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High-pressure behavior of a SiO_2 clathrate observed by using various pressure media

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Compression curves and stability of melanophlogite, a natural mineral formed by SiO_2 clathrate, have been studied up to about 25 GPa by using various pressure-transmitting media. We have studied both unheated and preheated samples to understand the role of guest gas molecules in clathrate. All the high-pressure experiments were made at room temperature using a diamond-anvil apparatus combined with synchrotron radiation. Unheated melanophlogite amorphized irreversibly without any structural transition at about 17 GPa, where the volume was decreased to about 70% of its original volume. Identical results were obtained in experiments using methane or an alcohol-water mixture as pressure-transmitting media or when direct compression was applied. Preheated melanophlogite, on the other hand, became much more compressible and amorphized only at around 3 GPa when the volume was decreased to 80%. The behavior changed completely when helium was used as the pressure-transmitting medium. The unheated sample was much less compressible but neither phase transition nor amorphization was observed up to about 25 GPa. Preheated samples had the same compression curve up to about 17 GPa, where an isostructural transition occurred, accompanied by a 10% increase in volume. This isostructural transition was a reversible process with a hysteresis of about 6 GPa. Completely different behaviors observed using helium media suggest that the small helium atom can penetrate into the cage structure of clathrate on compression. Present experimental results will provide useful information to consider the interaction of SiO_2 cages and guest molecules in the clathrate structure.

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I. INTRODUCTION

Many elements and molecules, such as carbon, silicon, germanium, and ice, among others, can crystallize into a clathrate structure, which is formed by the combination of various cages and elements or molecules encapsulated therein. By the combination of various materials forming cages and guests, clathrates exhibit a large variety of physical and chemical properties, and numerous studies have been made from the viewpoint of basic science as well as applied science. For example, methane hydrates, the clathrates formed by the combination of H_2O ice and methane gas, have been studied intensively because of its potential importance as an energy source in the next generation. It is also an important constituent of icy planets. Hydrogen clathrate is regarded as a potential material for hydrogen storage, and various studies are being made to clarify their high-pressure properties. Silicon clathrates with various guest molecules exhibit a variety of interesting physical properties including superconductivity, and intensive studies have been made. On the other hand, only a very limited study was reported on SiO_2 clathrate.

Melanophlogite is a rare mineral found in volcanic areas. It has type-I gas hydrate structure,[1,2] one of the clathrate structures, and is formed by the combination of two kinds of SiO_2 cages and gas molecules. Type-I gas hydrate structure has cubic symmetry, while melanophlogite is known to distort slightly[3] below around 80 °C. Therefore the structure at room temperature is usually described as tetragonal by doubling the *a* axis, but it can be regarded as pseudocubic. The type of gas varies depending on the locality and may be CO_2, N_2, NH_3, or yet another.[4] It has been argued that the existence of these guest molecules is crucial for the formation of melanophlogite,[2] but that once the cage is formed, these gas molecules can be expelled from the cage by heating, without destroying the clathrate structure.[3,5] Various studies have been made to clarify the formation mechanism,[2] high-temperature stability,[3,5] guest molecules,[6] Raman spectrum,[7] and so on, but no studies have yet been made on its behavior under high pressure. In the present study, we have clarified the compression behavior and stability of melanophlogite up to about 25 GPa using high-pressure *in situ* x-ray diffraction. In order to clarify the interaction of cage and surrounding material, three different pressure-transmitting materials were used. Moreover, to clarify the role of the guest molecule on stability and compressibility, some experiments were made using the sample from which the guest gases were first expelled by heating.

II. EXPERIMENT

Starting material is a natural mineral sample of melanophlogite from Fortullino, Italy. Powder x-ray diffraction pattern is in harmony with the type-I gas hydrate structure. Although the unit cell was analyzed as a tetragonal cell, the axial ratio (c/a) was very close to 0.5. The observed unit-cell dimensions were $a = 26.74$ Å and $c = 13.39$ Å, which are in good agreement with the previous report, $a = 26.79$ Å and $c = 13.37$ Å.[8] The Raman spectrum of this sample (Fig. 1) indicates that the main guest molecules are CO_2, with a minor amount of N_2, and CH_4. This result is in harmony with a previous report[9] on a sample from the same locality.

