The crystal chemistry of the sakhaite–harkerite solid solution

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ABSTRACT

Sakhaite, ca. Ca48Mg16(BO3)32(CO3)48(HCl, H2O)2, is a rare rock-forming borate-carbonate mineral typically occurring in high-temperature, low-pressure calcareous skarns. It forms a complete solid solution with harkerite, ca. Ca48Mg16[AlSi5(O,OH)16]4(BO3)16(HCl, H2O)2. The solid solution can be described with the general formula

\[
\text{Ca}_{48} \text{Mg}_{16} \text{Al}_{x} \text{Si}_{16-x} \text{(O,OH)}_{16} \text{BO}_{3y} \text{HCl, H}_2 \text{O}_n
\]

where \(y_{\text{max}} = 8\) and \(n_{\text{max}} = 16 - y\). In this study, we examine samples of sakhaite and harkerite from four localities worldwide: Titovskoye deposit, Sakha Republic, Russia (type locality for sakhaite); Solongo B deposit, Buryatia Republic, Russia; Camas Malag, Skye, Scotland (type locality for harkerite); as well as a sakhaite-like mineral from the Kombat Mine, Tsumeb. The Si:B ratios of the samples ranged from that of end-member sakhaite (containing B only) to that of end-member harkerite (Si:B = 1:1), with several intermediate compositions. All samples were deficient in B relative to the ideal composition, implying significant substitution for borate groups. The Si:Al ratio of silicate-containing samples ranged from the ideal 4:1 to 4:1.5, implying substitution of Al at the Si site. The cubic unit-cell parameter was found to increase linearly with increasing Si content, except for the sakhaite-like mineral from Tsumeb. This mineral was found to have significant substitution of Pb for Ca (0.4–0.5 apfu) and was poor in Cl, which in most sakhaite and harkerite samples occupies the interstitial site surrounded by four borate groups. This interstitial site in the Tsumeb samples appears to be, instead, mainly occupied by H2O, which may qualify the mineral as a distinct species.

Keywords: Sakhaite, harkerite, solid solution, crystal structure; Lithium, Beryllium, and Boron: Quintessentially Crustal

INTRODUCTION

The solid solution between sakhaite, ca. Ca48Mg16(BO3)32(CO3)48(HCl, H2O)2, and harkerite, ca. Ca48Mg16[AlSi5(O,OH)16](BO3)16(HCl, H2O)2, is distinctive in that the substitution involves entire clusters of polyhedra, instead of one or two sites as is typical of most natural solid solutions. The sakhaite-harkerite series is close to unique in containing essential carbonate, borate, and silicate groups; among other minerals, only britvinite and the related mineral roymillerite (IMA No. 2016-061) contain all three of these anion complexes. Originally the main structural difference between sakhaite and harkerite was interpreted to be a partial substitution of isolated BO3 triangles with isolated SiO4 tetrahedra (Ostrovskaya et al. 1966; Davies and Machin 1970). Subsequent crystallographic studies of synthetic sakhaite (Chichagov et al. 1974) and natural harkerite and sakhaite (Machin and Miehe 1976; Giuseppetti et al. 1977; Yakubovich et al. 1978, 2005), as well as the anomalous sakhaite-like mineral reported by Dunn et al. (1990), have revealed a far more complex relationship, which induced us to undertake this study of the crystal chemistry of the sakhaite-harkerite series.

Sakhaite and harkerite have been described from 14 localities worldwide of which 11 are skarns and other calcareous rocks formed at low pressures and high temperatures, whereas two are Mn-rich rocks metamorphosed under greenschist and amphibolite facies conditions, and one is a deep-seated granulite facies complex (e.g., Grew 1996; Grew et al. 1999).

PREVIOUS STUDY

Ostrovskaya (1969) was the first to consider the structures of sakhaite and harkerite, making use of powder X-ray diffraction, chemical, and infrared data. However, the sakhaite structure (Fig. 1) was revealed only in single-crystal refinements of synthetic sakhaite (Chichagov et al. 1974) and of natural sakhaite from Solongo, Buryatia, Russia (Yakubovich et al. 1978). This structure was found to be a framework composed of columns of Ca polyhedra oriented in all three crystallographic directions. The other constituents, i.e., Mg octahedra, BO3 and CO3 triangles, occupy the interstices of the framework, leaving two types of

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