Iron whiskers on asteroid Itokawa indicate sulfide destruction by space weathering

Toru Matsumoto1,2✉, Dennis Harries2, Falko Langenhorst2,3, Akira Miyake4 & Takaaki Noguchi1

Extraterrestrial iron sulfide is a major mineral reservoir of the cosmochemically and astrobiologically important elements iron and sulfur. Sulfur depletion on asteroids is a long-standing, yet unresolved phenomenon that is of fundamental importance for asteroid evolution and sulfur delivery to the Earth. Understanding the chemistry of such environments requires insight into the behavior of iron sulfides exposed to space. Here we show that troilite (FeS) grains recovered from the regolith of asteroid 25143 Itokawa have lost sulfur during long-term space exposure. We report the wide-spread occurrence of metallic iron whiskers as a decomposition product formed through irradiation of the sulfide by energetic ions of the solar wind. Whisker growth by ion irradiation is a novel and unexpected aspect of space weathering. It implies that sulfur loss occurs rapidly and, furthermore, that ion irradiation plays an important role in the redistribution of sulfur between solids and gas of the interstellar medium.
Energetic ions from various cosmic sources can significantly alter solid mineral grains in interplanetary and interstellar space. Within the solar system, solar wind ions are considered to be a main cause of space weathering, which alters the physical and chemical surface properties of airless bodies such as the Moon and asteroids. Iron sulfides such as troilite (FeS) are common minerals in solar system materials. Although iron sulfides are important solid reservoirs of the cosmically abundant elements sulfur and iron, their behavior in space-exposed environments is poorly constrained. Remote-sensing of the S-type asteroid 433 Eros indicates significant sulfur depletion in its surface regolith by space weathering of iron sulfides. One of the fundamental chemical characteristics of airless bodies are their volatile element abundances, including sulfur, which closely correlate with elemental fractionation during solid accretion in the solar nebula, subsequent thermal processing and gravitational differentiation. Moreover, the sulfur abundance of small airless bodies is of great importance to estimate the amount of sulfur delivered to the early Earth, which likely became a major ingredient of a habitable surface and life. However, the sulfur depletion by space weathering may obscure the detection of original sulfur abundances of airless bodies. Thus, the rates and modes of space weathering of iron sulfides are essential to understand the dynamics of asteroids, their relics of the early solar system and their impact on the terrestrial planets and life. Understanding the alteration of minerals by the solar wind is important for unveiling their surface evolution, because the altered regolith grains are key indicators of the timescales of geological processes on these dynamical bodies, such as motion, loss and replenishment of the regolith. Furthermore, knowledge of the interaction between solids and energetic ions may help to understand the chemistry of cosmic radiation environments in the interstellar medium (ISM), where molecular clouds and new stars are born and deliver chemical components to emerging planetary systems, such as the early solar system.

Regolith particles recovered from the S-type asteroid 25143 Itokawa by the Hayabusa mission are key samples to examine the space weathering of primordial minerals, especially the effects of solar wind implantation. Their mineralogy corresponds to LL4–6 ordinary chondrites, in which troilite is the major sulfide phase. The few previous studies of iron sulfides have reported little modifications by the solar wind compared to the distinctly radiation-damaged rims of silicate minerals, whereas earlier experimental studies have suggested chemical and structural changes of iron sulfides by ion irradiation. So far, naturally altered iron sulfide has not been comprehensively examined. Here we present systematical analyses of the surface features of troilite-bearing Itokawa particles. Field emission scanning electron microscopy (SEM), focused ion beam (FIB) sectioning and transmission electron microscopy (TEM) are used to better understand the surface modifications of space-exposed troilite (see the Methods section, Supplementary Notes 1–4, and Supplementary Figs. 1–3). We show that the wide-spread occurrence of metallic iron whiskers as a decomposition product formed through solar wind irradiation on the troilite. It implies that sulfur loss occurs rapidly on airless bodies and, furthermore, that ion irradiation plays an important role in the partitioning of sulfur and iron in interplanetary and interstellar space, if small dust particles are involved.

**Results**

The characteristics of troilite-bearing Itokawa particles. A striking feature of the troilite surfaces is the appearance of elongated whiskers of metallic iron protruding from the space-exposed surfaces (Fig. 1). They are present on 8 of 10 Itokawa particles we have investigated, suggesting their common appearance (Supplementary Table 1, Supplementary Note 1). The whiskers are thinnest at their tips, curved, and striated. Their length varies from several tens of nm to 2.8 μm. The whiskers often coexist with thin flat plates that are deficient in sulfur and possibly composed of iron (Fig. 1d). Troilite surfaces that have whiskers often exhibit vesicular textures (Fig. 1c, Supplementary Table 1).