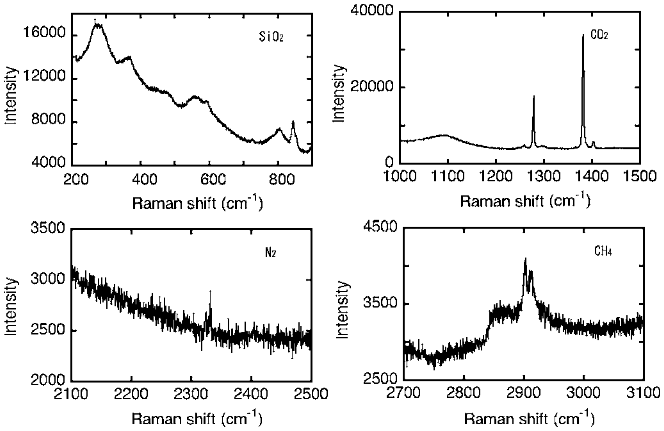

FIG. 1. Raman spectra of the starting sample of melanophrogite. All spectra were obtained before heating the sample. Guest gas molecules are mainly CO_2 together with small amounts of N_2 and CH_4.

By heating the sample in air at 650 °C for 7 h, the intensity of the Raman signal from CO_2 decreased considerably and that from N_2 and CH_4 became unobservable, while no meaningful change was observed for the Raman signal from the SiO_2 network (Fig. 2). Unit-cell dimensions observed by x-ray diffraction did not change either. This indicates that most of the guest gas molecules were expelled from the cage and that the SiO_2 cages became almost empty. We used two types of samples, unheated and preheated, as starting materials.

At first, we powdered the sample using a pestle and mortar but the x-ray diffraction peaks of this powdered sample became broad and weak, which makes the judgment of amorphization under pressure difficult. Later, the starting material was prepared by cutting and polishing the mineral sample into a rectangular shape of about $50 \times 50 \times 20$ μm^3. This sample is an aggregate of small crystals with some texture and gives a characteristic x-ray pattern as shown in Fig. 3. Although the Debye ring is not smooth and continuous, by integrating this two-dimensional pattern, we can get a sharp one-dimensional x-ray pattern as in the case of the powdered sample.

High-pressure experiments were performed by using lever and spring type diamond-anvil cell. Diamonds anvils with a 0.45 mm culet and a stainless-steel gasket with a 0.15 mm sample hole were used for the experiments. Starting material and several ruby balls, which work as pressure markers, were placed in the sample chamber and then it was filled with a pressure-transmitting medium. All the experiments were made at room temperature and the pressures were determined by using a ruby pressure scale under quasihydrostatic conditions.[10] Three different materials, helium, methane, and an alcohol/water mixture (ethanol:methanol:water =4:12:1), were used as a pressure-transmitting medium. Helium and methane were loaded at room temperature using a gas loading system modified from the one described before.[11] Some experiments were made by directly compressing the powdered sample without using any pressure-transmitting medium.

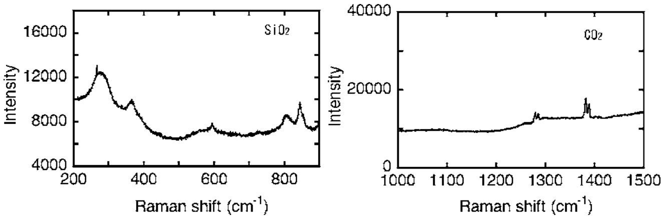

FIG. 2. Raman spectra of the preheated sample. After heating the sample at 650 °C for 7 h, the intensity of the Raman signal from CO_2 had decreased considerably and those from N_2 and CH_4 became weak and unobservable. The signal from the SiO_2 cage remained unchanged.

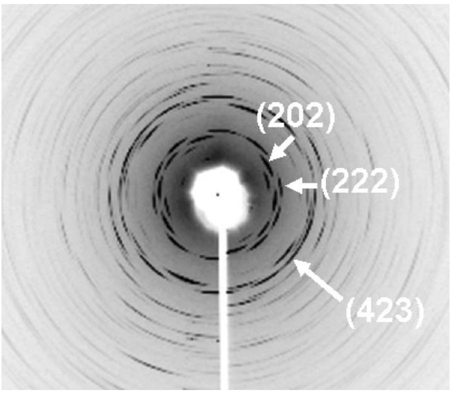

FIG. 3. Two-dimensional x-ray diffraction pattern of melanophlogite. Because of the texture of the sample, Debye rings are not uniform.

