

Minerals

PS08.02.01 RIETVELD-REFINEMENTS AND TEMPERATURE-DEPENDENT MOESSBAUER SPECTROSCOPIC INVESTIGATIONS OF SYNTHETIC C2/c CLINOPYROXENES. G. Amthauer, G. J. Redhammer, W. Lottermoser, Institute of Mineralogy, University of Salzburg, Austria

C2/c clinopyroxenes on the binary join hedenbergite $[M2]Ca[M1]Fe^{2+}Si_2O_6$ - acmite $Na+Fe^{3+}Si_2O_6$ were synthesized using standard hydrothermal techniques and investigated by means of temperature-dependent Moessbauer spectroscopy between 80 and 700K, revealing Fe^{2+} and Fe^{3+} on the octahedral M1 position only and showing additional resonant absorption with hyperfine parameters intermediate between Fe^{2+} and Fe^{3+} above 250K within the solid solution series, which gains intensity with increasing temperature. This is interpreted as thermally activated electron transfer between Fe^{2+} and Fe^{3+} statistically occupying the M1 sites. Syntheses were done at 4 kbar, 973K and the redox conditions of the nickel/nickeloxid solid state buffer. Run products were characterized by microprobe analyses and XRP-diffraction including Rietveld refinements on selected samples in addition to Moessbauer spectroscopy. The dependence of lattice parameters on chemical composition deviates from linearity. Mean M1-O distances decrease with increasing acmite component, whereas mean M2-O and mean T-O distances show no significant variation. Within the M1-zig-zag chain, which is parallel to the crystallographic c-axis and consists of edge-sharing octahedra, the shortest Fe-Fe distance is 3.112(2)Å in hedenbergite and 3.196(2)Å acmite. Room temperature Moessbauer spectra of the end-compositions show one narrow split doublet with hyperfine parameters characteristic for Fe^{2+} and Fe^{3+} respectively, whereas within the solid solution series the Fe^{2+} resonance absorption feature is broadened asymmetrically and can be refined into three doublets due to next nearest neighbour effects.

PS08.02.02 SPINEL FORMATION IN THE MESOSPHERE OF THE EARTH AFTER CRETACEOUS/TERTIARY IMPACT. S. Aslanian, A. Preisinger and L. Petrás, Institute of Mineralogy, Crystallography and Structural Chemistry, Tech. University of Vienna, A-1060 Vienna, Getreidemarkt 9, AUSTRIA.

Magnetic spinels separated from hemipelagic and pelagic sediments of the Cretaceous/Tertiary (K/T) boundary sections of Bjala, Bulgaria and Cerbara, Italy were analysed by X-ray powder diffraction and by a scanning electron microscope equipped with microprobe.

65 million years ago Bjala was located at a distance of about 10000 km and Cerbara about 8800 km from the impact structure in Yucatan, Mexico. It is proposed, that the spinels found in the K/T boundaries are formed as re-condensed material of a hot fire ball induced by the impact in the mesosphere of the Earth at an altitude of ~80-100 km.

The spinels were extracted with a strong magnet from a suspension of the K/T boundary clay. The spinels were crystallized as octahedra in the range of 1-20 µm in sizes. The magnetic minerals at both sites are principally nickel-rich (Ni>1%) magnesioferrite spinels with strong variation in the chromium content (0-10% Cr_2O_3). The octahedra from the K/T boundary sediment from Cerbara show a lower Cr content with lattice parameter of $a=8.366\text{Å}$ than those of the larger particles (5-20 µm) from Bjala with lattice parameter of $a=8.345\text{Å}$. However the smaller particles (1-3 µm) from the latter site show low Cr content. The octahedral faces of the large particles of Bjala show etch pits. This etching could be a consequence of sulphuric acid rain following the K/T impact.

