

高圧下での金の結晶弾性測定：~5GPa領域弾性異常と一次圧力スケールの構築

Single crystal elasticity of gold (Au) up to ~20 GPa: Bulk modulus anomaly below ~5 GPa and implication for a primary pressure scale

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We measured single crystal elasticity of gold (Au) as well as its lattice parameters simultaneously under high pressure by using inelastic X ray scattering (IXS) technique. Generated pressure and elastic moduli of gold were obtained only from the present experimental data at five pressure points between 0 and 20 GPa by direct numerical integration. Pressure variation of the bulk modulus displays an anomalous behavior; it is nearly constant up to ~5 GPa, and then steeply increases toward higher pressure. Similar anomaly is observed in independent first-principles calculations as well. The absolute pressure scale determined from the present results gives systematically lower pressures than those from the previous pressure scales owing to the bulk modulus anomaly founded in this study.

キーワード：金、結晶弾性、体積弾性率、圧力スケール、非弾性X線散乱、ダイヤモンド・アンビル・セル
Keywords: gold, single crystal elasticity, bulk modulus, pressure scale, inelastic X ray scattering, diamond anvil cell

High-pressure phase transitions of MgCO₃ under the lower mantle conditions

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MgCO₃ is one of the important carbonate minerals in the deep Earth because it can be a carbon carrier from the surface to the mantle in subduction processes. Such deep carbonates may be involved in melting of subducted rocks and formation of deep diamonds in the mantle transition zone or lower mantle. MgCO₃ has especially been suggested to be the most stable carbonate under the high-pressure and temperature conditions.

Recent experimental and theoretical studies reported high-pressure phase transitions of MgCO₃ under the lower mantle conditions. A report of the high-pressure polymorph was started from ‘magnesite II’ at 115 GPa in Isshiki et al. (2004). Several recent studies supported a monoclinic MgCO₃ (‘phase II’) as a post-magnesite phase above ~80 GPa.

Phase II was revealed to be composed of (C₃O₉)-ring units which were constituted by three CO₄ tetrahedra sharing three oxygen atoms. However, the structure of phase II has a little difference between the previous studies: the space groups of phase II were reported as C2/m and P2₁/c in Oganov et al. (2008) and Boulard et al. (2011), respectively. Moreover the latest study by Pickard and Needs (2015) observed a new high-pressure polymorph having a triclinic lattice as a post-magnesite phase above 85 GPa, which changed to phase II at 101 GPa.

In addition to the difference of the post-magnesite phase and phase-II structures, none of the above studies decided the phase boundary of the high-pressure phase transitions at high temperature.

Therefore, we have been studied the phase relation of MgCO₃ up to the lowermost mantle conditions based on high-pressure and temperature experiments. We especially focused on the phase boundary of the high-pressure polymorphs at high temperature and a true post-magnesite phase.

The starting material was a natural magnesite from Bahia in Brazil. The experimental conditions were up to 138 GPa and 2900 K generated using a double-sided laser-heated diamond anvil cell (LHDAC). Culet diameters of diamond anvils used were between 130 and 250 μm. The sample was loaded into a sample chamber in a tungsten gasket which was pre-indented to 40–60 μm in thickness and drilled a 60–80-μm hole in diameter. Laser heating was conducted using a fiber laser. Pt or Au was used as a laser absorber. Run products were detected using synchrotron X-ray diffraction (XRD) measurements at beamline BL10XU of SPring-8 in Hyogo, Japan. Experimental pressures were measured using a thermal equation of state of Pt or Au (Fei et al., 2007) and thermal pressures were calculated using Mie-Grüneisen-Debye model (e.g., Fei et al., 1992). XRD patterns were analyzed using IPAnalyzer and PDIndexer software (Seto et al., 2010).

We observed the two high-pressure polymorphs of MgCO₃, which might be monoclinic phase II and triclinic phase reported in Oganov et al. (2008) and Pickard and Needs (2015), respectively. Phase II was observed mainly above 90 GPa and the lattice constants were estimated to be $a = 8.209 \text{ \AA}$, $b = 6.575 \text{ \AA}$, $c = 6.978 \text{ \AA}$, $\beta = 104.06^\circ$, and $V = 365.3 \text{ \AA}^3$ at $100 \pm 2 \text{ GPa}$ and $2080 \pm 230 \text{ K}$ when fitted using the Oganov’s space group, C2/m. The triclinic phase might be appeared as a post-magnesite phase around 90 GPa: The XRD patterns were not explained only by magnesite and phase II. Strong peaks near 104 diffraction of magnesite are considered to be derived from the triclinic phase although we could not fit

their patterns and estimate the lattice constants due to lack of the peak number to fit the triclinic unit cell. We could estimate the phase boundaries of high-pressure polymorphs based on the above observations. The triclinic post-magnesite phase may have a very narrow stability field in the P-T phase diagram. The triclinic phase might buffer the significant structural change from magnesite (CO_4 triangles) to phase II (C_3O_9 rings composed of three CO_4 tetrahedra).

