

## Spodumene from granitic pegmatites of various genetic types: crystal chemistry and OH defects concentrations

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Intensive research in past few decades established that many nominally anhydrous minerals contain various concentrations of structurally incorporated hydrogen. Studies of hydrogen entering crystal structure of minerals have high geological importance because these minerals act as storage of significant quantities of water in the Earth's mantle and OH defects control their physical and chemical properties (Bell and Rossman 1992). In contrast to the petrologically important mantle pyroxenes (Skogby 1999), there is a lack of systematic studies of hydrogen contents in less common upper Earth's crust pyroxenes.

Lithium-bearing pyroxene - spodumene (ideally  $\text{LiAlSi}_2\text{O}_6$ ) - is a typical major to accessory mineral in complex (Li) granitic pegmatites of the rare-element class. Several distinct paragenetic types of spodumene were distinguished depending on the parent pegmatite, position of spodumene in pegmatite evolution and its origin: primary spodumene (A) from pegmatites of albite-spodumene type (A1); primary spodumene from complex pegmatites chiefly of the spodumene (A2) but also of petalite, lepidolite and elbaite subtype (A3) (minor to accessory spodumene), respectively; secondary spodumene after petalite mostly from petalite subtype pegmatites (B) and hydrothermal spodumene (C) from open vugs in a variety of complex pegmatites (cf. London and Burt 1982; Černý 1991). Thirty well-characterized spodumene samples covering defined genetic types were studied by electron microprobe and both polarized Fourier transform infrared spectroscopy on oriented single-crystals and  $^{57}\text{Fe}$  Mössbauer spectroscopy.

Samples are commonly homogeneous with respect to major and minor elements and have compositions close to ideal formula. The samples of individual genetic types exhibit more or less apparent differences in the concentrations of minor cations chiefly in Fe (0.00 up to 4.26 wt.%  $\text{Fe}_2\text{O}_{3\text{tot}}$ ) and Na (0.05 to 0.20 wt.%  $\text{Na}_2\text{O}$ ) (Fig. 1a). Trivalent iron represents 90 to 94 % of  $\text{Fe}_{\text{tot}}$  from Mössbauer spectroscopy. High Fe content is typical for primary spodumene (Fig. 1a), whereas moderate Fe content is in secondary spodumene and hydrothermal spodumene is mostly Fe-poor. Iron ( $\text{Fe}^{3+} \gg \text{Fe}^{2+}$  from Mössbauer spectroscopy) occupy largely the *M1* site by  $\text{Fe}^{3+}_{\text{tot}}\text{Al}_{-1}$  substitution, only minor contents of  $\text{Fe}^{2+}$  could enter also *M2* site. Coupled substitution ( $\text{NaFe}^{3+}$ )( $\text{LiAl}$ )<sub>-1</sub> could also participate. Trace amounts of Mn (up to 0.28 wt.% MnO), Ti (up to 0.15 wt.%  $\text{TiO}_2$ ) and Cr (up to 0.07 wt.%  $\text{Cr}_2\text{O}_3$ ) were found.

The studied spodumene samples contain extremely low spectroscopically determined OH defect concentrations, ranging from 0.11 to 4.7 ppm  $\text{H}_2\text{O}$  by weight. Apparent differences in hydrogen contents in spodumene from various genetic types were revealed: magmatic spodumene contains highest amounts (0.25 up to 4.7 wt ppm  $\text{H}_2\text{O}$ ), secondary spodumene exhibits low variation in hydrogen contents (0.18 to 1.1 wt. ppm  $\text{H}_2\text{O}$ ), and hydrothermal spodumene (C) contains only 0.11 to 0.40 wt. ppm  $\text{H}_2\text{O}$  (Fig. 1b). Pleochroic behavior of sharp narrow OH bands indicate that the OH dipole (incorporated as a point structural defects) in spodumene is crystallographically oriented approximately parallel to  $n_\gamma$  ( $n_\gamma > n_\alpha \sim n_\beta$ ).

