

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

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Thermodynamic properties of  $\text{MgSiO}_3$  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  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$ -bearing Pv[1,2,3] and  $\text{Fe}^{2+}$ -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,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , 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,  $\text{Fe}^{3+}$  ions substituted at Mg and Si site respectively have the high and low spin state within the deep LM pressure range, while  $\text{Fe}^{3+}$  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  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in PPv is found unfavorable.

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## Ca(OD)<sub>2</sub> の高圧下での熱膨張 Thermal expansion of Ca(OD)<sub>2</sub> at high pressure

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Ca(OH)<sub>2</sub> 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 Ca(OH)<sub>2</sub> 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<sub>2</sub>O 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<sub>2</sub>O water, and then dried at 383 K under vacuum for 3 hours. The products were confirmed to have the CdI<sub>2</sub>-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 Ca(OD)<sub>2</sub> at various P-T conditions from 2-4 GPa and 300-800 K. TOF neutron powder diffraction measurements of Ca(OD)<sub>2</sub> 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 Ca(OD)<sub>2</sub> peaks and no peaks from sample surrounding materials such as ZrO<sub>2</sub> 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 Ca(OD)<sub>2</sub> at high pressure will be discussed.

キーワード: ポートランドト, 熱膨張, 高圧, 放射光X線回折, TOF 中性子回折

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

## SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-RO (R=Mg, Ca, Sr, Ba) 系メルトの高温熱容量 High-temperature heat capacity of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-RO (R=Mg, Ca, Sr, Ba) melts

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シリケートメルトの熱容量はマグマの相関係の熱力学的考察や工業用ガラスの溶融プロセスでの熱流動シミュレーションにおける重要な物性のうちのひとつである。これまでの研究によれば、アルミニウムを含まないシリケートメルトの熱容量は温度に依存せず、また組成変化に対して線形的に変化するが、アルミノシリケートメルトの熱容量は正の温度依存性を有し、加えて複雑な組成依存性を示すことが知られている (Richet and Bottinga, 1985; Richet and Mysen, 2005)。しかしながら、ガラス転移領域からリキダス以上の広い温度範囲に渡る測定データが少ないために、その温度・組成依存性の詳細については不明な部分が多い。本研究では Ca, Sr, Ba を含むアルミノシリケートメルトについて新たな熱量測定を行った。

測定は 50SiO<sub>2</sub>-25Al<sub>2</sub>O<sub>3</sub>-25CaO (An), 36.5SiO<sub>2</sub>-27Al<sub>2</sub>O<sub>3</sub>-36.5CaO (Ca36.5), 8SiO<sub>2</sub>-30Al<sub>2</sub>O<sub>3</sub>-62CaO (Ca62), 75SiO<sub>2</sub>-12.5Al<sub>2</sub>O<sub>3</sub>-12.5SrO or 12.5BaO (Sr12.5, Ba12.5) 組成 (mol%) について行った。落下型熱量計を用いて 873K から 1889K の温度のメルトと 273K のガラスの間の相対エンタルピーを測定した。得られた相対エンタルピーを温度の関数として近似し、その微分から比熱を求めた。比熱は An について  $1.356+0.0001151T(K)$  (J/K-g) と求まり、Richet and Bottinga (1985) による測定値とよく一致した。Ca36.5, Ca62, Sr12.5, Ba12.5 については、それぞれ 1.532, 1.508, 1.313, 1.160 (J/g-K) と求まり、温度によらず一定であった。

本研究による測定結果を既報の落下熱量測定による高温熱容量データ (n=11, Richet and Bottinga, 1984; Courtial and Richet, 1993; Neuville and Richet, 1991; Richet and Neuville, 1992) および示差走査熱測定による T<sub>g</sub> よりやや上の熱容量データ (n=22, Webb, 2008; 2011) と組み合わせ、SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-RO (R=Mg, Ca, Sr, Ba) 系メルトの熱容量の温度・組成依存性を考察した。Courtial and Richet (1993) が報告したように、SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO 系メルトにおいては熱容量に正の温度依存性が観察される。一方、SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系で正の温度依存性を示すのは An 組成のみに限定される。熱容量の組成変化は symmetric solution モデルを用いておおよそ近似することができた。メルトの混合熱容量はいずれも負の非理想性を示し、負の程度は Ba>Sr>Ca>Mg の順に大きくなった。このことは Field strength の小さなアルカリ土類金属イオンほど Al の電荷補償イオンと成りやすく、原子配置の自由度が制約されることに起因するものと考えられる。Sr および Ba 含有メルトの熱容量の温度依存性の有無については、さらに組成範囲を広げて検証する必要がある。