キーワード：菱苦土石、高压多形、下部マントル、レーザー加熱式ダイヤモンドアンビルセル

Keywords: magnesite, high-pressure polymorph, lower mantle, LHDAC

What can mineral physics tell us about the origin of ULVZs? What can mineral physics tell us about the origin of ULVZs?

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The core-mantle boundary region is complex. In addition to large regions with reduced shear velocities (LLSVPs), there are small areas with shear velocities up to 30% lower than surrounding material, the so-called ultralow velocity zones (ULVZs). Although these heterogeneous regions are small (10 to 100 km), they have featured in speculation regarding an ancient global magma ocean, magnetic pole positions during reversals, core-mantle material exchange and the source of mantle plumes. Mineral physics provides important constraints in understanding the nature of ULVZs through the comparison of seismic data with experimental and computational studies of the relevant phases. Shear wave velocities are particularly important, and nuclear inelastic scattering (NIS) offers the attractive possibility to measure these velocities for iron-containing minerals in the laser-heated diamond anvil cell through direct measurement of the partial density of states (DOS). Complementary determination of the partial DOS using density functional theory (DFT) has shown the potential to identify experimental features that impact the velocity determination as demonstrated by our recent study on bridgmanite. We performed first-principles calculations to determine the iron partial DOS for $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{SiO}_3$ post-perovskite. We calculated Debye sound velocities (which are closely related to the shear wave velocities) using the same approach as for experimental NIS data, and obtained velocities for $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{SiO}_3$ post-perovskite that are consistent with literature values for MgSiO_3 and FeSiO_3 post-perovskite also calculated using DFT. In contrast, literature data on the Debye sound velocity determined experimentally using NIS is 35% lower than our calculated value, which led to previous suggestions that ULVZs originate from regions containing iron-rich post-perovskite. Our results show, however, that the lower NIS velocities in post-perovskite data likely arise from a similar artefact as the NIS bridgmanite data. The velocities derived from the DFT DOS of both bridgmanite and post-perovskite are consistent with seismic velocities of the bulk lower mantle, suggesting that ULVZs are likely not caused by iron-rich post-perovskite. Instead we favour previous suggestions that dense melts are a more plausible explanation.

キーワード : lower mantle, density functional theory, nuclear inelastic scattering, shear wave velocity, post-perovskite

Keywords: lower mantle, density functional theory, nuclear inelastic scattering, shear wave velocity, post-perovskite

Single crystal synthesis of δ -(Al,Fe)OOH using multi-anvil apparatus

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δ -AlOOH is an important hydrous mineral for understanding the water cycle in the deep Earth. In a descending slab, δ -AlOOH forms a solid solution with Phase H (MgSiO_4H_2) and ε -FeOOH [e.g., 1, 2]. This solid solution can transport water stored in its crystal structure to the deep mantle because it can be stable at the lowermost mantle conditions [1, 3]. Therefore, δ -AlOOH - Phase H - ε -FeOOH solid solution may affect the Earth's deep water cycles, chemical heterogeneity, and anomalies of seismic wave velocities at the lower mantle.

However, the stability, structure, elasticity, and spin state of this solid solution that are essential to discuss the issues above have not been constrained experimentally because of the difficulty to synthesize this solid solution as a homogeneous single phase.

In this study, we successfully synthesized Fe-bearing δ -AlOOH (δ -(Al, Fe)OOH) single crystals. Single crystals of pure δ -AlOOH and δ -(Al, Fe)OOH with dimensions up to ~ 0.6 mm were synthesized by a high-pressure hydrothermal method. Synthesis experiments were performed at 21 GPa and 1480 K for 4 h using a Kawai-type multianvil apparatus. Mössbauer spectra showed 95-100% $\text{Fe}^{3+}/\Sigma\text{Fe}$ at the octahedral site in δ -(Al, Fe)OOH. Unit-cell parameters of δ -AlOOH were consistent with those of previous studies, and they increased linearly with $\text{Fe}/(\text{Al}+\text{Fe})$ of the starting materials. The crystals contain 1-2 wt.% of excess water compared to their ideal water content. The syntheses of large single crystals of δ -(Al, Fe)OOH will facilitate investigations of their stability, elasticity, elastic anisotropy, spin state, and behavior of hydrogen bonding, which will improve our understanding of the water cycles, chemical heterogeneity, and anomalies of V_p and V_s in the deep Earth.

