Meteoritics & Planetary Science 38, Nr 11, 1579–1583 (2003)
Abstract available online at http://meteoritics.org

First discovery of stishovite in an iron meteorite

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(Received 26 March 2003; revision accepted 23 October 2003)

Abstract–The first occurrence of stishovite in an iron meteorite, Muonionalusta (group IVA), is reported. The mineral occurs intimately mixed with amorphous silica, forming tabular grains up to ~3 mm wide, with a hexagonal outline. It was identified using X-ray diffraction and Raman microspectroscopy. The unit-cell parameters of stishovite are a = 4.165(3) Å and c = 2.661(6) Å, and its chemical composition is nearly pure SiO_2. Raman spectra show relatively sharp bands at 231 and 754 cm^{-1} and a broad band with an asymmetric shape and a maximum around 500 cm^{-1}. The rare grains are found within troilite nodules together with chromite, daubreelite, and schreibersite. From their composition and morphology, and by comparisons with silica inclusions in, e.g., the Gibeon IVA iron, we conclude that these rare grains represent pseudomorphs after tridymite. The presence of stishovite in Muonionalusta is suggested to reflect shock metamorphic conditions in the IVA parent asteroid during a cosmic impact event.

INTRODUCTION

Stishovite, a high-pressure polymorph of SiO_2, is an exceptionally rare mineral in terrestrial environments and has only been found in association with a few meteorite impact structures (Chao et al. 1962; Koeberl 2002) and deposits of microtectites (e.g., McCall 2001). It forms at pressures in excess of 10 GPa, as a consequence of shock metamorphism of silica-bearing rocks following a hypervelocity impact event. Also, accessory stishovite has recently been detected in a group of martian meteorites, the basaltic shergottites (Langenhorst and Poirier 2000a, b; Jambon et al. 2002), along with other "post-stishovite" high-pressure polymorphs of SiO_2 (Sharp et al. 1999; El Goresy et al. 2000). Xie et al. (2002) found submicroscopic stishovite in a shocked L6 chondrite. Shock metamorphism is a fundamental process in the evolution of all planetary bodies (e.g., Bischoff and Stöffler 1992), but this unequivocal shock indicator has never been reported to occur in a differentiated meteorite of asteroidal origin. Here, we report the first find of stishovite in an iron meteorite, Muonionalusta, which is a fine octahedrite (Of) belonging to the well-populated IVA group.

THE MUONIONALUSTA METEORITES

The Muonionalusta iron meteorites have been found in the Pajala district, Norrbotten county, Sweden in a 25 × 15 km area situated approximately 140 km north of the Arctic circle. Drumlinized forms intersected by lakes and bogs dominate the landscape. The Quaternary deposits are mainly glacial till, glaciofluvial sediments, and peat. Glacial erosion has been very weak in the area; the bedrock is disintegrated by weathering in many places, and the saprolite can be up to several meters thick (Lagerbäck and Wickman 1997). The meteorites are scattered in the till and have been found to occur at different depths (0–2 m). Their supposed terrestrial age of >0.8 Ma, determined by ^{10}Be and ^{36}Cl methods (Chang and Wänke 1969), indicates that they have experienced at least 4 major glaciations (e.g., Andersen and Borns 1994).

The first find was made in 1906 (Högbom 1909), and about 40 meteorites have been found to date. The weights of the collected specimens range from 0.1 to 158 kg. Because of a sparsely populated area, only 4 meteorites had been found before the year 2001. These earlier finds were made by chance during road work and while digging the foundation of a new house (Wickman 1964; Lagerbäck and Wickman 1997). The new meteorite investigated here, with a total mass of 9.575 kg, was found after a systematic search in the area, which was carried out in the summer of 2001. The find occurred in sandy till at a depth of 25 cm, about 20 m from the 1906 find location (67°48′N, 23°6′E).

