Structural evolution of gypsum (CaSO$_4$·2H$_2$O) during thermal dehydration

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Herein, an in situ high-temperature synchrotron X-ray diffraction study of gypsum is performed in the temperature range of 30–200 °C to investigate the continuous structural change from gypsum to soluble anhydrite through hemihydrate. Thermogravimetric and differential thermal analysis curves reveal that dehydration occurs in two stages. The diffraction peaks of $\beta$-hemihydrate with the trigonal space group $P3_121$ gradually become sharper above 90 °C, whereas those of gypsum become less intense and cannot be distinctly observed at 160 °C. The CaO$_8$ dodecahedra and SO$_4$ tetrahedra in gypsum expand negligibly with temperature. The site occupancy parameter of the water oxygen (Ow) atom in gypsum remains at approximately 1.0, within the experimental error. When water molecules are lost from gypsum, it immediately transforms into $\beta$-hemihydrate, without maintaining its structure. The volumetric thermal expansion coefficient of gypsum is $1.31 \times 10^{-4}$ K$^{-1}$. The site occupancy of Ow in $\beta$-hemihydrate continuously decreases from 0.8 and reaches approximately 0.5 at temperatures of 130–140 °C, where soluble anhydrite with a hexagonal space group $P6_2$22 begins to form. Therefore, $\beta$-hemihydrate dehydrates can be translated by the chemical formula CaSO$_4$·$x$H$_2$O (0.5 $\leq$ $x$ $\leq$ 0.8). The volumetric thermal expansion coefficient of $\beta$-hemihydrate, determined at temperatures between 90 and 140 °C is $1.54 \times 10^{-4}$ K$^{-1}$. $\beta$-Hemihydrate coexists with soluble anhydrite above 140 °C; however, the amount of $\beta$-hemihydrate decreases with temperature. In $\beta$-hemihydrate, water molecules are continuously released from the CaO$_9$ tetra-decahedra, thereby resulting in its contraction. Consequently, the structural change to a smaller CaO$_8$ dodecahedron triggers its transformation into soluble anhydrite without the collapse of its one-dimensional linear chains. With further heating, $\beta$-hemihydrate completely transforms into soluble anhydrite at 170 °C. The volumetric thermal expansion coefficient of soluble anhydrite determined in the temperature range of 170–200 °C is $1.69 \times 10^{-5}$ K$^{-1}$, which is an order of magnitude smaller than the values of gypsum and $\beta$-hemihydrate.

**Keywords:** Gypsum, Hemihydrate, Soluble anhydrite, Dehydration, In situ high-temperature synchrotron X-ray diffraction

