Constraints on the origins of iron silicide spherules in ultrahigh-temperature distal impact ejecta

Sergei BATOVRIN*, Boris LIPOVSKY, Yury GULBIN, Yury PUSHKAREV, and Yury A. SHUKOLYUKOV

1Independent Researcher, 120 Casals Place, Bronx, New York 10475, USA
2The Mining Institute of St. Petersburg, Vasilevsky ostrov, 21 Liniya, Dom 2, St. Petersburg 199106, Russia
3Institute of Geology and Geochronology of Precambrian, RAS, Naberezhnaya Makarova 2, St. Petersburg 199034, Russia

*Corresponding author. E-mail: cosmogenica@gmail.com
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Abstract—Terrestrially occurring iron silicide spherules, described in the geological literature for 160 years as cosmogenic and approved as “extraterrestrial” minerals by IMA CNMMN in 1984, so far have escaped any serious examination by meteoriticists. Our isotopic and REE data, obtained for silicide spherules for the first time, disagree with the meteoritic origin of gupeiite (Fe₃Si) and xifengite (Fe₅Si₃) spherules from two continents. Despite departures from terrestrial norms (⁸⁷Rb/⁸⁶Sr—0.0174; ⁸⁷Sr/⁸⁶Sr—0.700181; ³He/⁴He—7.57×10⁻⁶; ⁴⁰Ar/³⁶Ar—325.9), the compositions of ¹⁴³Nd/¹⁴⁴Nd (0.512034) and ¹⁴⁷Sm/¹⁴⁴Nd (0.06357), as well as REE abundances, clarify provenance from upper crust sediments for samples with U/Pb age of 121–314 ka from the Ala-Tau range in the Urals. However, the morphology of flanged button shapes, ring waves, and eccentro-radiating ridges reliably constrains the origin of silicide spherules to distal meteoritic impact ejecta. Arc jet ablation experiments have previously demonstrated that similar morphologies, observed on australite tektites, reflect aerodynamic ablation rates corresponding to flight velocities well into orbital range. These features are generally accepted as conclusive evidence for hypervelocity atmospheric entry from space. Internal structure, consistent with accretion through the coalescence of 3–5 µm droplets, and composition, closely corresponding to 1893–1154 K span of C-type condensation sequences, indicate a high probability of processing through recondensation of ejecta vapor.

INTRODUCTION

It is astonishing that objects with aerodynamic morphology suspected by mineralogists for 160 years to be extraterrestrial minerals and approved as such over three decades ago by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA), could have escaped serious examination by meteoriticists and the cosmochemistry community.

Naturally occurring iron silicide spherules with SiC inclusions were discovered in 1859 by C.U. Shepard in North Carolina and were described as “meteoritic” (Shepard 1859). Until the turn of the century, these spherules were labeled as “meteoritic ferrosilicine” in the collection of the British Museum. However, the pioneering of industrial production of calcium carbide since 1895 at the Norwegian Aktieselskabet Meraker Smelteverk has encouraged doubts about the natural origins of any highly reduced materials (Spencer 1935). Thus, when Moss and Seymour (1909, 1910) found iron silicide in Ireland, their reports in Nature met with skepticism.

In 1924, H.N.G. Cobbe reported to the British Museum finding iron silicide spherules in concentrates from the gold dredges on the rivers and creeks in the jungles of British Guiana. Notably, the analysis of the spherules gave Fe—65%, Si—35% long before the time when technological means to manufacture synthetic
spherules and irregularly shaped grains (0.05–0.7 mm) of unknown iron silicide minerals with wustite and magnetite rims, in association with silicate glass and occasional aggregates of moissanite (SiC), barringerite, and cohenite in the Paleogene sedimentary formation of the North Azov maritime region in Ukraine (Gevorkian et al. 1969; Yeremenko et al. 1974). The specimens recovered from drill cores of 67 test wells revealed that a complex of highly reduced minerals, inconsistent with local geological conditions, was dispersed over an elliptical territory of 2 × 4 km at a depth of 90 m. The distribution field in Eocene sediments was found overlying the slumped granite megablocks of Ekaterinovsky Precambrian, which are terraced beneath the slope of the raised eastern edge of the Konsko-Yalynsky depression. However, the 20 km diameter of this depression was not as rigorously surveyed at any other location.

Iron silicide particles were initially described as an intergrowth of cubic (FeSi) and tetragonal (FeSi₂) phases. Fe₅Si₃ and Fe₃Si phases were identified in further studies. Magnetite-rimmed spherules displayed melt flow striations and sculptured exteriors, suggestive of ablation. Grains of greenish-gray silicate glass with flow patterns, and small shrapnel-like particles of nickel–iron, with a characteristic micro-octahedrite structure revealed by etching, were also occasionally found in association with iron silicide spherules. A small fraction included magnetite globules, sometimes with hollow interiors, and fragments of detached magnetite shells. Occasionally, silicide spherules occurred with silicate glass rims. Considering the inert nature of iron silicide minerals, such features seemed to indicate thermal decomposition of the surface, usually associated with aerodynamic processes. The burial depth, the large size of the territory in which the spherules were found, and the remote location in an unpopulated region excluded the possibility of technogenic contamination.

Similar mineral paragenesis, dominated by Fe₅Si₃ and Fe₃Si spherules of small size (<2 mm), strewn over a region of ~50 km, was subsequently reported in the Cretaceous sedimentary formation of the Isfara river in the Ferghana Valley of Uzbekistan (Nikolayeva and Shabanin 1971). Similar finds were reported in several other places: at a depth of 330 m in Lower Cambrian limestone of the Bazaihka river in the Eastern Sayan mountains (Novoselova 1975; Novoselova and Bagdasarov 1979), in Paleogene sediments of the Carpathian mountains (Makarova 1977), and in Devonian sandstone of the Chusovaya river in the Urals (Novoselova and Bagdasarov 1979). Wustite or magnetite rimmed silicide spherules with TiC inclusions were found as placer deposits in the Yunshan province of China (Zuxiang 1984). Morphological and compositional similarities, shared by iron silicides from various locations, were noted in the reports.