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Reference

- [1] Ohira et al. (2014) *Earth and Planet. Sci. Lett.*, **401**, 12-17
- [2] Liu et al. (2016) *Goldschmidt Conference 2016*, **04d**, 10:45-11:00
- [3] Sano et al. (2008) *Geophys. Res. Lett.*, **35**, L03303

キーワード：地球内部水循環、高温高圧実験、 δ -AlOOH、 ε -FeOOH、単結晶、川井型マルチアンビルプレス装置

Keywords: Water Cycle in the Earth's Interior, High Pressure and High Temperature Experiment, δ -AlOOH, ε -FeOOH, Single Crystal, Kawai-type Multianvil Apparatus

Boehmiteの圧力誘起積層不整と非対称な水素結合について

Pressure-induced stacking disorder and non-symmetric hydrogen bond in boehmite

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高温高圧実験やダイヤモンド包有物の研究から、地球内部に一特に沈み込み帯やマントル遷移層など一少なくとも局所的には、かなりの量の"水"が含水鉱物として存在していることが明らかになってきた (e.g., Peacock (2000) *Science*, **248**, 329; Pearson *et al.* (2014) *Nature*, **507**, 221)。地球深部の主要な造岩鉱物は酸化物やケイ酸塩であるから、含水鉱物中の水素は酸素に囲まれてO-H...O結合(O-Hは共有結合、H...Oは水素結合)を形成しながら存在していることになる。ところで高圧下では、O...O距離が短くなることで、水素結合と共有結合が等価となる水素結合の対称化が起こることが予想される。したがって、地球深部のような高圧条件下では、ある深度以深で水素結合の対称化が起きている可能性が高い。しかし、含水鉱物中の水素結合が高圧下で対称化するか、また、対称化にしたがってどのような物性変化を起こすかについての研究はdelta-AlOOH (e.g., Tsuchiya *et al.* (2002) *Geophys Res Lett*, **29**, 1; Sano-Furukawa *et al.* (2009) *Am Mineral*, **94**, 1255)やPhase H (Tsuchiya and Mookherjee (2015) *Sci Rep*, **5**, 15534)などについて、わずかに行われているのみであり、まだ理解が十分ではない。本研究では、層状水酸化物であるboehmite (gamma-AlOOH)に注目し、その高圧下での構造変化をX線・中性子回折およびラマン分光法により観察した。Boehmiteは、常圧下では空間群Cmcmの直方晶系で、AlO₆八面体が辺共有した層がb軸方向に積層した層状構造を成しており、水素結合はちょうど層と層との空隙に存在する。圧力をかけると、優先的に層間距離が縮まり、水素結合の圧力変化を効率的に観察できると予想した。

BoehmiteのX線回折実験の結果、加圧に伴い、0kl反射以外の反射、特に130反射について、顕著なブロードニングが見られた一方、0kl反射についてはブロードニングは見られなかった。この現象は、AlO₆八面体層が、隣り合う層についてa方向にdxだけ正負ランダムに変位する積層不整を考えることで説明可能であることがわかった。変位量dxを0 - 0.5まで変化させてシミュレーションした散乱パターンと、実測されたX線回折パターンとを比較することにより、変位量dxの圧力依存性を見積もった。また、10 GPa程度までの中性子回折実験から、O...O、O-D、D...O距離はそれぞれ線形に変化しており、これを単純に直線で外挿すると20 GPa程度でO-D距離とD...O距離は一致することになる。しかしながら、37 GPaまでのラマンスペクトルの結果からは、対称化の兆候は見られておらず、中性子回折の結果とは一見矛盾しているように見える。これは積層不整によって、ドナーとアクセプターの酸素が結晶学的に等価ではなくなり、O...O距離が短くとも水素を感じるポテンシャルは非対称のままになっていると解釈することができる。

