

Thermodynamic properties of Mg-postperovskite with Fe^{3+} and Al^{3+} dopant: an internally consistent LSDA+U study

WANG, Xianlong^{1*} ; TSUCHIYA, Taku¹

¹GRC, Ehime University and ELSI, Tokyo Institute of Technology

Thermodynamic properties of MgSiO_3 perovskite (Pv) and postperovskite (PPv) with Fe and Al incorporation at high pressure and high temperature are important to understand the Earth's lower mantle (LM). The thermodynamic properties of Fe^{2+} , Fe^{3+} , and Al^{3+} -bearing Pv[1,2,3] and Fe^{2+} -bearing PPv[4] have been investigated in our previous works uniformly based on first-principles method combined with the internally consistent LSDA+U method and quasi-harmonic approximation (QHA). However, to date, effects of trivalent ions, Fe^{3+} and Al^{3+} , on the thermodynamic properties of PPv are still unclear. In this work, by using the same methods with previous works, the structural, electronic, magnetic, and thermodynamic properties of $(\text{Mg},\text{Fe}^{3+})(\text{Si},\text{Fe}^{3+})\text{O}_3$ and $(\text{Mg},\text{Fe}^{3+})(\text{Si},\text{Al}^{3+})\text{O}_3$ PPv at several pressures, from 0 GPa to 180 GPa, are investigated. Our results show that for $(\text{Mg},\text{Fe}^{3+})(\text{Si},\text{Fe}^{3+})\text{O}_3$ PPv, Fe^{3+} ions substituted at Mg and Si site respectively have the high and low spin state within the deep LM pressure range, while Fe^{3+} in $(\text{Mg},\text{Fe}^{3+})(\text{Si},\text{Al}^{3+})\text{O}_3$ PPv remains in the high spin state. Furthermore, separated phase between Fe_2O_3 and Al_2O_3 in PPv is found unfavorable.

References:

- [1] Metsue, A. and Tsuchiya, T. (2012) *Geophys. J. Int.* **190**, 310.
- [2] Tsuchiya, T. and Wang, X. (2013) *J. Geophys.* **118**, 83.
- [3] Wang, X. and Tsuchiya, T. To be submitted.
- [4] Metsue, A. and Tsuchiya, T. (2011) *J. Geophys. Res.* **116**, B08207.

Keywords: First-principles method, Internally consistent LSDA+U, Thermodynamic properties, Postperovskite

Thermal expansion of $\text{Ca}(\text{OD})_2$ at high pressure

NAGAI, Takaya^{1*} ; SANO, Asami² ; IIZUKA, Riko³ ; KAGI, Hiroyuki³ ; HATTORI, Takanori⁴

¹Faculty of Science, Hokkaido University, ²Japan Atomic Energy Agency, ³Graduate School of Science, The University of Tokyo, ⁴Materials and Life Science Division, J-PARC Center

$\text{Ca}(\text{OH})_2$ is one of the important hydrous minerals to understand structural behavior at high pressure and high temperature, because this type of structure is a building unit in more complex hydrous phases such as chondrodite. It is surprising that only a few previous researches can be found on crystallography of $\text{Ca}(\text{OH})_2$ in the conditions of simultaneously high pressure and high temperature. We gave an oral presentation about some preliminary results in this conference last year. We have continued to analyze the data carefully and will add some new information.

Deuterated samples were prepared via hydrothermal treatment with CaO fine powders and excess D_2O water in a Teflon lined stainless steel autoclave at 493 K for 4 days. After the hydrothermal treatment was completed, precipitates were filtered out, washed with D_2O water, and then dried at 383 K under vacuum for 3 hours. The products were confirmed to have the CdI_2 -type structure by conventional powder X-ray diffraction measurements and were checked to be deuterated by IR absorption spectra. Synchrotron X-ray diffraction experiments were performed at the beamline AR-NE5C, KEK, Japan in order to obtain cell parameters of $\text{Ca}(\text{OD})_2$ at various P-T conditions from 2-4 GPa and 300-800 K. TOF neutron powder diffraction measurements of $\text{Ca}(\text{OD})_2$ were carried out from 300 to 773 K at high pressure at the PLANET beamline in J-PARC, Japan. Pressure was estimated by comparing unit cell parameters with those obtained by synchrotron experiments.

All our TOF data obtained include only $\text{Ca}(\text{OD})_2$ peaks and no peaks from sample surrounding materials such as ZrO_2 pressure medium, graphite furnace and WC anvils could be detected owing to radial collimators equipped with the 6-ram pressure apparatus (Atsuhime). The detailed structure parameters such as lattice parameters and atomic coordinates could be reasonably refined by the Rietveld method by using a program GSAS. It is an interesting result that thermal expansion along the *c*-axis seems to be suppressed at high pressure comparing to that at ambient pressure. Mechanism of the thermal expansion of $\text{Ca}(\text{OD})_2$ at high pressure will be discussed.

Keywords: portlandite, thermal expansion, high pressure, synchrotron X-ray diffraction, TOF neutron diffraction

High-temperature heat capacity of SiO₂-Al₂O₃-RO (R=Mg, Ca, Sr, Ba) melts

SUGAWARA, Toru^{1*}

¹Akita University

Heat capacity (C_p) of silicate melts is an important property in consideration of phase equilibria in magmatic system and a numerical simulation of flow and thermal structures in glass melting furnace. Heat capacity of aluminum-free melts can be expressed by an additive function of partial molar heat capacities for components (Richet and Bottinga, 1985). On the other hand, it has been reported that the heat capacities of aluminosilicate melts show complicated dependence on both temperature and composition (Richet and Mysen, 2005). However, they are still poorly understood due to the lack of calorimetric data. This study provides new experimental data for the high-temperature heat capacities of Ca, Sr and Ba-bearing aluminosilicate melts.

