vacant is not represented in this formula. The results in this study revealed not only the existence of Fe^{3+} in olivine but also of the short range order of laihunite structure.

Keywords: olivine, 57Fe Mossbauer, oxidized scoria and lava

P10.05.38

The oxidation state and distribution of Fe in pumpellyite from Chichibu belt, Ozu, Ehime, Japan

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Oxidation state and distribution of Fe in pumpellyite, $W_8X_4Y_8Z_{12}O_{56-n}(OH)_n$, was studied using Fe Mössbauer and X-ray Rietveld methods and semiquantitative analysis based on the intensity ratio of FeL_β and FeL_α lines. The pumpellyite studied was collected from basic semischist, Chichibu belt, Ehime, Japan. Pumpellyite associated with epidote contains about 7.5 to 14.0wt% total Fe_2O_3, and pumpellyite which is not associated with epidote about 6.0 to 17.5wt% total Fe_2O_3. The $Fe^{2+}:Fe^{3+}$ ratios estimated based on the ratios of the intensities of the FeL_β and FeL_α lines are $Fe^{2+}:Fe^{3+}$=11-24:89-76 (mean $Fe^{2+}:Fe^{3+}$=17:83). The $Fe^{2+}:Fe^{3+}$ ratio determined using Mössbauer method is 20(2):80(2). The Mössbauer doublet of Fe^{2+} (Isomer shift (IS)=1.22mm/s; Quadrupole splitting (QS)=2.82mm/s) was assigned to Fe^{2+} at the X site, and that of Fe^{3+} (IS=0.26mm/s; QS=1.06mm/s) to Fe^{3+} at the Y and X sites. The unit cell parameters were refined as a=8.8456(4)Å, b=5.9393(2)Å, c=19.1614(8)Å, β=97.462(3)°, V=998.14(7)Å^3. Rietveld refinements gave $Fe(X):Fe(Y)$ ratio of 43:57. By applying the $Fe^{2+}:Fe^{3+}$-ratio determined by the Mössbauer analysis, the site occupancies of Fe at X and Y sites given by Rietveld method and chemical analysis, the resulting formula is $(Ca_{7.95}Na_{0.01}K_{0.02})_{\Sigma 7.98}(Al_{1.58}Mg_{1.21}Fe^{3+}_{0.61}Fe^{2+}_{0.53}Mn_{0.09})_{\Sigma 4.02}(Al_{6.51}Fe^{3+}_{1.49}V_{0.02}Ti_{0.01})_{\Sigma 8.03}Si_{12.25}O_{40.75}(OH)_{15.25}$. The resulted intracrystalline distribution coefficient of Fe^{3+} and Al between the X and Y sites $(K_D=(Fe^{3+}/Al)^X/(Fe^{3+}/Al)^Y)$ is 1.69. The unit cell parameters and the cell volume increase with increasing Fe content in the pumpellyite. The mean Y-O distance increases with increasing mean ionic radii at the Y site. However, change of the mean X-O distance is not correlated with the mean ionic radii at the X site.

Keywords: pumpellyite, X-ray rietveld method, 57Fe Mossbauer method

P10.05.39

Crystal chemistry of chromian pumpellyite from Osayama, Okayama Prefecture, Japan

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Crystal structure of chromian pumpellyite was analyzed using single-crystal X-ray diffraction method in order to investigate behavior of chromium between two independent octahedral sites in pumpellyite,