キーワード: シリケートメルト, 比熱, 熱容量, 熱測定  
Keywords: Silicate melt, Heat capacity, Calorimetry

## チタンを含むマグマの高圧下での粘度 Viscosity of titanium-bearing silicate melts at high pressure

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TiO<sub>2</sub> は一般に地球のマグマでは副成分だが、月のマグマでは主成分である。特に高チタンマグマでは 10wt% を超える含有量であり、Apollo 14 black glass では 16wt% に達するものもある。マグマは惑星内部で岩石が溶けて生ずるため、噴出の過程を考える上で高圧高温下での物性を知ることは重要である。さて、マグマ中での Si は、地表付近の圧力において一般に 4 配位となることが知られており、SiO<sub>4</sub> 四面体がマグマ中ではネットワークを形成している。ネットワークを構成する陽イオン (T イオン) には Al などがあり、この TO<sub>4</sub> ネットワークの構造が粘度に大きな影響を与えている。Ti はマグマの組成、温度、圧力に依存して配位数が変わるため、Ti を含むマグマ (珪酸塩メルト) の粘度は複雑な挙動を示す。

そこで我々は、Ti を含む珪酸塩メルトの高圧下での粘度の変化を知るため、放射光を用いた X 線影像落球法で粘度測定を行っている。今回は K<sub>2</sub>TiSi<sub>4</sub>O<sub>11</sub> 組成のメルトについて報告する。実験は高エネルギー加速器研究機構 (KEK) の放射光実験施設である PF-AR の NE7A ステーションにおいて行った。試料容器中に K<sub>2</sub>TiSi<sub>4</sub>O<sub>11</sub> 組成の粉末と白金球を入れておき、高圧高温下においてメルト中を落下する白金球の速度を調べた。その後、落下速度とストークスの式から粘度を求めた。実験の結果、3GPa 付近で粘度が極小となることがわかった。3GPa 以上での粘度の増加は、メルト中の Ti の配位数や Ti を含むネットワーク構造が変化していることを示唆している。ところで、高い TiO<sub>2</sub> 含有量である Apollo 14 black glass 組成メルトの密度は Sakamaki et al. (2009) によって調べられ、地球のマグマと比べて圧縮率が大きいことが分かっている。このため、圧力の増加と共に急激に周囲のマントルとの密度差が小さくなり、やがて密度逆転を起こす。Apollo 14 black glass は本研究で用いた K<sub>2</sub>TiSi<sub>4</sub>O<sub>11</sub> と近い TiO<sub>2</sub> 量であるので、同様に高圧下で粘度が増加することが期待される。さらに、マントルとマグマの密度差の減少および粘度の増加によって、月深部では高チタンマグマが移動しにくくなると予想される。月深部の月震波高減衰域は、マントルの部分熔融が原因となった可能性がある。

キーワード: マグマ, 粘度, 月, マントル  
Keywords: magma, viscosity, moon, mantle

## 放射光メスバウア分光法を用いた高圧下における Fe-Si 合金の物性研究 Study of physical properties of Fe-Si alloy at high pressure using using synchrotron radiation Mossbauer spectroscopy

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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<sub>0.95</sub>Si<sub>0.05</sub> enriched with <sup>57</sup>Fe. The starting material was synthesized by melting the mixture of <sup>57</sup>Fe and Fe-Si alloys under the Ar-H<sub>2</sub> 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.