DESCRIPTION OF THE STISHOVITE-BEARING SAMPLE

The meteorite was cut into 8 mm slices, which were ground and finally etched with a mixture of ethanol and nitric acid. It shows a fine Widmanstätten pattern with long, usually straight kamacite lamellae with a weak tendency to subgrain development (cf., Buchwald 1975). The average (n = 20) width is 0.32 ± 0.07 mm; Buchwald (1975) gave 0.29 ± 0.05 mm. The Ni concentration of kamacite is 7.28 ± 0.2%, and Reed (1965) reported a similar figure for Muonionalusta (7.40%). Plessite and taenite cover ~30% of the full slices. Features are present that bear witness to a violent history of the meteorite (faults, bent kamacite lamellae, etc.).

In addition, note that much evidence for shock deformation in Muonionalusta has been reported previously, in particular the presence of ε-iron (Buchwald 1975) and X-ray asterism of kamacite (Jain and Lipschutz 1970). The latter authors estimated the shock pressure at 13–40 GPa.

The Fe, Ni metal mass of the examined slices has troilite inclusions (~8 per 100 cm^2) that are essentially rectangular in shape and 2–5 mm in their greatest dimension. A few rounded and irregular, somewhat larger (up to 10 mm) troilite nodules also occur. The troilite is polycrystalline (the optically coherent areas are ~50 µm wide) and commonly surrounded by a thin (0.2 mm) rim of kamacite. Subhedral chromite crystals usually accompany the sulphide phase. Equant chromite grains are located in the centers, while elongated varieties usually are found at the sulphide-metal boundaries and may protrude into metal. SiO_2 phases are rare and have been found in only 3 cases.

A polished mount (Swedish Museum of Natural History catalogue nr 20020049), ~8 × 4 mm in size, with a troilite nodule containing the silica component was prepared for close examination by reflected light microscopy and scanning electron microscopy (SEM). The sulphide-oxide assemblage has a somewhat shattered texture with many pervading cracks. The minerals of the fracture infillings are fine-grained and intimately intergrown; they may be partly of terrestrial origin, as the present section was originally located close (~10 mm) to the weathered surface of the meteorite. The largest silica grain in the section measures 330 × 150 µm (Fig. 1). It is closely associated with the 2 dominant minerals, troilite and chromite. As a result of brecciation of the SiO_2 phase, several smaller, angular fragments are scattered in the sulphide mass. A closer examination of the major grain shows that microcracks are abundant; some are the result of penetrative fracturing of the grain, while others have the appearance of contraction cracks, i.e., resembling fine cracks in glass originated by quenching and volume change. Troilite has injected some of the wider cracks. Narrow portions of the silica grains are replaced by a hydrous Fe-silicate along the grain boundaries toward troilite. This phase has a hisingerite-like composition (Fe:Si ratio ~1:1) according to preliminary electron microprobe analyses, and variable, but significant, Cl contents (0.3–1.2 wt%) suggest formation during terrestrial alteration.

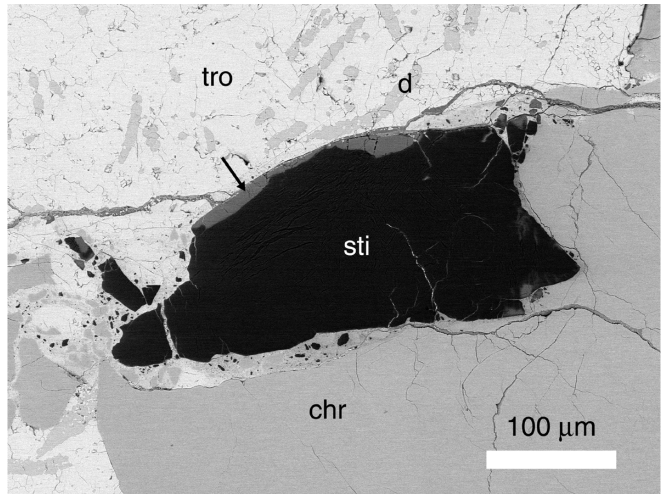

Fig. 1. Backscattered electron image of a polished section of Muonionalusta with troilite (tro), daubreelite (d), chromite (chr), and a stishovite (sti) grain. The black arrow points to the hydrous Fe-silicate that replaces marginal parts of silica.

