

CRYSTAL CHEMISTRY OF LITHIUM IN PEGMATITE PHOSPHATES: A SIMS INVESTIGATION OF NATURAL AND SYNTHETIC SAMPLES

Frédéric Hatert¹

Luisa Ottolini²

Paul Keller³ & André-Mathieu Fransolet¹

¹Laboratoire de Minéralogie, Département de Géologie, Bâtiment B18, Université de Liège, B-4000 Sart-Tilman, Belgium (fhatert@ulg.ac.be).

²C.N.R.-Istituto di Geoscienze e Georisorse (IGG), Unità di Pavia, Via Ferrata 1, I-27100 Pavia, Italy.

³Institut für Mineralogie und Kristallchemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany.

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INTRODUCTION AND ANALYTICAL PROCEDURE

Lithium plays an essential geochemical role in granitic pegmatites, and this element can be used to monitor the degree of pegmatite differentiation (Ginzbourg 1960). Among primary phosphates, Li mainly occurs in minerals of the triphylite-lithiophilite [$\text{LiFe}(\text{PO}_4)\text{-LiMn}(\text{PO}_4)$] and amblygonite-montebrazite [$\text{LiAl}(\text{PO}_4)\text{F-LiAl}(\text{PO}_4)\text{OH}$] series. Starting from the triphylite-lithiophilite series, a mechanism of oxidation coupled with Li-leaching is frequently observed, leading to the formation of ferrisicklerite-sicklerite [$\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})\text{PO}_4\text{-Li}_{1-x}(\text{Mn}^{2+}, \text{Fe}^{3+})\text{PO}_4$] and of heterosite-purpurite [$\text{Fe}^{3+}(\text{PO}_4)\text{-Mn}^{3+}(\text{PO}_4)$] (Quensel 1957, Mason 1941).

In order to constrain the conditions of temperature and oxygen fugacity which occurred in pegmatites, we decided to reproduce experimentally several associations of pegmatite phosphates. Primary alluaudite + triphylite assemblages were reported in the Hagedorf-Süd (Germany), Buranga,

and Kibingo (Rwanda) pegmatites, and the hydrothermal experiments ($P = 1$ kbar, $T = 400\text{-}800^\circ\text{C}$) lead to the crystallisation of alluaudite + triphylite at 400 and 500°C , and of alluaudite + triphylite + maricite at 600 and 700°C (Hatert et al. 2005). Triphylite and sarcopside, which show lamellar exsolution textures in several pegmatites, were reproduced between 400 and 700°C ($P = 1$ kbar), starting from the compositions $\text{LiFe}_{2.5}(\text{PO}_4)_2$, $\text{LiFe}_2\text{Mn}_{0.5}(\text{PO}_4)_2$, and $\text{LiFe}_{1.5}\text{Mn}(\text{PO}_4)_2$ (Hatert et al. 2007).

The aim of this study is to measure the Li-content of several natural and synthetic phosphates by SIMS, in order to shed some light on the crystal chemistry of lithium in pegmatite phosphates. The measurements were performed with a Cameca IMS 4f ion microprobe installed at CNR-IGG, Pavia (Italy). We used a 12.5-kV accelerated $^{16}\text{O}^-$ primary-ion beam with a current intensity in the range $0.8\text{-}4$ nA, corresponding to a beam diameter of $3\text{-}6$ μm . The samples were polished, washed in an ultrasonic tank with ethanol, and Pt coated (400 Å thickness) before analysis. Secondary-ion signals of the following

isotopes $^6\text{Li}^+$, $^31\text{P}^+$ and $^{57}\text{Fe}^+$ were detected at the electron multiplier. Acquisition times were 3 seconds for Li and P (each), and 6 seconds for Fe over 3 cycles. Analyses were done under *steady-state* sputtering conditions after 360-second sputtering using $\sim 75\text{--}125$ eV secondary ions. As it was demonstrated (Otolini et al. 1993, 2002), the choice of medium-to-high-energy (*energy filtering*) secondary ions as analytical ones is particularly useful to reduce matrix effects affecting light-element ionization and improve the reproducibility of analysis.

