Revision 1

Discovery of stishovite in Apollo 15299 sample

Shohei Kaneko[1], Masaaki Miyahara[1,2*], Eiji Ohtani[1,3], Tomoko Arai[4], Naohisa Hirao[5] and Kazuhisa Sato[6]

[1]Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

[2]Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan.

[3]V. S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Science, 630090 Novosibirsk, Russia.

[4]Planetary Exploration Research Center, Chiba Institute of Technology, Chiba 275-0016, Japan.

[5]Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto Sayo, Hyogo 679-5198, Japan.

[6]Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan.

*E-mail address: miyahara@hiroshima-u.ac.jp

ABSTRACT

High-pressure polymorphs recovered in terrestrial craters are evidence of meteoroid impact events on the Earth's surface. Despite countless impact craters on the Moon, high-pressure polymorphs have not been reported to date in returned Apollo samples. On the other hand, recent studies report that the high-pressure polymorphs of silica, coesite and stishovite occur in shocked lunar meteorites. We investigated regolith breccia 15299, which was returned by the Apollo 15 mission, using the combined techniques of focused ion beam (FIB), synchrotron X-ray diffraction (XRD), and transmission electron microscopy (TEM). The regolith breccia 15299 studied here consists of a mafic impact melt breccia with mm-sized, coarse-grained, low-Ti basalt clasts. The mafic melt breccia consists of fragments of minerals (olivine, pyroxene, plagioclase, silica, and ilmenite) and glass. Several quartz, tridymite, and cristobalite grains of 10–100 μm across occur in the mafic impact melt breccia. Vesicular melt veins of less than ~200 μm wide cut across the mafic melt breccia matrix and mineral fragments. Some silica grains are entrained in the melt veins. One of the silica grains entrained in the melt veins consist of stishovite (a = 4.190(1) Å, c = 2.674(1) Å, V = 46.95 Å^3, space group $P4_2/mnm$) along with tridymite and silica glass. This is the first report of high-pressure polymorphs from returned lunar samples. TEM images show that the stishovite is needle-like in habit, and up to ~400 nm in size. Considering the lithologies and shock features of 15299, it is inferred that the stishovite possibly formed by the Imbrium impact or subsequent local impact event(s) in the Procellarum KREEP Terrane (PKT) of the near side of the Moon.

Keywords: Apollo, stishovite, Imbrium impact, Procellarum terrane

INTRODUCTION

Numerous craters and a thick layer of soil (called regolith, hereafter) on the Moon indicate that the Moon has been heavily bombarded by meteoroids. It is expected that lunar surface materials are exposed to transient high-pressure and high-temperature conditions upon meteoroid impacts, and constituent minerals should transform into high-pressure polymorphs. Brecciated rocks (breccias) are products of meteoroid impacts in which rocks of the Moon are shattered by impact. Local pressure and/or temperature spikes occur during impact, thus allowing for the formation of high-pressure polymorphs in breccias. The shattered rock fragments are consolidated, being buried in mixed impact debris, megaregolith layers. Thus, breccias are among ideal reservoirs of impact-induced high-pressure polymorphs. However, no high-pressure polymorph has been reported to date in Apollo samples. We investigated the regolith breccia 15299, which was collected by the Apollo 15 mission, with a focused ion beam (FIB) system, synchrotron X-ray diffraction (XRD), and a transmission electron microscope (TEM). High-pressure polymorphs of silica have recently been found in shocked lunar meteorites (Ohtani et al. 2011; Miyahara et al. 2013), which were excavated and launched from the Moon by meteoroid impacts. Accordingly, we focused on silica minerals in the regolith breccia 15299. Here, we report the discovery of a high-pressure polymorph of silica, stishovite, in Apollo sample 15299.