All x-ray experiments were made at the BL13A beamline of the Photon Factory, KEK, Tsukuba. A monochromatic x ray of about 30 keV in energy was collimated to a 30 or 50 μm thick beam and then it was irradiated to the sample. Diffracted x rays were recorded by an imaging plate and the exposure time was from 15 to 30 min.

III. RESULTS

A. Unheated sample

When the unheated samples were compressed using methane or alcohol/water mixture as a pressure-transmitting medium, gradual broadening and weakening of all the diffraction peaks were observed even in the pressure range where the pressure-transmitting medium remained hydrostatic. As shown in Fig. 4(a), the diffraction peaks became weaker and weaker with increasing pressure and disappeared at around 17 GPa. The sample compressed directly without using a pressure-transmitting medium behaved almost in the same manner, although broadening of the diffraction peaks started at lower pressures, as shown in Fig. 4(b). This amorphization is an irreversible process, and once the sample was amorphized, the sample remained amorphous even after it was recovered to ambient pressure. Because of the broadening and weakening of the diffraction peaks associated with amorphization, the volume compression data obtained by these experiments are scattered. However, it is clear that the compression curves determined by these three types of experi-

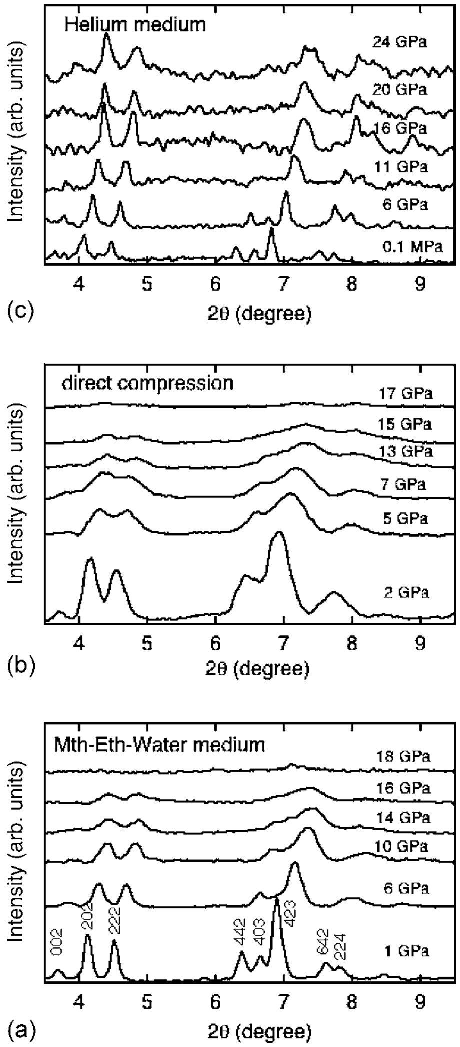

FIG. 4. One-dimensional x-ray diffraction patterns of melanophlogite compressed by using various pressure-transmitting media: (a) methanol:ethanol:water mixture medium, (b) direct compression, and (c) helium. In (a) and (b), diffraction peaks disappeared at around 17 GPa by amorphization of the sample, while clear diffraction peaks remained in (c) even at 24 GPa.

ments using methane media, alcohol/water media, and direct compression are very similar to each other, as shown in curve "A" of Fig. 5. Amorphization occurred when the volume of the sample was decreased to around 70% of the original volume. By fitting the Birch-Murnaghan equations of state, the bulk modulus K_0 of this compression curve "A" was determined to be 23(1) GPa when its pressure derivative, dK_0/dP, is assumed to be 4.

When the unheated samples were compressed using helium as a pressure-transmitting medium, the behavior was quite different. The diffraction peaks remained clear and sharp even at 24 GPa, as shown in Fig. 4(c). A small increase of the linewidth was observed, but there was no indication of a phase transformation or amorphization up to 26 GPa, the highest pressure in the present study. The volume compression curve was quite different as well, and the compressibility was much smaller compared to that obtained by using other pressure-transmitting media or by direct compression, as shown by curve "C" in Fig. 5. At 26 GPa, the unit-cell volume was compressed to about 77% of its original volume, and on decompression, it reverted to the original volume along the same compression curve. Bulk modulus K_0 was determined to be about 56(2) GPa for compression curve "C," which is more than twice bigger than the compression curve "A."