Drop calorimetry measurements were performed for 50SiO₂-25Al₂O₃-25CaO (An), 36.5SiO₂-27Al₂O₃-36.5CaO (Ca_{36.5}), 8SiO₂-30Al₂O₃-62CaO (Ca₆₂) and 75SiO₂-12.5Al₂O₃-12.5SrO or 12.5BaO (Sr_{12.5}, Ba_{12.5}) melts between 873K and 1889K using a Bunsen ice calorimeter. Heat capacity of melts was determined from the differential of measured relative enthalpy. The heat capacity of anorthite melt is 1.356+0.0001151T(K) (J/K-g), which is consistent with the value reported by Richet and Bottinga (1985). The heat capacities for Ca_{36.5}, Ca₆₂, Sr_{12.5} and Ba_{12.5} are 1.532, 1.508, 1.313 and 1.160 (J/K-g), respectively, and they are independent of temperature.

The temperature and compositional dependence of the C_p for SiO₂-Al₂O₃-RO (R=Mg, Ca, Sr, Ba) melts are considered by combining new calorimetric data and literature data by drop calorimetry (n=11, Richet and Bottinga, 1984; Courtial and Richet, 1993; Neuville and Richet, 1991; Richet and Neuville, 1992) and by differential scanning calorimetry (n=22, Webb, 2008, 2011). The positive temperature dependence is observed in the SiO₂-Al₂O₃-MgO melts as reported by Courtial and Richet (1993). In the system SiO₂-Al₂O₃-CaO, temperature dependence of the C_p is only observed at anorthite composition. The heat capacity of alkaline-earth aluminosilicate melts can be expressed by a symmetric solution model. The derived heat capacity of mixing is negative value in all of the systems. At constant temperature and oxide ratio, the heat capacity decreases with decreasing field strength of alkaline-earth elements (Ba < Sr < Ca < Mg), suggesting that configurational freedom is restricted in the cations with lower field strength due to the charge compensation effect of aluminum. Further experimental data for Sr and Ba-bearing melts are required to generalize temperature dependence of the heat capacity.

Keywords: Silicate melt, Heat capacity, Calorimetry

Viscosity of titanium-bearing silicate melts at high pressure

SUZUKI, Akio^{1*}

¹Tohoku University

Knowledge about viscosity of silicate melt is valuable for understanding the activity of magma in the planetary interiors. The high-Ti magmas erupted on the lunar surface. These magmas contains TiO₂ up to 16 wt%. Because the viscosity change at high pressure is affected by the structural change of TO₄-network, it is very interesting to know the influence of Ti on the pressure dependence of viscosity. We performed viscosity measurement of K₂TiSi₄O₁₁ melt as an analogue of the lunar high-Ti magmas. Viscosity was measured by the falling sphere method using an X-ray radiography system. Experiments were performed at the NE7A station of the PF-AR synchrotron radiation facility in KEK, Tsukuba, Japan. We found that the viscosity of K₂TiSi₄O₁₁ melt has a viscosity minimum at 3 GPa. Paris et al. (1994) reported that the coordination number of titanium increases with increasing pressure on the basis of the XANES spectra of glasses synthesized under high pressure. Our results suggest that the viscosity minimum of K₂TiSi₄O₁₁ is strongly related to the coordination change of titanium. The viscosity minimum is also found in the terrestrial MORB magma. Recently, Sakamaki et al. (2013) proposed that the viscosity minimum causes the low velocity zone of seismic wave in the upper mantle. The present study suggests that the high-Ti melt causes an attenuating zone in the deep lunar mantle.

Keywords: magma, viscosity, moon, mantle

Study of physical properties of Fe-Si alloy at high pressure using synchrotron radiation Mossbauer spectroscopy

SUZUKI, Nanami^{1*} ; OHTANI, Eiji¹ ; HIRAO, Naohisa² ; KAMADA, Seiji¹ ; HAMADA, Maki³ ; SAKAMAKI, Tatsuya¹ ; OHISHI, Yasuo² ; MASUDA, Ryo⁴ ; MITSUI, Takaya⁵

¹Department of Earth and planetary materials science, Graduate School of Science, ²Japan Synchrotron Radiation Research Institute, Hyogo, 679-5198, Japan, ³School of Natural System, College of Science and Engineering, Kanazawa University, Kanazawa, 920-119, ⁴Research Reactor Institute, Kyoto University, Osaka, 590-0494, Japan, ⁵Japan Atomic Energy Agency, Hyogo, 679-5148, Japan

The Earth's core is divided into the liquid outer core and solid inner core based on seismological observations. The Earth's core has been geochemically and cosmochemically thought to be mainly composed of Fe. The density of the core is smaller than that of pure iron under the core conditions. Therefore, the core has been considered to contain light elements, such as H, S, Si, C, and O. Si is one of the most important light elements in the core. Although the phase relations and compression behaviors in the Fe-Si alloy have been studied at high pressure and temperature in order to investigate properties of the inner core, magnetic properties of the alloys have not been studied well. In order to clarify the relationship between the magnetic transition and the structural transition of the Fe-Si alloy, we made simultaneous measurements of X-ray diffraction and synchrotron Mössbauer spectroscopy of the Fe-Si alloy up to 40 GPa at room temperature.

The Fe-Si alloy used for the measurements has a composition of Fe_{0.95}Si_{0.05} enriched with ⁵⁷Fe. The starting material was synthesized by melting the mixture of ⁵⁷Fe and Fe-Si alloys under the Ar-H₂ atmosphere by laser heating. Mössbauer spectra and XRD patterns were obtained at the beamlines, BL10XU and BL11XU of SPring-8 up to 40 GPa at room temperature. Our Mössbauer data together with X-ray diffraction data revealed that the magnetic transition from magnetic to non-magnetic phase occurs at 18 GPa simultaneously with the bcc to hcp transition. The change in the sound velocity and compression behavior of the Fe-Si alloy has been reported associated with the structural transformation of the alloy from bcc to hcp. The present results imply that the change in these physical properties is caused not only by the structural change but also by the magnetic transition.

Experimental determination of post-spinel transition boundary in Fe_2SiO_4

MATSUZAWA, Taisuke^{1*} ; KOJITANI, Hiroshi¹ ; AKAOGI, Masaki¹

¹Department of Chemistry, Gakushuin University

It is widely accepted that $(\text{Mg,Fe})_2\text{SiO}_4$ ringwoodite is the most abundant mineral in the mantle transition zone. Because spinel-type Fe_2SiO_4 is the endmember of $(\text{Mg,Fe})_2\text{SiO}_4$ ringwoodite, many investigators have been studied on phase transitions of Fe_2SiO_4 spinel (Kawada 1977, Ohtani 1979, Morooka 1992, Katsura et al. 1998). Spinel-type Fe_2SiO_4 decomposes into $2\text{Fe}_x\text{O} + \text{SiO}_2$ (stishovite) + $2(1-x)\text{Fe}$ above about 18GPa. However, the dissociation boundary has not yet been established well due in part to difficulty in oxygen fugacity control. In this study, we determined the post-spinel phase boundary in Fe_2SiO_4 by high-pressure experiments controlling oxygen fugacity with the Fe-FeO buffer.