## Fe<sub>2</sub>SiO<sub>4</sub> のポストスピネル転移相境界線の決定 Experimental determination of post-spinel transition boundary in Fe<sub>2</sub>SiO<sub>4</sub>

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(Mg,Fe)<sub>2</sub>SiO<sub>4</sub> カンラン石は、上部マントルで最も豊富な鉱物である。そのカンラン石は、マントル遷移層中で変形スピネル型を経て、スピネル型 (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> に相転移する。Fe<sub>2</sub>SiO<sub>4</sub> スピネルはその端成分であるため、Fe<sub>2</sub>SiO<sub>4</sub> スピネルの相転移は多くの研究者によって研究されてきた (Kawada 1977, Ohtani 1979, Morooka 1992, Katsura et al. 1998)。これらの研究によって、スピネル型 Fe<sub>2</sub>SiO<sub>4</sub> が約 18GPa で 2Fe<sub>x</sub>O+SiO<sub>2</sub>+2(1-x)Fe に分解することが明らかにされたが、2価鉄を含むために高温高压下での酸素分圧によって相境界線が変化し得ることから、その相境界線は十分には確定されていなかった。本研究では、Fe-FeO バッファーにより酸素分圧をコントロールし、Fe<sub>2</sub>SiO<sub>4</sub> のポストスピネル転移の相境界線を決定した。

出発物質は Fe<sub>2</sub>SiO<sub>4</sub>(fayalite)、Fe<sub>x</sub>O 及び Fe の混合物 (モル比 10 : 2 : 1) であり、Fe カプセルに詰められた。高温高压下で試料の酸素分圧は Fe-FeO バッファーでコントロールされた。川井型 6-8 マルチアンビル高压発生装置を用いて、出発試料を 16~19.5GPa、1000~1400 °C の条件下で 3~6 時間保持し、急冷し回収した。回収した試料について、微小領域及び粉末 X 線回折装置と SEM-EDS を用いて、相の同定と Fe<sub>x</sub>O の格子定数の決定を行った。McCammon(1993) による Fe<sub>x</sub>O の組成と格子定数の関係を用いて x の値を求めた。

Fe<sub>2</sub>SiO<sub>4</sub> のポストスピネル転移相境界線は 1000~1400 °C の温度領域において、 $P \text{ (GPa)} = -0.0021T \text{ (}^\circ\text{C)} + 19.85$  と決定され、小さな負の傾きを持つことが分かった。P - T 相図上での本研究の相境界線の位置は、Ohtani (1979) や Katsura et al. (1998) とほぼ調和的である。Katsura et al. (1998) では、従来の研究による Fe<sub>2</sub>SiO<sub>4</sub> ポストスピネル転移相境界線の負勾配の原因が Fe<sub>2</sub>SiO<sub>4</sub> の分解反応の遅さにあると解釈された。本研究では、1000 °C で 3 時間の実験で Fe<sub>2</sub>SiO<sub>4</sub> スピネルの分解反応が完全に進行し、1000 °C で 3 時間及び 6 時間保持された高压回収試料中の Fe<sub>x</sub>O の x 値が誤差範囲で等しい値を示した。これらのことより、1000 °C において少なくとも 3 時間加熱を行えば平衡に達したと考えられる。今回は、1000 °C で 6 時間、1200 °C で 3 時間、1400 °C で 3 時間保持した実験結果に基づき、小さな負の勾配を持つ相境界線を決めており、Fe<sub>2</sub>SiO<sub>4</sub> のポストスピネル転移相境界線の負勾配は、速度論による見かけのものではなく本質的なものと考えられる。

キーワード: Fe<sub>2</sub>SiO<sub>4</sub>, ポストスピネル, スピネル, 高压

Keywords: Fe<sub>2</sub>SiO<sub>4</sub>, post-spinel, spinel, high-pressure

## ラマンスペクトルと堇青石の結晶方位依存性 Relationship between Raman spectral pattern and crystal orientation of cordierite

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In the crystal structure of cordierite, six-membered rings of (Al, Si) O<sub>4</sub> are stacked along the *c*-axis and form a channel structure. This channel structure can trap volatiles such as H<sub>2</sub>O and CO<sub>2</sub>, and makes cordierite an important mineral for preserving the information of past fluid conditions during metamorphism. Earlier studies have shown that the intensity of CO<sub>2</sub> Raman band represents the contents of CO<sub>2</sub> 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 CO<sub>2</sub> at 1383cm<sup>-1</sup> 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 CO<sub>2</sub> in randomly oriented cordierite grains in metamorphic rocks. As a first step to accurately quantify the CO<sub>2</sub> 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<sup>-1</sup>, the peaks of 970 cm<sup>-1</sup> and 1180 cm<sup>-1</sup> changed its intensity drastically, whereas the peak at 670 cm<sup>-1</sup> remained constant. We selected five Raman peaks at 554 cm<sup>-1</sup>, 575 cm<sup>-1</sup>, 670 cm<sup>-1</sup>, 970 cm<sup>-1</sup>, and 1180 cm<sup>-1</sup> attributable to the cordierite (Al, Si)O<sub>4</sub> structure and analyzed the intensity ratio of these five peaks in different orientations. A parameter of  $\Delta$ 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