TEM observation showed that each whisker appears to be composed of a set of several sub-whiskers (Fig. 2a). Selected area diffraction (SAED) patterns of the whisker confirmed that they consist of bcc-structured metallic iron (Fig. 2b). Individual sub-whiskers show the same diffraction contrast in TEM images (Fig. 2a), suggesting that single crystals of iron are predominant within them. SAED patterns and diffraction contrast of thinner whiskers (<300 nm in width) even show that they are composed of almost one single iron crystal (Fig. 2e) or several crystals with slightly different crystallographic orientations. The metal of the whiskers is typically almost pure iron (<0.7 wt% Ni), only in a few cases minor Ni was concentrated near the uppermost surfaces of some sub-whiskers (~4.1 wt%; Fig. 2d, Supplementary Table 2).

Open vesicles on troilite surfaces are delimited by subparallel, scale-like structures (Fig. 3a), which are elongate perpendicular to the c-axis of the troilite (Fig. 3a, b). Dark-field TEM images of the vesicular regions show many bright spots corresponding to small crystalline sub-domains (>10 nm) having slightly different crystallographic orientations compared to the substrate troilite (Fig. 2f). This occurs within 80–100 nm in depth. In the case of troilite apparently showing a non-vesicular texture in SEM images, many internal vesicles appear beneath the troilite surface, which extend to ~50 nm in depth (Fig. 3c). Relatively large
vesicles are concentrated at depths between 10 and 20 nm (Fig. 4b). SAED patterns of troilite in the vicinity of the vesicles indicate slight crystallographic misorientations (Fig. 3d). No discernable relationship in orientation between the iron whiskers and the troilite is evident in SAED patterns. The Fe/S ratio increases in the surface region with open vesicles as compared with the bulk troilite (Fig. 4a). In contrast, the Fe/S ratio of the surfaces with internal vesicles appears to be constant (Fig. 4b).

The whiskers, troilite, and silicate surfaces are covered with O- and Si-rich layers that are 7–15 nm thick (Fig. 2c, d). Such layers on troilite contain O, Si, and Mg (Fig. 4), and in some cases, Na, Cl, and Ca. These rims are probably vapor-deposited coatings generated by solar wind sputtering and/or micrometeorite impacts on nearby regolith grains. The accumulation of vapor-deposited materials appears to have occurred after whisker growth. The olivine and low-Ca pyroxene coexisting with troilite have outermost vapor-deposited rims and lower polynanocrystalline rims that are generally interpreted as products of solar wind damage (Supplementary Fig. 4).

The residence times of the examined Itokawa grains within a few millimeters of the uppermost regolith surface were estimated to be ~1000 to ~8000 yr, calculated from solar flare track densities in silicates (Supplementary Table 1 and Supplementary Fig. 5).

**Discussion**

Polynanocrystalline rims and vesicles are known to be typical damage features of experimentally ion-irradiated materials and solar-wind-irradiated minerals. Vesicles might expand through the coalescence of implanted atoms and/or by the clustering of induced vacancies. Expansion of vesicles along [uv0] crystallographic directions and/or simultaneous surface sputtering by ion implantation likely produced the open vesicles on Itokawa troilite. Troilite possesses a strong anisotropy between the [001] and [uv0] directions due to its hexagonal NiAs-type base structure, which quite certainly enhances elongation of open vesicles. The solar wind is a stream of charged ions from the Sun, composed mainly of \(^{4}\)He (~95.4%) and \(^{4}\)He (~4.6%) with typical kinetic energies peaking at ~1 keV/nucleon. The depth of vesicles in the troilite (up to 40–50 nm) broadly matches the penetration depth of 4 keV He\(^{+}\) of 47 nm, whereas large vesicles (Fig. 4b) in troilite are located at the penetration depth of 1 keV H\(^{+}\) of 22 nm (Supplementary Fig. 6). These depths support the notion that vesicles developed through accumulation of solar wind gases.