INTRODUCTION

Calcium sulfate dihydrate, gypsum CaSO$_4$·2H$_2$O, is the most common sulfate mineral. Therefore, considerable attention has been paid to the dehydration of gypsum. Numerous studies on the mechanisms and products of dehydration of calcium sulfates under various conditions have been published (Lager et al., 1984; Abriel et al., 1990; Strydom et al., 1995; Schofield et al., 1996; Sarma et al., 1998; Ballirano et al., 2001; Prasad et al., 2005; Carbone et al., 2008; Jacques et al., 2009; Ballirano and Melis 2009a, 2009b, 2009c; Azimi and Papangelakis 2011; Tang et al., 2019; Vimmrová et al., 2020). Gypsum crystallizes in monoclinic space groups $I2/a$ (Pedersen and Semmingsen, 1982) and $C2/c$ (Boeyens and Ichhar-am, 2002), which are essentially the same space group but in different settings. With increasing temperature, it begins to dehydrate and forms calcium sulfates with a lower H$_2$O content. Calcium sulfate hemihydrate, bassanite CaSO$_4$·0.5H$_2$O, generally occurs as $\alpha$- or $\beta$-hemihydrate, depending on the dehydration conditions (Follner et al., 2002; Christensen et al., 2008). $\alpha$-Hemihydrate is formed by dehydration in an acidic water suspension of
gypsum or under hydrothermal conditions in the presence of electrolytes (Azimi and Papangelakis, 2011). It crystallizes in the monoclinic space groups $C12_1$ (Gallitelli, 1933), $I2$ (Ballirano et al., 2001), and $I12_1$ (Bezou et al., 1995), which are different settings for space group $C2$. In contrast, $\beta$-hemihydrate is formed by the dehydration of gypsum in a water-vapor atmosphere (Jacques et al., 2009; Ballirano and Melis, 2009a). It crystallizes in two different space groups: the trigonal space group $P3_121$ (Abriel and Nesper, 1993) and monoclinic space group $I12_1$ (a pseudo-orthorhombic cell with $\beta = 90^\circ$) (Bezou et al., 1995). These $\alpha$- and $\beta$-hemihydrates have nearly identical structures but exhibit different chemical behaviors upon reaction with water. Different physical properties, such as nuclear magnetic resonance (NMR) spectroscopic parameters and X-ray diffraction (XRD) patterns (Christensen et al., 2008), are also observed. In addition to hemihydrates, subhydrates with the general formula $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ ($0.5 \leq x \leq 0.8$) have been reported (Abriel et al., 1990; Bezou et al., 1995; Schmidt et al., 2011). Upon heating, hemihydrates dehydrate to form calcium sulfate (soluble anhydrite $\gamma$-$\text{CaSO}_4$) with a hexagonal space group $P6_22$ (Lager et al., 1984) or an orthorhombic space group $C222$ (Bezou et al., 1995). Upon further heating, $\gamma$-$\text{CaSO}_4$ finally transforms into insoluble anhydrite $\beta$-$\text{CaSO}_4$ with orthorhombic space group $Amma$ (Kirfel and Will, 1980). Zero-water hemihydrates have been observed immediately before the occurrence of anhydrites (Jacques et al., 2009).

The crystal structure of gypsum is composed of one-dimensional linear chains of alternating edge-sharing $\text{CaO}_8$ dodecahedra and $\text{SO}_4$ tetrahedra along the $a$ axis (Fig. 1a). The chains are held together by the shared edges of adjacent $\text{CaO}_8$ dodecahedra and by the shared corners of $\text{CaO}_8$ dodecahedra and $\text{SO}_4$ tetrahedra, which stack to form a two-dimensional sheet parallel to (101). These sheets are connected via hydrogen bonding. Because the $\text{H}_2\text{O}$ molecules are located between the sheets, the structural features allow the $\text{H}_2\text{O}$ molecules to escape during thermal dehydration without the collapse of the one-dimensional linear chains. Hemihydrates and soluble anhydrites are composed of essentially the same linear chain structure of alternating $\text{CaO}_9$ tetradecahedra and $\text{SO}_4$ tetrahedra, which extend along the $c$ axis (Figs. 1b and 1c). The chains are arranged to form channels, which eventually accommodate guest-water molecules in hemihydrate but without water molecules within the channels in soluble anhydrite. By contrast, the structure of insoluble anhydrite is composed of more regularly arranged $\text{CaO}_8$ polyhedra and $\text{SO}_4$ tetrahedra than that of soluble anhydrite (Fig. 1d).

Although much work has been devoted to identifying the phases occurring in the $\text{CaSO}_4$-$\text{H}_2\text{O}$ system during dehydration and determining their atomic configurations, studies addressing the continuous structural change of gypsum to anhydrite through hemihydrate are limited.

![Figure 1](image_url)

Figure 1. Comparison of one-dimensional linear chains in (a) gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, (b) hemihydrate $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, (c) soluble anhydrite $\text{CaSO}_4$, and (d) insoluble anhydrite $\text{CaSO}_4$. 
The thermal expansion and structural evolution of gypsum in the low-temperature range of 4.2–320 K have been studied (Schofield et al., 1996; Knight et al., 1999). The respective thermal behaviors of gypsum, β-hemihydrate, and soluble anhydrite have been reported by Ballirano and Melis (2009a, 2009b, 2009c). Herein, we performed in situ high-temperature synchrotron XRD to investigate the continuous structural change from gypsum to soluble anhydrite during two thermal dehydrations. Further, we focused on the variations in the coordination environment around the Ca site.