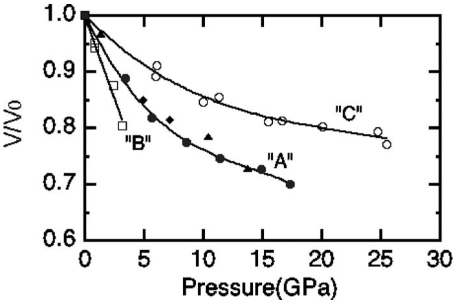

FIG. 5. Compression curves of melanophlogite obtained by using various pressure media. ●, methane; ▲, alcohol-water mixture; ♦, direct compression; □, methane (preheated sample); and ○, helium (preheated sample). Curve "A" represents the compression curve of normal melanophlogite, while "B" represents the compression curve of empty SiO$_2$ clathrate. Curve "C" represents melanophlogite with helium in it (see text).

B. Preheated sample

When the preheated sample was compressed using methane as a pressure-transmitting medium, amorphization occurred at a much lower pressure, below 5 GPa. This amorphization was also an irreversible process. Compressibility increased enormously as well, as shown by line "B" in Fig. 5, and the volume decreased to 80% of the starting sample at only about 3 GPa, following which it was amorphized. The bulk modulus of this compression curve is about 14(1) GPa.

A completely different behavior was observed when the same preheated sample was compressed using helium as a pressure-transmitting medium. As shown in Fig. 6, the x-ray diffraction peaks remained sharp and shifted to a higher angle with increasing pressure and the compression curve was identical, up to about 17 GPa, with that observed by the

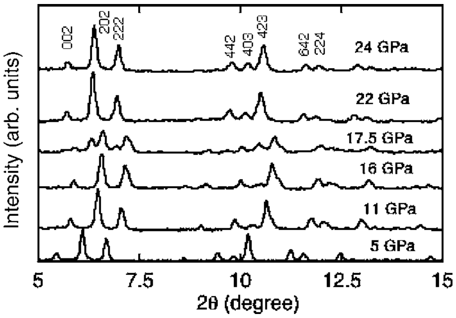

FIG. 6. X-ray diffraction patterns of preheated melanophlogite under pressure obtained by using helium as a pressure-transmitting medium. Isostructural transition occurs at about 17 GPa and no amorphization was observed even at 24 GPa.

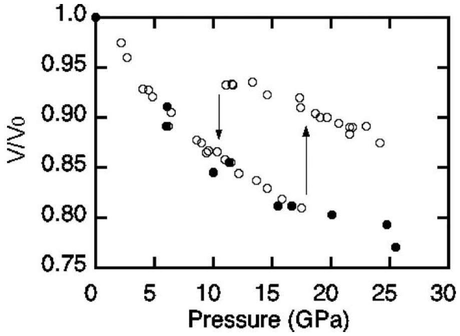

FIG. 7. Compression curves of preheated melanophlogite obtained by using helium as a pressure-transmitting medium (open symbols). With increasing pressure, a discontinuous increase in volume occurs at about 17 GPa while the volume reverts to the original compression curve at about 11 GPa on decreasing pressure. Solid symbols are the volume compression data of unheated melanophlogite obtained by using the same pressure medium, and no discontinuous volume change occurs in this case.

unheated sample using helium pressure medium. However, when the pressure exceeded about 17 GPa, new diffraction peaks appeared in the low-angle side of each diffraction. Two kinds of peaks coexisted in a narrow pressure range of less than 1 GPa, while only the new peaks remained above about 18 GPa. These new peaks can be explained by the same indexing as with melanophlogite, but the unit-cell volume calculated by these peaks had increased by about 10% more than before the transition, as shown in Fig. 7. By further increasing the pressure, this large unit cell was compressed in a normal manner up to 24 GPa. In the pressure-decreasing cycle, the sample was decompressed along the compression curve of the large unit cell until the pressure has decreased to 11 GPa, where a sudden decrease of the unit cell volume to the original compression curve was observed. These behaviors are summarized in Fig. 7, together with the compression curve of the unheated sample. On further decompression, the volume changed along the original compression curve and reverted to the original value at ambient condition.