Here we discuss the feasibility of iron whisker growth from the liquid, vapor and solid states. Aqueously mediated formation of iron whiskers appears highly unlikely, because of the dry...
fractured surfaces that formed by the fragmentation of larger
with whisker distribution. The majority of Itokawa grains display
the troilite surface (Supplementary Table 1), they do not correlate
volume36, the Si-bearing rims on Itokawa grains do not balance
which iron sulphides deposited rims have the bulk composition of LL chondrites, in
most likely source of a vapor. However, assuming that the
necessary for vapor
preferential iron condensation on troilite, such as droplets
these rims are quite thin (<15 nm). Additionally, the whiskers do
the widespread occurrence of iron whiskers on troilite, because
have been reported in lunar samples, all of which were regarded
as condensation products. Although the iron stalks consist of
metallic iron, they do not correspond to iron whiskers on Itokawa,
because they clearly show a droplet at their tip indicating VLS growth.

The remaining and most plausible mechanism for iron whisker
formation is growth from a solid substrate that is supersaturated
with cations, as proposed for the metallic whisker growth in
sulphides or oxides44–46. This inference is supported by the fact that
the iron whisker growth appears to be associated with the pro-
gressive irradiation-damage, given the lack of whiskers on troilite
with minor damage16. Metallic iron may form when troilite
comes into contact with H2 gas47. The H2 gas trapped in the
vesicles may cause the reaction, FeS + H2 = H2S + Fe2+ + 2e−
under solar heating (Supplementary Note 5, Supplementary
Fig. 7). Shifting the equilibrium towards H2S requires removal of
the H2S produced from the vesicle. This process takes place most
efficiently where an escape path for H2S gas is available such as
along sub-grain boundaries, cracks, or open vesicles, while H2 is
replenished by solar wind irradiation. Additional heating by
micrometeorite bombardment and larger impact events may play
a role for increasing the replacement of these gases by accelerating
the diffusion rate of hydrogen atoms and H2S in troilite. Fur-
thermore, these heating events may raise the reaction rate and
subsequent diffusion of iron atoms. The acceleration of the
reaction can also happen by solar heating when the asteroid has
an orbit with a lower heliocentric distance16. The action of the
solar wind can selectively sputter sulfur atoms. The S/Fe ratio of
troilite decreased to 0.55 ± 0.55 after experimental 4 keV He
irradiation2 with a dose of 17 × 1017 ions/cm², which corresponds
to an exposure time of 4 × 107 yr to the solar wind at 1 AU.

Energy transfer to sulfur atoms could result in the sulfur escape in
the form of H-, S-bearing radicals and/or molecules48,49. Figure 7 shows the equilibria
air reaction
The oxidation of sulphur into H2S requires removal of
the H2S produced from the vesicle. This process takes place most
efficiently where an escape path for H2S gas is available such as
along sub-grain boundaries, cracks, or open vesicles, while H2 is
replenished by solar wind irradiation. Additional heating by
micrometeorite bombardment and larger impact events may play
a role for increasing the replacement of these gases by accelerating
the diffusion rate of hydrogen atoms and H2S in troilite. Fur-
thermore, these heating events may raise the reaction rate and
subsequent diffusion of iron atoms. The acceleration of the
reaction can also happen by solar heating when the asteroid has
an orbit with a lower heliocentric distance16. The action of the
solar wind can selectively sputter sulfur atoms. The S/Fe ratio of
troilite decreased to 0.55 ± 0.55 after experimental 4 keV He
irradiation2 with a dose of 17 × 1017 ions/cm², which corresponds
to an exposure time of 4 × 107 yr to the solar wind at 1 AU.

Energy transfer to sulfur atoms could result in the sulfur escape in
the form of H-, S-bearing radicals and/or molecules48,49. Figure 7 shows the equilibria
air reaction
Fe$^{2+} + 2e^-$. Assuming that $S_2$ escape from the space-exposed troilite surface occurs at zero ambient $S_2$ partial pressure, the Hertz–Knudsen–Langmuir relationship results in an estimated a maximum evaporative flux of $\sim 3 \times 10^{-3}$ S atoms/cm$^2$/yr at the maximum surface temperature of Itokawa of 130 °C (Supplementary Note 6). This corresponds to $\sim 1 \times 10^{-18}$ nm/yr, which is an extremely low rate. Submicron-sized impact craters on troilite in Itokawa particles show no evidence for whisker growth\textsuperscript{51}. Moreover, examined troilite surfaces with iron whiskers do not correspond to crater floors. Somewhat larger impacts might locally induce a transient temperature rise of the regolith and could increase the equilibrium pressure of $S_2$, such that thermal evaporation could become more efficient. However, this process should take place at relatively greater depths in the regolith, where the temperature increases and the permeability required for $S_2$ loss are low. In addition, the temperature increase would be rather short in duration and long-term temperatures at depth are much lower than at the surface. Increased solar heating at possible lower heliocentric distances\textsuperscript{16} might be insufficient for a fast recession of the troilite surface (Supplementary Note 6). Hence, selective sulfur loss appears not to be caused solely by heating events on the asteroid. Based on the discussion above, sulfur loss and supersaturation of Fe$^{2+}$ just beneath the surfaces of troilite grains very likely occurred as a consequence of solar wind

