

vacant is not represented in this formula. The results in this study revealed not only the existence of Fe³⁺ in olivine but also of the short range order of laihunite structure.

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

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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 Fe₂O₃, and pumpellyite which is not associated with epidote about 6.0 to 17.5wt% total Fe₂O₃. The Fe²⁺:Fe³⁺ ratios estimated based on the ratios of the intensities of the FeL_β and FeL_α lines are Fe²⁺:Fe³⁺=11-24:89-76 (mean Fe²⁺:Fe³⁺=17:83). The Fe²⁺:Fe³⁺ ratio determined using Mössbauer method is 20(2):80(2). The Mössbauer doublet of Fe²⁺ (Isomer shift (IS)=1.22mm/s; Quadrupole splitting (QS)=2.82mm/s) was assigned to Fe²⁺ at the X site, and that of Fe³⁺ (IS=0.26mm/s; QS=1.06mm/s) to Fe³⁺ 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)Å³. Rietveld refinements gave Fe(X):Fe(Y) ratio of 43:57. By applying the Fe²⁺:Fe³⁺-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})_{Σ7.98}(Al_{1.58}Mg_{1.21}Fe³⁺_{0.61}Fe²⁺_{0.53}Mn_{0.09})_{Σ4.02}(Al_{6.51}Fe³⁺_{1.49}V_{0.02}Ti_{0.01})_{Σ8.03}Si_{12.25}O_{40.75}(OH)_{15.25}. The resulted intracrystalline distribution coefficient of Fe³⁺ 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

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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 Cr₂O₃ content is highest around chromite, reaching 13.3 wt%. The Cr₂O₃ 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})_{Σ8.10}(Mn²⁺_{0.03}Fe²⁺_{0.32}Ni_{0.04}Mg_{1.91}Cr_{0.15}Al_{1.42})_{Σ3.87}(Cr_{0.30}Al_{1.70})_{Σ8.00}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 Å³] 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

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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. TiO₂ 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-