$^{VII}W_8{}^{VI}X_4{}^{VI}Y_8{}^{IV}Z_{12}O_{56-n}(OH)_n$ (Z=1). The chromian pumpellyite was collected from basic schists in the Osayama ultramafic body, Okayama Prefecture, Japan. It is reddish gray. The Cr distribution is heterogeneous, and Cr_2O_3 content is highest around chromite, reaching 13.3 wt%. The Cr_2O_3 content of the chromian pumpellyite available for the structural analysis was 1.78 wt%. The structure was refined by a least-squares method, where Ca, Mg and Si were fixed at the W, X and Z, respectively, and the occupancies of Cr and Al at the X and Y sites were refined. The R-index for the non-hydrogen atoms is 5.03% for 1243 unique reflections. The refined occupancies of Al_X, Cr_X, Al_Y and Cr_Y are 0.22, 0.08, 0.94 and 0.04, respectively. By applying this result and EPMA data, the formula is established as $(K_{0.02}Na_{0.07}Ba_{0.01}Ca_{8.00})_{\Sigma 8.10}(Mn^{2+}_{0.03}Fe^{2+}_{0.32}Ni_{0.04}Mg_{1.91}Cr_{0.15}Al_{1.42})_{\Sigma 3.87}(Cr_{0.30}Al_{7.70})_{\Sigma 8.00}Si_{12.04}O_{41.66}(OH)_{14.34}$. The distribution coefficient of Cr and Al between the X and Y sites $[(Cr/Al)_X/(Cr/Al)_Y]$ is 2.70, indicating a stronger preference of Cr for the X site than the Y site. The unit cell parameters [a 8.854 (1), b 5.9209(5), c 19.1927(6) Å, β 97.460(2)°, V 997.68 Å^3] are greater than those of Mg-Al-pumpellyite, because of Cr substitution for Al. It is consistent with mean Y-O distances of 1.932Å for the Osayama chromian pumpellyite and 1.918Å for Mg-Al-pumpellyite. The calculated bond balance sums are consistent with the refined occupancies of Al and Cr in the X and Y sites and the locations of OH at O5, O7, O10 and O11.

Keywords: pumpellyite, chromium, crystal chemistry

P10.05.40

Phase composition of natural imenites used in white pigment production

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Ilmenites as a natural source of titanium oxide are widely use in pigments production. TiO_2 is produced mainly by sulphate method, where reaction of titanium raw material with sulphuric acid is the first step of the process. Knowledge about the phase content and the ionic states of elements in ilmenites is fundamental to proper adjustment of the chemical reactions. The origin of the minerals influence the composition through the distribution of main phases and minority elements and thus have a large influence on efficiency, safety, kinetics of reaction and the quality of products. Due to complicated morphology of these minerals standard procedures used in industrial's chemical analysis provides the element content in form of common oxides. This is far away from real phase content and ionic state. We present the studies of ilmenites form Norway, China, Australia and India. The main phases which involve Fe and Ti are usually easy to estimate but estimation of content and chemical state of minority elements is much more complicated. The x-ray powder diffraction (XRD) pattern is very complicated due to many diffraction peaks as well as similarity of phases, which are formed by substitution of minority elements into the majority phase lattice. In the presented work phases based on major and minor elements in minerals listed above were studied using XRD and x-ray absorption (XAS). Elemental composition was estimated using single particle electron probe microanalysis. XAS analysis allowed to identify phases based on major elements like Fe, Ti as well as minor elements like Mg, Mn and Cr. In some of the minerals minor elements were found in more than one phase. This work was partially supported by European Community under Contract RII3-CT-2004-506008 (IA-

SFS).

Keywords: ilmenites, X-ray absorption, phase composition

P10.05.41

Low temperature structural distortions of brucite

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Neutron powder diffraction studies of brucite, $Mg(OD)_2$, indicate subtle structural anomalies at 100K revealed by the temperature dependence of the anisotropic atomic displacement parameters (ADPs). Over the temperature interval 135K to 75K, the anisotropic ADP ellipsoid of the oxygen atom in the single D/H site model changes from prolate to oblate. The anisotropic ADPs of the D/H atom also exhibit anomalous temperature dependence below 135K. In addition, the alpha-angle, defined as the angle between the single-site DO bond and the split-site DO bond, decreases from 300K to 75K then increases at lower temperatures, and below 135K the thermal contraction of the octahedral layer thickness ceases. Additional understanding of this structural behavior is being sought from Raman spectroscopy and heat capacity measurements. The brucite layer is a fundamental building unit of a great variety of geologically important hydrous phyllosilicates, which include micas and clays. Brucite has P3barm1 space group symmetry with 3 atom positions all on 3-fold axes in the asymmetric unit. The Mg atom is at the origin, and the O and D/H atoms have variable z-coordinates. Typically, the D/H position is moved off from the three-fold axis into a fractionally occupied split-position to better accommodate the large ADP found in the single-site model. Oak Ridge National Laboratory is supported by the Division of Materials Sciences, U.S. D.O.E. (contract DE-AC05-00OR22725 with UT-Battelle, LLC).