Troilite contains elongate, slightly curved inclusions of daubreelite up to 100 µm long. Small areas contiguous with troilite consist of a fine-grained assemblage of a metallic Fe phase low in Ni coexisting with Fe sulphide (in appearance, similar to the intricate metal-troilite textures reported by Scott [1982], which are ascribed to impact melting). A few schreibersite grains, up to 80 µm wide, occur at the edge near kamacite; this mineral has also been observed in the enclosing metal matrix, a few mm from the troilite nodule itself. Chromite and daubreelite lie near their ideal compositions, $FeCr_2O_4$ and $FeCr_2S_4$, respectively. Troilite varies from $Fe_{0.97}Cr_{0.02}S$ to near-end member composition, and schreibersite is ~$(Fe_{1.56}Ni_{1.44})P$.

From the opposite piece of the polished section, the remaining part of the silica inclusion was extracted by dissolution of the metal-sulphide host in concentrated hydrochloric acid. The freed fragment has a maximum dimension of 3 mm, but the complete grain could have been slightly larger (the major, central part was destroyed by the saw during the cutting process). The original inclusion obviously had a tabular habit with a typical hexagonal outline (Fig. 2). The bulk of the material is milky white, turbid, and very hard (H >8).

CHARACTERIZATION OF STISHOVITE

X-ray Diffraction

A sub-mm fragment of the loose SiO_2 inclusion was crushed and spread on to a silicon 9 1 1 monocrystal disc. An

X-ray diffraction pattern was produced using an automated powder diffractometer and monochromated CuKα-radiation (40 mA, 40 kV). The data were collected in step scans at room temperature in the 2θ-range 15–80°, the step width and counting time being 0.02° and 5 sec, respectively. The pattern is composed of a broad diffraction maximum at 2θ ~18°, attributed to amorphous (glassy) SiO_2, and several sharper peaks at higher angles. Except for a moderately intense peak corresponding to d = 3.34 Å (presumably the 1 0 1 reflection of quartz), the pattern matches the published data for stishovite (Table 1). The most prominent stishovite peak (1 1 0) is about half as intense as the amorphous "bump" of the X-ray diffractogram. An observed general broadening of the diffraction peaks is attributed to either small average crystallite size or an overall poor crystallinity. The tetragonal unit-cell parameters for stishovite were refined from 7 unambiguously indexed reflections to a = 4.165(3) Å and c = 2.661(6) Å, in good agreement with available data for synthetic material, a = 4.179 Å and c = 2.667 Å (Ross et al. 1990).

Chemical Analysis

Chemical analysis was carried out with a wavelength-dispersive Cameca SX50 electron microprobe run at 20 kV and 15 nA on a carbon-coated polished section. Components other than SiO_2 that could be detected were, on average, 0.08 wt% Al_2O_3, 0.10 wt% Fe_2O_3, and 0.08 wt% Cr_2O_3.