We used as reference material for SIMS Li-analyses triphylite from the Buranga pegmatite, Rwanda. The wet chemical analysis of this sample was performed by Héring (1989) and shows a Li content of 9.96 wt% Li_2O . The calibration factor for Li in the standard was obtained through the calculation of the experimental Li ion yield after choosing P and Fe as the inner elements for the matrix. We thus derived the $\text{IY}(\text{Li}/\text{P})$ and the $\text{IY}(\text{Li}/\text{Fe})$. Here we remember, as an example, the definition of the relative-to-P ion yield of Li, $\text{IY}(\text{Li}/\text{P})$, as $(\text{Li}^+/\text{P}^+)/(\text{Li}(\text{at})/\text{P}(\text{at}))$ where Li^+ , P^+ are the current intensities detected at the electron multiplier and (at) represents the elemental atomic concentration. The $\text{IY}(\text{Li}/\text{P})$ and $\text{IY}(\text{Li}/\text{Fe})$ were thus calculated for the triphylite standard. The two IYs were used to calculate the Li_2O concentrations (wt%) in the "unknown" compounds, concentrations which were thus cross-checked by means of two independent inner references for the matrix: P and Fe. The final Li_2O (wt%) data for each crystal analysed was averaged between those two quantified by means the $\text{IY}(\text{Li}/\text{P})$ and $\text{IY}(\text{Li}/\text{Fe})$. For Li_2O concentration values at percent level, the analytical uncertainty is always very low, i.e., on the order of few percent relative as 1 st.dev.%.

Electron-microprobe analyses were performed with a Cameca SX-50 instrument located in Bochum, Germany (analyst H.-J. Bernhardt), which operated in the wavelength-dispersion mode with an accelerating voltage of 15 kV and a beam current of 15 nA. The standards used were fraconite from Kabira (sample KF16, Françoislet 1975) (for Fe, Mn, P), pyrope (Mg, Al, Si), ZnO (Zn), andradite (Ca), jadeite (Na), and a K-glass (K).

OLIVINE-TYPE PHOSPHATES

Analyses of 6 natural triphylite samples show lithium contents from 9.51 to 9.88 wt. % Li_2O , while the analyses of 4 lithiophilites show higher Li_2O contents ranging from 10.23 to 11.15 wt. %. These compositions correspond to 0.99-1.04 Li *a.p.f.u.* in triphylites, and 1.07-1.15 Li *a.p.f.u.* in lithiophilites. The significant Li enrichment of lithiophilites indicates that Li can also occur in the M(2) site of the olivine structure. 11 ferrisicklerite samples show Li_2O -contents from 1.65 to 2.84 wt. % (= 0.17 to 0.29 *a.p.f.u.*), and 3 heterosite samples contain 0.16 to 0.21 wt. % Li_2O (= 0.02 *a.p.f.u.*). The presence of significant amounts of Li in heterosites was unexpected, and the low Li content of ferrisicklerites indicates that trivalent manganese also occurs in this mineral. The formula of Li-poor ferrisicklerite corresponds to $\text{Li}_{0.17}\text{X}_{0.75}\text{Mn}^{3+}_{0.10}\text{Mn}^{2+}_{0.0}\text{Mg}_{0.06}(\text{PO}_4)$.

Synthetic triphylites, associated with alluaudites, maricites and X-phase, show a decrease of the $\text{Li}/(\text{Li} + \text{Na})$ ratio, from 0.96-0.97 at 600°C, to 0.92-0.94 at 800°C. This decrease of the Li content in triphylites is correlated with an increase of the Li content in alluaudites, maricites, and X-phase, and can be used for geothermometric applications (Hatert et al. 2005).

Alluaudite-type phosphates

The SIMS analyses of natural alluaudites from Buranga, Kibingo, and Hagendorf-Süd, show Li_2O contents between 0.004 and 0.010 wt. %. The presence of lithium in natural alluaudite-type phosphates is mentioned in the literature (Moore & Ito 1979), but the high Li_2O contents, up to 0.06 wt. %, are certainly due to impurities, difficult to avoid when minerals are mechanically separated for wet-chemical analyses. Our SIMS measurements on natural alluaudites are consequently the first confirmed occurrences of lithium in these phosphates. This result is not really surprising, since Hatert et al. (2000, 2002) and Hatert (2004) inserted up to 1 Li *a.p.f.u.* in the $(\text{Na}_{1-x}\text{Li}_x)\text{MnFe}(\text{PO}_4)_2$, $(\text{Na}_{1-x}\text{Li}_x)\text{CdIn}_2(\text{PO}_4)_3$, and $(\text{Na}_{1-x}\text{Li}_x)\text{Mn}_{1-x}\text{Fe}_{1-x}(\text{PO}_4)_3$ alluaudite-type solid solutions.