**EXPERIMENTAL METHODS**

Natural gypsum obtained from the Kan-nondo ore deposit of Hanaoka mine, Akita Prefecture, Japan, was purchased from Takeda Mineral Specimen Co. Ltd., Ibaraki, Japan. Thermal analysis was performed using thermogravimetry (TG) and differential thermal analysis (DTA) (TG/DTA-7300, Seiko Instruments Inc. Japan). Approximately 10 mg of gypsum and α-alumina reference were placed into flat-bottomed aluminum pans. The samples were heated from 50 to 500 °C at a heating rate of 10 °C min⁻¹ under airflow (200 mL min⁻¹).

In situ high-temperature synchrotron powder XRD measurements were performed at BL-8B at the Photon Factory (PF), High Energy Accelerator Research Organization (KEK), Japan. The incident beam was monochromatized using a Si(111) double-crystal monochromator. The X-ray wavelength was determined to be 0.6507(1) Å using CeO₂ (NIST Standard Reference Material 674a). The X-ray beam was collimated to 0.5 mm in diameter. The gypsum powder was inserted into a Lindemann glass capillary (ϕ = 0.7 mm); subsequently, the capillary end was fully opened. Furthermore, it was mounted and aligned with a goniometer and then introduced into a heating furnace. Next, it was heated under an ambient atmosphere at a fixed temperature step of 10 °C from 30 to 200 °C. The actual temperature was estimated in advance by direct measurement at the sample position using a chromel-alumel thermocouple. After reaching the target temperature, the sample was maintained for 5 min before the measurements. The exposure time was set at 3 min.

The obtained XRD data were analyzed by the Rietveld method using GSAS software (Larson and Von Dreele, 2004). The structural parameters were refined using the XRD data in the 20 range of 2–60°, corresponding to the sinθ/λ range from 0.027 to 0.768 Å⁻¹. The background was modeled with 36 terms using the Chebyshev polynomial function. The peak shape was modeled using the pseudo-Voigt function described by Howard (1982) and Thompson et al. (1987). The peak cut-off was set at 0.1% of the peak maximum. Structural refinements were performed using isotropic displacement parameters for all atoms, except H atoms. Negative isotropic displacement parameters were fixed. The initial lattice parameters and atomic coordinates of gypsum were adopted from Comodi et al. (2008). Because β-hemihydrate and soluble anhydrite were indistinguishable from the powder XRD pattern, an attempt to calculate the two-phase mixture model of β-hemihydrate and soluble anhydrite did not yield reliable quantitative values during refinement. Therefore, a single-phase model was employed at higher temperatures to determine the crystal structure. The structures of β-hemihydrate with trigonal space group P3₁21 (Abriel, 1983) and soluble anhydrite with hexagonal space group P6₃22 (Lager et al., 1984) were adopted at higher temperatures for the dehydrated phase. The S–O bond distances in gypsum, β-hemihydrate, and soluble anhydrite were refined with the distance restraints of 1.48 ± 0.02, 1.47 ± 0.02, and 1.47 ± 0.02 Å, respectively. The volumes of the coordination polyhedra of the Ca and S sites were calculated using the VESTA3 program (Momma and Izumi, 2011).