Raman Microspectroscopy

Raman spectra of the largest silica grain in the polished mount were recorded between 180 and 1300 cm^{-1} using a Dilor XY Laser Raman spectrometer (similar to the one described by Burke and Lustenhouwer [1987]). Spectra were obtained with the 514.5 nm (green) line from an Innova 70 Ar ion laser. To focus the light to ~2 μm on the sample, an optical microscope with an 80× objective was used. The laser power was 300 mW at the entrance of the microscope, and spectra were collected during 20 cycles with an integration time of 5 sec. Wave number calibration was made using a Ne lamp and a Si standard. No treatment of the raw data was made. The obtained Raman spectrum shows a generally weak band intensity, but 2 relatively sharp bands can be seen at 231 and 754 cm^{-1}, respectively (Fig. 3). The 754 cm^{-1} band is the most intense. These 2 bands agree with literature values of crystalline stishovite (Grimsditch et al. 1994), while the third main band of stishovite at 590 cm^{-1} is obscured in the present spectrum by a broad band with an asymmetric shape and with a peak maximum of ~500 cm^{-1}. This feature is unrelated to known crystalline forms of SiO_2 but is characteristic for SiO_2 glasses (Dolino and Vallade 1994). The band broadening indicates a disordered structure, and the obtained spectrum is similar to those recorded for partially amorphized stishovite (Grimsditch et al. 1994; Liu et al. 1997).

Table 1. X-ray powder diffraction data.

d_{meas} (Å)	d_{calc} (Å)	d_{litt} (Å)	h	k	l	I_{meas} (%)	I_{litt} (%)
3.34[a]						23	
2.947	2.956	2.959	1	1	0	100	100
2.249	2.234	2.246	1	0	1	24	18
1.977	1.971	1.981	1	1	1	50	35
1.861	1.870	1.870	2	1	0	17	14
1.525	1.526	1.530	2	1	1	51	50
1.475	1.478	1.478	2	2	0	27	18
1.329	1.322	1.333	3	1	0	21	18
1.229	1.233	1.235	3	0	1	26	25

[a]Probably from quartz. Stishovite literature data are from PDF 15–26.

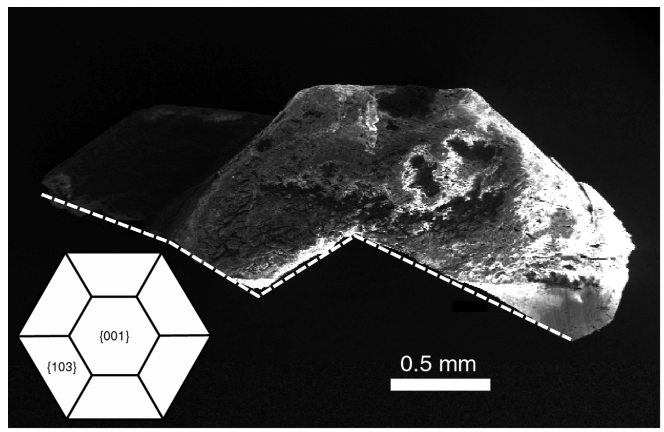

Fig. 2. Scanning electron micrograph of the freed stishovite grain. Uncoated specimen at 15 kV. The dashed white line shows where the specimen was cut. A small "twin" is indistinctly seen to the left. Note the similarity to a perfectly grown high-tridymite crystal, as seen in the schematic drawing included in the left corner (with the {hkl} form symbols for the faces indicated).

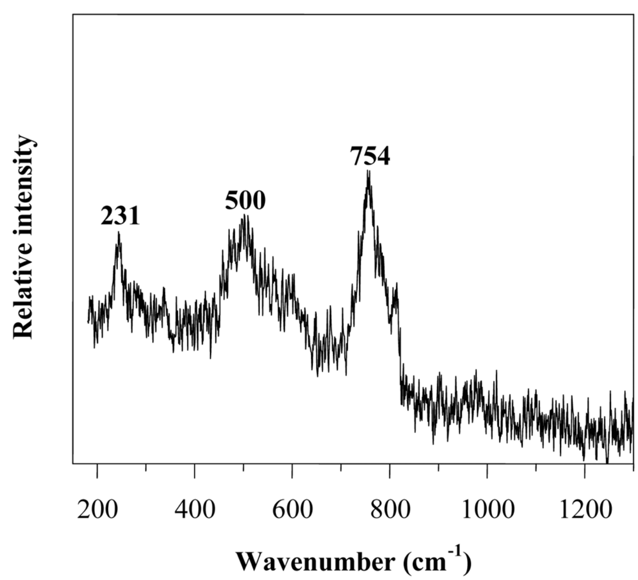

Fig. 3. Raman spectrum of the Muonionalusta stishovite.