MATERIALS AND EXPERIMENTAL METHODS

We observed the detailed fine textures of Apollo 15299,200 polished thin section using a field-emission gun scanning electron microscope (FEG-SEM), JEOL JSM-71010 and 7100 F with an accelerating voltage of 15 kV. A laser micro-Raman spectroscope, JASCO NRS-5100 was used for the identification of minerals in the sample. A microscope was used to focus the excitation laser beam (532 nm lines of a green laser). The laser beam was focused through microscope objectives (x100) to ~1 μm on the sample. The laser power was kept at 6.7 or 7.3 mW.

A part of the sample was excavated with a FIB system, FEI Quanta 200 3D for synchrotron X-ray diffraction (XRD) analysis. We placed the extracted block piece (~15 × ~7 × ~5 μm) on a culet of single diamond plate using a micromanipulator attached to a dedicated optical microscope. The extracted block piece on the diamond was scanned at the SPring-8 BL10XU beam line. A monochromatic incident X-ray beam with a wavelength of 0.41360(7) Å was collimated to less than 10 μm. XRD spectra were collected on an imaging plate (IP) using an exposure time of 10 or 15 min. The XRD spectrum of cerium dioxide (CeO_2) was used to determine the wavelength and the distance between the sample and the IP.

A slice for TEM observation was prepared from the excavated block piece on the diamond after XRD analysis using a FIB system, JEOL JEM-9320FIB. The slice was ~100 nm thick. An field-emission gun (FEG) scanning TEM (FEG-TEM/STEM), JEOL JEM-2100F operating at 200 kV, was used for conventional TEM observations, selected area electron diffraction (SAED) analysis, and high-angle annular dark field (HAADF) observation. We also checked the chemical compositions of minerals in the slice using an energy dispersive X-ray spectrometer (EDS) attached to the FEG-TEM/STEM under STEM mode. The chemical compositions were calculated using theoretical *k*-factors.

RESULTS

A regolith breccia 15299, which was collected near the Hadley valley of the Moon in 1971, consists of a mafic impact melt breccia and mm-sized, coarse-grained, low-Ti basalt clasts (Taylor et al. 1973; McKay et al. 1989). The Apollo sample 15299 was recovered on top of the regolith at station 6, which was about 100 m up the North slope of the Hadley Delta (Swann et al. 1972). Sample 15299 is a regolith breccia with a brown-colored glassy matrix, including welded regolith components, which is similar to the representative regional regolith (McKay et al. 1989). According to a previous report (McKay and Wentworth 1983; McKay et al. 1989), sample 15299 consists of compact breccias with minor shock features and low fracture porosity (Bulk density: 2.49 g/cm^3). The breccia portion has a chemical composition similar to the bulk chemical composition of regolith at station 6 (Taylor et al. 1973). We studied a polished thin section 15299,200, which is dominantly breccia with coarse-grained, low-Ti, basalt clast of 8 mm × 2 mm in size with a clear boundary between the two. The breccia portion consists of fragments of minerals (olivine, pyroxene, plagioclase, silica, and ilmenite) and glass. Vesicular melt veins of less than ~200 μm wide cut across the breccia matrix and mineral fragments. The low-Ti basalt clast mainly consists of pyroxene, plagioclase, and ilmenite. Some grains of feldspar in both the breccia portion and the low-Ti basalt clast are amorphous (maskelynite). Several silica grains of 10–100 μm across occur in the mafic impact melt breccia portion. Some silica grains are entrained in the melt veins. Raman spectroscopy analyses indicate that most silica grains are quartz, tridymite, or cristobalite. Using Raman spectroscopy, we could not identify mineral species for several silica grains that were smaller (< 1 μm) than the probe size. One of the silica grains in a melt vein of the breccia matrix consisted of an assemblage of fine-grained silica crystals coexisting with ~30 μm quartz and tridymite crystals (Fig. 1). |Therefore, we prepared a block piece of the silica grains including the fine-grained assemblage for synchrotron XRD analysis using a focused ion beam (FIB) system. The block piece was placed on a culet of a single-crystal diamond plate and scanned with a synchrotron X-ray beam. The XRD profile of the extracted block piece showed that the fine-grained silica assemblage consisted of stishovite (a = 4.190(1) Å, c = 2.674(1) Å, V = 46.95 Å^3, space group $P\ 4_2/mnm$) (Fig. 2) and tridymite. All the indexed diffraction peaks are shown in Table 1. α-PbO_2-type silica, seifertite is one of the high-pressure polymorphs of silica, and has been reported in Martian and lunar meteorites (El Goresy et al. 2013; Miyahara et al. 2013). A diffraction peak appeared around 7.4° (2θ), which can be assigned to the d_{110} of seifertite. However, several more peaks would be required to unambiguously identify the presence of this mineral in this sample. We prepared a slice for TEM observation from the block piece using a FIB system after having performed the XRD analysis. The TEM images showed that stishovite is needle-like in habit, and up to ~400 nm in size, coexisting with poorly crystallized (or amorphous) silica (Fig. 3).