A starting material of high-pressure experiments was a mixture of Fe_2SiO_4 (fayalite), Fe_xO and Fe with molar ratios of 10:2:1, and it was packed in a Fe capsule. Oxygen fugacity of the sample at high pressure and high temperature was controlled by the Fe-FeO buffer. The high-pressure experiments were performed using a Kawai-type 6-8-type multi-anvil apparatus at 16-20GPa and 1000-1400 °C. The starting samples were heated at the desired conditions for 3-6 hours, and then quenched and decompressed to ambient conditions. Recovered samples were identified by using powder XRD method and SEM-EDS, and then lattice parameters of Fe_xO were determined by using powder XRD. The x values in Fe_xO were estimated from the composition-lattice parameter relationship of Fe_xO by McCammon (1993).

The post-spinel transition boundary in Fe_2SiO_4 was determined to be $P(\text{GPa}) = -0.0021T(^{\circ}\text{C}) + 20.0$ in the temperature range of 1000-1400 °C. The phase boundary has a negative slope. Our boundary is almost consistent with those of Ohtani (1979) and Katsura et al. (1998). Katsura et al. (1998) interpreted that the negative slope of the boundary in the previous studies was apparent which was caused by slow kinetics of spinel decomposition. Because our study indicated that the decomposition of Fe_2SiO_4 spinel completed in the runs for 3 hours at 1000 °C and that x values of Fe_xO in the run products for 3 and 6 hours at the 1000 °C were approximately equal, we conclude that heating at 1000 °C for at least 3 hours was enough to reach the equilibrium. Because our transition boundary was determined by the runs for 6 hours at 1000 °C, 3 hours at 1200 °C, and 3 hours at 1400 °C, we suggest that the negative slope of the post-spinel transition boundary in Fe_2SiO_4 is not apparent but the essential feature.

Keywords: Fe_2SiO_4 , post-spinel, spinel, high-pressure

Relationship between Raman spectral pattern and crystal orientation of cordierite

ABE, Miyako^{1*} ; MADHUSOODHAN, Satish-kumar¹ ; KAGI, Hiroyuki²

¹Niigata University, ²Tokyo University

In the crystal structure of cordierite, six-membered rings of (Al, Si) O₄ are stacked along the *c*-axis and form a channel structure. This channel structure can trap volatiles such as H₂O and CO₂, and makes cordierite an important mineral for preserving the information of past fluid conditions during metamorphism. Earlier studies have shown that the intensity of CO₂ Raman band represents the contents of CO₂ inside the channel (e.g. Kaindl et al., 2006). Carbon dioxide is aligned linearly along the *a*-axis in the channel (Aines and Rossman, 1984), and therefore the peak intensity of CO₂ at 1383cm⁻¹ in the Raman spectra varies considerably depending on the crystal orientation of cordierite (Kolesov and Geiger, 2000). Thus, it is necessary to correct the effect of crystal orientation for the determination of true contents of CO₂ in randomly oriented cordierite grains in metamorphic rocks. As a first step to accurately quantify the CO₂ content in cordierite using Raman spectroscopy, we analyzed euhedral crystals of cordierite for revealing the relationship between Raman spectral patterns and crystal orientation.

In this study, euhedral cordierite crystals collected from the volcanic ash deposit in the Takiga swamp, Gunma Prefecture, Japan were examined in detail using micro-Raman spectroscopy. Raman spectra were observed with different conditions for each analytical point to check the effect of polarization and crystal orientation. Mineral chemical analyses of cordierite crystals indicate homogeneity in its composition ($X_{Mg} = 0.735 \pm 0.14$). However, different Raman spectral patterns were obtained for (001) plane and (100) plane; the (001) plane show only one pattern, but the (100) plane showed three different patterns. Peak splitting between 554 and 575 cm⁻¹, the peaks of 970 cm⁻¹ and 1180 cm⁻¹ changed its intensity drastically, whereas the peak at 670 cm⁻¹ remained constant. We selected five Raman peaks at 554 cm⁻¹, 575 cm⁻¹, 670 cm⁻¹, 970 cm⁻¹, and 1180 cm⁻¹ attributable to the cordierite (Al, Si)O₄ structure and analyzed the intensity ratio of these five peaks in different orientations. A parameter of Δ intensity was defined, where the intensity ratios of (001) plane were concentrated around 0, and those of (100) plane deviates from 0. This parameter can be used to identify the crystal orientation of cordierite. The spectral variations observed in cordierite and its relationship with crystal orientation are interpreted based on the stretching and/or bending vibrations of cordierite unit cell structure

Keywords: Cordierite, Raman spectroscopy, Crystal orientation

References

Aines, R. D. and Rossman, G. R. (1984) The high temperature behavior of water and carbon dioxide in cordierite and beryl. *American Mineralogist*, 69, 319-327

Kaindl, R., Tropper, P. and Deibl, I. (2006) A semi-quantitative technique for determination of CO₂ in cordierite by Raman spectroscopy in thin sections. *European Journal of Mineralogy*, 18, 331-335

Kolesov, B. A. and Geiger, C. A. (2000) Cordierite II: The role of CO₂ and H₂O. *American Mineralogist*, 85, 1265-1274

Keywords: Cordierite, Raman spectroscopy, Crystal orientation

The low-temperature Moessbauer spectroscopy of an M3' epidote from Osayama, Okayama prefecture, Japan

YAMAKAWA, Junji^{1*}; KAWASE, Masaya²; KUROKUZU, Masayuki³; MORIMOTO, Shotaro⁴; SAITO, Tadashi⁵

¹Graduate School of Natural Science and Technology, Okayama University, ²Nagahama Institute of Bio-Science and Technology, ³Research Reactor Institute, Kyoto University, ⁴Faculty of Pharmacy, Osaka Ohtani University, ⁵Radioisotope Center, Osaka University

Epidote, $\text{Ca}_2(\text{Al,Fe}^{3+},\text{Fe}^{2+})\text{Al}_2\text{SiO}_4\text{Si}_2\text{O}_7(\text{O,OH})$ is a common rock forming mineral found low-grade metamorphic rocks. The chemical compositions of the epidote vary with the formation conditions and make some complex zoning textures. The distribution of Fe^{2+} - Fe^{3+} ions in the crystal structure will be able to analyze by the Mössbauer spectrometry and the stability/unstability of the sample can be estimated from the distribution.

