der Vegetationsintensität, einem wichtigen Parameter im   Rahmen des Rekultivierungsmonitoring.

^{57}Fe- and ^{119}Sn- Mössbauer study on stannite (Cu$_2$FeSnS$_4$) - kesterite (Cu$_2$ZnSnS$_4$) solid solution

F. Benedetto[1], G.P. Bernardini[1], D. Borrini[1], W. Lottermoser[2], G. Tippelt[2], G. Amthauer[2]

[1] Dipartimento di Scienze della Terra, Università di Firenze, Italy, [2] Institut für Mineralogie, Universität Salzburg, Austria

Stannite (Cu$_2$FeSnS$_4$) is a very important sulfide both for its occurrence in tin-bearing ore and for its physical and chemical properties. The stannite structure (Brockway, 1934) can be derived from that of chalcopyrite, substituting half of the Fe atoms by Sn atoms, with a change of the symmetry from $I\bar{4}2d$ to $I\bar{4}2m$. This model was confirmed by Hall et al.´s (1978) structural refinement. In the pseudobinary system Cu$_2$FeSnS$_4$ (stannite) - Cu$_2$ZnSnS$_4$ (kesterite), a rearrangement of Cu and Zn atoms would lead to the space group 14. Such a rearrangement in the kesterite structure implies that half stannite Cu-sites are occupied by Zn atoms, while all the stannite Fe-sites become Cu-sites. On the other hand, Chicagov et al. (1986), studying the Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ series, found no evidence supporting the structural model for kesterite proposed by Hall et al. (1978) and assigned kesterite to the same space group as stannite, 142 m. Both Hall et al.´s (1978) structural models for stannite and kesterite are very similar in that Cu, Fe, Zn and Sn cations are in tetrahedral coordination, but these tetrahedra differ in dimension and bond angles. ^{57}Fe and ^{119}Sn Mössbauer spectra and magnetic susceptibility data collected firstly on stannite by Eibschütz et al. (1967) suggested the cation valences Cu$_2^+$Fe^{2+}Sn^{4+}S$_4$.

  Kissin and Owens (1979), in their study on the pseudobinary system stannite - kesterite, proposed the existence of a miscibility gap from x$_{Zn}$ $\cong$ 0.25 to x$_{Zn}$ $\cong$ 0.40. On the other hand Corazza et al. (1986) and

Bernardini et al. (1990) suggested the presence of a complete solid solution, as shown by XRD analyses both on single crystal and powdered samples.

  In the present study, a combined ^{57}Fe and ^{119}Sn Mössbauer study has been performed on the whole solid solution stannite - kesterite consisting of natural and synthetic samples. No discontinous change of the Mössbauer parameters of ^{57}Fe as well as of ^{119}Sn as function of the composition has been observed, thus confirming the existence of a complete solid solution between both compounds.

Bernardini, G.P., Bonazzi, P., Corazza, M., Corsini, F., Mazzetti, G., Poggi, L., Tanelli, G., 1990: Eur. J. Mineral. 2, 219-225.

Brockway, L.O., 1934: Z. Kristallogr. 89,.434-441.

Chicagov, A.V., Osadchii, E.G., Usyakovskaya, Z.V., 1986: N. Jb. Miner. Abh. 155, 15-22.

Corazza, M., Corsini, F., Tanelli, G., 1986: Rend. SIMP 41, 217-222.

Eibschütz, M., Hermon, E., Shtrikman, S., 1967: J. Phys. Chem. Solids. 28, 1633-1636.

Hall, S.R., Szymanski, J.T., Stewart, J.M., 1978: Can. Mineral. 16, 131-137.

Kissin, S.A., Owens, D.R., 1979: Can. Mineral. 17, 125-135.

H$_2$O in synthetic Mg-cordierite

C. Bertoldi[1], N.-S. Rahmoun[1], C.A. Geiger[1], E. Dachs[2]

[1] Institute for Geoscience, Department of Mineralogy, University of Kiel, Germany
[2] Institute of Mineralogy, University of Salzburg, Austria

Anhydrous Mg-cordierite was synthesized at 1 bar and 1380°C for 240 hr. from a glass of bulk composition 2MgO*2Al$_2$O3*5SiO$_2$. The run product was investigated with X-ray powder diffraction and electron microprobe analysis. The powder X-ray pattern was refined by using the Rietveld method yielding the following cell parameters a = 17.0657(4) Å, b = 9.7208(2) Å, c =

9.3406(2) Å (R$_{wp}$=8%, R$_B$=3%). The distortion index as defined after Miyashiro (1957) is Δ = 0.25 indicating complete Al/Si ordering. The formula derived by EMPA, on the basis of 18 oxygens, is Mg$_{1.98(1)}$Al$_{3.97(2)}$Si$_{5.03(1)}$O$_{18}$. Water was incorporated into the structural channels by hydrothermal experiments made at 1, 2, 3, 4 and 5 kbar and 600°C. The water content was determined by Karl