**RESULTS AND DISCUSSION**

**Two-step process in the dehydration of gypsum**

Supplementary Figure S1 (Fig. S1–S4 are available online from https://doi.org/10.2465/jmps.220811) shows the TG and DTA curves of gypsum. In general, gypsum dehydration involves a two-step process: CaSO₄·2H₂O → CaSO₄·0.5H₂O → CaSO₄. The TG curve revealed a total mass loss of 21.0% in the temperature range between 90 and 200 °C, which approximately corresponds to the loss of two molecules of structural water (theoretical mass loss of 20.9%). In addition, two endothermic peaks were observed in the DTA curves; the first peak located at 135 °C could be assigned to the dehydration of gypsum. The mass loss was approximately equal to the theoretical value of 15.7% for the dehydration reaction of CaSO₄·2H₂O → CaSO₄·0.5H₂O + 1.5 H₂O. Whereas the second peak, located at 150 °C, could be attributed to the dehydration reaction of CaSO₄·0.5H₂O → CaSO₄ + 0.5H₂O. However, Lou et al. (2011) reported that the actual dehydration of gypsum partly overlaps, thus indicating that β-hemihydrate begins to transform into soluble anhydrite before gypsum completely transforms into β-hemihydrate. Therefore, the three phases (gypsum, β-hemihydrate, and soluble anhydrite) would coexist during certain dehydration periods.

Figure 2 shows the continuous variation in the XRD pattern with increasing temperature. The XRD pattern
observed at 30 °C was identical to that of gypsum; however, very small peaks were detected at 6.2° and 10.7° owing to the existence of β-hemihydrate, which will be referred to as ‘hemihydrate’ throughout this study for clarity. The peak intensities of hemihydrate remained substantially unchanged until 80 °C, thus suggesting that hemihydrate was present from the beginning. Above 90 °C, the peaks gradually became more intense. By contrast, the gypsum peaks became less intense and were no longer observed at 160 °C. Regarding the transformation temperatures, Abriel et al. (1990) reported that hemihydrates began to appear at 75 °C and gypsum completely disappeared at 101 °C, whereas Jacques et al. (2009) reported that the transformation from gypsum to hemihydrate began at 158 °C and was completed at 171 °C. As Carbone et al. (2008) reported, the induction and completion times for gypsum dehydration decreased as a function of temperature (e.g., the induction time was 3 h at 40 °C but reduced to only 1 min at 80 °C). Therefore, the dehydration of gypsum is highly dependent on the measurement conditions, such as the heating time or \( P_{120} \) in the atmosphere. Hence, the transformation temperatures were not directly comparable. Herein, gypsum completely disappeared above 160 °C; however, precisely evaluating the transformation temperature of hemihydrate to soluble anhydrite using the XRD pattern is challenging because the peak positions of these phases almost coincide. Carbone et al. (2008) described that the dehydration of hemihydrate can be visually monitored from the evolution of the intensity ratio for the reflection indexing of 100 and 110 of the trigonal hemihydrate (these reflections were observed at 6.2° and 10.8°, respectively, in Fig. 2S). The authors proposed that the intensity ratio increased from approximately 1:1 to 2:1 owing to the transformation of hemihydrate to soluble anhydrite. Herein, the intensity ratio was approximately 2:1 at 130 °C (Fig. 2S). By contrast, Jacques et al. (2009) reported that the transformation of hemihydrate to soluble anhydrite causes peak shifts of 200 and 210 reflections to lower and higher angles, respectively. Herein, because this peak shift was observed at 140 °C (Fig. 2S), we concluded that the transformation from hemihydrate to soluble anhydrite began at 130–140 °C.