Clues to the nature of relations between silicides and associated materials were suggested by Novoselova and Bagdasarov (1979). They had shown in experimental work that heating at temperatures >1500 °C in air decomposes iron silicide into silicate glass and magnetite, the same phases found occasionally in association with iron silicide spherules. In the process, Fe₅Si₃ phases, nonstoichiometric Fe₅Si₂, Fe₃Si, and occasional inclusions of FeSi₂ and SiC were produced as transitional stages of decomposition.

In discussing the origin of the iron silicides, all the authors mentioned above excluded any likelihood of technogenic or geological processing for these objects. Considering the geological settings, the aerodynamic morphologies, and the composition, they argued instead for an extraterrestrial origin.

A similar opinion had been previously summarized in the words of C.U. Shepard, who wrote: “The strangeness of external aspect was regarded as affording a certain degree of probability in favor of its meteoritic origin; since all who have studied these objects attentively have recognized in them traits, wholly inexplicable from our knowledge of merely terrestrial matter” (Shepard 1859).

In 1984, the samples from Yunshan province of China were submitted to and approved as new minerals by the International Mineralogical Association (IMA) and were given the names gupeiite (Fe₃Si) and xifengite.
for the eastern passageways of the Great Wall (Gupeite Fe₂Si [Dana ID: 1.1.23.2] should not be confused with suessite [Fe, Ni]₂Si [Dana ID: 1.1.23.1]). The CNMMN interpreted iron silicide spherules as “extraterrestrial,” despite low Ni contents (0.3 wt%), basing their conclusion primarily on the “surface characteristics and minerals present” (Dunn et al. 1986). Over the past three decades, this interpretation has entered every comprehensive mineral record. However, the origin of iron silicide spherules has still not been discussed in the cosmochemistry literature.

Eventually, several other phases previously observed in iron silicide spherules were approved by IMA as minerals: luobusaite Fe₀.₈₃Si₃ (IMA 2005-052a), zangboite TiFeSi₃ (IMA2007-036), naquite Fe₅ (IMA 2010-010), linzhiite Fe₂Si (IMA 2010-011). Yet, discussion of silicide compounds was limited in the meteoritic community to discoveries of highly reduced phases in well-known extraterrestrial objects.

Submicrometer grains of stoichiometric MnSi manganese silicide were discovered within an interplanetary dust particle believed to have originated from comet 26P/Gregg-Skjellerup. Formation as a high-temperature condensate was suggested (Nakamura-Messenger et al. 2010). It was approved as a new mineral (IMA 2008-011) and was named brownleeite in honor of Donald E. Brownlee, the founder of the field of IDP research. Iron silicide globules of a small fraction (2–30 µm) were reported in anorthositic regolith breccia clast of a lunar highland meteorite Dhofar 280 (Anand et al. 2004). The spherules composed of a two-phase intergrowth of FeSi, Fe₂Si, and FeSi₂ phases, previously reported in terrestrial finds, were suggested to condense in lunar conditions through vaporization of lunar soil by a micrometeorite impact. Fe₂Si phase was approved as a new mineral by the IMA and was named hapkeite (IMA 2003-012) after Bruce Hapke, who predicted vapor-deposited coatings on lunar soil grains. Silicide globules with structural and compositional similarities to terrestrial finds were also found in complex anorthositic grain from the Apollo 16 samples of lunar regolith (Spicuzza et al. 2011) and were described as impactite. Additional examples of Fe-Si compounds have been identified in a survey of particles from Apollo 16 sample 61501.22 (Gopon et al. 2017) and were explained as an example of impact vaporization of lunar soil. Despite compositional similarities with previously reported terrestrial finds, no comparison was made by the authors.

Meanwhile, a similar mineral complex with iron silicide microspherules of small diameter (3–100 µm) was found in Ordovician siltstone beds of Manitairid ridge in the Polar Urals (Nikulova et al. 2011), in Permian red shale of Fore-Sudetic monocline at the Polkowice-Sieroszowice mine in SW Poland (Muszer 2014), in Miocene gypsum at a depth of 290 m at Koshava mine in Bulgaria (Yanev et al. 2016), in lower Miocene limestone at a depth of 64 m in Yevpatoria district of Crimea (Tishchenko et al. 2016), in mid-Paleocene impact ejecta layer of the Isle of Sky in Scotland (Drake et al. 2017), and in hard sediments from various locations in Hungary (Szőör et al. 2001). All authors of these reports in geological literature had considered their finds as “extraterrestrial” minerals or markers of meteoritic impact.

More recently, submillimeter iron silicide spherules (50–150 µm) with aerodynamic surface melt features, discovered in association with silicate glass and magnetite globules, were recovered from a 7 m depth of upper Cretaceous chalk in Ranmore Common, Surrey, UK, and interpreted as diagenetically altered fossil micrometeorites (Suttle and Genge 2017). Large iron silicide spherules (0.5–10 mm) with surface morphologies suggestive of ablation, in association with TiC and SiC, calcium-aluminum-rich inclusions, detached magnetite shells, and silicate glass were recently reported occurring within diamond-bearing lower Paleozoic clastic sediments in various locations of the Krasnovishersky region in North-West Urals (Chaikovsky and Korotchenkova 2012). Geological settings in both locations were described as impact ejecta layer. Impact ejecta layer with submillimeter iron silicide spherules in silicate glass globules and ropy clay-melts was reported occurring in road-cuts of Blacksville, South Carolina (Wittke et al. 2007). However, limited data on iron silicide spherules, published in geological literature, failed to find the attention of meteoriticists and the cosmochemistry community.