キーワード：ベーム石、高圧、積層不整

Keywords: Boehmite, High Pressure, Stacking disorder

ベーマイトとダイアスポアの脱水反応の速度論的研究 Dehydration kinetics of boehmite and diaspore

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Boehmite and diaspore are polymorphs of AlOOH . Dehydration kinetics of boehmite (H-boehmite), deuterated boehmite (D-boehmite) and diaspore were investigated by thermogravimetric measurements with various heating rates. During dehydration treatments, boehmite and diaspore convert to $\gamma\text{-Al}_2\text{O}_3$ and corundum, respectively. The extent of dehydration as a function of temperature and heating rate was analyzed by integral isoconversional methods proposed in Vyazovkin et al.(2011). Because obtained isoconversional activation energies vary significantly with conversion extent, dehydration processes of these hydrous minerals are dominated by not a single reaction but multiple reaction steps. Comparison between H-boehmite and D-boehmite suggests the early stage of dehydration process is controlled by hydrogen migration from one O-H group to adjacent O-H (formation of adsorbed water molecule). On the other hand, comparison between H-boehmite and diaspore suggests the latter stage of dehydration process is controlled by migration of the adsorbed water molecule.

キーワード：脱水反応の速度論、ベーマイト、ダイアスポア

Keywords: dehydration kinetics, boehmite, diaspore

Molecular Dynamics Study of Soret Effect in Calcium-Aluminosilicate glass

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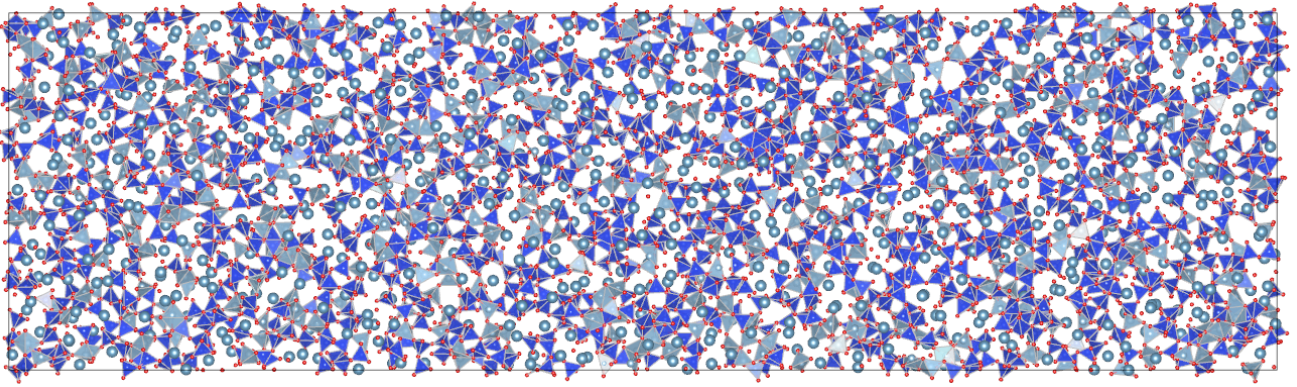
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There are various transportation phenomena driven by a potential gradient. The Soret effect has been known as the diffusion driven by a temperature gradient (Soret, 1879; Ludwig, 1856). While the inverse one is known as Dufour effect. The Soret effect is sometime used in the explanation of fractionation phenomena in geology (Leshner, 1986; Dominguez et al., 2011). Recently Kishi et al. (2016, conference abstract) reports a distribution anomaly of composition around the trace of the migration of high-temperature metal sphere induced by laser irradiation in calcium aluminosilicate glass (Hidai et al., 2016). The rate of fractionation by temperature gradient is determined by both thermal diffusivity (D_T) and mass diffusivities (D) because the total net flux must be zero in a steady state. Consequently, understanding the Soret effect and determination of Soret coefficient (D_T/D) are difficult because the coefficient is affected by not only atomic mass and inter-atomic interaction that affect activation energy but also geometric/structural factor. Calcium-aluminosilicate system is suitable for the investigation of the Soret effect because three oxides have different characteristics; namely, network former, network modifier, and intermediate oxide.

We applied the molecular dynamics (MD) simulations for this system to investigate the mechanism of fractionation by temperature gradient. The MD simulation is an appropriate method for this study because it gives trajectories of each atoms in the simulation cells and potentials of each atom at any point in simulation time. MD simulations of $\text{Ca}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ glass were performed using MXDORTO code (Sakuma & Kawamura, 2009). The simulation conditions are as follows: The inter-atomic potential model was taken from Noritake et al. (2015). System of approximately 30000 particles in rod-shaped (approximately 5 x 5 x 17 nm) simulation cell in periodic boundary condition was firstly annealed for 2 ns at 1873 K from randomly generated structure. Then the liquid was quenched to room temperature at the rate of 10^{12} K/s. Then we started the simulations in temperature gradient. The temperatures in sliced regions (approximately 0.35 nm thickness) perpendicular to the longest axis at the end and the center of simulation cell were maintained 300 and 3500 K using the scaling procedure, respectively. After several tens nano-second simulations, we confirmed the changes in distribution of composition. The concentration of SiO_2 in the high-temperature center part slightly increases as simulation proceeds. In contrast the concentration of CaO in that part slightly decreases. The distribution of concentration of Al_2O_3 does not change apparently. Quantification of coefficient and mechanisms will be discussed in this presentation.