Fig. 4 Depth profiles of major elements detected near the troilite surface. X-ray intensity counts of O, Mg, Si, S, Fe and the count ratio of Fe/S near the troilite surface with (a) open vesicles and with (b) internal vesicles are shown. The vertical axis is X-ray count and the horizontal axis is distance (nm). The lower subfigure is a BF-STEM image of investigated area corresponding to upper count profiles. a was obtained from a FIB section RA-QD02-0325-01 (Supplementary Fig. 1). b was obtained from FIB section RA-QD02-0286-01 (Supplementary Fig. 4).
irradiation on Itokawa. Heating events might have contributed to promote the chemical reaction and/or atomic and molecular diffusion in troilite. The iron-supersaturated zone may have been the relaxation of the compressive stress induced by thermal cycling during the rotation of Itokawa.

From a calculation of the total whisker volume per unit area of troilite, the production rate of excess iron was estimated to be -0.04 nm/yr or -0.13 troilite monolayers/yr assuming a space-exposure age of 10^3 yr (Supplementary Note 7; Supplementary Fig. 8; Supplementary Table 3). The average characteristic length of iron diffusion in troilite on Itokawa’s surface in its present-day orbit is the order of 10 nm/yr on average (Supplementary Note 8; Supplementary Fig. 9). This indicates that whisker growth is not controlled by cation diffusion, but rather by the production of excess cations. The rapid iron diffusion enables accumulation of sufficient excess Fe^{2+} for whisker growth. Hence, the total volume of whiskers at a given surface area might be a novel proxy for the duration of regolith space exposure that corresponds to the amount of excess iron accumulated. The net growth mechanism of iron whiskers on Itokawa appears to be unique among the extraterrestrial whiskers, which have been widely considered as vapor condensates.

Solar wind irradiation has had a limited effect on the sulfur abundance on the surface of Itokawa, because the estimated sulfur loss is negligible compared with the total troilite volume. This is probably due to a short exposure time. Therefore, it is interesting that sulfur depletion was detected in the uppermost 10 μm of regolith on the S-type asteroid Eros that occupies heliocentric distances similar to Itokawa. Deeper sulfur loss is possible but not accessible to remote X-ray analysis. Adopting the sulfur loss rate due to solar wind on Itokawa (0.04 nm/yr), sulfur depletion to 10 μm depth takes about 2.5 × 10^5 yr. Given that the regolith ages of Eros is 3–50 million years, this indicates that substantial amounts of sulfur could have been lost through regolith gardening. Sulfur loss through other processes, such as impact vaporization, may have occurred additionally. The solar wind may be most effective on bodies at low heliocentric distances, where the increased ion flux and surface temperature can exponentially enhance H2 formation and sulfur loss. Alteration rims on iron sulfide might provide a clue for past orbital states of airless bodies with secular variations of their perihelia, as proposed for silicates. Effective solar wind irradiation may also occur in small interplanetary dust due to their high surface-to-volume ratio. Sulfur loss by the irradiation could contribute to the sulfur abundance of the Earth, if irradiated small grains were involved in accretion of the Earth.