Incidental discovery of iron silicide spherules in Pleistocene sediments of the Ala-Tau range of the Southern Urals and in Cretaceous silty glauconitic sands of the Wenonah formation at Laurel Hills in Holmdel on the east coast of New Jersey presented the authors with an opportunity to examine and compare the finds from two continents. For the first time, a broad scope of isotopic, major, minor, and trace element compositional data, previously not available for iron silicide spherules, was obtained. Here, we compare how our findings correspond with previous reports in geological literature and IMA conclusions regarding the “extraterrestrial” nature of these objects.

METHODS

Field Survey and Sample Recovery

During the fieldwork of four expeditions to the Ala-Tau site, iron silicide specimens with a combined weight of 4.8 and 0.3 kg of associated materials were collected.
Several recovery methods were alternatively used for sample collection depending on terrain, burial depth, and other field conditions.

Vertical natural exposures of the Pleistocene alluvial layer along the stream bed and on the mountain slope were located and scanned for samples of iron silicide spherules with metal detectors: Minelab XT-1800, White’s Electronics GM3, Falcon MD10 operating accordingly on 60, 50, 300 kHz frequencies and Minelab SD2100 operating in multi-period sensing mode. Fisher M-Scope Gemini 3 two-box metal detector with transmitter operating on 82 kHz frequency in narrow scan inductive trace mode and FX-3 Ferro Probe magnetometer were used for locating alluvial concentrations of iron silicides in correlating Pleistocene burial layer.

Test trenches and pits were excavated in a radius of 300 m ranging between 50 cm × 50 cm and 1 m × 5 m. Cuts through silicide-bearing clayey sand bed were exposed, scanned with metal detectors, and excavated. The removed aggregate of sedimentary material was separated by size through mesh 2 classifier screen and sluiced in the stream through a double-sluice concentrate system additionally equipped with 3.4 megagauss plastic-coated samarium cobalt magnetic traps for separation of a magnetic fraction. Recovered silicide particles were wet sieved using mesh screens between sizes 4 (4.75 mm) and 16 (1 mm). Concentrate of a small fraction (<1 mm) was panned, separated optically, and wet sieved using mesh screens between sizes 20 (850 µm) and 100 (150 µm). To avoid contamination of samples, plastic hand sluices were employed for dredging of the sediments; plastic pans and classifiers were used for panning; and plastic sieves were used for grading. All specimens were collected manually.

Guldstrom electronic prospecting instrument employing 280 cm × 2 cm carbide-tipped probe with a sensor for measuring electrochemical potential and the conductivity of particles >0.05 mm was used for probing sediments. A 38 mm × 305 mm sand auger with a set of extension tubes of small aperture and 32 mm × 305 mm tube sampler attachment was used for manual drilling and sampling sediments at depths up to 300 cm. A Falcon MD 10 metal detecting probe with 27 mm diameter coil was lowered into the test well to scan for silicide particles >150 µm. The well cuttings were disaggregated in a container with water and a handheld magnet was passed through loose sediments to recover magnetic fraction.

U, Pb, Rb, Sr, Sm, Nd Analyses

The U, Pb, Rb, Sr, Sm, and Nd isotopic compositions were analyzed at the Laboratory of Isotopic Geochemistry and Geochronology in the Institute of Geology and Geochronology of Precambrian, Russian Academy of Sciences, by Y.D. Pushkarev with the assistance of K.I. Lokhov. The determination of Sr and Pb isotopic compositions as well as Rb, Sr, Pb, U, Sm, and Nd concentrations (method of isotopic dilution) was

Fig. 1. Aerodynamic ablation morphologies of iron silicide spherules. Reflected light images. A) Posterior of button-shaped Ala-Tau spherule with broken flanges. Nodules of textured melt attached to the remnants of the flanges suggest disintegration in flight as ablation continued in the final stage at lower temperatures. B) Anterior of button-shaped Ala-Tau spherule with densely arranged ring waves (right), granular melt texture at stagnation point and ring-wave structure, altered by the melt-flow on the left flange, indicating that the projectile tumbled after the loss of flight stability. C) Profile of ablated Laurel Hills spherule with wustite surface rim, melt-flow ridges, internal vesicle opened by surface recession on anterior (left), and a nodule of accumulated melt, transferred from anterior, protruding on the posterior surface (right). D) Profile of a flanged Ala-Tau spherule. Ablated anterior (bottom) forms an equatorial flange structure composed of vesicular wustite/magnetite aggregate produced in the thermal decomposition of iron silicide surface layers. Posterior (top) demonstrates internal cavity opened by surface recession and attached splashes of textured ablation-melt transferred from anterior. E) Anterior of Laurel Hills spherule with eccentric-radiating melt-flow ridges. F) Profile of Laurel Hills spherule with a stepped flange. Cone-shaped oriented anterior (bottom) with wustite fusion crust of fine-grained granular texture. Posterior (top) shows original smooth surface, hemispherical pits connected by U-shaped grooves, internal cavities opened by surface recession and likely expanded in turbulent airstreams by trapped vortices. G) Ala-Tau spherule with textured magnetite surface rim and internal vesicle exposed by the surface recession. H) Posterior of button-shaped Ala-Tau sample with parasitic spherule and remnants of detached flanges. The remnant of the original flange (bottom) marks the initial diameter of the structure. Smoothed fracture on broken edge (left) suggests disintegration in flight as ablation continued. Melt flow from parasitic spherule to the surface of the host suggests that the particle has attached in flight at the ablation stage. I) Anterior of Ala-Tau spherule with melt-flow ridges radiating from stagnation point. J) Oriented Laurel Hills spherule with dark magnetite surface rim. Abundant schlieren and raised flow ridges suggest turbulent melt-flow on the solid surface at relatively low quenching rates in the final stage of deceleration when ablation ceased. K) Fragment of a broken Laurel Hills button-shaped spherule with flange remnant, thin fusion crust, and magnetite melt-flow on posterior surface contrasting with iron silicide of conchoidal fracture. The polygonal pattern of raised magnetite flow ridges was probably formed when the lower layer of surface melt was squeezed through contraction cracks during the secondary quenching episode. L) Profile of a broken Ala-Tau spherule with wustite/magnetite fusion crust, conchoidal fracture, internal vesicles, smooth posterior (left), and frothy anterior surface (right). Remnants of an initial polygonal pattern of contraction fissures on the posterior are altered by a magnetite rim formed in a secondary heating event.
performed on a Finnigan MAT 261 8-collector mass spectrometer in static mode. Rb and Sr were separated using conventional cation-exchange techniques (Bio-Rad AG50 Wx8). Sm and Nd were separated from REE fraction using a two-step procedure: first, conventional cation-exchange chromatography, and then, extraction chromatography on HDEHP-covered teflon powder. Conventional sample preparation for isotopic analyses was used according to Richard et al. (1976). Total blanks during the course of this study were estimated as 0.05 ng for Rb and 0.2 ng for Sr, 0.03 ng for Sm, and 0.08 ng for Nd. The quality of isotopic analyses was controlled by measurements of isotopic standards. The mean values for 10 runs in the last series of standard measurements for Sr (SRM-987) were $^{87} \text{Sr} / {^{86} \text{Sr}} = 0.710241 \pm 15 \sigma$ and for Nd standard (La Jolla) were $^{144} \text{Nd} / {^{143} \text{Nd}} = 0.511908 \pm 8$. Sr isotopic ratios were normalized to $^{88} \text{Sr} / {^{86} \text{Sr}} = 8.37521$ and Nd ratios were normalized to $^{148} \text{Nd} / {^{144} \text{Nd}} = 0.24157$ (Neymark et al. 1994). Additionally, Nd isotopic ratios were normalized to La Jolla standard ($^{143} \text{Nd} / {^{144} \text{Nd}} = 0.512865 \pm 8$). The results for