キーワード：分子動力学法、珪酸塩ガラス、珪酸塩メルト、ソレー効果

Keywords: Molecular Dynamics, Silicate Glass, Silicate Melt, Soret Effect



AlPO₄モガナイト相における相転移：高温その場ラマン分光法による研究

Phase transition of AlPO₄-moganite: In-situ high-temperature Raman spectroscopic study

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Moganite構造のAlPO₄が高圧相の1つとして発見された(Kanzaki and Xue, 2012)。MoganiteはSiO₂のレアな多形の1つであり、その構造は石英（の双晶）と密接な関係がある。SiO₂やAlPO₄の多形と同様に、温度による変位型相転移が予想される。SiO₂-moganiteについては既に相転移が報告されている(Heaney et al., 2007)。SiO₂-moganiteは単相を得ることが困難なためにラマンおよび回折実験で良質のデータを得ることが難しい。AlPO₄-moganiteは単相として合成できる利点があるが、常圧では準安定である（この点はSiO₂-moganiteも同じであるが）。本研究ではAlPO₄-moganiteにおける相転移の存在を確かめるために、高温その場ラマン測定を800 °Cまで常圧で行った。なお、2011年の同セッションの講演でこの相転移に簡単に触れているが、今回は測定をやり直し、低周波数におけるソフトモードの存在についても調べた。

使ったAlPO₄-moganite相は以前に5 GPa, 1500 °Cで合成したものである(Kanzaki and Xue, 2012)。加熱にはワイヤーヒーターを使った(Kanzaki et al., 2012)。温度校正には5~6種類の融点既知の物質を使った。ラマン測定には自家製の共焦点顕微ラマン分光法システムを使った(488 nmレーザー, ~80 mW, f=500 mmポリクロメーター、液体窒素冷却CCD検出器)。最初は100 cm⁻¹以上の周波数領域での測定を行ったが、その後、低周波数領域の測定ができるようになり、室温において2つのラマンピーク（約60と73 cm⁻¹）を新たに見つけた（2016年同セッション講演参照）。これらのピークがソフトモードかどうかを調べるために100 cm⁻¹以下領域の高温測定を追加で実施した。アンチストークス側も同時に測定することで、ラマンピークを装置起因ノイズと区別した。室温から25 °Cステップで800 °Cまでの昇温過程で測定した。

100 cm⁻¹以上の周波数領域で測定したラマンスペクトルを解析したところ、いくつかのピークが温度とともにわずかに低周波数側にシフトすることが観察され、425 °C付近でシフト方向が反転するか、ほぼ一定になった。しかし不連続は見つからなかった。これらのハードモードの結果から、高次の相転移の存在が明らかとなり、転移点は約425 °Cと推定された。一方、100 cm⁻¹以下における測定では、73 cm⁻¹ピークは温度とともに大きく低周波数側へシフトし、同時にピーク幅が急激に増加することが観察された。約475 °Cではピークは消失した。これらの結果から73 cm⁻¹ピークはソフトモードと考えられる。一方、60 cm⁻¹のピークは、温度により少し低周波数にシフトし、73 cm⁻¹ピークと一時オーバーラップするが、73 cm⁻¹ピーク消失後も残り、温度によるシフトはほぼ一定になった。こちらは上記ハードモードの振る舞いとよく似ている。800 °C付近では常圧安定相であるberlinite（石英相）の出現が観察された。

本研究でAlPO₄-moganite相においても高次の相転移が存在することが確認された。また、ソフトモードを観察することができた。SiO₂-moganiteについてはハードモードの測定結果があり、転移点は~570 Kとされている(Heaney et al., 2007)。低周波数領域が測定されていないこともあり、ソフトモードは観察されていないが、AlPO₄同様にソフトモードが存在する可能性がある。なお、ハードモードとソフトモードで転移温度が異なるが(425 °C vs 475 °C)、これは後者の測定時間間隔が短かったため、測定上の問題（熱的非平衡）である可能性が高い。今回の実験はberliniteが生じたために加熱過程のみであったが、冷却過程での測定を含め研究を続ける予定である。