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キーワード: 堇青石, ラマン分光法, 結晶方位

Keywords: Cordierite, Raman spectroscopy, Crystal orientation

## 岡山県新見市大佐山産緑簾石の低温メスbauer分光 The low-temperature Moessbauer spectroscopy of an M3' epidote from Osayama, Okayama prefecture, Japan

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緑簾石は低変性度の変成岩等に普通に見られる鉱物である。化学組成は  $\text{Ca}_2(\text{Al,Fe}^{3+},\text{Fe}^{2+})\text{Al}_2\text{SiO}_4\text{Si}_2\text{O}_7(\text{O},\text{OH})$  で、生成条件に対応してゾーニング組織を形成する。結晶格子中の  $\text{Fe}^{2+}$  と  $\text{Fe}^{3+}$  の M1 および M3 サイトへの分配比率はメスbauer分光法で検出可能であり、緑簾石の安定/準安定に関する情報を得ることが出来る。

さらにいくつかの緑簾石ではメスbauer分光法のみで同定可能なサイトである M3' サイトに Fe が分配されている。Fe の M3' サイトへの分配率は X 線結晶構造解析法では推定できないため、微小な秩序構造を形成すると同時に結晶中で均質に分散していると考えられている。また Fe の M1/M3/M3' サイトへの分配率は緑簾石の生成温度を反映していると考えられている。今回、M3' サイトを持つ緑簾石サンプルについて低温でメスbauerスペクトルと磁化率を測定し、M3' サイトの性質について検討を行った。

本研究で用いた緑簾石サンプルは岡山県産 (Ep1) および岩手県産 (Ep2) である。化学組成は EPMA と CHNS/O アナライザで決定した。結晶構造は単結晶法を用いて決定した。メスbauerスペクトルは Rh マトリックスを使用し  $^{57}\text{Co}$  を線源とした測定システムにより 0K-300K で測定した。また磁気物性を検討するために、同様の温度範囲で磁化測定を行った。

解析の結果、低温では Ep1 の磁気物性が Ep2 と異なることが判明した。そこで各サンプルの M1 および M3 サイトの磁気緩和時間を低温メスbauerスペクトルから求め、温度依存性を検討した。その結果、比較的低温で形成された岩体由来である Ep1 の M3 サイトと比較的高温で形成された岩体由来である Ep2 の M3 サイトで磁気緩和挙動が異なっていた。これは Ep1 の M3 サイトにおいて、岩体の形成温度に応じた X 線回折法では検出できない構造変形が発生して磁気環境が変化したため、メスbauerスペクトルのみで検出可能な M3' サイトに変化していることを示唆している。

キーワード: 緑簾石, メスbauer分光, M3' サイト, 磁気緩和

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



## 氷点近傍でのイカ石 ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) の結晶構造変化 Structural change in ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) near the freezing point temperature of water

