High-pressure Al-rich hexagonal phases—What are their kin?

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ABSTRACT

The hexagonal Al-rich high-pressure phases are members of a structural family with the same type of framework composed of double-ribbons of edge-sharing octahedra, but variably occupied trigonal and hexagonal channels. This family includes jaffeite, fluoborite, yeremeyevite, painite, and synthetic Ba indates. This kinship broadens the spectrum of elements potentially accommodated by these phases in the mantle.

Keywords: Al-rich high-pressure phases, jaffeite, fluoborite, painite, framework of octahedra

INTRODUCTION

Miyajima et al. (1999) synthetized “NAL,” M$_3$Al$_2$Si$_4$O$_{12}$ (M = Mg,Fe,Ca,Na,K), $P6_3/m$ or $P6_3$, $a = 8.85$ and $c = 2.78$ Å at 30–50 GPa (Table 1). Gasparik et al. (2000) published the crystal structure of a similar high-pressure phase, $K_{0.3}Na_{0.7}Mg_{2.4}Fe_{0.6}Al_{1.5}Si_{3.5}O_{12}$, with traces of Ca and octahedrally coordinated Si, obtained at 24 GPa and 1700 °C. Miura et al. (2000) published the structure of CaMg$_2$Al$_2$O$_{12}$, $P6_3/m$, $a = 8.76$, $c = 2.79$ Å, synthesized at 21.8 GPa and 1200 °C. Shimmei et al. (2005) derived the high-temperature/high-pressure equation of state for the Al-rich hexagonal phase Na$_2$Mg$_{1.5}Al_2$Si$_3$O$_{12}$ and suggested that in this phase a part of the Na must occur in the trigonal channels. Syntheses prior to these publications were made without exact crystallographic characterizations. They are summarized in the contributions cited above.

These high-pressure structures are frameworks of double columns of octahedra (cf. hollandite- and Ca$_2$Fe$_5$O$_{12}$-structure types) that share corners to produce tunnel structures with trigonal and hexagonal channels (Fig. 1). The coordination octahedra contain primarily Al and Si. Six-coordinated Mg occupies the trigonal channels and (K, Na) and Ca atoms reside in the hexagonal channels. The latter cation arrays are disordered for steric reasons and these channels also contain vacancies (Gasparik et al. 2000). Both Gasparik et al. (2000) and Miura et al. (2000) assumed this to be a novel structure type; discussion of this claim is the rationale for the present contribution.

In their paper on the crystal structure of painite, Moore et al. (1976) recognized that several seemingly very different compounds, all of them borates of widely different stoichiometries (Table 1), have the same framework composed of double columns of octahedra, and differ primarily in the occupancy of the trigonal channels. Yamnova et al. (1993) widened this relation to include jaffeite, Ca$_2$[(OH)$_3$Si$_3$O$_9$], a sorosilicate from low-grade metamorphic rocks, which also is a component of hydrated cement under the name “triclicium silicate hydrate.” The framework of octahedra contains Ca in this compound (Yamnova et al. 1993) and is identical to that of the high-pressure Al-rich phases listed above, in which the framework hosts Al and Si. The relation between fluoborite (Table 1) and jaffeite is the same as that between the Zr disilicates of the làvenite-wöhlerite family and the borate mineral, warwickite (Strunz and Nickel 2001): in trigonal channels, regularly stacked BO$_3$ groups are substituted by disilicate groups Si$_2$O$_5$. Other borates of the hexagonal family contain more complicated sequences in the trigonal channels: alternation of BO$_3$ groups with trigonal prisms containing Zr in painite (Moore and Araki 1976; Armbruster et al. 2004) or alternation of these groups with F, which replaces O in the vertices of octahedra in yeremeyevite (Rodellas et al. 1983). In yeremeyevite every third octahedron in each column is vacant and the octahedral wall facing the hexagonal channel is occupied by a BO$_3$ group. These compounds were quoted as an example of a higher-order, plesiotypic family by Makovicky (1997) and Ferraris et al. (2004). Homologous expansion of the fluoborite framework toward structures known for barium-bismuth sulfides (Aurivilius 1983) has been described by Makovicky (1985).

FIGURE 1. Projection of the crystal structure of the high-pressure phase (K,Na)$_3$(Mg,Fe)$_2$(Al,Si,Mg,Fe)$_2$O$_{12}$ (Gasparik et al. 2000) on (0001). Shaded = Si, Al octahedra, cross-hatched = Mg coordination prisms in trigonal channels, circles = K, Na in hexagonal channels.