Heaney, P.J. et al. (2007) *Am. Mineral.*, 92, 631

Kanzaki, M. and Xue, X. (2012) *Inorg. Chem.*, 51, 6164

Kanzaki, M. et al. (2012) *J. Min. Petrol. Sci.*, 107, 114

キーワード：モガナイト型AlPO₄、ソフトモード、ラマン分光法
Keywords: AlPO₄-moganite, soft mode, Raman spectroscopy

Symmetry reduction of analcime with Al/Si ordering

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Analcime is a sodium aluminosilicate hydrate ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) with the ANA type of zeolite framework. It occurs widely in hydrothermal and diagenetic environments. Symmetry of analcime is well known to be changed with distribution of framework cations and extra-framework cations. Naturally occurring analcime generally exhibits cubic symmetry space group $Ia-3d$, which is the maximum topological symmetry, but it can crystallize in at least three different symmetries; tetragonal space group $I4_1/acd$, orthorhombic space group $Ibca$, and monoclinic space group $I2/a$. However, crystallization conditions affecting the symmetry change have not been fully understood yet. In the study, we hydrothermally synthesized single crystals of analcime and hydrothermally re-heated under various heating time. Single crystals obtained from the different processes were refined by using single-crystal X-ray diffraction method.

Single crystals ranging in size from 50 to 120 μm were grown from gels of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SiO_3 . They show deltoidal icositetrahedron habit with well-developed 24 equivalent $\{2\ 1\ 1\}$ crystal faces. Single crystals grown from gels possess cubic $Ia-3d$ symmetry, in which Si and Al are totally disordered over the framework T sites. Single crystals of analcime hydrothermally reheated for 24h, however, exhibit tetragonal $I4_1/acd$ symmetry. The tetragonal analcime shows a weak site preference of Si for $T1$ site and Al for $T2$ site. Single crystals of analcime hydrothermally reheated for 48h display orthorhombic $Ibca$ symmetry. In the orthorhombic analcime, Si and Al are strongly ordered over the T sites. Si is preferentially distributed into $T11$ and $T12$ sites whereas Al is into $T2$ site. The crystal structural analysis revealed continuous symmetry reduction from cubic $Ia-3d$ to orthorhombic $Ibca$ through tetragonal $I4_1/acd$ depending on heating time. On the other hand, Na atoms are equally distributed over the extra-framework sites during the symmetry reduction. The result of the study clearly shows the heating time significantly influences the Al/Si ordering over the framework T sites rather than the ordering of extra-framework cations. The symmetry reduction in analcime would be useful for understanding of petrological and geochemical history of rocks.

キーワード：アナルサイム、単結晶X線回折、Al/Si秩序配置

Keywords: analcime, single-crystal X-ray diffraction, Al/Si ordered distribution

Artinite, $\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ の $\text{H}_2\text{O}/\text{CO}_3$ の秩序配列の再検討

Reexamination of the crystal structure of artinite, $\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, with two-dimensional disorder

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【はじめに】

炭酸マグネシウム水和物には、多様な相が存在する (Hopkinson et al. 2012). その中で、artiniteは結晶構造中で H_2O 基と CO_3 基が無秩序配列する極めてユニークな構造を持つことが知られている (Akao and Iwai 1977). しかしながら、その特異性について十分な検討はなされていない. そこで、本研究ではartiniteの結晶構造中で H_2O 基と CO_3 基が無秩序配列しているのか、秩序配列しているのかを解明するという目的のもとに実験を行った.

【実験方法】

実験には、天然のartinite (San Benito, USA) を用い、高輝度単結晶自動X線回折装置 (Bruker APEXII ULTRA) により測定を行った. 単結晶構造解析は、固有位相決定法により原子位置を決定し、最小二乗プログラムShelxl-97 (Sheldrick 1997) により原子位置の精密化を行った. また、結晶構造解析は、無秩序配列モデルと秩序配列モデルについてそれぞれ行った. 第一原理計算は、汎用量子化学計算プログラムGaussian 09 (Frisch et al. 2009) を用いた. 波動関数には密度汎関数 (DFT), 基底関数には6-31Gを用いて有効電荷解析を行った.

