of Mg or Al between the tetrahedral and octahedral sites is almost constant against Ga content in the MgAl$_{2-x}$Ga$_x$O$_4$ solid solution. A compositional variable of the Ga/(Mg+Ga) ratio in the octahedral site is not influenced by the occupancy of Al. The occupancy of Al is independent of the occupancy of Ga, though it depends on the occupancy of Mg according to thermal history. The local Al-O bond length in the tetrahedral site is 0.15 Å longer than the expected bond length. The nature that Al in spinel structure occupies mainly the octahedral site arises from the character of Al itself.

Keywords: spinel, crystal structure, NMR spectroscopy

P10.05.35

Soft synthesis and crystallographic characterization of calcium magnesium mixed carbonates

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It seems to be generally accepted that smithsonite, magnesite, siderite, as well as mixed carbonates like dolomite (MgCaCO$_3$) or huntite (Mg$_{0.75}$Ca$_{0.25}$CO$_3$) have been formed in the nature under hydrothermal conditions. Rao et al. developed a general soft synthesis procedure for obtaining anhydrous carbonates by precipitation from solution at normal pressure. They had success in the synthesis of smithsonite and siderite, but failed in the magnesite synthesis. This finding questions that the hydrothermal synthesis were the only way of genesis of some of these minerals in nature. The scope of this work is to apply the Rao et al. method to the synthesis of double carbonates of general formula Mg$_x$Ca$_{1-x}$CO$_3$. The compounds obtained have been characterized by X-ray fluorescence, atomic absorption analysis, TG and X-ray powder diffraction. The results obtained clearly demonstrate that anhydrous double calcium magnesium carbonate minerals can be obtained by soft synthesis for x composition ranging from 0 to 0.7. Hydroxysalts instead of anhydrous salts are obtained for larger values of x. The crystallographic parameters of the anhydrous compounds have been calculated and it has been shown that the volume of the cell accomplishes with the Veggard law.

Keywords: alkaline-earth double carbonates, lattice parameters

P10.05.36

Synchrotron X-ray diffraction studies of two olivines from the comet Wild 2

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Introduction and Experimental Methods: We have analyzed a collection of the Comet Wild 2 coma grains returned by the NASA Stardust Mission. This is the first solid sample return mission since Apollo 17. The purpose of the diffraction experiment is to permit the structure refinement of olivine including site occupancies. In addition to the intrinsic importance of the olivine structures for revealing the thermal history of Wild 2 materials, we wish to test reports that olivine recovered after hypervelocity capture in silica aerogel has undergone a basic structural change due to capture heating [Foster N.J. et al. (2007) MAPS 42, A51]. The diffraction equipment placed at beam line BL4B1 of the Photon Factory, KEK was developed for microdiffraction studies of materials. [Ohsumi K. et al. (1991) J. Appl. Cryst., 24,340 & (1995) Rev. Sci. Instru., 66(2),1448]. This equipment has been successfully applied to various extraterrestrial materials [Ivanov A. V. et al. (2000) Amer. Min. 85,1082]. Two Laue patterns of the samples (C2054,0,35,4 and C2067,1,111,4) were taken on an IP after 90 and 120 minutes exposures respectively. Structure refinements and Results: All Laue spots of both patterns are indexed by the traditional cell parameters of olivine. Structure refinements were carried out by a least-squares method minimizing the residual factor(R) based on the integrated intensities of Laue spots. The results of the several cycles of least-squares refinements including site occupancies of both samples lead the chemical formura as (Mg$_{0.89}$Fe$_{0.11}$)$_2$SiO$_4$ for C2054 and (Mg$_{0.71}$Fe$_{0.29}$)$_2$SiO$_4$ for C2067. Success of the refinement assuming the traditional cell parameters implies that the cell parameters of Wild 2 olivine cannot be significantly different from its typical values.

Keywords: synchrotron X-ray diffraction, microcrystallography, mineralogy and crystallography using X-ray diffrac

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Olivine from highly oxidized scoria and lava of Kasayama volcano, Hagi, Japan

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Oxidation state and distribution of Fe in olivine, $M2M1Z$O$_4$, in the andesitic scoria and lava oxidized at high temperature were investigated using FeL_β/FeL_α-intensity ratio, X-ray Rietveld and ^{57}Fe Mössbauer methods. Olivine samples were collected from the reddish black and black scorias, and the reddish black and black Opx-andesites in Kasayama volcano, Hagi, Yamaguchi Prefecture. The Fo contents of olivine in reddish scoria exceeded 91 mol%, while those of reddish black and black scorias are 83-85 and 79-81mol%, respectively. The Fe^{2+}:Fe^{3+} ratios in olivine of reddish black and black scoria determined using FeL_β/FeL_α-intensity ratio are Fe^{2+}:Fe^{3+}= 92(3)-93(3):8(3)-7(3) and Fe^{2+}:Fe^{3+}= 93(3)-98(3):7(3)-1(3), respectively. On the other hand, the Fo contents of olivine in reddish black and black lava were 91-99, 79-80 and 73-80, respectively. The Fe^{2+}:Fe^{3+} ratios of olivine in reddish black and black lava are 92(3)-99(3):8(3)-1(3) and 93(3)-99(3):7(3)-1(3), respectively. Mg and Fe occupancies at $M1$ and $M2$ in olivine refined by the X-ray Rietveld method (Rwp=4.89, Re=3.79, S=1.29) are Mg($M1$)=0.835 (7), Fe($M1$)=0.165 (7), Mg($M2$)=0.830 (6), Fe($M2$)=0.170 (6). The ^{57}Fe Mössbauer spectrum of olivine in the reddish black scoria consists of three doublets which are assigned to Fe^{2+}($M1,M2$) and Fe^{3+}($M2$) in olivine and Fe^{3+}($M2$) in laihunite. The Fe^{2+}($M1,M2$):Fe^{3+}($M2$) ratios determined by ^{57}Fe Mössbauer method for olivine in the black scoria is Fe^{2+}:Fe^{3+}=69:31, and the resulting chemical formula of the olivine is[^{M1}(Mg$_{0.835}$Fe$^{2+}_{0.165}$) ^{M2}(Mg$^{2+}_{0.830}$Fe$^{2+}_{0.053}$Fe$^{3+}_{0.117}$)]$_{\Sigma 2.000}$Si$_{1.000}$O$_4$, although the amount of

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-