(A) (B) (C)

(D) (E) (F)

(G) (H) (I)

(J) (K) (L)

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measurements of BCR-1 were Sr = 330.7 ppm, Rb = 47.46 ppm, Sm = 6.47 ppm, Nd = 28.13 ppm, \(^{87}\text{Rb} / ^{86}\text{Sr} = 0.40615\), \(^{87}\text{Sr} / ^{86}\text{Sr} = 0.70536 \pm 22\), \(^{143}\text{Nd} / ^{144}\text{Nd} = 0.1380\), \(^{143}\text{Nd} / ^{144}\text{Nd} = 0.512642 \pm 14\).

Isotopic analyses of Pb were carried out with the aid of a silica gel emitter. The total Pb blank was 0.5 ng. Mass discrimination of 0.0013 ± 0.0003 per amu, determined by numerous measurements of SRM-982, was used to correct for fractionation in the samples. Average ratios for SRM-982 measured during the course of these analyses were \(^{206}\text{Pb} / ^{204}\text{Pb} = 36.643\), \(^{207}\text{Pb} / ^{204}\text{Pb} = 17.092\), and \(^{208}\text{Pb} / ^{204}\text{Pb} = 36.551\). External 2σ error of 0.05% per amu was accepted for real samples.

**Noble Gas Analyses**

Ar and He isotopic compositions were analyzed on our request at the Laboratory of Isotopic Geochemistry, Geochronology and Cosmochemistry in the Vernadsky Institute of Geochemistry, Russian Academy of Sciences, by Y.A. Shukolyukov and A.M. Pleshakov.

Ar and He isotopic analyses were performed using experimental facilities on the platform of MI.1201.IG mass spectrometer, including (1) resistance-heated double-vacuum Ta furnace equipped with Eurotherm temperature stabilization and control system; (2) a purification system equipped with Balzers TMU-260 turbomolecular pump and Varian-SD90 rotary pump; (3) an MI.1201.IG mass spectrometer equipped with ion source (ionization by electron impact) and two-channel ion detection system with Faraday collector and Balzers SEV-218 electron multiplier in integral and ion counting modes; (4) a computer system, providing control over functional parts and process of measurement.

Gas standards were used for the determination of absolute sensitivity and discrimination effects. Atmospheric helium \(^3\text{He} / ^4\text{He} = 1.4 \times 10^9\), \(^4\text{He} = 4.22 \times 10^{-6}\) cm\(^3\) was taken as the standard for He. Atmospheric argon \(^{40}\text{Ar} = 4.59 \times 10^{-6}\) cm\(^3\) was adopted as the standard for Ar. Fusion system blanks were performed before each test of the samples. The values for the blanks were \(^4\text{He} = 4.6 \times 10^{-10}\) cm\(^3\) and \(^{40}\text{Ar} = 1.9 \times 10^{-10}\) cm\(^3\). The samples were step-heated to 800 °C, 1200 °C, and 1600 °C. Each heating step was preceded by degassing procedure at \(t = 200\) °C for 1 h to expel absorbed atmospheric gases (Verkhovsky and Shukolyukov 1991).

**REE Analysis**

REE data were obtained at the Laboratory of Isotopic Geochemistry and Geochronology in the Institute of Geology and Geochronology of Precambrian, Russian Academy of Sciences, by Y.A. Shukolyukov. The determination of REE concentrations was performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using a NewWave UP266 MACRO 266nm, short UV laser ablation system coupled to a high-resolution ICP-MS ThermoElement-XR (spot size: 515 µm; 10 Hz; fluence: 13.3 J cm\(^{-2}\); scan speed: 70 µm s\(^{-1}\)). Calibration was performed using NIST 612 glass reference (Campbell and Humayun 1999). Analytical sensitivity: 0.001 ppm. NewWave UP266 MACRO 266nm instrument sensitivity: 3σ detection limit for NIST glass calculated well below ppb level in the solid to 2.5 ppt.

**Analyses of Chemical Composition**

Abundances of major and minor elements were measured in the Laboratory of Mineralogy, Crystallography, and Petrography at the Mining Institute of St. Petersburg by Y.L. Gulbin with the assistance of I.A. Gaydamako. Quantitative analyses of chemical composition were performed with a JEOL JXA 8600 S electron microprobe operating at 15 kV, a probe current of 1.206 \(\times 10^{-7}\) A, and 2 µm beam diameter. During these tests, Ni abundances were not measured due to the presence of Ni in the coating applied to polished samples. Detection limits were 0.01 wt%.