Our observations have strong implications for the alteration of iron sulfides in the interstellar environments. Iron sulfides have been detected in the outflows of evolved stars and are likely injected into the interstellar medium. An unsolved question regarding the chemical composition of the ISM is the unique role of sulfur in the gas phase. In the diffuse ISM sulfur is barely depleted from the gas phase. On the contrary, in dense molecular clouds sulfur is strongly depleted in the gas, which has been attributed to complex astrochemical reactions involving organo-sulfur compounds. Here it is not entirely clear how sulfur can be transferred between inorganic sulfides, the gas and, eventually, organics in these environments. Submicron-sized silicate dust in the diffuse ISM has been considered to become amorphous by the irradiation of H+ and He^{+} accelerated by shockwaves from supernovae. The flux of ions with energies of 1 keV/nucleon in the shockwave models (10^7–10^9 ions/cm^2/s) and their total ion dose (up to 10^{18}–10^{19} ions/cm^2) are similar to the solar wind (flux = 2 × 10^3 H^+ ions/cm^2/AU^2/s, dose = 6 × 10^{20} H^+ ions/cm^2, assuming an exposure age of 10^3 yr at 1 AU). Our observation supports the hypothesis that sulfur is supplied to the gas phase of the ISM via the destruction of iron sulfides due to ion irradiation. Rapid whisker growth as opposed to the formation of a protective iron shell implies that sulfides are easily destroyed under such conditions. Metallic iron is predicted to appear as a byproduct of this alteration process in the ISM and might exist there even though its primary formation by homogenous nucleation from supernova ejecta appears to be highly ineffective. Metallic iron in the ISM can be an important catalyst for molecule formation and can produce magnetic dipole emissions that disturb the cosmic microwave background.

Therefore, the alteration of iron sulfides by ion implantation could have a large impact on the chemistry and electromagnetic properties of the ISM.

From our study, we conclude that, contrary to previous evidence, iron sulfides are highly susceptible to decomposition by ion irradiation in space. Sulfur loss from iron sulfides by solar wind could cause a remarkable decrease of sulfur abundances on airless bodies at low heliocentric distances. Their susceptibility to this process implies that ion irradiation plays an important role for the partitioning of iron and sulfur in interplanetary and interstellar environments. Iron whiskers are newly recognized features of space weathering and could become distinctive indicators to interpret the history of airless bodies, such as the C-group asteroids currently studied by Hayabusa2 and OSIRIS-REx. The appearance of whiskers induced by ion irradiation has never before been found in the fields of mineralogy and material science —potentially their further study will provide new insights into whisker growth mechanisms and corrosion processes due to ion irradiation.

**Methods**

**Samples.** The Itokawa particles investigated in this study were collected from room A of the sample catcher and were captured during the second touchdown in the MUSES-C Region on Itokawa. The mineral phases and average diameters of the Itokawa particles were investigated during their initial description at the Extra-terrestrial Sample Curation Center (ESCuC) of the Japan Aerospace Exploration Agency (JAXA).

**SEM analysis.** We examined surface features of 10 regolith particles (average diameters = 68–241 μm) including iron sulfide (Supplementary Table 1) using a field emission SEM (FE-SEM; Hitachi SU6600) at the ESCuC after the initial routine description. The particles were placed on an Au-coated holder for SEM observations, without a conductive coating, using an electrostatically controlled micromanipulation system. Until these SEM observation, the Itokawa particles had never been exposed to an atmospheric environment, thus minimizing the contamination and alteration of the studied particles. We performed secondary electron (SE) imaging at accelerating voltages of 1.5 and/or 2.0 kV under high vacuum with an electron beam current of ~10 pA.

Three Itokawa particles (RA-QD02-0286, RA-QD02-0292, and RA-QD02-0325) were transferred onto an adhesive carbon-conductive tape for further analysis. We determined the elemental compositions of their surfaces with an energy-dispersive X-ray spectrometer (EDX) using an FE-SEM (Hitachi SU6600) equipped with a X-Max® 150 mm² Oxford Instruments) in JAXA and an FE-SEM (Hitachi SU6600) equipped with a Bruker XFlash® FlatQUAD detector at the Institute for Molecular Science (IMS, Higashi-Ozakazi, Japan). The accelerating voltage for SE imaging was 1.5 kV, whereas for EDX analysis we used 5 and 10 kV.
TEMA analysis. We then extracted electron-transparent sections for transmission electron microscopy (TEM) studies of regions of interest on iron sulfide surfaces, using focused Ga ion beam systems (FEIs). The FIB systems were a FEI Quanta 200 3D at Kyoto University, Japan, and a FEI Quanta3D FEG at the University of Jena, Germany. To protect the particle surfaces during FIB processing and enhance the electrical conductivity, the particles were coated with carbon (~20 nm thick). We then coated the particle surfaces with an electron-beam-deposited Pt layer (at 3kV) followed by a Ga ion-beam-deposited Pt layer (at 30 kV). For each particle, sections that were a few tens of micrometers in size were extracted using a microsampling manipulator and mounted onto TEM copper grids. After the target samples were attached to the TEM grids, they were thinned to ~100 nm using a 30 kV Ga+ beam and were finally cleaned using a 53 kV Ga+ beam at 40–80 pA.

