal charge +1 to +4 and ionic radius 0.25 to 1.6 Å. Inspection of proposed average compositions of the crust (Holmes 1965, Ringwood 1969) shows that all major cations fall within this range, reflecting the ubiquity of these minerals. Despite the complexity of the amphiboles, they have been the object of considerable attention in the past hundred years. Schaller (1916) was first to derive the formula of tremolite when he recognized that hydroxyl is an essential constituent of that mineral. Tschermak (1872) recognized that there is a strong relationship between the chemistry, physical properties and paragenesis of the pyroxenes and the amphiboles. Warren (1929) and Warren & Modell (1930b) showed that this relationship also extended to the unit-cell dimensions and diffraction patterns, and solved the structures of tremolite and anthophyllite by analogy with the known structures of diopside (Warren & Bragg 1928) and enstatite (Warren & Modell 1930a). Warren (1930) and Kunitz (1930) showed the structural and chemical homology of the amphiboles, emphasizing the importance of both homovalent and heterovalent substitutions to the chemistry of this group.

The considerable effort expended on the structural chemistry of the amphiboles in the past fifteen years has been aided by extensive automation of equipment in the fields of X-ray diffraction and mineral analysis, and by the application of spectroscopic techniques to problems in amphibole chemistry. The resulting proliferation of structural and chemical data has led to an increase in our understanding of the complexity of these minerals. The structural details of a considerable number of natural (and synthetic) amphiboles have now been fairly well characterized, and a general survey of the results is presented here.

Structural, chemical and spectroscopic data are listed and cross-correlated in a series of appendices. In the numbering system used, [ ] and ( ), respectively, denote orthorhombic and monoclinic amphiboles for which crystal-structure data are available; { } and < > denote amphiboles characterized by Mössbauer and infrared spectroscopy, respectively; the keys to this system are found in Appendices A–E → { } and ( ), Appendices F and G → { }, Appendix G → < >. All isomer shifts have been normalized relative to that of metallic iron. A synopsis of the information presented here is given by Hawthorne (1981a, b); however, it should be stressed that the latter articles are instructional and do not incorporate the amount of critical assessment given here.