**Thermal expansion behavior in the dehydration process of gypsum**

Figure S3 shows the results of the Rietveld refinement analysis at 120 °C. The powder XRD patterns were well-fitted with gypsum and trigonal hemihydrate with space group \( P_3 \text{1}\text{2}1 \). The final \( R \)-factors, lattice parameters, and mass fractions are presented in Table S1 (Tables S1–S7 are available online from https://doi.org/10.2465/jmps.220811). The atomic coordinates, isotropic displacement parameters, and site occupancy parameters are listed in Tables S2, S3, and S4, respectively. Figure 3 shows the variations in the lattice parameters of gypsum. The lattice parameters obtained at 30 °C were \( a = 6.29130(17), b = 15.2366(5), c = 5.68489(19) \) Å, \( \alpha = 114.07(3)^\circ \), and \( V = 497.566(16) \) Å³, which were larger than the initial lattice parameters of gypsum: \( a = 6.277, b = 15.181, c = 5.672 \) Å, \( \alpha = 114.11^\circ \), and \( V = 493.36 \) Å³ (Comodi et al. 2008). The volumetric thermal expansion coefficient between 30 and 120 °C calculated by the equation \( \alpha_V = \frac{1}{V} \sum_i \frac{V_i - V_0}{V_0} \), was \( 1.31 \times 10^{-5} \) K⁻¹. This value was larger than that of 8.21 \( \times 10^{-5} \) K⁻¹ at temperatures between 20 and 100 °C (Balirano and Melis, 2009a). For the lattice parameters \( a, b, \) and \( c \), the values obtained were \( a_0 = 3.85 \times 10^{-5} \) K⁻¹, \( a_b = 6.11 \times 10^{-5} \) K⁻¹, and \( a_c = 2.46 \times 10^{-5} \) K⁻¹, respectively. Therefore, the thermal expansibilities followed the order \( b/b_0 > a/a_0 > c/c_0 \). The structural characteristic that thermal expansion was the most sensitive to temperature along the \( b \) axis is in good agreement with previous reports (Schofield et al., 1996; Knight et al., 1999; Bal-
As several researchers have already specified, this anisotropic thermal expansion of gypsum is ascribed to the weakening of the hydrogen bonds between the sheets. Here, note that the monoclinic angle $\beta$ exhibited a decreasing trend in the temperature range of 30–140 °C; however, this trend is contrary to the results of previous studies (Schofield et al., 1996; Knight et al., 1999; Ballirano and Melis, 2009a), wherein it decreased up to approximately 0 °C and then increased. This discrepancy might be because of the initial values of the starting model employed in each experiment. Herein, gypsum coexisted with hemihydrate at temperatures ranging from 90 to 160 °C. The phase fraction of gypsum decreased monotonously with increasing temperature. Note that the site occupancy parameter of $O_w$ was refined, but it always remained at approximately 1.0 within the experimental error, even during heating. Essentially, when water molecules were released, gypsum immediately transformed into hemihydrate, without maintaining its structure.

Figure 4 shows the variations in the lattice parameters of hemihydrate. Notably, the increasing trends of the $a$ and $c$ lattice parameters appear to lie on the logistic and logit function curves, respectively. Because soluble anhydrite occurred at 130–140 °C, it may have affected the increasing trend of the curves of the lattice parameters. The volumetric thermal expansion coefficient determined at temperatures between 90 and 140 °C was $\alpha_v = 1.54 \times 10^{-4}$ K$^{-1}$. The lattice parameters $a$ and $c$ were $\alpha_a = 6.70 \times 10^{-5}$ K$^{-1}$ and $\alpha_c = 1.94 \times 10^{-5}$ K$^{-1}$, respectively. Ballirano and Melis (2009b) also investigated the thermal expansion behavior of hemihydrates, but a hemihydrate sample was prepared by rehydrating $\gamma$-anhydrite at room temperature (humidity of approximately 5%). Therefore, the thermal expansion of hemihydrate was measured in the temperature range of 30–110 °C. Consequently, unit cell volume of the hemihydrate monotonously increased from 1057.00 to 1060.40 Å$^3$ in the temperature range, but the volumetric thermal expansion coefficient obtained from Ballirano and Melis (2009b) was $\alpha_v = 4.02 \times 10^{-5}$ K$^{-1}$, which is an order of magnitude smaller than the value in our study. The variations in the $O_w$–site occupancy parameters are shown in Figure 4d. The site occupancy of $O_w$ in the hemihydrate was directly correlated with the dehydration reaction. Upon dehydration, the number of water molecules in the hemihydrate decreased from approximately 0.8. When the transformation from hemihydrate to soluble anhydrite began at 130–140 °C, the site occupancy of $O_w$ in hemihydrate was approximately 0.5. This result indicates that hemihydrate having the chemical formula CaSO$_4$·$x$H$_2$O ($0.5 \leq x \leq 0.8$) dehydrates, which is strongly supported by previous studies (Abriel...
Hemihydrate and soluble anhydrite coexisted above 140 °C; however, because of the limited ability of the Rietveld technique, assessing whether the hemihydrate of CaSO₄·0.5H₂O continuously dehydrates until all water molecules are lost or if the ratio between the hemihydrate of CaSO₄·0.5H₂O and soluble anhydrite of CaSO₄ continuously decreases with temperature is challenging. Upon adopting a single-phase hemihydrate model above 140 °C, the site occupancy of Ow in the hemihydrate continuously decreased with temperature. Consequently, it became approximately zero at temperatures above 170 °C. Considering the flattened TG-DTA curve at temperatures above 170 °C (Fig. S1), we conclude that the transformation from hemihydrate to soluble anhydrite was complete at approximately 170 °C.