Bulk composition measurements including Ni values were obtained by X-ray fluorescence spectrometry performed with a Thermo Fisher ARL-2800 X-ray analyzer in the XRF department of the central analytical lab at the Russian Geological Research Institute (VSEGEI) in St. Petersburg. Standard procedures were applied for sample preparation. Four large Ala-Tau iron silicide samples of 1.9–2.3 cm sizes were powdered to 40 µm particle size and mixed with 50% lithium tetraborate and 50% lithium metaborate flux at 1:9 proportion in preparation of four beads. Au/Pt crucibles were used to form beads in Classe Fluerx-Bis automatic fusion instrument. Also, in preparation of pellets for the test of materials associated with iron silicide spherules, Herzog HP 40 press was applied. A 3.1 cm sample of limonite nodule with silicide inclusions and a 3.2 cm sample of vesicular magnetite were powdered to 30 µm particle size and were used to form 32 mm pellets.

 Further investigation of chemical composition was conducted by Y.L. Gulbin with the assistance of O.L. Galankina using JEOL JSM-6510LA scanning electron microscope, equipped with JED-2200 EDS spectrometer, operating at 20 kV accelerating voltage, a probe current of 1.5 nA, and 2 µm beam diameter. The ZAF corrections method was applied for EDS measurements. Detection limit was 0.01 wt%. Natural mineral, oxide, and metal reference standards designed for SEM/EDS system calibration were used, including olivine—for Si,
Flanged iron silicide spherules

Mg, Fe; kaersutite—for Al; diopside—for Ca; jadeite—for Na; orthoclase—for K; and spessartine—for Mn. Carbon was used for sample coating.

Photomicrography

Reflected light images were obtained with LM Photomacroscope lens on Nikon D800 and Sony a7R II digital cameras by the photographic method of focus stacking automated by StackShot macro rail with StackShot 3x controller. Photographic images were also produced with Leica M205 C and LOMO MBS-10 binocular microscopes. Backscattered and secondary electron images were obtained with JEOL JXA 8600 S and JEOL JSM-6510LA scanning electron microscopes.

Fig. 2. Morphological variations of iron silicide samples from Ala-Tau and Laurel Hills locations. Reflected light images. A) Profile of a broken Ala-Tau iron silicide spherule with granular texture of wustite/magnetite fusion crust, conchoidal fracture, internal cavities, internal vesicle opened by the surface recession. B) Iron silicide samples from Ala-Tau location, including wustite-rimmed spherule with melt droplets attached to surface, anhedral irregular shaped fragment, and angular conchoidal flake. C) Large Ala-Tau silicide particle of an irregular shape with regmaglypts. D) Limonite nodule from Ala-Tau location with inclusions of iron silicide spherules. E) Pyramidal crystals of iron silicide on Ala-Tau sample of irregular shape. F) Posterior of button-shaped Laurel Hills spherule with broken flanges. Textured lumps of melt attached to the edge of broken flanges (left) suggest that disintegration of the flange structure took place in flight when ablation continued at the lower end of ablation temperatures. G) Anterior of Laurel Hills spherule with eccentro-radiating ridges oriented at the stagnation point of the particle. H) Conical anterior of oriented Laurel Hills spherule with radiating ridges. I) Anterior of disk-shaped Laurel Hills sample with densely arranged rows of ring-wave ridges indicating rhythmic transfer of thin melt layers over a solid surface.
RESULTS AND DISCUSSION

Location, Settings, and Sample Recovery

Iron silicide spherules, subsequently identified as a two-phase intergrowth of gupeiite, xifengite, and other mineral variations of silicides, including hapkeite, were incidentally found in 1981 by one of the authors (S.B.) in the remote unpopulated region of the Southern Urals, isolated between Ala-Tau and Kalu ranges 19 km southeast from an abandoned village of Utar-Yurt. The undisturbed natural settings of the find were protected by a lack of roads and trails in the mountainous forested terrain, accessible only on foot along the streambeds of non-navigational Shesheniak Major or Shesheniak Minor rivers. Initially, several spherules with metallic luster and no visible signs of oxidation were noticed eroding out of the high banks of a small mountain stream tributary to rivers. During the initial survey of the site, iron silicide spherules of a wide variation in size (0.05–8 mm) and their articulated or disarticulated fragments were recovered from the bank cuts along ~200 m stretch of the streambed. Some silicide objects had distinctive aerodynamic shapes and surface features typical for tektites. Other silicide particles demonstrated features previously observed only in australite tektites: flanged button shapes (Fig. 1A) and ring waves (Fig. 1B). Magnetite globules and fragments of detached magnetite shells were also found in the area. Occasionally, the samples were found in association with nodules of limonite matrix enclosing submillimeter iron silicide, alumina, spinel, and silicate glass globules. The mineral complex, inconsistent with geological conditions and known terrestrial processes, was dispersed in the undisturbed clayey sand layer of Pleistocene alluvium overlying Riphean aleuritic sandstones, crinoidal limestones, and stromatolitic dolomite beds of the Katavsky Formation in Proterozoic of Alatau anticlinorium.

Further study of the site and samples was interrupted and postponed by political persecution of the author as a Soviet dissident and expulsion from the USSR in 1983. Three expeditions to the location that followed two decades later recovered iron silicide particles in the streambed, in the bank cuts, and the corresponding layer at a depth of 0.5–1.5 m within an ~300 m radius. The spherules were found individually dispersed or clustered in concentrations on perimeters of 1 × 1 m to 2 × 5 m separated by distances between 40 and 210 m. Small clusters of particle concentration appeared as alluvial deposits. The sharp conoidal fractures on spherule fragments and lack of signs of abrasion on the surface of silicide spherules indicated that the objects were not transported a significant distance since their original deposition.

