INTRODUCTION

Li-bearing amphibole minerals belong to two main groups: Fe-Mg-Mn-Li (holmquistite) and sodic amphiboles. Holmquistite has been described from some thirty localities around the world (London 1986), whereas Li-rich sodic amphiboles have been described from igneous rocks (Questa Caldera, Hawthorne et al. 1996a; Hurricane Mountain, Hawthorne et al. 1996b; Strange Lake, Hawthorne et al. 2001), and from metamorphic rocks (Kajlidongri, India, Hawthorne et al. 1992). Both amphibole types are typical of highly fractionated syenites and alkali syenites, and granitic pegmatites (Deer et al. 1999; London 1986).

Before the 1990s, the distribution and the crystal-chemical behavior of Li in amphiboles was poorly characterized, primarily because of the difficulties in analyzing Li at the micrometer scale. These problems have been resolved with the application of micro-analytical techniques and detailed crystal-structure refinements of suites of samples from petrologically well-characterized environments. In holmquistite, Li$_2$(Mg,Fe$^{2+}$)$_3$(Al,Fe$^{3+}$)$_2$Si$_8$O$_{22}$(OH)$_2$, Li is a B-group cation and is completely ordered at M4. In sodic amphiboles such as leakeite, Na$_2$[Na$_2$(Mg,Fe$^{2+}$)$_2$(Al,Fe$^{3+}$)$_2$Li]Si$_8$O$_{22}$(OH)$_2$, Li is a C-group cation and is strongly ordered at M3 (Hawthorne et al. 1993, 1994).

The available data show that Li can enter the amphibole structure through two main exchange reactions: (1) 2[M$_{2,3}$Fe$^{3+}$, Mg] = [M$_3$]Li + [M$_2$]Fe$^{2+}$, Al], connecting arfvedsonite (eckermannite) with leakeite (Hawthorne et al. 1994); and (2) Na$_2$[M$_{2,3}$Fe$^{2+}$, Al]Si$_8$O$_{22}$(OH)$_2$ (Oberti et al. 2002; Caballero et al. 2002), has Li at both the M4 and M3 sites, thus bridging the Mg-Fe-Mn-Li and the Na amphibole groups.

The apparent exchange vector $^8$Na + $^6$Li is the sum of different mechanisms and has no crystal-chemical significance, as it does not allow for local charge balance (Caballero et al. 2002; Oberti et al. 2003).

Holmquistite and riebeckite are classified in two different groups (Leake et al. 1997) and it has been assumed that there is a miscibility gap between these two amphiboles (Deer et al. 1999). However, recent investigation of amphiboles from the Pedriza Massif, Sierra de Guadarrama, Spain (Caballero et al. 1998; Oberti et al. 2000; Caballero et al. 2001) showed complete miscibility between Na and Li at the B-group sites (Caballero et al. 2002; Oberti et al. 2003).

There are no experimental studies concerning the relation

ANAB$^8$Na–BLi solid-solution in A-site-vacant amphiboles: synthesis and cation ordering along the ferri-clinoferroholmquistite–riebeckite join

GIANLUCA IEZZI,1 † GIANCARLO DELLA VENTURA,2, * FERNANDO CÁMARA,3 GIUSEPPE PEDRAZZI,4 AND JEAN-LOUIS ROBERT1

1ISTO, UMR 6113, 1A, Rue de la Férollerie, F-45071 Orléans Cedex 2, France
2Dipartimento di Scienze Geologiche, Università di Roma Tre, Largo S. Leonardo Murialdo 1, I-00146, Italy
3CNR-Istituto di Geoscienze e Georisorse, sezione di Pavia, via Ferrata 1, I-27100 Pavia, Italy
4Dipartimento di Sanità Pubblica, Sezione di Fisica, INFM Università di Parma, Via Volturno, 39, I-43100 Parma, Italy

ABSTRACT

Amphiboles were hydrothermally synthesized at 500 °C and 4 kbar in the system Li$_2$O-Na$_2$O-FeO-Fe$_2$O$_3$-SiO$_2$-H$_2$O, with nominal compositions along the riebeckite [Na$_2$Fe$^{2+}$Fe$_2$Si$_8$O$_{22}$(OH)$_2$]-ferri-clinoferroholmquistite [Li$_2$Fe$^{2+}$Fe$_2$Si$_8$O$_{22}$(OH)$_2$] join, where the exchange vector is NaLi at the B-site. Experimental products were characterized by powder XRD and SEM-EDAX, confirming very high amphibole yield along the join (>95%, plus minor quartz). The XRD patterns can be indexed in $\text{C}_2\overline{2}m$, and the refined cell parameters show linear variation as a function of composition. For the $^8$Li end-member, the IR spectrum shows a single sharp main band at 3614 cm$^{-1}$, which is assigned to the FeFeFe-OH-A$^+$ configuration. With increasing $^6$Na in the mineral, this band broadens and shifts 4 cm$^{-1}$ to higher frequencies. This effect can be attributed to the change in M4 site occupancy. Minor $^8$Na (partial solid-solution toward arfvedsonite) is also observed with increasing sodium in the system. Mössbauer spectroscopy confirms the cation distribution provided by IR data, and shows that a small, but significant amount of Fe$^{2+}$ occurs at M4 along the join. Infrared spectroscopy shows that the Li end-member has a very ordered structure, whereas intermediate compositions show local heterogeneities associated with the presence of two different B sites occupied by Na or Li.

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