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炭酸カルシウムのひとつであるイカ石 (ikaite) は、氷点下から氷点付近で熱力学的に安定であり、常温になると急速に脱水し方解石やバテライトへと相転移する。奇岩として知られるグレンドン石や玄能石岩は、結晶外形のみを残して方解石に相転移したイカ石の仮像であると考えられている。本研究は、合成イカ石 ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) の単結晶 X 線回折実験によって、イカ石の温度変化に伴う脱水分解メカニズムを解明することを目的として行った。イカ石の結晶構造は、 $-50^\circ\text{C}$  で、単斜晶系、空間群  $C2/c$ ,  $a = 8.8134(1)$ ,  $b = 8.3108(1)$ ,  $c = 11.0183(1) \text{ \AA}$ ,  $\beta = 110.418(1)^\circ$  であり、単位格子中に存在する 4 個の  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  分子が互いを水素結合のネットワークで支え合うことで構造を形成している。低温単結晶 XRD 測定の結果、単位格子体積は  $-50^\circ\text{C}$  から  $-10^\circ\text{C}$  までは連続的に増加し、その増加率は  $-50^\circ\text{C}$  から  $-20^\circ\text{C}$  までは  $756.3$  から  $758.0 \text{ \AA}^3$  と非常に僅かであった。しかし、単位格子体積は、 $-10^\circ\text{C}$  で  $771.0 \text{ \AA}^3$  に著しく膨張し、その後  $0^\circ\text{C}$  で回折点が消失し、イカ石の結晶性は失われた。単位格子は、温度上昇に伴って異方的に膨張し、 $c$  軸が最も大きな伸長を示し、 $a$  軸も大きく伸長したが、 $b$  軸はほぼ一定であった。分子内結合の変化は、 $-10^\circ\text{C}$  で  $\text{Ca-O}(5)$  結合距離が著しく伸長し、これは、イカ石の脱水プロセスの最初が  $\text{Ca}$  原子と  $\text{O}(5)$  原子との結合の解離であることを示唆している。また、分子間距離は、 $\text{O}(2)\text{-O}(3)$ ,  $\text{O}(2)\text{-O}(5)$ ,  $\text{O}(4)\text{-O}(5)$  間距離が伸長し、 $\text{O}(4)\text{-O}(5)$  間距離は収縮した。分子間の  $\text{O}(2)\text{-O}(5)$  距離の増加は、温度上昇に伴う単位格子の  $a$  軸方向への伸長の直接的な原因である。さらに、分子間の原子間角度は、 $\text{Ca-O}(3)\text{-O}(2)$  間角が、温度上昇に伴って単調に増加した。これは、温度増加により  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  分子が  $b$  軸に平行に回転運動していることを意味し、この運動が単位格子の  $c$  軸方向への大きな伸長の原因となっている。

キーワード: イカ石, バテライト, 炭酸カルシウム, 仮像, 低温単結晶 X 線回折

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

## 放射光 X 線粉末回折によるハイドログロッシュラー構造中の水素原子の挙動の解明 Synchrotron powder X-ray diffraction study of the structural thermal properties on hydrogrossular

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合成 hydrogrossular, katoite  $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$ , の 10 K から 300 K までの低温放射光 X 線粉末回折測定を行い, リートベルト解析によって結晶構造精密化を行った. 低温下での katoite の構造相転移の可能性を検証するために, 10 K で測定した X 線回折パターンに対して, 常温での空間群  $Ia-3d$ , 高压相の空間群  $I-43d$ , majorite の空間群  $I4_1/acd$  の 3 つの構造モデルを用いて結晶構造解析を行った. 解析の結果, 残差の  $R_w$  値は  $Ia-3d$  のとき最小 ( $R_w=9.4\%$ ) となり, したがって低温下では構造相転移をせず常温常圧の結晶構造を維持していることがわかった. これは, katoite の高压相転移の単位格子の収縮率と比較した場合に低温下では単位格子の収縮率が 1/8 倍と非常に小さいため, 構造相転移に至らなかったと推測される. しかし, 温度低下に伴う格子定数の変化は, 100 K を境に体積変化率が急激に変化して不連続となった. Katoite の単位格子体積は温度低下の過程で 100 K から単調に減少し 10 K で最小値を示したが,  $\text{O}_4\text{H}_4$  四面体内の O-H 結合距離は 40 K から 10 K まで連続的に増加した. さらに,  $\text{O}_4\text{H}_4$  四面体体積は 100 K から 20 K まで連続的に減少したが, 10 K で著しい増加に転じた. このとき, 40 K 以下での O-H 結合距離の増加は, katoite の単位格子の収縮に伴って生じる原子同士の反発によるものと考えられる. 一方,  $\text{O}_4\text{H}_4$  四面体体積の変化は,  $\text{AlO}_6$  八面体体積の変化と常に逆相関の関係を示した. したがって, katoite が極低温下でも構造相転移せずにその構造を維持できる理由は,  $\text{O}_4\text{H}_4$  四面体と  $\text{AlO}_6$  八面体が katoite に相転移を及ぼすような収縮を打ち消しあうためだと考えられる. 極低温下での水素原子の挙動は, katoite の結晶構造の大きな変化を与えるには及ばないが,  $\text{O}_4\text{H}_4$  四面体内の OH 基の結合の対称性に関しては変化が生じていると推察される.