All recovered samples were located with methods of reconnaissance sediment sampling and electronic prospecting equipment. Sluicing and other techniques of concentration were used only with precautions to avoid sample contamination. Silicide specimens with a combined weight of 4.8 and 0.3 kg of associated materials were collected at the site during four field seasons. Similar iron silicide spherules, composed as a two-phase intergrowth of gupeiite, xifengite, or occasionally hapkeite and other silicide minerals, were independently discovered in 1997 by the co-author (B.L.) on another continent. The samples were found incidentally on his private land, at a depth of 2.5 m, in undisturbed Cretaceous silty glauconitic sands of the Wenonah formation, under the slopes of Laurel Hills in Holmdel,
New Jersey. Fifty-seven spherules of a small diameter ~4 mm were extracted by a magnet from the 25 m x 5 m area. This prompted consultations of the authors and further study of iron silicide spherules from both locations.

**Morphological Characteristics**

Examined samples from the Urals and New Jersey comparably vary widely in grain size and morphology (Fig. 2). Ala-Tau samples are typically represented as
spherules (0.05–8 mm) (Figs. 1G, 2A, and 3A) and as irregular-shaped particles (maximum 2.7 cm) (Figs. 2B and 2C). Samples from Laurel Hills in Holmdel are smaller (0.05–4 mm) (Figs. 2F–I and 4). Irregular particles demonstrate a range of morphological variations between anhedral and highly angular shrapnel-shaped types. Passing hand-magnet over typical sluice concentrate has shown that over 98% of silicide samples are ferromagnetic or paramagnetic. The finely textured spherules are the characteristic type for samples from both locations. But the textural patterns of these spherules usually vary on anterior and posterior.

Due to the common occurrence of moderately dark rims, the strong metallic luster of iron silicide is visible primarily on fragments of broken spherules (Figs. 1L and 2A). Some spherules have a porphyritic surface. Occasionally observed crystals include polycrystalline aggregates of pyramidal crystals (Fig. 2E) or tetragonal prisms. The spherules are predominantly dark-rimmed and occur with surface textures of several variations, complicated by hemispherical pits and U-shaped meandrine grooves (Fig. 3C), recognized for the hemispherical bottom and smooth walls of the cavities and fissures. Small Ala-Tau spherules, which are occasionally found as inclusions in limonite nodules (0.2–3 cm) with enclosed grains of alumina, spinel, and silicate glass, do not have these features and are smooth surfaced.

Iron silicide spherules display apparent aerodynamic morphologies that are similar to typical shapes and surface textures of tektites (Figs. 1, 3, and 4). These morphologies of silicide spherules closely reproduce aerodynamic features considered unique for australites: flanged structures of button shape (Figs. 1A, 1H, 2F, 3E, 4E, 5A and 5D) and circular ring waves (Figs. 1B and 2I). The spherules demonstrate sculptured anterior surface (Figs. 3E and 4E), melt flow ridges (Fig. 1C), radiating flow striations (Figs. 1E, 1I, 2G, 2H and see Fig. 7E), and other surface characteristics commonly associated with aerodynamic ablation during a high-velocity atmospheric passage. Large specimens (>5 mm) occasionally have surface depressions of plastic configuration resembling regmaglypts (Fig. 2C). More often samples have shapes that appear flight-oriented: cone, lens, dumbbell, disk, teardrop, peanut, elliptical, and elongated forms (Figs. 1F, 3B, 3F, and 6A–D [and see Fig. 8A–D]). Impact marks such as pits, fractures, fissures, or indentations are occasionally present on the apparent stagnation point of particles with oriented shapes (Figs. 6A and 6E). Surface features, resembling contorted schlieren (Fig. 1J) and other textural patterns similar to tektite morphology, suggest the flow of molten material. However, melt-flow extrusions on the surface indicate that liquated material was streaming over a solid object (Fig. 1C).

All mentioned surface features of iron silicide spherules also display a thin layer of dark fusion crust as an affirmation of aerodynamic origin. Evidence of aerodynamic heating is visible on silicide spherules in the thermal decomposition of the surface layer. This will be addressed further in the discussion.

Ala-Tau and Laurel Hills samples share similar morphology (Figs. 3 and 4). Differences may be accounted for by lack of representation in the sampling of particles from New Jersey. Morphology of previously reported finds of iron silicide particles is closely corresponding. Principal compositional differences between the amorphous siliceous glass of tektites and the complex crystalline aggregate composition of iron silicide spherules exclude any close analogy in processing. Meanwhile, morphological similarities of aerodynamic features indicate parallels in aerodynamic conditions of formation.

Meteorites offer an affirmative answer to the question of whether implications of tektite aerodynamic features can be safely extrapolated to a fundamentally different material with similar morphology. Ablation flanges similar to circumferential flange structures
characteristic for australite tektites occasionally occur on meteorites of various compositions. For example, Nallah H chondrite and Miller Range 07666 IIAB iron are perfectly button shaped (McCall and Cleverly 1969; Corrigan and Welzenbach 2008). Pronounced flange structure is present on Allan Hills 84165 IIIAB octahedrite (Clarke 1986), Allan Hills 84190 acapulcoite achondrite (Score and Mason 1988), Salem L6 chondrite (Clarke and Pugh 1988), Wood’s Mountain IVA iron (Buchwald 1975), and other meteorites. Definitive work
on tektite aerodynamics compared circular ring waves of australite tektites to examples of similar morphology on such dissimilar meteorites as Boogaldi and Nedagolla irons or the Orleans stone (Chapman et al. 1962). Also, despite principal differences in composition and size with australite tektites, arc-jet ablation experiments have successfully simulated the formation of flanges on iron and stone meteorite models (Shepard et al. 1965). Hitherto the consensus has associated flange structure and circular ring waves with hypervelocity atmospheric entry regardless of projectile material.