When the sample was compressed again during the decompression process, just after the volume had decreased to the original compression curve at about 11 GPa, the same discontinuous increase of volume was observed at about 17 GPa. This sudden increase in volume is thus a reversible process with a large hysteresis of about 6 GPa. No meaningful change of the intensities of the diffractions peaks were observed to be associated with this transition. The axial ratio c/a of the tetragonal unit cell was 0.500 ± 0.001 and remained unchanged across this transition.

IV. DISCUSSION

A. Compressibility and stability of melanophlogite

A variety of compression behaviors of melanophlogite were observed by the combinations of various pressure-transmitting media and heat treatment of the starting sample. These results provide interesting information about the intrinsic nature of melanophlogite under pressure, and about the interaction between SiO_2 cages and gas molecules. Compression behavior, observed by direct compression without using a pressure-transmitting medium, was basically identical to that observed by using either methane or an alcohol/water mixture as a pressure-transmitting medium. Therefore it is reasonable to conclude that the compression curve "A" in Fig. 5 represents the intrinsic compression behavior of melanophlogite under pressure. This means that the clathrate structure formed by the SiO_2 cages with encapsulated gas molecules is stable until the volume is decreased to less than about 70% of its original volume and amorphizes irreversibly without transforming to another structure.

There is a wide variety of high-pressure behavior of compounds with a clathrate structure. Tse *et al.*[12] compressed Clathrasil dodecasil, a new class of porous tectosilicate which is structurally isomorphic with type-II hydrates, using NaCl as a pressure-transmitting medium. They observed pressure-induced amorphization at above 6 GPa. The transition was reversible when the guest molecule exists in the cage while it was irreversible for the empty cage. Our present results are very similar in a sense that pressure-induced amorphization occurs. However, in our study all the amorphizations were irreversible irrespective of the presence of guest molecules. Many silicon clathrates also assume a type-I structure and, on compression to 35 GPa, they amorphize gradually.[13] Unlike melanophlogite, however, many of them have a reversible structural phase transformation before amorphization,[14,15] and many discussions are made on its possible origin.[16] Pressure-induced amorphization is a common phenomenon observed in many polymorphs of silica when they are compressed at room temperature.[17] Most of them are believed to occur because the transition into a thermodynamically stable phase is hindered by the lack of thermal energy and, on heating, these amorphous phases of silica crystallize into stishovite.

Gas hydrate assume either type-I or type-II clathrate structure at ambient condition, depending on the guest gas molecule. At room-temperature compression, most of these gas hydrates transform into a hexagonal sH structure and then into a filled ice structure.[18] Some of them decompose into H_2O ice plus a gas phase, but in methane hydrate, the filled ice structure remains stable even at 42 GPa, where the volume decreases to about 50% of the original volume.[19]

The variety of high-pressure behaviors of various clathrates reflects the variety of bonding and interaction of cages and guest molecules in these clathrates. The present results on SiO_2 clathrate will provide additional information to understand the nature of these bonds and the interaction of clathrate-structured compounds.

B. Role of guest gas molecules

Curve "B" in Fig. 5 represents the compression behavior of "empty" melanophlogite, which is formed by the network of pure SiO_2. Much bigger compressibility compared to normal melanophlogite indicates that the gas molecules in SiO_2 cages play an important role in making the whole structure incompressible. Moreover, empty melanophlogite amor-

TABLE I. Bulk modulus K_0 of SiO_2, Si clathrate, and various SiO_2 minerals.

Cage material and minerals	Guest molecule	Pressure media	Bulk modulus (GPa)	Reference
SiO_2	CO_2	CH_4, Ar, direct	23	Present study
SiO_2	None	CH_4	14	Present study
SiO_2	None	He	56	Present study
Si	None		87	Ref. 13
Cristobalite			18	Ref. 20
Quartz			38	Ref. 21
Coesite			96	Ref. 22
Stishovite			313	Ref. 23

phizes when the volume is decreased to only 80% of its original volume, compared to 70% of normal melanophlogite. Thus, volume compression is not the sole factor in determining the stability of the structure, and gas molecules in the cages play a significant role in maintaining the clathrate structure.