Soluble anhydrite with a hexagonal space group of P6₂22 was used to fit the XRD data at temperatures above 170 °C. Figure 5 shows the variations in the lattice parameters of the soluble anhydrite. Compared with gypsum and hemihydrate, the temperature dependence of the lattice parameters for soluble anhydrite was not observed in the temperature range of 170–200 °C. The resulting volumetric thermal expansion coefficient of the soluble anhydrite was \( \alpha_v = 1.69 \times 10^{-5} \ \text{K}^{-1} \), which was approximately half of that reported by Ballirano and Melis (2009c). In the previous study, however, the anhydrite sample was prepared by heating gypsum in an oven at 150 °C for 2 weeks before the experiment (Ballirano and Melis, 2009c) and inserted into a capillary before measurement. These experimental differences might justify the discrepancy in the thermal behavior of soluble anhydrite between the previous study and our results.

The crystal structural evolution in the dehydration of gypsum

The variations in the Ca-O and S-O bond distances in gypsum, hemihydrate, and soluble anhydrite are presented in Tables S5, S6, and S7, respectively, and are shown in Figure S4. Ballirano and Melis (2009a) mentioned that the individual Ca-O bond distances in gypsum remained substantially unchanged until 130 °C. The tetrahedral S-O bond distance changed above 130 °C, although this may have been an analytical error. In a previous study on hemihydrates (Ballirano and Melis, 2009b), the Ca-O and S-O bond distances were almost constant within the range of 0.015 and 0.003 Å, respectively, owing to the lower and narrower temperature range of the measurement. However, in this study, the Ca-O bond distances significantly changed in the range of 0.05–0.167 Å, whereas the Ca-O bond distances in soluble anhydrite remained unchanged. Figure 5 shows the variations in the coordination volumes of the Ca and S sites in the gypsum, hemihydrate, and soluble anhydrite. Ballirano and Melis (2009a) reported that the CaO₈ dodecahedra and SO₄ tetrahedra in gypsum did not exhibit distinct thermal expansion with temperature. They were alternately linked to form one-dimensional linear chains, which were joined laterally into two-dimensional sheets parallel to the ac plane. The Ow atoms were coordinated with the Ca atoms and were involved in interlayer hydrogen bonding in the b axis direction. Therefore, the slight thermal expansion of these polyhedra resulted in slight lattice parameter changes along the a- and c-axes. Essentially, the CaO₈ dodecahedra and SO₄ tetrahedra in gypsum expanded negligibly with temperature.

