Refinement of the crystal structure of zinnwaldite $2M_1$

MILAN RIEDER$^1$, JIRÍ HYBLER$^2$, L’UBOMÍR SMRČOK$^3$ and ZDENĚK WEISS$^4$

$^1$Department of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, CZ-128 43 Praha 2, Czech Republic
e-mail: Rieder@prfdec.natur.cuni.cz or Rieder@mbox.cesnet.cz
$^2$Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-162 00 Praha 6, Czech Republic
$^3$Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 5, SK-842 36 Bratislava, Slovak Republic
$^4$Central Analytical Laboratory, Technical University Ostrava, CZ-708 33 Ostrava-Poruba, Czech Republic

Abstract: Crystal structure of zinnwaldite $2M_1$ was refined in the $Cc$ space group with $R$ equal to 5.8% and $R_w$ 7.5%. Its octahedral sheet is hetero-octahedral, with octahedra around M1 and M3 having the same mean cation-anion bond length, whereas the third (around M2) has the mean bond significantly shorter. In terms of electrons, the cation ordering between M1 and M3 is less pronounced (16.2 e- vs 17.4 e-) than that between M1 (M3) and M2 (14.3 e-). Li and Fe$^{2+}$ prefer M1 (M3) to M2, Al does the opposite. Thus, like zinnwaldite $1M$ (Guggenheim & Bailey, 1977), the $2M_1$ polytype is hetero-octahedral. This is the first two-layer hetero-octahedral mica polytype known to date. The degree of tetrahedral cation ordering is very low in both zinnwaldites. Also, distortion characteristics of individual octahedra and tetrahedra in these zinnwaldites are very close to each other.

A comparison of the details of structures of $1M$ and $2M_1$ biotite and $1M$ and $2M_1$ zinnwaldite gave no indication that a geometrical or other advantage is associated with either $2M_1$ or $1M$ stacking in zinnwaldite.

Key-words: zinnwaldite, crystal structure, cation ordering, polytypism.

Introduction

To date, four structures of lithium-iron micas have been refined, zinnwaldite (Guggenheim & Bailey, 1977) and three “protolithionites” (Pavlishin et al., 1981; Weiss et al., 1993). The most interesting feature of the structures of these micas is the ordering of octahedral cations. When Durovič et al. (1984) examined a set of 51 refined structures, they noticed that octahedral sheets of all $3T$ structures are hetero-octahedral$^1$ and that micas with two-layer structures all have meso-octahedral sheets. They noticed that the obverse was not true: not all polytypes with hetero-octahedral sheets are $3T$ nor are $2M$ all those with meso-octahedral sheets. All refined micas with homo-octahedral sheets are $1M$ polytype, but micas with the $1M$ structure may also be meso- or hetero-octahedral.

The aim of the present research was to refine the structure of a different lithium-iron mica polytype, $2M_1$, to supplement the $1M$ and $3T$ structures refined earlier, to examine the cation ordering patterns and compare them with the known ones.

Experimental techniques

A single-crystal $0.63 \times 0.36 \times 0.012 \text{mm}$ in size was selected that gave sharp reflection spots. The zinnwaldite originates from mine Barbora, Krupka, Czech Republic. Recalculation of its