**Morphological Evidence for Ablation**

The occurrence of eccentric radiating ridges, flanges, button shapes, and ring waves among aerodynamic features of iron silicide spherules suggests surface ablation of a solid projectile with a cold interior (Glass et al. 1996). The sensitivity of these ablation morphologies to a complex of conditions specific for hypervelocity aerodynamic processes guarantees their reliability as evidence. While the anterior surface of the projectile is heated by atmospheric friction in flight, a thin layer of ablation-melt is removed, limiting the heat-affected zone. Formation of eccentric-radiating ridges, flanges, button shapes, and ring waves (Figs. 1, 3, and 5) requires the flow of molten material over a solid surface. When a thin layer of ablation melt flows toward the posterior of an aerodynamically stable decelerating object, it may accumulate to form a flange around the boundary of temperature and pressure differences. A completely molten object, whether natural or man-made, cannot mimic morphologies resulting from the surface ablation of a solid projectile.

Unlike siliceous glass of tektites, the complex mineral composition of iron silicide particles offers a record of surface pyrolysis. Exposure of iron silicide to temperatures >1800 K leads to unmixing of solid solution, progressive stages of Si depletion, and Fe oxidation to wustite and magnetite. This chemical record of selective heat exposure of the surface layer cannot be reproduced by industrial or endogenic melt products. An association of known aerodynamic surface features with the chemical record of peripheral thermal decomposition presents conclusive evidence for aerodynamically controlled ablation. Such patterns of heating and loss of surface melt would be impossible without hypervelocities.

Arc jet ablation experiments have shown that flanged button shapes, ring waves, and eccentric-radiating ridges of australite tektites provide tight constraints on the hypervelocity entry into the terrestrial atmosphere from space (Chapman 1960; Chapman et al. 1962). These experiments have demonstrated that aerodynamic ablation rates of button-shaped australite tektites correspond to flight velocities well into orbital range (11–12 km s\(^{-1}\)) and high temperatures of the atmospheric entry (2500–2800 K; Chapman et al. 1962). Arc jet experiments have shown that atmospheric entry is the only process capable of providing the combination of extreme conditions necessary to form an ablation flange. Accordingly, a similar circumferential flange structure at the equatorial regions of iron silicide spherules is the evidence for an atmospheric entry from space to no lesser degree.

Aerodynamic evidence for atmospheric entry of australite tektites hinges on the magnitude of the velocity. The acquisition of a similar button shape by iron silicide spherules required velocities even higher than computed for australites. Formation of the flanges retaining observed highly reduced silicide composition necessitates significantly higher temperatures (>3700 K) of ablation process (Yakovlev et al. 1992) and corresponding hypervelocities in the orbital range.

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Fig. 5. Variations of flange structures on iron silicide spherules. Backscattered electron and reflected light images. A) Posterior of button-shaped Ala-Tau spherule with broken flanges. The rounded edge on the remnant of the original flange (top left corner) marks the initial diameter of ablation-melt coiling in the solidified toroidal vortex of molten iron silicide. Smoothed edge of a flange remnant (bottom left corner) indicates that disintegration of the flange structure took place in flight as ablation continued. Textured lumps of melt attached to the edge of the flange remnant (right) indicate lower temperatures before ablation ceased. A dark layer of magnetite flow on the posterior surface suggests tumbling of the object after the loss of stabilization in flight. B) Posterior of Laurel Hills spherule with partially detached flange. Flange structure composed of accumulated nodules of textured ablation-melt indicates ablation at the lower end of ablation temperatures. C) Posterior of Ala-Tau spherule with smooth original surface, large magnetite flow rollover lip, small remnants of detached flanges, and raised melt-flow vein. D) Posterior of Ala-Tau button-shaped spherule with partially detached flange. Scalloped sculpturing of the retained flange structure and U-shaped grooves on the posterior were probably formed by turbulence after the loss of flight stability and tumbling due to partial detachment of the flange. E) Semi-profile of Laurel Hills sample at the final stage in ablation of the flanged button shape. Inverted flanges of the anterior (left) are forming a bowl with a remnant of the spherule protruding at the posterior center (right) on the bottom of the bowl. The anterior surface is sculptured with large folds of ablation texture. The posterior surface is partially covered with wustite/magnetite aggregate crust formed by micro-droplets of melt conveyed from the anterior. F) Ala-Tau spherule with oriented anterior and corona-shaped remnants of stepped flange structure. Chemically inert properties of iron silicide exclude terrestrial weathering of the object and suggest that corona formed when the flange was ablated at aerodynamic stress points by trapped vortices in turbulent airstreams. (Color figure can be viewed at wileyonlinelibrary.com.)
Morphological differences with button-shaped australite tektites are also apparent. The anterior of the flanged silicide spherules is not reminiscent of the smooth surface characteristic for the anterior of australite buttons (Figs. 1B, 1D, 3E, and 4E). Significant differences in chemical and physical properties between tektites and iron silicide spherules cannot be expected to produce completely identical morphology under similar aerodynamic conditions. However, products of thermal decomposition of iron silicide mark heat-affected zone on
the surface of the particles and offer certain flight records. For example, an occurrence of a thin layer of magnetite amidst the surface melt-flow patterns on the samples (Fig. 5A) is a marker of temperature decrease below 3700K in the course of deceleration.

A number of morphological surface features observed on iron silicide spherules offer further insights into the conditions of ablation. Some samples have multiple ring waves (Figs. 1B and 2f) indicating that the ablation-melt proceeded from the stagnation point to the flanges during an aerodynamically stable hypervelocity flight (Glass et al. 1996). The ring-wave flow ridges clarify the possible atmospheric entry angles. Arc jet ablation experiments have demonstrated that multiple ring waves form on the exterior of ablated objects at high stagnation-point pressures exceeding 1 atm on shallow atmospheric flight trajectory, while at low stagnation-point pressures on the order of 0.1 atm, such morphologies do not form (Chapman and Larson 1963). The occurrence of multiple ring waves on the surface of some iron silicide spherules correspondingly indicates a shallow entry angle of the object decelerating in the atmosphere and velocity sufficient for high stagnation-point pressures, approaching 1 atm, until ablation ceased.

