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Lithium extraction from the mineral zinnwaldite: Part I: Effect of thermal treatment on properties and structure of zinnwaldite[☆]

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ABSTRACT

Lithium has become an energy critical element and thus the security of supply is of great importance. As a local German resource, attention was directed towards the mica-type mineral zinnwaldite. It represents a lithium-rich siderophyllite and corresponds to an intermediate polylithionite–siderophyllite solid solution with high contents of fluoride. Mineral samples from the deposit Zinnwald/Cínovec at the German/Czech border were analyzed and characterized by a variety of methods, particularly concerning its thermal behavior. Understanding the thermal behavior of the mica gives the opportunity to develop new and cost-efficient methods for lithium extraction.

Investigations with different spectroscopic methods revealed the decomposition mechanisms. Starting at 300 °C, oxidation of Fe^{2+} catalyzed the dehydroxylation of the mica by dehydrogenation. This is followed by a dehydroxylation similar to the mechanism of dioctahedral micas. At higher temperatures, the release of HF was detected. At about 800 °C the precipitation of hematite was observed. The complete decomposition of Zinnwaldite takes place at 900 °C, it is accompanied by the liberation of SiF_4 and leads to the formation of several solid decomposition products.

By means of single-crystal diffraction using X-rays and neutrons the structural changes could be identified after annealing at 700 °C. The results point to a transformation into a polylithionite-like structure, the end member of the solid solution series.

1. Introduction

Due to the growing market of rechargeable lithium batteries for electronic devices and electric vehicles, lithium has become an element of high interest (Choubey et al., 2016; Jaskula, 2016). Due to this, lithium supply security has become of increased importance, especially as European deposits of lithium are limited.

As one of the oldest raw materials for the industrial lithium salt production (Girsewald and Weidmann, 1933; Voigt, 2014), zinnwaldite was rediscovered. The deposit Zinnwald/Cínovec at the German/Czech border appears profitable for lithium recovery.

Zinnwaldite represents a trioctahedral mica with an average of 2–4 wt% Li_2O and belongs to the polylithionite–siderophyllite solid solution series (Tischendorf et al., 2007). The crystal structure of the zinnwaldite 1 M polytype was published by Guggenheim and Bailey (Guggenheim and Bailey, 1977). It displays an octahedral and tetrahedral ordering pattern, which causes an octahedral flattening und tetrahedral rotation. Rieder suggested that the ordering will be broken at higher temperatures (Rieder, 1968). This would cause a change in symmetry and thus in space group of the crystal structure.

Due to its high fluorine content zinnwaldite is of high thermal stability (Ogorodova et al., 2010). Therefore, applied and suggested processes for lithium recovery are based on high temperature calcination or the use of strong acids (Schneider, 1955; Alex and Suri, 1996; Jandová et al., 2009; Jandová et al., 2010; Siame and Pascoe, 2011; Jandová et al., 2012; Vu et al., 2013).

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Table 1
Chemical composition and calculated formula coefficients.

Chemical composition wt%		Formula coefficients	
SiO_2	50.45	Si	3.44
Al_2O_3	20.28	Al	0.46
FeO	9.71	$^{[IV]}$Sum	3.90
Fe_2O_3	0.33	Fe^{2+}	0.55
K_2O	9.11	Fe^{3+}	0.02
Li_2O	3.38	Al	1.17
Rb_2O	0.33	Li	0.93
Na_2O	0.12	Mn	0.07
MnO	1.46	Ti	0.01
MgO	0.02	Mg	0.00
CaO	0.15	$^{[VI]}$Sum	2.75
TiO_2	0.21	K	0.79
F	7.58	Na	0.02
H_2O	0.46	Rb	0.01
		Sum	0.82
Sum	103.61	OH	0.37
2F = O	−3.19	F	1.63
Sum	100.42	O	10.00
		Sum	12.00

Starting in 1923 a roasting process with 30% K_2SO_4 at 900 °C was applied (Motock, 1946; Schneider, 1955). The roasted mixture was boiled in water and the solution was concentrated by evaporation before Li_2CO_3 was precipitated using K_2CO_3.

Understanding the thermal behavior of the mica gives the opportunity to develop new and cost-efficient methods for lithium extraction.

This work focuses on the structural changes of zinnwaldite when heated, particularly the mechanism of iron oxidation and dehydroxylation. For this aim, a variety of methods were applied. A subsequent article (Part II: "Lithium carbonate recovery by direct carbonation of sintered zinnwaldite concentrate") will present a new process for lithium extraction based on this research (Martin et al., 2017).