Moreover, in some sample, the Fe ions are distributed in the characteristic M3' site that can be detected by the Mössbauer spectroscopy. The distribution ratio of the Fe ions in the M3' site can not be estimated by the X-ray structure analysis, so the M3' sites are making a small ordering structures and distribute homogeneously in the crystal. Distribution ratio of Fe in the site of M1/M3/M3' corresponds to the formation conditions of the sample.

In this study, the low-temperature Mössbauer spectrum and Magnetic susceptibility of the M3' epidote sample was measured and the characteristics of the M3' site were analysed.

Keywords: Epidote, Moessbauer spectroscopy, M3' site, Magnetic susceptibility

Structural change in ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) near the freezing point temperature of water

TATENO, Natsuki¹ ; KYONO, Atsushi^{1*}

¹Div of Earth Evolution Sciences, Grad Sch of Life & Environmental Sciences, Univ of Tsukuba

Ikaite, one of the calcium carbonate minerals, is thermodynamically stable only at near-freezing temperature and transformed rapidly into calcite and vaterite at ambient temperature. During the phase transformation with dehydration, its crystal shape is preserved as pseudomorphs, termed glendonite, thinolite, and gennoishi. This study aims to clarify the structure change and dehydration mechanisms by using low-temperature single-crystal X-ray diffraction study. At -50 °C, the crystal structure of ikaite is monoclinic, space group $C2/c$ with the unit cell parameter $a = 8.8134$ (1), $b = 8.3108$ (1), $c = 11.0183$ (1) Å, $\beta = 110.418$ (1) °. It is composed of four $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ molecules in the cell. With increasing temperature, the unit cell volume is increased monotonously from 756.3 to 758.0 Å³ between -50 and -20 °C, and then jumped to 771.0 Å³ at -10 °C. The unit cell lattice anisotropically expands mainly along the c -axis, followed by the a -axis. The intramolecular Ca-O(5) bond distance is drastically elongated at -10 °C, which is associated with elongations of the intermolecular O(2)-O(3), O(2)-O(5), O(4)-O(5) distances. The a unit cell expansion is directly due to the elongation of the O(2)-O(5) aligned parallel to the a -axis. The drastic elongation of the Ca-O(5) bond distance gives rise to an initial dehydration of the $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ molecule. The intermolecular Ca-O(3)-O(2) angle is constantly increased with temperature, leading to rotational motion of the $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ molecule along b -axis. This is responsible for the highest expansion coefficient of the c lattice parameter.

Keywords: ikaite, vaterite, calcium carbonate, pseudomorph, low-temperature X-ray diffraction study

Synchrotron powder X-ray diffraction study of the structural thermal properties on hydrogrossular

KATO, Masato^{1*} ; KYONO, Atsushi²

¹Graduate School of Life and Environmental Science, ²Graduate School of Life and Environmental Science

Synchrotron powder X-ray diffraction study on synthetic Si-free hydrogrossular, katoite $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$, were performed at temperature range from 300 to 10 K. The temperature dependence of structure parameters was refined by Rietveld analysis. Since structural contraction with decreasing temperature would directly cause a phase transition on the hydrogrossular structure, three candidates for space group: $Ia-3d$ (katoite at ambient), $I-43d$ (katoite at high pressure), and $I4_1/acd$ (majorite), were applied to the X-ray diffraction profile fitting collected at 10 K. The final R_w with the $Ia-3d$ space group consequently results in the smallest value, which suggests that the katoite structure remains unchanged up to the lowest temperature of 10 K. However, the temperature dependence of the unit cell volume shows two different expansion coefficients at temperatures above and below 100 K. It can be accounted for by the effect of the repulsion between atoms of the same species. Whereas the unit cell of katoite is monotonously contracted with decreasing temperature, the O_4H_4 tetrahedron and AlO_6 octahedron are alternatively expanded and contracted. Compared with the phase transition in katoite under high pressure, moreover, the unit cell volume contraction up to 5 GPa is about eight times larger than that under low temperature. The structural characteristics could therefore explain the reason why no phase transition occurs in katoite at low temperature condition.

Keywords: katoite, synchrotron powder X-ray diffraction, Rietveld analysis, O_4H_4 tetrahedron

Structural study on the phase transformation of natural scolecite with increasing temperature

UCHIDA, Takahiro^{1*}; KURIBAYASHI, Takahiro¹; NAGASE, Toshiro²

¹Department of Earth Science, graduate school of science, Tohoku University, ²The Tohoku University Museum, Tohoku University

Scolecite, $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$ is classified to fibrous zeolite group. The sequence of general phase transformation with increasing temperature has been reported for natural scolecite: scolecite \rightarrow meta-scolecite \rightarrow amorphous phase and decomposes to An + Qtz (Rykl *et al.* 1986; Gottardi and Galli 1985).

In this study, the high-T evolution of the structure of natural scolecite from Poona, India were studied up to 573 K to reevaluate the dehydration process of scolecite using TG-DTA and in situ single crystal X-ray diffraction experiments.

As the results from structural refinement at room temperature, the lattice constants of the sample are determined as follows : $a = 18.504(3)\text{Å}$, $b = 18.971(2)\text{Å}$, $c = 6.5262(9)\text{Å}$ and $\beta = 90.558(5)^\circ$. The crystal structure of scolecite, $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$, was refined with the space group $F1d1$ from 3567 reflections with $I_o > 2\sigma(I)$, yielding $R = 4.62\%$, $wR = 11.41\%$. At $\sim 423\text{K}$, the space group was changed to $Fd11$ from $F1d1$, and scolecite underwent a phase transformation to meta-scolecite phase.