Keywords: brucite, thermal expansion mechanism, neutron powder diffraction

P10.05.42

Simulation of powder XRD patterns from disordered phyllosilicates using information from HRTEM

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Stacking disorder is a common phenomenon in phyllosilicates but its nature is difficult to be deduced using conventional diffraction techniques. In contrast, recent investigations using high-resolution transmission electron microscopy (HRTEM) have elucidated the structure of stacking disorder in various phyllosilicates, by directly observing individual layers and stacking sequences. Furthermore, simulations of X-ray diffraction (XRD) patterns using the information from the HRTEM results can complement the limited analysis area in TEM and quantify the density of the stacking disorder. In this paper, we describe several successful results to reproduce experimental powder XRD patterns from 2:1 phyllosilicates (pyrophyllite, talc, celadonite, etc.) including

considerable stacking disorder, using the DIFFaX program (Treacy et al., 1991) whose calculation parameters were derived from direct observation of stacking by HRTEM. The attached figure is an example of our results, comparison between the experimental and simulated patterns of disordered talc.
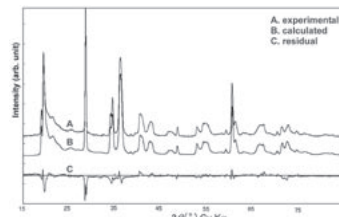
Keywords: stacking faults, high-resolution transmission electron microscopy, simulation X-ray diffraction

P10.05.43

Rietveld and ^{57}Fe Mössbauer study of babingtonite from Shimane Peninsula, Japan

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Oxidation state and distribution of Fe between two independent octahedral sites, Fe1 and Fe2, in babingtonite from Shimane Prefecture, Japan, were investigated using Rietveld and ^{57}Fe Mössbauer method. Bubingtonite occurs in cavities of hydrothermally altered gabbro or dolerite, and is associated with prehnite and calcite. It is rhombic in form with edge length of 0.5-1 mm. This mineral has sector zoning, where Fe and Mn contents are different from each other, and compositional zonal structure with Mn and Al-rich core and Fe-rich rim.The chemical formula based on the average composition is $(K_{0.004}Na_{0.006}Ca_{2.009})(Mg_{0.113}Mn_{0.094}Fe_{1.696}Ni_{0.002}V_{0.003}Cr_{0.001}Ti_{0.009}Al_{0.058})Si_{5.005}O_{14}(OH)$. The $Fe^{2+}:Fe^{3+}$-ratio based on the assumption that Fe1 and Fe2 sites are occupied by divalent and trivalent cations, respectively, is 45.2:54.8, which was consistent with the result by ^{57}Fe Mössbauer analysis: $Fe^{2+}:Fe^{3+}$-ratio determined from the area ratio of the doublets of Fe^{2+} (IS = 1.160 mm/s, QS = 2.482 mm/s)and Fe^{3+} (IS = 0.424 mm/s, QS = 0.797 mm/s) is 45:55. The site occupancies of cations at the Fe1 and Fe2 sites given by the X-ray Rietveld analysis (R_{wp} = 11.84 %, R_e = 6.86 %, S = 1.73) are $(Fe0.82Mg0.18)^{Fe1}(Fe0.89Al0.11)^{Fe2}$. Unit-cell parameters are a 7.4656(5), b 12.1761(8), c 6.6816(4) Å, α 86.156(5) °, β 93.881(3) °, γ 112.257(4) °, V 560.27(6) Å^3, and average Fe1-O and Fe2-O distances are 2.15 and 2.03 Å, respectively. The crystallographic features are nearly the same as those of babingtonite from other localities.

Keywords: babingtonite, Rietveld analysis, Mossbauer spectral analysis

P10.06.44

Single-crystal X-ray diffraction study of chabazite at 123 K

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