キーワード: katoite, 放射光 X 線粉末回折, リートベルト解析,  $\text{O}_4\text{H}_4$  四面体

Keywords: katoite, synchrotron powder X-ray diffraction, Rietveld analysis,  $\text{O}_4\text{H}_4$  tetrahedron

## スコレス沸石における加熱脱水に伴う相変化に関する研究 Structural study on the phase transformation of natural scolecite with increasing temperature

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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  $\text{H}_2\text{O}$  site in meta-scolecite phase. This may be a key to solve the dehydration process of scolecite.

キーワード: スコレス沸石, 脱水, 相変化, 単結晶X線回折実験, 双晶, 高温実験

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

## 氷 VII 相の高温高圧下でのプロトンネリングーホッピング転移の可能性について Near-infrared spectra of ice under high pressure and high temperature

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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<sup>-</sup> and H<sub>3</sub>O<sup>+</sup>. 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.

キーワード: 氷, プロトン, 氷衛星, 近赤外分光, 高温高圧

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

## ゲスト分子の配向秩序化による Filled Ice Ih 構造メタンハイドレートの相変化 Phase changes of filled ice Ih methane hydrate induced by the orientational ordering of the guest molecules

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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.

キーワード: メタンハイドレート, X 線回折, 高圧, ラマン分光

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

## テクトタイトと衝撃関連性自然ガラス中のZr局所構造のXAFS法による解析 Zirconium local structure in tektite and impact-related natural glasses probed by XAFS

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テクトタイトと自然ガラスの局所構造はZr k端XANESとEXAFSを研究することで配位数と原子間距離の量的データを得ることが出来る。XAFS法はKEKの(筑波, 日本)PF-ARのBL-NW10Aビームラインで行われた。テクトタイト中のZr<sup>4+</sup>イオンは形成するガラスごとに異なる配位環境を持つ。様々な自然ガラスは異なる物理環境下で形成されている。衝撃関連性ガラス、火山ガラス、閃電ガラスは典型的な自然ガラスである。ガラスを構成するときと急冷過程でガラス構造は温度と圧力条件の影響を受ける。本研究では自然ガラスの異なる形成過程が異なるジルコニウムの局所構造を作り出すと示している。

テクトタイトのZrK端XANESスペクトルは異なる二つ高さのピークエッジを持つ。全てのテクトタイトは同じタイプに分類される。テクトタイトにおけるZr-O距離は2.198-2.215 ÅでテクトタイトのXANESスペクトルも似たようなスペクトルを持つ。火山ガラスは同じタイプに分類される。衝撃関連性ガラスのKofelsite, SueviteとLDG, Darwin glassは異なるタイプに分類されている。衝撃関連性ガラスは隕石衝突イベントにおける異なる地学的過程で形成されて、異なる物理的環境を経ている。

キーワード: XAFS, Zr局所構造, テクトタイト, 自然ガラス, XANES, EXAFS

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

## Os 蒸着膜を用いたマイクロプローブ法による軽元素定量 Light element quantification using electron microprobe and Os surface coating

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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 CaCO<sub>3</sub>.

## 地球試料および隕石試料に見出されるアルカリ塩化物鉱物のカソードルミネセンス Cathodoluminescence characterization of terrestrial and extraterrestrial alkali-halide minerals

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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.



## Mn アクチベータおよび分配率がドロマイトのカソードルミネッセンスに及ぼす効果 Effects of Mn activator and site occupancy on cathodoluminescence of dolomite

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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.

## 高温スカルン中のドロマイト起源カルサイトのカソードルミネッセンス Cathodoluminescence of calcite decomposed from dolomite in high-temperature skarn

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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.

## 地球試料および隕石試料に見出されるエンスタタイトのカソードルミネッセンス Cathodoluminescence characterization of terrestrial and extraterrestrial enstatite

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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, Sri Lanka 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.

## 愛媛県岩城島のエジリン閃長岩に伴う長石のカソードルミネッセンス Cathodoluminescence study of metasomatic feldspar in aegirine syenite from Iwaki Is- land, Ehime Prefecture

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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 (Ab<sub>80</sub>, An<sub>20</sub>) characterized by divalent Mn activator at 556 nm, and the latter to alkali feldspar (Or<sub>90</sub>, Ab<sub>10</sub>) 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.

## 石英のカソードルミネッセンスを用いた砂漠風成層の起源地推定 Provenance study of quartz grains in aeolian desert sediments using cathodoluminescence method

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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.