As the results from structural refinement at 523 K, the lattice constants of the sample are determined as follows : $a = 18.122(3)\text{Å}$, $b = 18.847(3)\text{Å}$, $c = 6.5408(11)\text{Å}$ and $\alpha = 88.948(7)^\circ$. The crystal structure of scolecite, $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, was refined with the space group $Fd11$ from 2782 reflections with $I_o > 2\sigma(I)$, yielding $R = 10.72\%$, $wR = 28.85\%$. When phase transformation occurs, OW2 in scolecite is expelled and then the half of Ca ions move by $\sim 1/2c$. At 573 K, the number of observed reflections was decreased dramatically.

Under high-T experiments from 423 to 523 K, two reciprocal lattices were observed, each lattice is corresponding to twin component with the [00-1] twin law. The [00-1] twinning could be associated with the dehydration mechanism. The X-ray diffraction data suggest the possibility of exist of a new H_2O site in meta-scolecite phase. This may be a key to solve the dehydration process of scolecite.

Keywords: scolecite, dehydration, phase transformation, single crystal X-ray diffraction, twin, high temperature

Near-infrared spectra of ice under high pressure and high temperature

NOGUCHI, Naoki^{1*} ; KOMATSU, Kazuki² ; SHINOZAKI, Ayako² ; SHINODA, Keiji³ ; KAGI, Hiroyuki²

¹Graduate School of Engineering, Hiroshima University, ²Geochemical Laboratory, Graduate School of Science, The University of Tokyo, ³Department of Geosciences, Faculty of Science, Osaka City University

The physical properties of ice VII under high pressure and high temperature (HP-HT) conditions are important to planetary science. Ice VII is considered a primary constituent of the interior of giant icy satellites and planets (e.g., Podolak et al. 1998). Thus, understanding the physical properties of ice VII will contribute to better knowledge about the structure and dynamics of other satellite and planetary interiors. In particular, the ionic conductivity of ice VII, which affects the magnetic fields of these bodies (Stevenson 2003), is controlled by ionic and rotational defects in the ices (Jaccard 1959); moreover, ionic defects have two types: OH^- and H_3O^+ . The probability of forming defects in ice VII under the HP - HT conditions that typify the interiors of icy satellites and planets is surely increased by thermal activation.

In the near-infrared (NIR) region, the spectrum of ice VII shows absorption bands of the bending-stretching combination ($\nu_2 + \nu_3$) and stretching overtone ($2\nu_3$) modes of the normal vibration of water molecules (Larsen and Williams 1998). These modes correspond to the high vibrational energy level of the potential well, and provide information regarding the potential barrier along the O...O axis. To determine the probability of forming ionic defects in the ice VII structure at elevated temperatures, the NIR spectra of ice VII must be measured. The aim of this study is to investigate the state of protons in ice VII under HP-HT conditions. Thus, we measured the NIR absorption spectra of water at pressures up to 16 GPa and temperatures up to 368 °C using an external heating diamond anvil cell and synchrotron NIR radiation of BL43IR at SPring-8.

The absorption band of the first OH stretching overtone mode divided into doublet peaks above 5 GPa at room temperature, suggesting that proton tunneling occurs at the overtone level. As the temperature increased, the doublet peaks gradually reduced to a singlet. This result implies that thermally activated protons hop between the two potential minima along the oxygen-oxygen axis. A P-T diagram for the proton state was constructed from the changing band shape of the overtone mode.

Keywords: ice, proton, icy satellite, near-infrared spectroscopy, high pressure and high temperature

Phase changes of filled ice Ih methane hydrate induced by the orientational ordering of the guest molecules

TANAKA, Takehiko^{1*} ; HIRAI, Hisako¹ ; MATSUOKA, Takahiro² ; OHISHI, Yasuo³ ; YAGI, Takehiko¹ ; OHTAKE, Michika⁴ ; YAMAMOTO, Yoshitaka⁴ ; NAKANO, Satoshi⁵

¹Geodynamics Research Center, Ehime University, ²Gifu University, ³Japan Synchrotron Radiation Research Institute, ⁴The National Institute of Advanced Industrial Science and Technology, ⁵National Institute for Materials Science

Oriental ordering of guest methane molecules in a filled ice Ih structure of methane hydrate (MH) was observed above 15 to 20 GPa at room temperature in a previous Raman study. However, the change in the fundamental structure was not observed at the pressure region by X-ray diffractometry. In this study, low-temperature and high-pressure experiments were performed with filled ice Ih structure of methane hydrate under pressure and temperature conditions of 2.0 to 77.0 GPa and 30 to 300 K, respectively, using diamond anvil cells and a helium-refrigeration cryostat. Distinct changes in the axial ratios of the host framework were revealed by In-situ X-ray diffractometry. Splitting in the CH vibration modes of the guest methane molecules, which was previously explained by the orientational ordering of the guest molecules, was observed by Raman spectroscopy. The pressure and temperature conditions at the split of the vibration modes agreed well with those of the axial ratio changes. The results indicated that orientational ordering of the guest methane molecules from orientational disordered-state occurred at high pressures and low temperatures, and that this guest ordering led to the axial ratio changes in the host framework. Existing regions of the guest disordered-phase and the guest ordered-phase were roughly estimated by the X-ray data. In addition, above the pressure of the guest-ordered phase, another high pressure phase was developed at a low-temperature region.

Keywords: Methane Hydrate, X ray diffraction, high pressure, Raman spectroscopy

Zirconium local structure in tektite and impact-related natural glasses probed by XAFS

TOBASE, Tsubasa^{1*} ; YOSHIASA, Akira¹ ; WANG, Ring¹ ; HIRATOKO, Tatsuya¹

¹Graduate School of Science, Kumamoto University, ²Materials and Structures Laboratory, Tokyo Institute of Technology

The local structures of tektite and natural glasses were studied by Zr K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) in order to provide quantitative data on bonding distances and coordination numbers. The XAFS measurements were performed at the beam line BL-NW10A of the PF-AR in National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. Zr⁴⁺ ion in tektite has different kinds of coordination environment. Various natural glasses are formed under different physical conditions. Impact-related glass, fulgurite and volcanic glasses are typical natural glasses. Glass structure is affected by the pressure and temperature conditions during the glass formation and annealing process. This study indicated that different formation process of natural glasses gives different local structure of zirconium ions.