The Li_2O contents of alluaudites, hydrothermally synthesized during the investigation of the alluaudite + triphylite

assemblage, range from 0.06 wt % at 500°C, to 0.22 wt. % at 700°C. This last value corresponds to 0.072 Li *a.p.f.u.*. The temperature dependence of the $\text{Li}/(\text{Li} + \text{Na})$ ratios shows that the Li contents of alluaudites progressively increase with temperature, while the Li content of triphylite-type phosphates decreases due to the $\text{Li} \rightarrow \text{Na}$ substitution (Hatert et al. 2005).

SYNTHETIC TRIPHYLITE + SARCOPSIDE ASSEMBLAGES

The experiments, performed between 400 and 700°C (1 kbar) during the investigation of the triphylite + sarcopside assemblage, show that the Li content of triphylites significantly decreases with temperature, from 0.72 *a.p.f.u.* at 400°C, to 0.37 *a.p.f.u.* at 700°C, for the $\text{LiFe}_{2.5}(\text{PO}_4)_2$ starting composition (Hatert et al. 2007). The Li content of sarcopside, however, is relatively low, and increases from 0.01 *a.p.f.u.* at 400°C, to 0.05 *a.p.f.u.* at 600°C (Fig. 1).

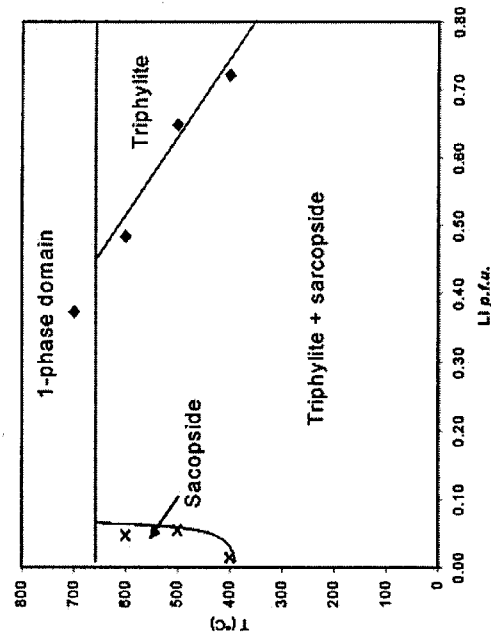


Figure 1.- Experimental phase diagram obtained hydrothermally at 1 kbar, from the $\text{LiFe}_{2.5}(\text{PO}_4)_2$ starting composition.

REFERENCES

Fransolet A-M 1975. Etude minéralogique et pétrologique des phosphates de pegmatites granitiques. PhD thesis, University of Liège, 333 p

Ginzbourg AI 1960. Specific geochemical features of the pegmatitic process. International Geological Congress, report of the twenty-first session, Norden, Part 17, 111-121

Hatert F 2004. The crystal chemistry of lithium in the alluaudite structure: a study of the $(\text{Na}_{1-x}\text{Li}_x\text{Li}_{1.5}\text{Mn}_{1.5}\text{Fe}^{3+}(\text{PO}_4)_3$ solid solution ($x = 0$ to 1). Mineral Petrol 81: 205-217

Hatert F, Keller P, Lissner F, Antenucci D, Fransolet A-M 2000. First experimental evidence of alluaudite-like phosphates with high Li-content: the $(\text{Na}_{1-x}\text{Li}_x)\text{MnFe}_2(\text{PO}_4)_3$ series ($x = 0$ to 1). Eur J Mineral 12: 847-857

Hatert F, Antenucci D, Fransolet A-M, Liégeois-Duyckaerts M 2002. The crystal chemistry of lithium in the alluaudite structure: a study of the $(\text{Na}_x\text{Li}_{1-x})\text{CdIn}_2(\text{PO}_4)_3$ solid solution ($x = 0$ to 1). J Solid State Chem 163: 194-201

Hatert, F & Fransolet A-M 2005. Stability of the alluaudite + triphylite paragenesis in granitic pegmatites, and first experimental evidence of sodium incorporation into triphylite. ELBA 2005 - Crystallization processes in granitic pegmatites, Abstract Book, 16-17