【結果】

Artiniteは、単斜晶系、空間群 $C2/m$ 、格子定数は、 $a=16.468(8) \text{ \AA}$, $b=3.1352(15) \text{ \AA}$, $c=6.184(5) \text{ \AA}$, $\beta=98.702(5)^\circ$ であった. $\text{CO}_3/\text{H}_2\text{O}$ の無秩序配置モデルで結晶構造を精密化した結果、 $R_1=0.0339$, $wR_2=0.0937$, $GooF=1.013$ であった. 一方で、 $\text{CO}_3/\text{H}_2\text{O}$ を秩序配置モデルで結晶構造を精密化した結果、構造精密化をすることができなかった. 第一原理計算により、無秩序配列モデルの電荷分布を計算した結果、 CO_3 基同士が隣り合うO原子の電荷が-0.378, 隣り合わないO原子の電荷が-0.721, MgO_6 八面体に配位しているO原子の電荷が-0.845, C原子の電荷が1.296となった.

【考察】

Akao and Iwai (1977)では、artiniteの結晶構造中で $\text{H}_2\text{O}/\text{CO}_3$ は無秩序配列していると結論付けている. 本研究の結果は、彼らの結果を支持するものとなった. Mgの配位多面体の結合距離(\AA)は、2.0345(9) ($\times 2$), 2.0610(13), 2.1641(9) ($\times 2$), 2.0135(13), Cの結合距離(\AA)は、1.227(3), 1.2920(18) ($\times 2$)であり、この結合距離は、Akao and Iwai (1977)の結果と類似している. 一方、配位多面体の歪みを他のマグネシウム炭酸塩と比較すると、Nesquehonite $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ と Hydromagnesite $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ と同様にMagnesite MgCO_3 の配位多面体に比べ歪んでいることがわかる. また、第一原理計算の結果は、 CO_3 基同士の隣り合うO原子の有効電荷が隣り合わないO原子の有効電荷より小さくなっており、O原子同士の反発が抑制されていることを示唆する. このことは、無秩序配列している場合に CO_3 基同士が隣り合えることを示している.

キーワード : Artinite、無秩序配列、単結晶構造解析、第一原理計算

Keywords: Artinite, disordered configuration, single crystal structure analysis, ab initio calculation

Experimental investigation of the Fe₂O₃-As₂O₅ system in air

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Arsenic is notoriously harmful to the environment. In numerous deposits and mining concentrates, it is usually present in the form of sulfides such as arsenopyrite (FeAsS) and enargite (Cu₃AsS₄), arsenides such as loellingite (FeAs₂) and nickeline (NiAs), arsenates such as scorodite (FeAsO₄·2H₂O), annabergite (Ni₃(AsO₄)₂·8H₂O) and erythrite (Co₃(AsO₄)₂·8H₂O) and solid solution in ore minerals such as chalcopyrite (CuFeS₂), pyrite (FeS₂), and sphalerite (Zn, Fe)S, for example. Currently, scorodite is the mineral of choice to immobilize arsenic from mine wastes because it has a very low solubility in water. Scorodite is also the most common arsenate known in nature where it is found in hydrothermal deposits and as a secondary mineral in gossans. Unfortunately, there is a lack of information in the literature regarding arsenate systems, which hamper the understanding of the complex chemical reactions involved in their genesis. In the last decades, much effort has thus been devoted to determine the thermodynamic properties and phase relations of arsenates in hydrous and anhydrous conditions. In this regard, the Fe₂O₃-As₂O₅ system is of particular interest because it contains the compound FeAsO₄, the anhydrous analog of scorodite. Surprisingly though, the system Fe₂O₃-As₂O₅ is still poorly known. This is due to the hygroscopic nature, slow kinetics, and high volatility of its phases, and to the presence of iron, which prevent the use of platinum crucibles at high temperature. The first (and only) experimental investigation of the whole phase diagram was performed by Kasenov and Mustafin [*Russ. J. Inorg. Chem. (Engl. Transl.)*, 1997, 42, 1598-1599] using differential thermal analysis (DTA) and X-ray diffraction (XRD) up to 1100 °C. Unfortunately, experiments were performed in sealed but evacuated (to 10⁻⁶ bar, i.e. 10⁻³ mm Hg) silica crucibles and as a result, evaporation probably occurred during the runs. Moreover, the silica crucibles may have reacted with the starting materials, modifying the melting point of the solid phases and the oxidation state of both As and Fe in the system. Consequently, the experimental data collected by Kasenov and Mustafin (1997) may have produced a very different phase diagram than the one expected in air. To determine the correct Fe₂O₃-As₂O₅ phase diagram in air and minimize most of the problems cited above (hygroscopicity, slow kinetics, high volatility, and presence of Fe reacting with crucibles), we prepared dry starting materials, carried out long duration experiments (up to 36 days) with non-evacuated sealed Au₇₅Pd₂₅ crucibles up to 1000 °C using the quenching method and accomplished phase characterization using XRD, backscattered electron (BSE) imaging, and electron probe microanalysis (EPMA). Based on our experiments, new subsolidus phase relations are proposed for the Fe₂O₃-As₂O₅ phase diagram in air, which are significantly different from the ones published earlier by Kasenov and Mustafin (1997). We also report the existence of a new compound, Fe₆As₄O₁₉ (F₃A₂), which is a potential candidate for arsenic sequestration.