Thin sections from the three particles were labeled RA-QD02-0286-01, RA-QD02-0291-01, and RA-QD02-0325-01. These sections were prepared in order to sample surface features of the iron sulfide initially detected by SEM, and also typically included also space-exposed silicates. We extracted an additional section (RA-QD02-0325-02) from pyroxene next to the iron sulfide sampled by RA-QD02-0325-01, because the latter did not contain any exposed silicates. Prepared sections were examined using a FE-TEM (FEI Tecnai G2 FEG) equipped with an Oxford 80 mm2 energy-dispersive SDD X-ray detector and a Gatan UltraScan 2k CCD camera at the Institute for Geosciences, University of Jena, Germany. EDX analysis was performed in scanning TEM (STEM) mode aided by high-angle annular dark-field (HAADF) imaging. Quantitative elemental abundances within the whisker metal were calculated using the Clift-Lorimer thin film approximation with k-factors determined from an artificial Fe–Ni–Co–Cr alloy of known composition29. High-resolution elemental profiles (Fig. 4) were obtained by acquiring laterally extended multispectral X-ray images in STEM mode, followed by segmenting, lateral integration, and fitting of extracted X-ray spectra. These spectra were evaluated semi-quantitatively to provide X-ray intensities and intensity ratios across surface layers with spatial resolutions of a few nanometer in the direction perpendicular to the surface. Compared with spot measurements, this approach minimizes beam damage. We performed further quantitative EDX analysis of the iron sulfide using a FE-TEM (JEOL JEM-3200FSK) equipped with an EDX detector at Kyushu University, Kyushu, Japan. The elemental compositions of the iron sulfides were calculated using the Clift-Lorimer thin film approximation. We used trolite nodules in the Cape York iron meteorite and a terrestrial mellite from Sanany, Ural in Russia, as standards for the factors. EDX detection limits depend on the counting statistics and we achieved down to 0.1 wpp for Cr, Ni and P in metal and sulfides (Cr and P were not detected at this level). Co and Cu have substantially higher detections limits (at least one order of magnitude) due to overlap of X-line series and spurious contributions from the sample environment (TEM column and Cu TEM grids). Densities of solar flare tracks (SFT) in silicate grains of each particle were determined using low-angle annular dark-field (LAADF) imaging in the STEM mode at a long camera length. SFTs were counted in the resulting images and we estimated the ratio of SFTs to the visible area of the track-sensitive mineral.

**Data availability**

The data that support this study are available from the corresponding author upon request.

Received: 5 August 2019; Accepted: 29 January 2020; Published online: 28 February 2020