There are many polymorphs in silica, and although all of them are made of a pure SiO_2 network, the bulk modulus and density vary widely depending on the structure. The bulk modulus of SiO_2 clathrate observed in the present study is compared with various silica polymorphs, together with Si clathrate, in Table I. The bulk modulus of cristobarite, a high-temperature polymorph of silica and having a very open structure, is about 18 GPa.[20] Quartz is the most stable form of silica at ambient condition and the bulk modulus is about 38 GPa.[21] High-pressure polymorphs of silica have close packing and, consequently, the bulk modulus becomes much larger. Coesite, which is stable from 3 to 10 GPa, has about 96 GPa,[22] increasing to about 300 GPa in stishovite.[23] The bulk modulus of empty melanophlogite, $K_0=14$ GPa, is slightly smaller than that of cristobalite ($K_0=18$ GPa), which is quite reasonable because the density of melanophlogite is also slightly smaller than that of cristobalite. Silicon clathrate has much bigger bulk modulus compared with SiO_2 clathrate (87 vs 23 GPa). This is again reasonable if we consider the fact that oxygen is much bigger than silicon and the unit-cell volume of silicon clathrate is only 47% of the SiO_2 clathrate.

C. Intrusion of helium into the crystal

The compression behavior of melanophlogite obtained in helium pressure-transmitting medium differs completely from that in other pressure media. This is probably because the small helium atom can penetrate into the cage during compression, although we have no direct evidence of the existence of helium in the cage. No difference of the compression curve was found among the experiments in methane or in alcohol/water mixture, or in direct compression. This suggests that methane, alcohol, or water molecules cannot get into the cages of melanophlogite under pressure. The compression curve "C" in Fig. 4, which was obtained in helium, is quite different from other compression curves. The difference began from the low-pressure region. Moreover, no difference was found between unheated and preheated samples. These facts suggest that helium can enter the cage even at a low pressure from almost the beginning of the compression and that unheated melanophlogite has some space in its cage(s) to accommodate helium, even though other gases are already present within it. In other words, the cages in melanophlogite are not fully packed by the guest gas molecules. This is in harmony with the fact that at atmospheric pressure, neither the structure nor the unit-cell volume changes before and after heating, even though the guest gas molecules are expelled from the cages by heating. Similar intrusion of pressure-transmitting medium in nanoporous materials is reported by Merlen *et al.*[24] on the intrusion of argon in carbon nanotubes. Stability of the structure is largely influenced by the intrusion and this phenomena looks common in many nanoporous materials.

A sudden increase in volume observed in helium pressure medium may be caused by the intrusion of additional helium into the cage. The number of helium atoms in the cage is difficult to estimate at this moment. However, it is interesting to note that the sudden increase was observed only in the heated sample and not in the unheated sample, although the compression curves below 17 GPa are indistinguishable between these two samples. A preliminary experiment in which the heated sample was compressed in a hydrogen pressure medium clarified that the compression curve is the same as in helium, but that there is no discontinuous increase of volume up to 25 GPa. All these experimental results will provide interesting information to estimate the effective volume of various gas atoms or molecules, and also the energy change associated with the accommodation of these gases in the SiO_2 cages. Helium solidifies at about 11.5 GPa at room temperature, and the observed volume change of melanophlogite occurs above and below this pressure. It is known that very often the melting point of material changes significantly when it is isolated in a nanostructure. Therefore it is interesting to know the state of helium within the nanocage of clathrate structure, but unfortunately, it is difficult to get information about it either by x-ray or Raman spectroscopy.

D. Potential problem of the helium pressure-transmitting medium

Present experimental results indicate the potential problem of using helium as a pressure-transmitting medium. In high-pressure experiments, hydrostaticity of pressure is very important for obtaining accurate results, and helium has been regarded to be the best pressure-transmitting medium to avoid the complexity of nonhydrostaticity.[25] However, the present results suggest that in some cases helium gets into the crystal structure of the sample and alters the compressibility considerably. Melanophlogite is probably an extreme case, but there are many crystal structures which have space to accommodate small gas molecules. Careful experiments using various pressure-transmitting media will be required to obtain results free from such effects.

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