DISCUSSION

While high-pressure polymorphs are present around many terrestrial impact craters (Chao et al. 1962; Martini et al. 1978; Stähle et al. 2008; Biren and Spray 2013), they have not been recovered in the returned Apollo samples in spite of abundant meteoroid impacts indicated by numerous impact craters on the Moon. No intensive effort has been undertaken to explore the high-pressure polymorphs in returned lunar samples, including breccias, which are products of meteoroid impacts. Nonetheless, we confirmed the existence of stishovite in the sample recovered from the Moon by the Apollo 15 mission. Although the original provenance of lithic clasts and mineral fragments in breccias is not known even in the Apollo samples (e.g., Norman et al. 2010), our discovery of a high-pressure polymorph of silica in returned Apollo 15 breccia would provide a critical constraint for the magnitude of meteoroid impact, lithology, and geologic history of the impact target site on the Moon.

It is likely that the present stishovite has transformed from quartz (Fig. 1b). The needle (or lamellar) shaped stishovite habit, accompanying silica glass is similar to those found in eucrite and lunar meteorite (Miyahara et al. 2013, 2014). Needle shaped stishovite occur also in the shock-melt veins or melt-pockets of shocked Martian meteorites (Langenhorst and Poirier 2000; Beck et al. 2004). The needle shaped stishovite in shock Martian meteorites is a liquidus phase. Present stishovite appears to occur along the fractures of the silica grain (Fig. 1b). The silica grain might be melted once along the fractures due to friction during an impact event. Although the thermal history of the silica grain is not clear, we could not rule out the possibility that present stishovite formed from melted silica. The pressure (P)–temperature (T) phase diagram deduced from static high-pressure and high-temperature synthetic experiments using quartz or silica glass as a starting material show that stishovite appears at pressures above 8 GPa (Akaogi and Navrotsky 1984; Zhang et al. 1993), giving a lower bound to the shock pressure condition experienced in the silica grain of the15299 breccia.

In the K-, rare-earth elements (REE)-, and P-rich (KREEP) basalts from Apollo 15 samples, the modal abundance of silica minerals is around 10 vol. % (Papike et al. 1991), whereas in typical mare basalts they are less than 1 vol. %. The relatively high abundance of silica minerals in sample 15299 appears to be consistent with KREEP basalts or impact melt from derived from KREEP basalts. It has been postulated that KREEP-rich igneous rocks were likely concentrated in the Imbrium/Procellarum area prior to the Imbrium impact (e.g., Jolliff et al. 2000). The stishovite in sample 15299 might be a product of the Imbrium impact or subsequent local cratering events that occurred in the Procellarum KREEP Terrane (PKT) of the near side of the Moon. However, a final conclusion depends on isotopic age and petrographic studies of 15299 breccia and impact melt.