The Zr K-edge XANES spectra of tektite have the double post-edge peaks with different heights. All tektites are classified in same types. Zr-O distances in tektite are 2.198-2.215 Å and XANES spectra of tektite have similar shape. It indicates that tektites have similar Zr local structure with 7-fold coordination Zr ions. Volcanic glasses are classified same type. Impact-related glasses are classified to different types. Impact glasses are formed under different geological process at impact event and are experienced different physical environments.

Keywords: XAFS, Local structure of Zr, Tektite, Natural glass, XANES, EXAFS

Light element quantification using electron microprobe and Os surface coating

OHFUJI, Hiroaki^{1*} ; YAMAMOTO, Masashi¹ ; KOJIMA, Yohei¹

¹Geodynamics Research Center, Ehime University

Electron microprobe analysis is a non-destructive method widely used for determining the chemical composition of solid materials such as not only minerals and rocks but also industrial and biological materials. Recent advances of solid-state detectors for energy dispersive spectroscopy (EDS) analysis allow us to readily collect precise quantitative data. For SEM and EDS analysis of non-conductive (insulating) materials such as minerals and rocks, surface coating of a thin conductive layer is a prerequisite for sample preparation. For this purpose, carbon and gold are most commonly used; the former with low atomic (*Z*) number is suitable for microprobe chemical analysis, while the latter is preferable for textural observation of samples with rough, uneven surfaces and/or with high porosity. Recently, osmium coating prepared by chemical vapor deposition (CVD) has been a focus of attention and found to be effective for high-resolution SEM observation of samples with uneven surfaces. In the present study, we applied the sample preparation technique using very thin osmium surface coating for chemical quantification of various mineral samples by EDS.

The SEM-EDS analysis was performed by using FE-SEM (JEOL, JSM-7000F) equipped with a silicon-drift-type EDS detector (Oxford Instruments, X-Max 20). Accelerating voltage and probe current were 15 kV and 1 nA, respectively. Osmium coating of 5 nm thick was carefully made by using a Neoc-ST osmium coater (Meiwafosis). Quantification analyses were conducted on a variety of mineral samples, silicate (including hydrous silicates), carbonate and oxide minerals.

The results showed that the quantification data obtained from samples with osmium coating are as accurate as those from samples with conventional carbon coating for principle elements such as Na, Mg, Al, Si, K, Ca and Fe. With respect to the quantification of light elements such as C, N and O, the results from osmium-coated samples are found to be closer to their stoichiometric values than those from carbon-coated samples. This is likely caused by the absorption correction of the X-rays passing through each coating layer. The thickness of the surface coating layer can be precisely controlled in the case of osmium coating prepared by the CVD technique, but not readily adjusted in carbon coating. As the result, the deviation of the estimated thickness of the coating layer from the actual thickness over/underestimates the effect of X-ray absorption correction, in which low-energy X-rays from light elements are more significantly influenced by the correction. We found that the precise quantification of oxygen as a separate element (not as oxide forms of cations) using osmium surface coating might be helpful and effective in estimation of the valence state of iron in iron-bearing minerals and water (hydrogen) content in hydrous minerals. We also confirmed that the present technique is also useful for precise quantification of carbonate minerals such as CaCO₃.

Cathodoluminescence characterization of terrestrial and extraterrestrial alkali-halide minerals

YOSHIDA, Eisuke^{1*}; NISHIDO, Hirotsugu¹; NINAGAWA, Kiyotaka¹

¹Okayama University of Science

Luminescence of natural alkali halides such as halite and sylvite is characterized by structural defects related to F-center (+p) and V-center (+e). On their CL (cathodoluminescence), however, scarcely has been reported so far. Since asteroidal water was discovered as fluid inclusion in halite from H5 chondrite, Monahans (1998), alkali halides in meteorites have been extensively investigated for understandings of aqueous alteration and thermal metamorphism on the parent body. Therefore, luminescence features of halides can provide valuable information on such issues. In this study we have measured CL spectra of terrestrial and extraterrestrial halite samples to clarify luminescence centers in various types of halite.

Halite crystals of terrestrial origin and small halite particles in ureilite meteorites were selected for CL measurements. All samples were prepared using oil while cutting and polishing without water. Also cleavage fragments of terrestrial samples were used for CL spectral measurements after carbon coating.

All samples exhibit weak blue to greenish blue CL with broad band emissions from 350 to 650 nm. CL spectra corrected for total instrumental response were converted into energy units for spectral deconvolution using a Gaussian curve fitting, because Gaussian curve in energy units can be assigned to one specific type of emission center (Stevens-Kalceff, 2009). The deconvoluted components can be assigned to the emission centers related to V_k (+e), F (+p), V_F (+e), Mn^{2+} (Na^+) and Mn^{2+} (interstitial) by referring to Gorobets and Rogojine (2002).

The CL spectra of terrestrial halite at room temperature are consisted of five components at 3.34 eV, 3.05 eV, 2.46 eV, and 2.28 eV and at 2.00 eV. At low temperature the emission of Mn^{2+} impurity center is enhanced due to an increase in the probability of radiation transition. In the case of high-energy emission, a decrease in sample temperature reduces the intensity of F-center emission, but sensitizes the intensity of V_k -center emission, suggesting the energy transfer from F-center to V_k -center. The CL spectral analysis of terrestrial sylvite at room temperature confirms four emission components at 3.32 eV, 2.97 eV, 2.53 eV and 1.89 eV.

Halite in the meteorite of polymict ureilite (Dar al Gani 319) gives a broad emission band in blue region, which is deconvoluted into two components at 2.70 eV for unknown center and at 3.11 eV for F-center. However, no emission in red region associated with Mn impurity center has not recognized in ureilite halite. It implies that high-energy radiation in cosmic space might break up the crystal fields around Mn ions.