Fischer Titration (Behrens, 1995). Powder FT-IR spectra (Fig.1) show two bands at about 3595 cm^{-1} (symmetric ν_1 mode) and 3690 cm^{-1} (asymmetric ν_3 mode) defining Class I-Type 1,2 H$_2$O (Kosolev and Geiger, 2001). We observed no band for Class I-Type 3 H$_2$O. The absorptivity coefficient, $\varepsilon_{H2O, \nu3}$, on a molar basis for the I ν_3

mode at 3690 cm^{-1} was calculated as $\varepsilon_{H2O, I \nu3} = 92$ L mol^{-1} cm^{-1}, which is in slight contrast to the value at Vry et al. (1990), whose absorptivity coefficient, $\varepsilon_{H2O, I \nu3}$, is 77 L mol^{-1} cm^{-1}. We present an IR working curve for Class I-Type 1,2 H$_2$O in synthetic alkali free hydrous Mg-cordierite (Fig. 2).
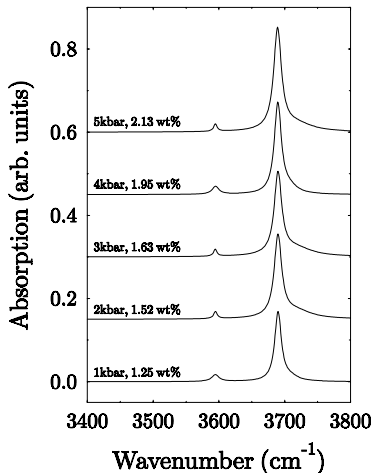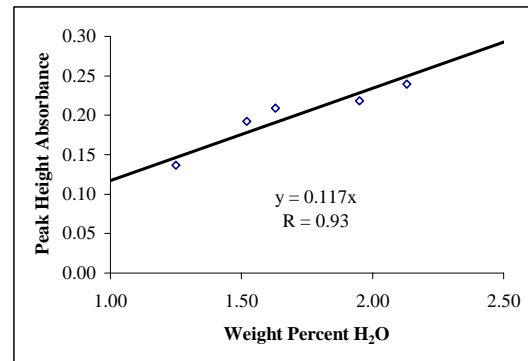

Fig. 1: *FT-IR powder spectra (KBr pellet technique 3mg: 200mg) of hydrous Mg-Cordierites synthesized at different pressures and 600° C.*

Fig. 2: *IR working curve for H$_2$O in syn. Mg-cordierite. Total H$_2$O contents determined by KFT.*

Behrens, H., 1995: Determination of water solubilities in high-viscosity melts: An experimental study on NaAlSi$_3$O$_8$ and KAlSi$_3$O$_8$ melts. Eur. J. Mineral., 7, 705-920.

Kosolev, B.A., Geiger, C.A., 2001: Cordierite II: The role of CO$_2$ and H$_2$O. Am. Min. 85,1265-1274.

Miyashiro, A., 1957: Cordierite-indialite relations. Am. J. Sci., 255: 43-62.

Vry, J.K., Brown, P.E., Valley, J.W., 1990: Cordierite volatile content and the role of CO$_2$ in high grade metamorphism. Am. Min., 75, 71-88.

Zeolith-ähnliche mikroporöse Phosphatstrukturen

A. Bieniok, G. Amthauer

Institut für Mineralogie, Universität Salzburg, Österreich

Ähnlich wie von aluminosilikatischen Zeolith-Mineralen bekannt, können Metallphosphate poröse Gerüste mit Käfigen und Kanälen bilden, in denen dann die für den Ladungsausgleich notwendigen Kationen und zusätzlich kleinere Moleküle eingelagert sind. Nicht nur bekannte Zeolith-Typen mit neuer Gerüstchemie, sondern auch völlig neue poröse Strukturen können aus den neuen Syntheseansätzen resultieren. Die porösen Metallphosphate sind von besonderem Interesse für neue Anwendungsmöglichkeiten in katalytischen Prozessen und als Ionenaustausch-Material.

Hydrothermale und solvothermale Synthesemethoden in Stahlautoklaven unter autogenen Drücken und moderaten Temperaturen (bis ~250°C) werden zur Herstellung von solchen mikroporösen Verbindungen eingesetzt. Im System Na$_2$O-Cs$_2$O-ZnO-P$_2$O$_5$ kann unter hydrothermalen Bedingungen die hexagonale Verbindung Na$_6$Cs$_2$[Zn$_6$P$_6$O$_{24}$](OH)$_2$ x 5H$_2$O hergestellt werden, die den gleichen Gerüstaufbau wie das Mineral Cancrinit

besitzt, aber aus Zinkat- und Phosphat-Tetraedern aufgebaut ist. Strukturgebendes Templat für die Cancrinit-Käfige sind hierbei Cs-Ionen. Solvothermale Synthesen mit Gallophosphaten eignen sich gut, um Eisen in Gerüststrukturen einzubauen. Die dabei entstandene Phase NH$_4$[FeGa$_2$P$_3$O$_{12}$(H$_2$O)$_2$] ist ein neues Ammoniumeisengallophosphat, das aus einem Gerüst aus verschiedenen Polyederarten aufgebaut ist. Phospat-Tetraeder verknüpfen hier pseudo-trigonale GaO$_5$-Bipyramiden und verzerrte FeO$_4$(H$_2$O)$_2$-Oktaeder. Dieses heterogene Gerüst bildet aber ebenfalls mikroporöse Kanäle aus, in denen die für den Ladungsausgleich notwendigen Ammoniumgruppen lokalisiert sind. Die Materialchemie dieser Verbindungen zeigt, dass man, ausgehend von den Bildungsbedingungen natürlicher Minerale, durch die entsprechende Variation der Syntheseparameter eine Vielzahl von neuen, interessanten Phasen herstellen und dadurch Materialeigenschaften verändern bzw. optimieren kann.