IMPLICATIONS

A high-pressure polymorph of silica, stishovite, has been discovered for the first time in a lunar regolith sample recovered through Apollo 15 mission. This is the first discovery of a high-pressure polymorph from an ex-terrestrial sample, other than in meteorites. The collection sites and occurrences of Apollo samples are described in detail by astronauts. Enormous petrological, mineralogical and radio-isotopic studies using the Apollo samples have been conducted for several decades. The nucleation and grain-growth rate of a mineral is controlled by kinetics. Our finding suggests that we may constrain a specific impact event on the Moon by combining geological information, radio-isotope age and the kinetics of high-pressure polymorphs. We should revisit Apollo samples from the standpoint of high-pressure mineralogy.

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Figure captions

Figure 1. BSE images of a) a mafic impact melt breccia portion, and b) a silica grain including stishovite. A block piece excavated by the FIB system for XRD analysis is shown by the white box. Qtz = quartz, Sti = stishovite, Tr = tridymite, Pyx = pyroxene.

Figure 2. XRD patterns (λ = 0.41360(7) Å) of a silica grain including stishovite and seifertite. Sti = stishovite, α-PbO_2 = seifertite, Tr = tridymite.

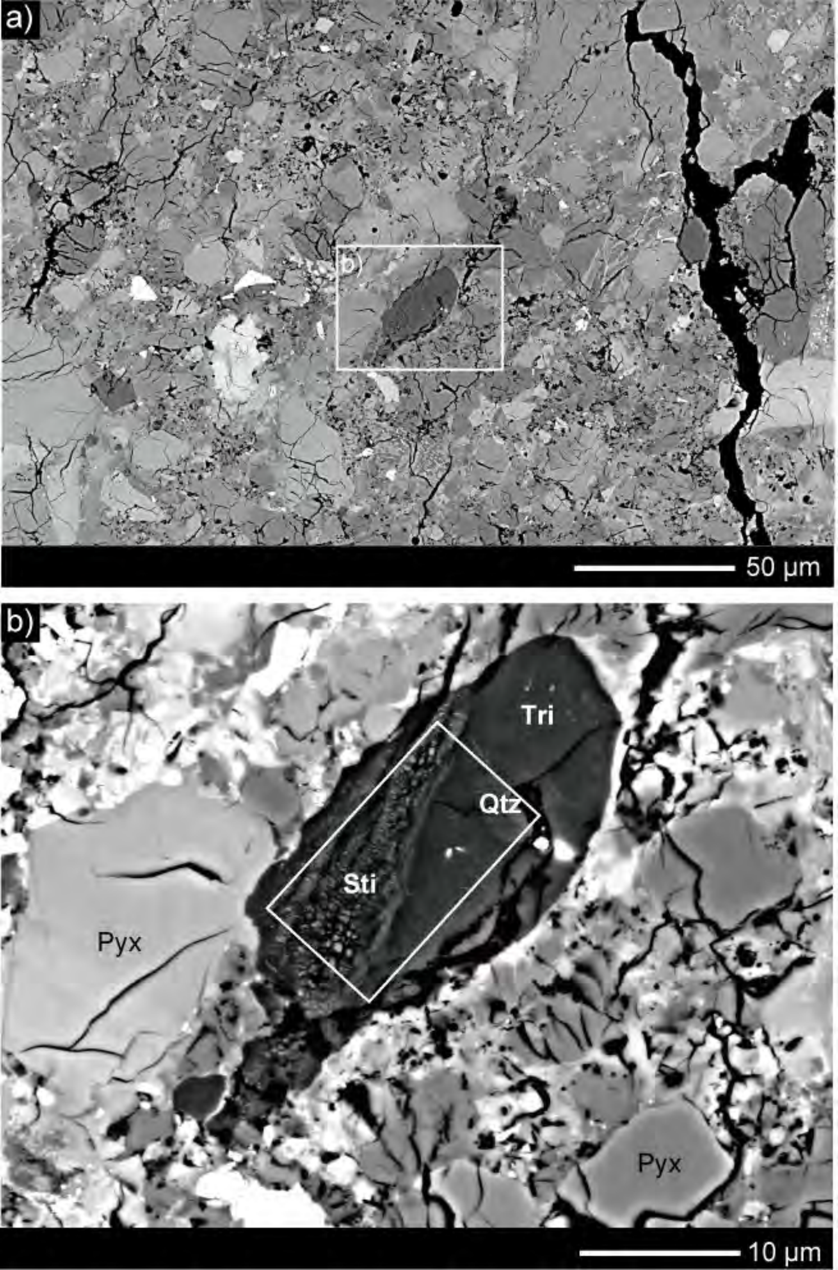
Figure 3. TEM results: a) Bright-field TEM image of stishovite; b) SAED patterns corresponding to stishovite. Sti = stishovite, Si-gla = silica glass.