Effects of Mn activator and site occupancy on cathodoluminescence of dolomite

KUSANO, Nobuhiro^{1*}; NISHIDO, Hirotsugu¹; NINAGAWA, Kiyotaka¹

¹Okayama University of Science

Cathodoluminescence (CL) has been widely applied in mineralogical and petrological investigations, especially for carbonates. Dolomite commonly red CL emission related to an impurity center of divalent Mn in Ca-site and Mg-site (Sommer, 1972; Walker et al, 1989). Furthermore, temperature effect on CL efficiency has not been discussed in spite of potentially important function to control CL emission mechanism. In this study we have clarified luminescent mechanism of dolomite in a wide range of temperature using a SEM-CL, and confirmed a temperature quenching of its emissions. The quenching process has been quantitatively evaluated by CL spectral deconvolution method assuming the Mott-Seitz model.

Five dolomite samples from Hase, Japan (D01), Nakase, Japan (D02), Raura, Peru (D03), Binntal, Switzerland (D04), Arizona, USA (D05) were selected for CL measurements after carbon-coating on their polished surfaces. SEM-CL analysis was conducted using an SEM (JEOL:JSM-5410) combined with a grating monochromator (Oxford: Mono CL2) to measure CL spectra ranging from 300 to 800 nm in 1 nm steps with a temperature controlled stage from -190 to 250 °C. The dispersed CL was collected by a photon counting method using a photomultiplier tube (R2228) and converted to digital data. All CL spectra were corrected for the total instrumental response.

CL spectra of all samples at room temperature exhibit almost similar pattern with a broad band at 525-800 nm in a red region. The spectral peaks are sharpened and enhanced at lower temperature due to reduction of thermal lattice vibration and an increase in luminescent efficiency, suggesting high spectral resolution of the emission bands at low temperature. Therefore, a Gaussian fitting was conducted to quantitatively deconvolute spectral data obtained at low temperature in an energy unit. The results confirmed that CL of all samples consist of two emission components at around 1.84 eV (Mg-site) and 2.15 eV (Ca-site) in red region, of which variation might be attributable to crystal field (Mn-ligands distance). In general, luminescence efficiency of the material decreases with a rise in temperature due to an increase in non-radiative transitions. This phenomenon has been recognized in several minerals such as quartz, cristobalite and tridymite as temperature quenching. Furthermore, an increasing temperature makes a shift of the emission peak to a higher wavelength side. The emission intensity varies depending on the samples with different concentrations of activator (Mn^{2+}) and quencher (Fe^{2+}), and site occupancy of the Mn^{2+} ion between two cation sites in dolomite structure. The facts suggest that the behavior of the emission intensity with changes in temperature is not explained on the basis of a temperature quenching theory based on an increase in the probability of non-radiative transition with the rise of temperature (Mott-Seitz model). Probably activator (Mn^{2+}) concentration affects temperature quenching effect on CL of dolomite considerably.

Cathodoluminescence of calcite decomposed from dolomite in high-temperature skarn

KUSANO, Nobuhiro^{1*} ; NISHIDO, Hirotsugu¹ ; INOUE, Koichi¹

¹Okayama University of Science

Purple luminescent calcite associated with periclase has been found from the high-temperature skarn in Kanehira mine located in the eastern part of Hiroshima Prefecture. Calcite usually emits red to orange in cathodoluminescence (CL), but scarcely purple to blue. In this study we have conducted to clarify the emission center related to purple luminescence by using CL spectral analysis and the origin of the calcite during skarn mineralization.

The specimens collected from the skarn zone in the limestone contacted with intrusive granodiorite in the outcrop of the pit-tunnel. The polished thin sections of the selected samples were employed for optical observation and CL measurements. Color CL images were obtained using a cold-cathode type Luminoscope with a cooled-CCD camera. CL spectroscopy was made by a SEM-CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating monochromator (OXFORD: Mono CL2). The CL emitted from the samples was dispersed by a grating monochromator (1200 grooves/mm), and recorded by a photon counting method using a photomultiplier tube. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp.

Color CL imaging reveals two types of CL emission, red and purple, in calcite closely associated with spotted periclase. The CL spectra of both calcite show a broad emission band at 620 nm in a red region, which is assigned to an impurity center derived from an activator of divalent Mn ion substituted for Ca, where the intensity of red CL is higher than that of purple CL. Furthermore, the calcite with purple calcite exhibits a broad emission band at 400-500 nm in a blue region, which might be related to a defect center such as "back-ground blue" found in low-Mn activated calcite.

The calcite with purple CL is accompanied by spotted periclase grains, which is usually found as a component of metamorphosed dolomitic limestone. If the hydrate condition would be presumed during its formation, periclase could easily hydrate and alter to brucite and other magnesium minerals by action of the humidity. According to the results of heating experiments of dolomite, dolomite decomposes to calcite and periclase at around 750 °C, whereas calcite causes its decarbonation above around 850 °C. It implies that the calcite with purple CL might be persisting after the decomposition of dolomite under a dry condition at relatively high-temperature near 800 °C, and leave the defects in the calcite structure during thermal decomposition of dolomite, which can be assigned to the component of an emission band in a blue region.

Cathodoluminescence characterization of terrestrial and extraterrestrial enstatite

OHGO, Syuhei^{1*} ; MISHIMA, Maki¹ ; NISHIDO, Hirotsugu¹ ; NINAGAWA, Kiyotaka¹

¹Okayama University of Science

Enstatite occurred in meteorite shows various cathodoluminescence (CL) emissions, whereas CL emission in terrestrial enstatite has not been reported so far. We have confirmed several luminescent enstatite in terrestrial samples. In this study, we have conducted to clarify the luminescence centers of terrestrial enstatite and comparatively discuss the CL of terrestrial enstatite and extraterrestrial ones in enstatite chondrite (E-chondrite).

Three enstatite with CL emission from Morogoro, Tanzania and Chandrika, SriLanka were selected for CL measurements. The samples were fixed on a brass disk with low-luminescent epoxy resin, and polished with a diamond paste. The polished thin sections of E-chondrite (Dar al Gani 734 and Y-86004) and Aubrite (Al Haggounia 001) were employed for CL examination. Color CL images were obtained using a cold-cathode type Luminoscope with a cooled-CCD camera. CL spectroscopy was made by a SEM-CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating monochromator (OXFORD: Mono CL2). The CL emitted from the samples was dispersed by a grating (1200 grooves/mm), and recorded by a photon counting method using a photomultiplier tube. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp.