DISCUSSION AND CONCLUSION

The present study presents clear evidence for the occurrence of stishovite in an iron meteorite. Free SiO_2 is a very uncommon component in iron meteorites (Buchwald 1975), but at least 2 of ~60 members of the IVA group, Gibeon and Bishop Canyon, are known to contain rare, but large (up to 35 mm), plate-like inclusions of tridymite (e.g., Marvin et al. 1997). The tridymite grains have parageneses very similar to that found for the stishovite-glass grains in Muonionalusta (i.e., they are typically associated with troilite, chromite, and daubreelite). Their trace element contents are generally low, with maximum impurity levels of: 0.4 wt% FeO, 0.09 wt% Al_2O_3, 0.03 wt% MgO (Ulff-Møller et al. 1995; Scott et al. 1996). Marvin et al. (1997) reported minor quartz intergrown with tridymite in Gibeon. From the similarities with Gibeon tridymite and the characteristic habit of the studied silica inclusion in Muonionalusta, we have concluded that stishovite represents a pseudomorph after tridymite.

Clearly, the meteoritic stishovite cannot have formed by the isostatic pressure prevailing in the core of the parent asteroid; to reach pressure levels >10 GPa, the planetary radius must exceed 300 km (Luo et al. 2002). Estimations of the IVA parent body, based on metallographical cooling histories, give the radius range 7–49 km (Haack et al. 1990). One can safely assume then that stishovite formation is connected with an impact event. The glass component might have formed directly (as a shock melt) or by post-shock processes (e.g., by partial amorphization in a later thermal event). The relation between glass and the high-pressure mineral in Muonionalusta samples should be studied in more detail (preferably down to the level of atomic resolution). The minor quartz indicated by the diffraction pattern might be a result of devitrification of the SiO_2 glass over time.

Some circumstances (particularly the large size of the present strewn field and the undisturbed nature of the saprolite of the area) presented by Wickman (1964) and Lagerbäck and Wickman (1997) suggest that the Muonionalusta meteoroid was not a cratering one but broke up in the atmosphere and created a significant shower. Even if the incoming body experienced an extremely violent break-up, conditions necessary for stishovite formation would not be attained. This conclusion is supported by the fact that tridymite is preserved in Gibeon, a meteorite that probably has a similar history of disruption (Buchwald 1975).

Cosmic ray exposure ^{41}K–^{40}K ages of most IVA meteorites cluster around 0.4 Ga, which is interpreted to reflect a fragmentation event of the parent body (Voshage and Feldmann 1979; Lavielle et al. 1999). Although the possibilities of both multiple break-ups and of minor collisions on the path to Earth must be considered, we find it plausible that the 0.4 Ga cataclysm is the event at which the stishovite was formed. Over 60% of the IVA irons can be considered strongly shocked, and in the case of Muonionalusta, the peak pressure may have reached 40 GPa (Jain and Lipschutz 1970). A well-known spread exists in the cooling rates of the IVA irons (e.g., Rasmussen et al. 1995). One recent explanation for this was given by Haack et al. (1996), who suggest that a first catastrophic break-up of the parent asteroid occurred when ~95% of the core had crystallized and that it shortly thereafter reassembled due to gravitational forces. The thus formed "rubble pile" could explain the thermal anomalies and also how the Muonionalusta meteoroid, originally a part of the asteroid core, could be situated at a level shallow enough to become affected by a foreign impactor.

Acknowledgments–This work is dedicated to the memory of Prof. Frans Erik Wickman (1915–2003), an eminent scholar and an ardent early investigator of the Muonionalusta meteorites. We thank J. G. Spray, an anonymous reviewer, and Associate Editor E. Scott for their constructive comments on the manuscript.

Editorial Handling—Dr. Edward Scott

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