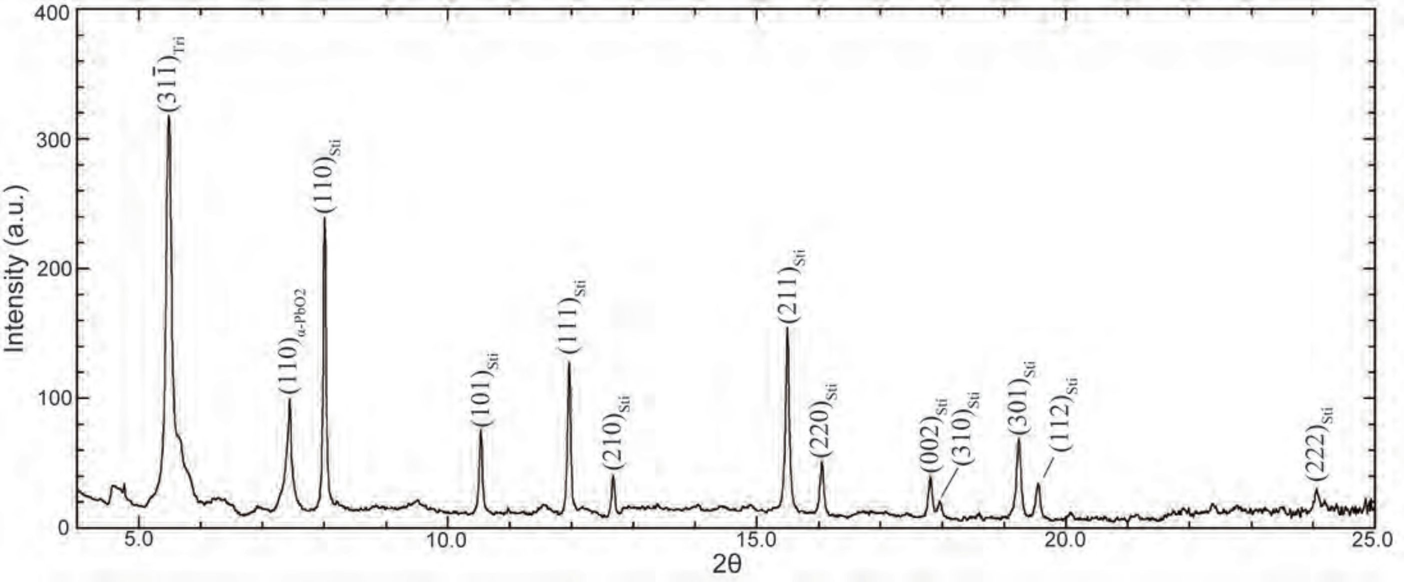
Table 1. The indexed XRD patterns of stishovite in Apollo 15299,200.