Color CL imaging reveals various types of CL emissions, red, blue and purple in the both of terrestrial and extraterrestrial samples. The CL spectra of these enstatite show a broad emission band at 670 nm in a red region, which is assigned to an impurity center derived from activated divalent Mn ion substituted for Mg, and a broad emission band at around 400 nm in a blue region, which might be related to a defect center such as "intrinsic defect center" possibly raised during crystal growth.

CL spectra corrected for total instrumental response were converted into energy units for spectral deconvolution using a Gaussian curve fitting, because Gaussian curve in energy units can be assigned to one specific type of emission center (Stevens-Kalceff, 2009). The deconvoluted components can be assigned to the emission centers related to impurity centers of trivalent Cr ion (1.71 eV) and divalent Mn ion (1.87 eV) and to defect centers (3.18 eV). Furthermore, enstatite in Y-86004 E-chondrite gives additional emission component (3.87 eV) in a blue to UV region, which might be characteristic of the enstatite formed under the condition of low-oxygen partial pressure.

Cathodoluminescence study of metasomatic feldspar in aegirine syenite from Iwaki Island, Ehime Prefecture

MAKI, Seiya^{1*} ; NISHIDO, Hirotsugu¹ ; KAYAMA, Masahiro²

¹Okayama University of Science, ²Hiroshima University

In Iwaki Island, aegirine syenite was emplaced in the Ryoke granite during late Cretaceous time by alkali-rich hydrothermal metasomatism. The syenite and related rocks show various types of petrographic textures in response to the process of hydrothermal alteration, e.g. feldspar minerals. Feldspar exhibits a variety of cathodoluminescence (CL) colors depending on kinds of impurity elements and their concentrations, and defect densities related to Si-Al ordering and other structural disorder. Recently, the deconvolution method of CL spectra enables to assign the luminescence centers characteristic of the feldspar with satisfactory reliability (Kayama et al., 2010). In this study, we have conducted to clarify the metasomatic process through granite to syenite by CL spectral analyses for various types of feldspar.

Polished thin sections of the rock samples collected from granite, altered granite and syenite were employed for petrographic observations under a polarizing light microscope, CL measurements, and electron microprobe analyses (EPMA). Color CL images were obtained using a cold-cathode type Luminoscope with a cooled-CCD camera. CL spectroscopy was made by a SEM-CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating (OXFORD: Mono CL2). The CL emitted from the samples was dispersed by a grating monochromator (1200 grooves/mm), and recorded by a photon counting method using a photomultiplier tube. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp.

The feldspar in the unaltered granite shows apple green and blue CL emissions. The former is identified to plagioclase (Ab80, An20) characterized by divalent Mn activator at 556 nm, and the latter to alkali feldspar (Or90, Ab10) by defect center at 417 nm related to Al-O-Al. Altered granite has albite with red CL emission at around 750 nm, and alkali feldspar with inhomogeneous color of red to violet-blue emissions at around 400 nm and 720 nm. These CL emissions in a red region can be assigned to trivalent Fe activator in tetrahedral sites. The feldspar in syenite are mostly altered to albite with enhanced red emission at 748 nm, but minor alkali feldspar as residual after hydrothermal alteration exhibits dull red emission at 722 nm. The results of the spectral deconvolution reveals oxygen defect centers associated with Al-O-Al and Al-O-Ti bridges and impurity centers of trivalent Fe ions substituted for tetrahedral Al sites according to Kayama et al. (2010). Kayama et al. (2010) investigated the peak changes of a blue emission peak at 420 nm in alkali feldspar and they found that the elimination of Al-O-Al defect center was affected by hydrothermal metasomatism possibly at 250 °C. Therefore, the disappearance of blue emission in alkali feldspar in syenite implies that alkali-rich (sodium-rich) hydrothermal metasomatism for the formation of syenite could act at relatively high temperature above 250 °C successively after granitic magmatism.

Provenance study of quartz grains in aeolian desert sediments using cathodoluminescence method

MASUDA, Risa^{1*} ; SANEYOSHI, Mototaka¹ ; NISHIDO, Hirotsugu¹ ; TSOGTBAATAR, K.² ; CHINZORIG, T.² ; MAINBAYAR, B.²

¹Okayama University of Science, ²Mongolian Academy of Sciences, Mongolia

Cathodoluminescence (CL), the emission of light caused by electron irradiation, has been widely applied in earth science, most extensively used in sedimentology. In such studies CL has the advantage that it can reveal characteristics which are invisible using transmitted light, e.g. growth zones of the crystals such as silica and carbonate minerals. In the case of quartz, its CL spectral feature is so complicated to be simply used for the identification of the provenance due to many emission centers related to various types of structural defects. In this study, we have conducted to clarify the luminescence centers in quartz selected from desert sediments using SEM-CL and evaluate quantitative ratios of the emission components of the CL spectra by the deconvolution method.

The quartz grains (#60-80 mesh size) in the aeolian sediments collected from Djadokhta formation (upper Cretaceous) in the Gobi desert were fixed on the slide glass with low-luminescent epoxy resin, of which surfaces were polished with 1 micron diamond paste. Color CL images were obtained using a cold-cathode type Luminoscope with a cooled-CCD camera. CL spectroscopy was made by a SEM-CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating monochromator (OXFORD: Mono CL2). The CL emitted from the samples was dispersed by a grating monochromator (1200 grooves/mm), and recorded by a photon counting method using a photomultiplier tube. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp.

All samples show dark blue CL emission, and exhibit two broad bands at 400 nm in a blue region and at 600-650 nm in a red region. CL spectra corrected for total instrumental response were converted into energy units for spectral deconvolution using a Gaussian curve fitting, because Gaussian curve in energy units can be assigned to one specific type of emission center (Stevens-Kalceff, 2009). The deconvoluted components can be assigned to the emission centers related to trivalent Fe at 1.65 eV, NBOHC at 1.89 eV, tetravalent Ti at 2.75 eV and trivalent Al at 3.19 eV by referring to Stevens-Kalceff (2009). We employed 10 grains randomly selected from collected 80 grains for each sample, and determined quantitative ratios of the emission components for these quartz grains using their integral intensities. We discuss variations of characteristic components among the sediments based on the results by a statistical analysis.