Hatert, F, Roda-Robles E, Keller P, Fontan F & Fransolet A.-M. 2007. Petrogenetic significance of the

triphylite + sarcopside intergrowths in granitic pegmatites : an experimental investigation of the $\text{Li}(\text{Fe,Mn})(\text{PO}_4)(\text{Fe,Mn})_3(\text{PO}_4)_2$ system. Granitic pegmatites: the state of the art, Book of Abstracts, 44

Héring P 1989. Contribution à l'étude minéralogique de phosphates de fer et de manganèse de la pegmatite de Buranga, Rwanda. Master thesis, University of Liège, 101 p

Mason B 1941. Minerals of the Varuträsk pegmatite. XXIII. Some iron-manganese phosphate minerals and their alteration products, with special reference to material from Varuträsk. Geol Fören Stockholm Förh 63: 117-175

Moore PB, Ito J 1979. Alluaudites, wylleites, arrojadites: crystal chemistry and nomenclature. Mineral Mag 43: 227-235

Ottolini L, Bottazzi P, Vannucci R 1993. Quantification of Lithium, Beryllium and Boron in Silicates by Secondary Ion Mass Spectrometry Using Conventional Energy Filtering. Anal Chem 65: 1960-1968

Ottolini L, Camara F, Hawthorne FC, Stirling J 2002. SIMS matrix effects in the analysis of light elements in silicate minerals: Comparison with SREF and EMPA data. Am Mineral 87: 1477-1485

Quensel P 1957. The paragenesis of the Varuträsk pegmatite, including a review of its mineral assemblage. Arkiv för Mineralogi och Geologi 2(2): 9-125

FIRST FIND OF KRISTIANSENITE IN SPAIN: COMPARISON WITH THE TYPE SPECIMEN BY NON-DESTRUCTIVE TECHNIQUES

P. Prado-Herrero¹
 J. García-Guinea²
 E. Crespo-Feo²
 V. Correcher³
 C. Menor⁴

¹ MICINN, Albacete 5, Madrid 28027, Spain. (pedro.prado@micinn.es)
² Museo Nacional de Ciencias Naturales (CSIC), José Gutiérrez Abascal 2, Madrid 28006, Spain
³ CIEMAT, Av. Complutense 22, 28040 Madrid, Spain
⁴ Centro de Astrobiología (CSIC-INTA) Ctra. Torrejón-Ajalvir, Km 4 Torrejón de Ardoz, Madrid, Spain

ABSTRACT

We report herein a new find of kristiansenite from a pocket in an intra-granite pegmatite from Cadalso de los Vidrios, near Madrid, Spain. This specimen of a late hydrothermal scandium silicate has been studied by Environmental Scanning Electron Microscopy with Energy Dispersive Spectrometry probe (ESEM-EDS), Micro-Raman Spectrometry and ESEM-Cathodoluminescence (ESEM-CL), all of them non-destructive techniques. The sample is a single perfect pyramidal monocrystal found in a small cavity less than one mm across. The experimental chemical, molecular and spectral luminescent information was later compared with the type specimen from Norway and the second find, at Baveno, Italy. Our Raman spectrum matches the spectrum of the Norwegian specimen, with minor variation in the intensity of the peaks; the chemical composition recorded by EDS also shows minor variations. In addition, the CL spectrum displays several narrow peaks, probably associated with REE in Ca positions. The geochemical framework of this new locality, with pegmatite pockets in A-type granites rich in Sc-bearing minerals and other REE, have many similarities with those of Norway and Italy.

Keywords: kristiansenite, cathodoluminescence, Raman, REE

INTRODUCTION

Approved by the IMA in 2000 (#2000-51), the name *kristiansenite* honours Mr. Roy Kristiansen (born in 1943), a Norwegian mineralogist who first noticed the new mineral collected from the Heftefjern pegmatite (of amazonite-“cleavelandite” type) 200–250 m long and 3–4 m wide, in the Tørdal area, Drangedal, Telemark County (southern Norway), the

type locality for this disilicate species. It is a triclinic C1 (pseudomonoclinic) sorosilicate, with theoretical formula $\text{Ca}_2\text{ScSn}(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})$, described as new mineral species by Raade et al. (2002); the crystal structure was determined by Ferraris et al. (2001).

The second find of kristiansenite was described in the Miniera Seula (Montecatini quarry), Baveno, Verbano-Cusio-Ossola, Piemonte, Italia (Guastoni & Pezzotta,