**References**

1. Keller, L. P. & McKay, D. S. The nature and origin of rims on lunar soil grains. Geochim. Cosmochim. Acta 61, 2331–2341 (1997).
2. Noguchi, T. et al. Incipient space weathering observed on the surface of an Itokawa regolith particle. Icarus 257, 230–238 (2015).
3. Tsujiyama, A. et al. Three-dimensional structure of Hayabusa samples: origin and evolution of Itokawa regolith. Science 333, 1125–1128 (2011).
4. Nakamura, T. et al. Itokawa dust particles: a direct link between S-type asteroids and ordinary chondrites. Science 333, 1113–1116 (2011).
5. Christofferson, R. S. & Keller, L. P. Space radiation processing of silicates and silicates in primitive solar system materials: comparative insights from in situ TEM irradiation experiments. Meteorit. Planet. Sci. 46, 950–969 (2011).
6. Keller, L. P., Loeffler, M. J. & Christofferson, R. Irradiation of FeS: implications for the lifecycle of sulfur in the interstellar medium and presolar FeS grains. Icarus 217, 361–379 (2011).
7. Keller, L. P., Loeffler, M. J. & Christofferson, R. Space weathering and the major role of FeS. 44th Lunar Planetary Science Conference Abstracts, Vol. 2404 (2013).
8. Keller, L. P., Berger, E. L. & Christofferson, R. Surface exposure ages of space-weathered grains from Asteroid 25143 Itokawa. European Planetary Science Congress Abstracts, Vol. 558, 2015.
9. Carrez, P. et al. Low-energy helium ion irradiation-induced amorphization and chemical changes in olivine. Insights for silicate dust evolution in the interstellar medium. Meteorit. Planet. Sci. 37, 1599–1614 (2002).
10. Was, G. S. Fundamentals of Radiation Materials Science (Springer, New York, 2016).
11. Reisenfeld, D. B. et al. Elemental abundances of the bulk solar wind: analyses from genesis and ACE. Space Sci. Rev. 130, 79–86 (2007).
12. Ziegler, J. F. TRIM. www.crim.org (2008).
13. Harries, D. & Langenhorst, F. Carbide-metal assemblages in a sample returned from asteroid 25143 Itokawa: Evidence for methane-rich fluids during metamorphism. Geochim. Cosmochim. Acta 222, 53–73 (2018).
14. Bradley, J. P., Harvey, R. P. & McSween, H. Y. Magnetite whiskers and platelets in the ALH84001 Martian meteorite: evidence of vapor phase growth. Geochim. Cosmochim. Acta 60, 5149–5155 (1996).
15. Bradley, J. P. Epitaxial growth of nanophase magnetite in Martian meteorite condensates. Earth Planet. Sci. Lett. 177, 293–301 (1999).
16. Dobric, E. et al. Collisonal history of itokawa regolith. Geology 45, 819–822 (2017).
17. Terada, K. et al. Thermal and impact histories of 25143 Itokawa recorded in Hayabusa particles. Sci. Rep. 8, 1–7 (2018).
18. Fries, M. & Steele, A. Graphite whiskers in CV3 meteorites. Science 320, 91–93 (2008).
19. Dodd, R. T. & Hutchison, R. Meteorites: a Petrologic, Chemical and Isotopic Synthesis (Cambridge University Press, 2004).
20. Wagner, R. S. & Ellis, W. C. Vapor-liquid-solid mechanism of single crystal growth. Appl. Phys. Lett. 4, 89–90 (1964).
21. Laurita, D. S., Lodders, K., Fegley, B. & Kresner, D. T. The origin of sulfide-rimmed metal grains in ordinary chondrites. Earth Planet. Sci. Lett. 151, 289–301 (1997).
22. Dobric, E. & Ogliore, R. C. Adhering grains and surface features on two Itokawa particles Space science Science of solar system materials examined from Hayabusa and future missions (II). Earth Planets Space 68 (2016).
23. Keller, L. P. & McKay, D. S. Discovery of vapor deposits in the lunar regolith. Science 261, 1305–1307 (1993).
24. Steele, A. et al. Graphite in an Apollo 17 impact melt breccia. Science 329, 51 (2010).
25. Analysis of Surveyor 3 Material and Photographs Returned by Apollo 12 Mission. NASA, Washington, DC (1972).
26. Carter, J. L. VLS (vapor-liquid-solid): newly discovered growth mechanism on the lunar surface? Science 181, 841–842 (1973).
44. Wagner, C. Mechanism of the reduction of oxides and sulphides to metals. JOM 4, 214–216 (1952).
45. Nicolle, R. & Rist, A. The mechanism of whisker growth in the reduction of wüstite. Metall. Trans. B 10, 429–438 (1979).
46. Ohachi, T. & Taniguchi, I. The growth and morphology of silver whiskers. J. Cryst. Growth 24–25, 362–366 (1974).
47. Tachibana, S. & Tsuchiyama, A. Incongruent evaporation of troilite (FeS) in the terrestrial solar nebula: an experimental study. Geochim. Cosmochim. Acta 62, 2005–2022 (1998).
48. Bennett, C. J., Jamieson, C. S., Osamura, Y. & Kaiser, R. I. Laboratory studies on the irradiation of methane in interstellar, cometary, and solar system ices. Astrophys. J. 653, 792–811 (2006).
49. Gillis-Davis, J., J., et al. Laboratory space weathering induced formation of sulfides in the murchison (CM2) meteorite. 50th Lunar Planetary Science Conference Abstracts, Vol. 2019, 2132 (2019).
50. Tsuchiyama, A., Uyeda, C. & Makoshi, Y. Incongruent evaporation experiments on iron sulfide (Fe1-8S) under H2-rich (at 1 atm) and evacuated conditions. Geochem. J. 31, 289–302 (1997).
51. Matsumoto, T., Hasegawa, S., Nakao, S., Sakai, M. & Yurimoto, H. Population characteristics of submicrometer-sized craters on regolith particles from asteroid Itokawa. Icarus 303, 22–33 (2018).
52. Tu, K. N. Irreversible processes of spontaneous whisker growth in bimetallic Cu–Sn thin-film reactions. Phys. Rev. B 49, 2030–2034 (1994).
53. Bradley, J. P., Brownlee, D. E. & Veblen, D. R. Pyroxene whiskers and platelets in interplanetary dust: evidence of vapour phase growth. Nature 301, 473–477 (1983).
54. Kracher, A. & Sears, D. W. G. Space weathering and the low sulfur abundance of Eros. Icarus 174, 36–45 (2005).
55. Korycansky, D. G. & Asphaug, E. Simulations of impact ejecta and regolith accumulation on Asteroid eros. Icarus 171, 110–119 (2004).
56. Toguchida, J., Kunz, J., Clague, D. A., Harrison, D. & Allegre, C. J. The nature of pristine noble gases in mantle plumes. Science 288, 1036–1038 (2000).
57. Hony, S., Bouwman, J., Keller, L. P. & Waters, L. B. F. M. The detection of iron sulfides in Planetary Nebulae. Astron. Astrophys. 393, L103–L106 (2002).
58. Keller, L. P. et al. Identification of iron sulphide grains in protoplanetary disks. Nature 417, 148–150 (2002).
59. Sembach, K. R. & Savage, B. D. The gas and dust abundances of diffuse halo clouds in the milky way. Astrophys. J. 457, 211 (1996).
60. Jenkins, E. B. A unified representation of gas-phase element depletions in the interstellar medium. Astrophys. J. 700, 1299–1348 (2009).
61. Laas, J. C. & Caselli, P. Modeling sulfur depletion in interstellar clouds. Astron. Astrophys. 624, A108 (2019).
62. Goldstein, B. E. et al. Ulysses plasma parameters: latitudinal, radial, and temporal variations. Astron. Astrophys. 316, 296–303 (1996).
63. Kimura, Y., Tanaka, K. K., Nozawa, T., Takeuchi, S. & Inatomi, Y. Pure iron grains are rare in the universe. Sci. Adv. 3, e1601992 (2017).
64. Johnson, N. M., McCarthy, M. & Nuth III, A. Rate comparisons of magnetite and iron catalysts during Fischer–Tropsch type reactions. 45th Lunar Planetary Science Conference Abstracts, Vol. 270 (2014).
65. Hoang, T. & Lazarian, A. Polarization of magnetic dipole emission and spinning dust emission from magnetic nanoparticles. Astrophys. J. 821, 91 (2016).
66. Yada, T., et al. Hayabusa-returned sample curation in the planetary material sample curation facility of JAXA. Meteorit. Planet. Sci. 49, 135–153 (2014).
67. Harries, D. Interface processes and anomalous oxygen transport in rapid metal oxidation and magnetite formation at protoplanetary conditions. ACS Earth Space Chem. 3, 2207–2224 (2019).