Keywords: Phase diagram, Iron arsenates, Scorodite, Fe₆As₄O₁₉

HARECXs法を用いた珪線石の微小領域におけるAl/Si秩序度の定量的決定

Quantitative determination of Al/Si-order parameter in sillimanite from micrometric region using HARECXs method

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Sillimanite is one of the polymorphs of Al_2SiO_5 which are valuable as indicators of pressure and temperature. Structure of sillimanite consists of AlO_6 octahedral chains and Si/AlO_4 tetrahedral double chains parallel to the *c*-axis. Although the tetrahedral Si/Al ions are normally ordered, a possibility of its disordering at high temperatures has been suggested (e.g. Zen, 1969). However, the Al/Si-order parameter of sillimanite has not been successfully quantified. The main problems are that one is the difficulty of separating mullite ($\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x}$, $x \approx 0.17-0.59$) from sillimanite, because mullite is very similar to sillimanite crystallographically, and another is the difficulty to distinguish Al from Si using XRD experiments because of similarity of their X-ray scattering factor.

On the other hand, Atom location by channeling-enhanced microanalysis (ALCHEMI) using TEM-EDS was carried out for determination of Al/Si-order parameter in orthoclase by Taftø & Buseck (1983). By ALCHEMI, it can distinguish the elements with similar atomic number, e.g. Al and Si, and it can be quantified the Al/Si-order parameter from the only sillimanite micrometric region. Furthermore, HARECXs (High Angular Resolution Electron Channeling X-ray Spectroscopy), which was developed from ALCHEMI recently (e.g. Soeda, 2000; Yasuda *et al.*, 2006), provides more quantitative information, because of many EDS measurements by varying the direction of incident electron beam. In this study, therefore, HARECXs experiments were carried out on sillimanite to establish the determination procedure for the Al/Si-order parameter in sillimanite.

Sillimanite crystals in Rundvågshetta, East Antarctica, which are homogeneous without characteristic textures, were examined using TEM-EDS (JEOL JEM-2100F, JED-2300T). HARECXs profiles were obtained by collecting X-ray signals as a function of electron-beam direction. The Al/Si-order parameter was determined by comparison between the obtained HARECX profiles and simulated HARECXs profiles by program ICSC (Oxley & Allen, 2003). Additionally, CBED (convergent-beam electron diffraction) patterns were also obtained to estimate sample thickness. Moreover, single crystal X-ray diffraction experiment using an automated four-circle X-ray diffractometer (Rigaku, AFC-7S, Tohoku Univ.) with $\text{MoK}\alpha$ Radiation ($\lambda = 0.71069 \text{ \AA}$) was also carried out in order to evaluate the result obtained by HARECXs.

As the result, the HARECXs profiles were successfully obtained from $1.5 \mu\text{m}$ diameter region. For quantitative analysis, two types of profiles were simulated; a profile of ordered sillimanite and that of disordered sillimanite, using the sample thickness determined by CBED. The experimental profiles were successfully fitted to linear combination of the two simulated profiles, and Al/Si-order parameter was determined. The determined results of 18 measurements were converged around 0.80 regardless of sample thickness. However, single crystal XRD experiment showed the Al/Si-O bond distances corresponding to the Al/Si-order parameter of 0.88. The discrepancy are thought to be caused by estimation error of absorption coefficient of incident electron for sillimanite which is one of the simulation parameter to affect the HARECXs simulation. It suggests that the additional absorption should be required for more precise simulation.

The above analytical procedure was also successfully applied to experimentally heat-treated sillimanite,

avoiding mullite or glasses formed by heat-treatment. Furthermore, the HARECXS method can also apply to various other minerals to determine site occupancies and estimate formation environment.

キーワード：アルケミ法、高角度分解能電子チャネリングX線分光法、珪線石、秩序度、透過型電子顕微鏡
Keywords: ALCHEMI, HARECXS, sillimanite, order parameter, TEM