2. Material and methods

2.1. Zinnwaldite sample

For all annealing experiments a homogenized mineral powder of the size fraction x < 45 µm was used. The powder was produced by magnetic separation of the mineral and subsequent crushing and milling (Chehreh Chelgani et al., 2015). The samples were collected from an old underground mine "Tiefe-Hilfe-Gottes-Stollen“ located in Zinnwald-Georgenfeld in the Ore Mountains (Erzgebirge) at the German/Czech border.

For single crystal analysis, samples from drill cores of the same deposit were used. The single crystals were obtained by high voltage pulse fragmentation (see Sandmann and Gutzmer (2013) for more information).

Table 2
Overview of the characteristics of the DTA/TG measurements of zinnwaldite in different atmospheres.

	N_2	Air
Initial weight [mg]	15.043	13.004
Total mass loss [%]	2.1	1.2
Onset DTA [°C]	894 (endo), 951 (exo)	911
Minima DTA [°C]	912	923
Maxima DTA [°C]	961	–

Table 3
Band assignment of the observed vibration bands in the DRIFT-spectra of zinnwaldite samples after annealing at different temperatures.

Wave number [cm^{-1}]	Band assignment	Reference
3480	ν H_2O (adsorbed)	(Madejová, 2003)
3557	ν (Al, Fe^{2+}, □)–OH, ν (Fe^{3+}, Fe^{3+}, □)–OH	(Goldstein et al., 1995; Besson and Drits, 1997)
3572	ν (Al, Fe^{3+}, □)–OH,	(Besson and Drits, 1997)
3594	ν (Al, Fe^{2+}, □)–OH	(Goldstein et al., 1995; Zviagina et al., 2004)
3620	ν (Al, Al, □)–OH, ν (Li, Al, Al)-OH	(Goldstein et al., 1995; Madejová, 2003)
3651	ν (Li, Al, Fe^{2+})	(Goldstein et al., 1995; Madejová, 2003)
3700	ν (M^{2+}, M^{2+}, M^{2+})–OH	(Vedder, 1964)

The chemical composition and the calculated formula are reported in Table 1. They are based on electron-microprobe and wet chemical analysis and the recommendations of Rieder (1970). The proportion of Fe^{2+}/Fe^{3+} and $^{[IV]}Al/^{[VI]}Al$ were determined by Mössbauer spectroscopy and ^{27}Al-MAS-NMR spectroscopy, respectively. With the coefficients from Table 1 the chemical formula would be written as $Li_{0.93}Fe_{0.57}Al_{1.17}Mn_{0.07}Ti_{0.01}Si_{3.44}Al_{0.46}O_{10}(OH)_{0.37}F_{1.63}$.

2.2. Annealing experiments

Zinnwaldite powder was tempered in corundum crucibles with the help of a muffle furnace for five and ten hours, respectively. Samples were prepared in steps of 100 K from 100 °C up to 1000 °C. The samples were cooled down to room temperature and then studied by a variety of different methods. Additionally, three samples were prepared in evacuated, sealed quartz ampoules which were kept in a muffle furnace at 300 °C, 600 °C and 800 °C for five hours.

2.3. Thermal analysis

Thermal analyses were carried out by using a TG/DTA 220 from SEIKO. About 15 mg of the zinnwaldite were poured into a platinum crucible and heated up to 1000 °C with a heating rate of 10 K/min. Nitrogen, air and argon gas flows of 300 mL/min were applied (see Table 2). Dry gases as well as gases with defined humidities were used. From the TG and DTA curves the measurements of an empty crucible were subtracted.

For the mass-spectrometric measurements of the gas phase released during heating a Hiden HPR20 triple-quadrupole mass analyzer was used. The sample was located in an evacuated quartz tube which was heated in a Xerion RO tubular furnace. It was held at 150 °C for 6 h before the measurements started. Then the oven was heated to 1000 °C with a heating rate of 1 K/min. This temperature was held for one hour before being allowed to cool down.

The thermal behavior of sheet silicates has been widely studied (Grim and Rowland, 1942b; Guggenheim and Koster van Groos, 2001; Brigatti and Guggenheim, 2002; Smykatz-Kloss et al., 2003). It is known that endothermal effects can be assigned to desorption and dehydration of water from the surface or the interlayer. At higher temperatures they are attributed to the dehydration and dehydroxylation and finally the melting of the mineral. Exothermal effects are assigned to the