Systematic study of the variation of trace hydrogen distribution in spodumene has revealed that spodumene of higher P-T origin is among the most hydrous spodumene samples. Relative to other pyroxenes containing from 20 to 1200 wt. ppm  $\text{H}_2\text{O}$  depending on their geological environment (e.g., Skogby 1999) spodumene contains significantly lower OH defect concentrations. It is in agreement with the general trend that LT/LP pyroxenes (Skogby 1999), as well as most of other nominally anhydrous minerals (see Bell and Rossman 1992) contain lower hydrogen contents compared to their HT/HP counterparts. We suggest that differences among particular genetic types of spodumene do not reflect the actual activity of hydrous components during crystallization from pegmatitic melt or fluid, but the OH concentrations in spodumene are related to maximum solubility of OH in spodumene structure at given temperature/pressure. Moreover, crystal-chemical factors may have also played an indispensable role. Low hydrogen and Fe concentrations in secondary spodumene could easily be explained by low OH and Fe contents in primary petalite – a spodumene precursor. Low OH defect concentrations relative to HT/HP pyroxenes e.g., from mantle rocks (Skogby 1999) are in agreement with petrological models of formation of granitic pegmatites at PT conditions of the upper crust where  $P \sim 1\text{-}6$  kbar and  $T \sim 650\text{-}400^\circ\text{C}$ .

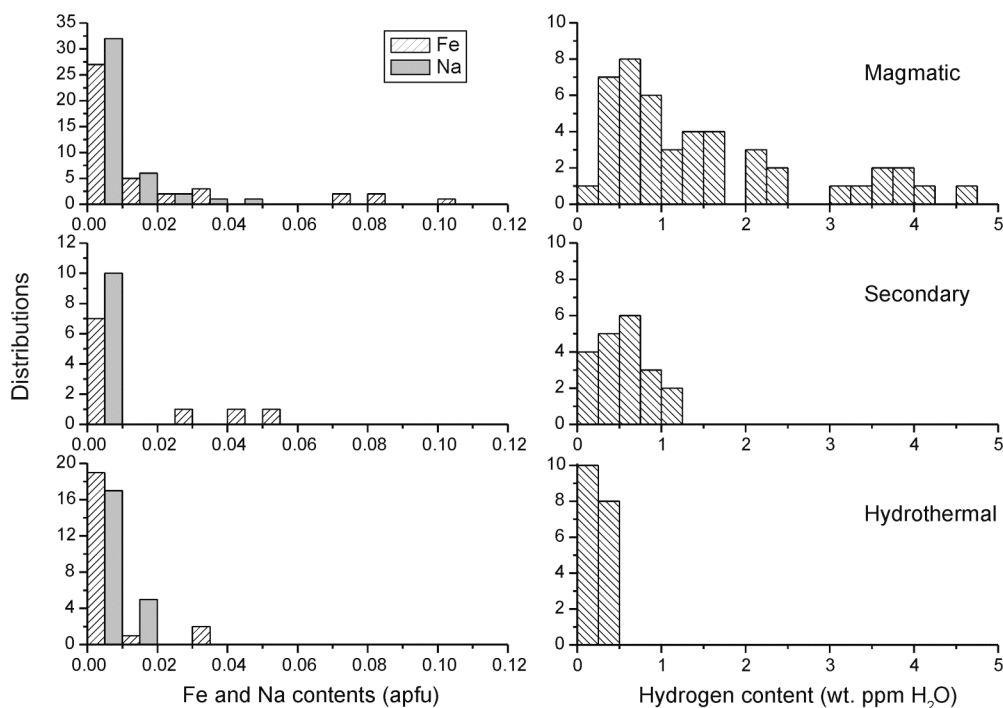


Figure 1: a) Variations of Fe and Na and b) OH defect concentrations for defined genetic types of spodumene.

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