PS08.02.03 STRUCTURAL VARIATIONS IN THE ZEOLITE PAULINGITE. A. Bieniok, W. Joswig and W. H. Baur, Univ. Frankfurt, Institut f. Kristallographie, Senckenberganlage 30, 60054 Frankfurt, Germany.

The Ca- and Ba-rich forms of paulingite were studied by X-ray single crystal methods. The refinements¹ converged to wR 0.085 and 0.077. This is the first structural information on chemically different paulingite crystals since introducing this natural zeolite and its complicated aluminosilicate crystal structure in 1966². Paulingite is a medium pore size zeolite constructed from 7 different cages (*opr*; *grc*, *pau*, *plg*, *cpa*, *oto*, *gsm*)³. The access to all cages is controlled by plane or deformed single eight rings (S8R). Preferred cation sites are the saddle shaped S8R openings from the open double eight rings (*oto*) to the *pau* cages (K1) and the compressed *pau* cages (*cpa*) (Ba1, K2). Two strong bonds to framework oxygen atoms and four to water molecules are possible at this site. The *plg* cages are stuffed by Ca cations coordinated by eight water molecules. An additional cation position occupied by K is located in the big channel of the structure in the S8R connecting the great rhombicuboctahedron (*grc*) with a double eight ring (*opr*). All other cages are stuffed with highly disordered and weakly bonded water molecules. The Si and Al atoms (ratio 2.9) are statistically distributed over 8 different T sites. The individual T-O distances of 1.64 Å ($\pm 0.01\text{Å}$) and ($\pm 0.02\text{Å}$), and the T-O-T angles of 146° ($\pm 3^\circ$) and 145° ($\pm 3^\circ$) respectively, show that the different cation populations in the pores do not affect the geometry of the framework of paulingite appreciably. The narrow distribution of the T-O-T angles shows that the framework is relaxed compared with the wide range of T-O-T angles observed in zeolites at large (116° to 180°)⁴.

(1) S.R. Hall, J.M. Stewart: Xtal3.0 (1990) Univ. Western Australia and Maryland. (2) E.K. Gordon, S. Samson, W.B. Kamb: Science **154** (1966) 1004. (3) J.V. Smith: Studies Surf. Sci. & Cat., **49A** (1989) 29. (4) W.H. Baur, Proc. 2nd Polish-German Zeol. Coll. (1995) 171.

PS08.02.04 THE INTERMEDIATE MEMBERS OF WAGNERITEZWIESELITE MINERAL SERIES. Dmitrieva M.T., Fin'ko V.I., IGEM Russian Acad.Sci. Staromonetny 35 Moscow Zh-17 109017 Russia.

The X-ray diffraction study of two ferroan wagnerite samples from Kyakhta (Russia) have been carried out with the intention to clarify the crystallochemical relationship between rare minerals: wagnerite Mg_2PO_4F , ferroan wagnerite $(Mg,Fe)_2PO_4F$, triplite $(Mn,Fe)_2PO_4F$, magniotriplite $(Mn,Mg,Fe)_2PO_4F$ and zwieselite Fe_2PO_4F . In spite of the fact, that all these minerals are characterized by the same general formula $Me_2PO_4(F,OH)$, (where $Me=Mg^{+2}$, Fe^{+2} , Fe^{+3} , Mn^{+2}) the crystal structure data reported by different authors have not shown the identity of all these structures. According to the chemical composition the two ferroanwagnerite $(Mg_{1.83}Fe^{+2}_{0.12}Fe^{+3}_{0.04}Mn_{0.01})PO_4(F_{0.93}OH_{0.07})$ and $(Mg_{1.71}Fe_{0.24}Mn_{0.05})PO_4F$ are the intermediate members of wagnerite-zwieselite series. The long exposure experiment of the ferroan wagnerite permitted to register the faint reflections at low angle area, which had not been observed by previous studies and the conclusion was made, that the ferroan wagnerite distinguishes from wagnerite and is identical with magniotriplite. This study showed that namely these samples belong to the wagnerite group rather than to magniotriplite one.