In hemihydrates, the Ca atoms are coordinated by eight O atoms and one water molecule, thus forming a CaO₈ tetradecahedron. Ballirano and Melis (2009b) reported that the thermal expansion of a hemihydrate was not related to the expansion of CaO₈ tetradecahedra. However, their experiment was performed in a lower and limited temperature range of 30–110 °C. As shown in Figure 5, the volume of the CaO₈ tetradecahedron depends on the temperature. The CaO₈ tetradecahedron continuously contracted with increasing temperature. The most striking observation and point to note here are that the CaO₈ tetradecahedra continuously released water molecules and simultaneously contract with temperature. As the number of water molecules in the CaO₈ tetradodecahedron decreases, the Ca-O bond distances decrease to satisfy the bond valence sum around the Ca atom. The ideal bond

**Figure 5.** Variation in the lattice parameters of \( a, c \), and \( V \) in soluble anhydrite in the temperature range of 170-200 °C; error bars are smaller than the symbols on the graphs.
strength of Ca is 2.0 valence units (v.u.). At 90 °C, the site occupancy of Ow in hemihydrate was 0.83 (Table S3), and the resulting bond strength was 2.07 v.u. (Brese and O’Keeffe, 1991), which is similar to the ideal bond strength. At 160 °C, the site occupancy of Ow became 0.115, but it resulted in a bond strength of 1.99 v.u. (Brese and O’Keeffe, 1991), which is almost equal to the ideal value. These values suggest that the CaO9 tetradecahedra continuously contracted during dehydration to maintain the bond strength of the Ca atom. Because the SO4 tetrahedron is sandwiched between the CaO9 tetradecahedra along the one-dimensional linear chain, the expansion of the SO4 tetrahedron can be caused by the pulling force from the shrinking CaO9 tetradecahedra. When the site occupancy of Ow reached 0.5, the hemihydrate was transformed into soluble anhydrite: $\beta$-CaSO4·0.5H2O → $\gamma$-CaSO4 + 0.5H2O. After soluble anhydrite was formed, the CaO9 tetradecahedron continuously contracted (Fig. 5). In the dehydration of hemihydrate, the CaO9 tetradecahedron lost one water molecule; thus, the coordination environment around the Ca site changed from 9- to 8-fold without the collapse of the one-dimensional linear chains. After being completely transformed to soluble anhydrite at 170 °C, the bond valence sum around the Ca site was 2.03 v.u. (Brese and O’Keeffe, 1991), which still maintained the ideal valence. Because soluble anhydrite no longer dehydrated, the CaO8 dodecahedra did not shrink with temperature (Fig. 6).

**CONCLUSIONS**

Figure 7 summarizes the mechanism of the dehydration of gypsum to soluble anhydrite. With increasing temperature, the unit cell of gypsum expanded along the b axis owing to the hydrogen bonds between the sheets; however, the CaO8 dodecahedron coordinated with six O atoms and two water molecules expanded negligibly. As the water molecules of gypsum began to dehydrate, the CaO8 dodecahedron was immediately reconstructed into a CaO9 tetradecahedron composed of eight O atoms and one water molecule. Consequently, gypsum transformed into hemihydrate. With further heating, water molecules in the hemihydrate were continuously released from the CaO9 tetradecahedra, accompanied by continuous contraction. When the site occupancy of Ow decreased from 0.8 and to 0.5, the CaO8 tetradecahedron released the remaining water molecules and transformed into a smaller CaO8 dodecahedron without the collapse of the one-dimensional linear chains. Ballirano and Melis (2009a, 2009b, 2009c) investigated the thermal behavior and dehydration kinetics of gypsum, hemihydrate, and soluble anhydrite. We performed an in situ high-temperature synchrotron X-ray diffraction study to investigate the continuous structural change of gypsum to soluble anhydrite through hemihydrate during thermal dehydration. Our findings provide further insight into the dehydration mechanism and structural evolution of gypsum.

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**SUPPLEMENTARY MATERIALS**

Supplementary Figure S1–S4 and Tables S1–S7 are available online from https://doi.org/10.2465/jmps.220811.
Figure 7. Thermal structural change in the coordination polyhedron of Ca atom from gypsum to soluble anhydrite through hemihydrate

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