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)*	h	k	l

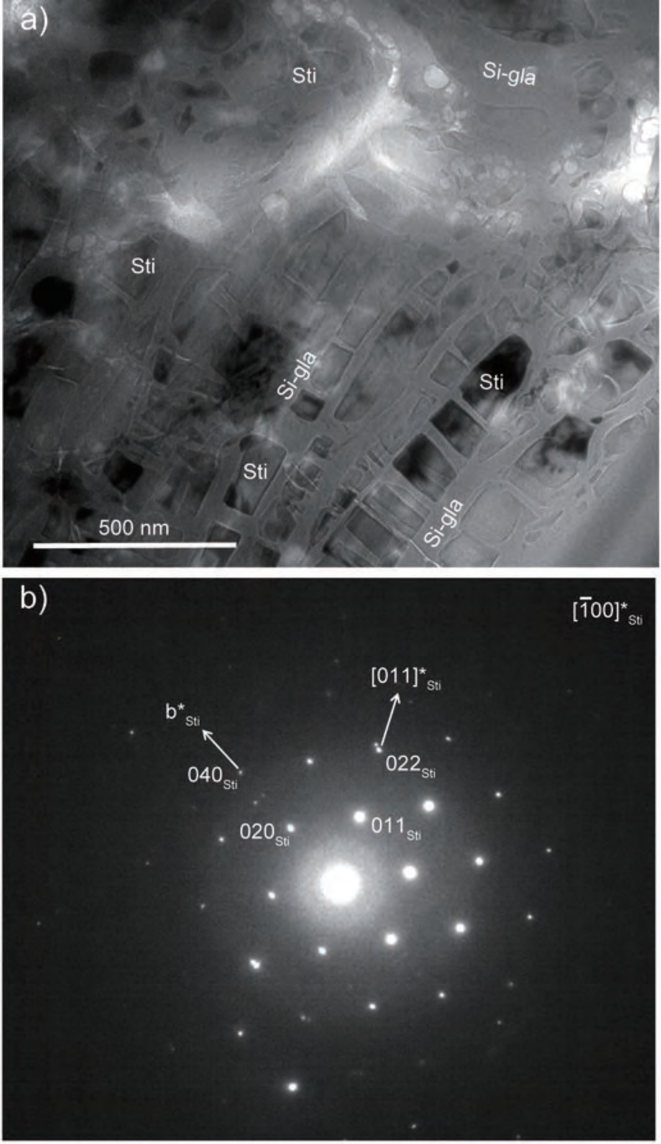
2.964	2.963	1	1	0
2.255	2.254	1	0	1
1.986	1.985	1	1	1
1.874	1.874	2	1	0
1.535	1.535	2	1	1
1.482	1.482	2	2	0
1.337	1.337	0	0	2
1.325	1.325	3	1	0
1.238	1.238	3	0	1
1.219	1.219	1	1	2
1.187	1.187	3	1	1

*a = 4.190(1) Å, c = 2.674(1) Å. Lattice parameters were calculated by PD-indexer software programmed by Y. Seto.


a)
b)
50 µm
b)
Tri
Qtz
Sti
Pyx
Pyx
10 µm



400
300
200
100
0
Intensity (a.u.)
5.0
10.0
15.0
20.0
25.0
2θ
(31$\bar{1}$)Tri
(110)α-PbO2
(110)Sti
(101)Sti
(111)Sti
(210)Sti
(211)Sti
(220)Sti
(002)Sti
(310)Sti
(301)Sti
(112)Sti
(222)Sti



a)
Sti
Si-gla
Sti
Si-gla
Sti
Sti
Si-gla
500 nm
b)
[$\bar{1}$00]*Sti
[011]*Sti
b*Sti
040Sti
022Sti
020Sti
011Sti

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2.964	2.963	1	1	0
2.255	2.254	1	0	1
1.986	1.985	1	1	1
1.874	1.874	2	1	0
1.535	1.535	2	1	1
1.482	1.482	2	2	0
1.337	1.337	0	0	2
1.325	1.325	3	1	0
1.238	1.238	3	0	1
1.219	1.219	1	1	2
1.187	1.187	3	1	1

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