**Acknowledgements**

We appreciate the JAXA curation team for giving us an opportunity to study Itokawa samples and for assisting the study. We also thank Dr. Satoshi Nakao and Dr. Masahiro Sakai for supporting SEM observations in the IMS. The present study is supported by Grant-in-Aid for JSPS Fellows (18H00579) and JSPS Early Career Scientists (18K13610), and the JSPS core to core program: International Network of Planetary Sciences. F.L. thanks the Deutsche Forschungsgemeinschaft for funding the SEM/FIB and TEM facilities at the University of Jena via the Gottfried Wilhelm Leibniz prize (LA830/14-1).

**Author contributions**

T.M. designed the research, carried out the analysis, and wrote the manuscript. D.H. processed the FIB sectioning and performed TEM observations at the University of Jena. F.L. provides advice on the interpretation of the TEM analysis. A.M. assisted FIB sample preparation at Kyoto University. T.N. supported TEM analysis at Kyushu University. All authors contributed to write and edit the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-14758-3.

**Correspondence** and requests for materials should be addressed to T.M.

**Peer review information** Nature Communications thanks Jeffrey Gillis-Davis, Dante Lauretta, Timothy McCoy and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

**Reprints and permission information** is available at http://www.nature.com/reprints

**Publisher’s note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

---

© The Author(s) 2020

---

© Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2020