Besides similarity with australites in a symmetrical pattern of circular distribution on the anterior surface, ring waves of iron silicide particles have their distinctions. They are more densely arranged and more convex. However, a similar principle of circular distribution on flanged australites and silicide spherules reflects a common pattern of surface melt-flow transfer suggesting analogous aerodynamic conditions of formation. The variance may be due to pressure difference. Arc jet ablation experiments have demonstrated that progressively closer spacing of ring waves is associated with pressure increase (Chapman and Larson 1963). Other examples of nonconformity to the appearance of australites on the part of silicide spherules point to compositional distinctions. Materials of significant differences in chemical and physical properties may hardly be expected to respond completely identically to similar aerodynamic conditions of formation.

Arc jet ablation experiments have shown that the formation of ring waves and flanges on button-shaped tektites required temperatures above 2100 K. Simulation of conditions at the lower limit in the range of ablation temperatures produced flanges formed by viscous beads of melt. Some of them detached and repositioned to the posterior. Flanges of this type are also observed among Ala-Tau samples (Fig. 5B), although the thermal range and viscosity–temperature relationship of silicide ablation were certainly different.

Another peculiar variation of flanges on silicide spherules is formed without accumulation of ablation-melt. In this case, the loss of surface melt from a cone-shaped anterior is emphasized by a flange produced as a stepped boundary between ablated anterior and distinctly larger diameter of an unaffected posterior hemisphere (Figs. 1F, 3B,F, 4B, 6E, 7B, and 7C). Flange features of this type were previously not observed on tektites. However, australites of lens and core shapes bear some structural similarity. The absence of melt accumulations or any melt-flow striations on ablated silicide spherules with stepped flanges suggests that material was probably lost through evaporation at higher velocities than experienced by typical flanged projectiles of button shape.

A fundamental characteristic of aerodynamically ablated material is that the entire flow of fluid melt is conveyed away in a thin layer. Flanges form in stabilized flight when transferred liquid adheres by surface tension to the object’s core at the equatorial boundary of temperature and aerodynamic pressure.

Fig. 6. Variations in ablation patterns of iron silicide spherules. Reflected light images. A–C: anterior, posterior, and profile of Ala-Tau lens-shaped ablated spherule. A) Anterior of lens-shaped Ala-Tau particle. Frothy fusion crust indicating violent volatilization of melt at the final stage of deceleration. Shallow impact pit at the stagnation point. B) Posterior of ablated lens-shaped Ala-Tau particle with an original smooth surface, polygonal pattern of fine contraction fissures, and secondary thermal alterations of the surface. Splashes of ablation-melt from anterior attached to posterior overlay parts of the pattern of contraction fissures, indicating that the primary quenching event preceded ablation. C) Lens-shaped profile of ablated Ala-Tau spherule with smooth posterior (top) and frothy wustite/magnetite fusion crust on anterior (bottom). The sharp equatorial boundary between morphological surface patterns of anterior and posterior suggesting stabilized flight. D) Profile of a segment from a large broken Ala-Tau lens-shaped disk with smooth posterior (top) and granular wustite/magnetite aggregate fusion crust on the anterior surface (bottom). Frothy magnetite accumulations, conveyed from anterior over the equatorial boundary, protrude on the posterior surface. The sharp equatorial edge of the boundary between morphological surface patterns of anterior and posterior suggests stabilized flight. E, F: profile and posterior of ablated Ala-Tau spherule. E) Profile of Ala-Tau spherule with stepped flange, an oblique orientation of ablated anterior, U-shaped grooves and pits on the smooth original surface of posterior. Wustite and magnetite fusion crust on anterior, shallow impact pit with a conchoidal fracture at stagnation point, and internal vesicle opened by the surface recession. Note that gray color wustite visually differs from black magnetite by greenish tint in reflected light. F) Structures on the posterior surface of the Ala-Tau spherule suggest that if oblique orientation persists long enough, the hemispherical pits are elongated into U-shaped meandrine grooves by a sequence of vortices trapped at aerodynamic stress points.
differences. Australite buttons often retain the bulk of the ablated material in the flanges. Flanged iron silicide buttons show far more efficient loss of anterior surface melt, probably due to elevated rates of vaporization at higher velocities and temperatures.

Unlike flanged australite tektites, button-shaped Ala-Tau silicide spherules occur in a narrow size range (3–10 mm). Flanged Ala-Tau samples are larger in size than small australite buttons (1–5 mm) reported from Lake Kutchel in the Kalgoorlie region (Pillans et al.)
Variations of Aerodynamic Ablation Features

U-shaped meandrine grooves and hemispherical pits on the surface of tektites were alternately explained by etching in acidic soil and by ablation in turbulent airstreams. Chemical weathering explanation dominates in the present time. Meanwhile, identical morphological features present on the surface of iron silicide spherules (Figs. 3C, 3D, 4C, and 4D) from Ala-Tau and Laurel Hills locations offer clarification. Unlike siliceous glass of tektites, iron silicide is chemically inert to aqueous acidic solutions of any kind. Iron silicide is insoluble in oxidizing and non-oxidizing acids with the exception of concentrated heated hydrofluoric acid. This excludes chemical weathering and constrains the origin of U-shaped meandrine grooves as well as hemispherical pits to ablation in turbulent airstreams. The existence of close morphological similarities between objects with principal compositional differences, like tektites and silicide spherules, suggests that similar physical conditions of formation are responsible. However, this

Fig. 7. Variations in surface recession patterns of iron silicide spherules. Backscattered electron images. A) U-shaped meandrine groove overlaying the polygonal pattern of contraction cracks on the original smooth surface of Ala-Tau spherules suggests that primary quenching preceded the ablation process. Considering chemically inert properties of silicide, terrestrial leaching is excluded. Note that the U-shaped groove terminates in large hemispherical pits. Several small hemispherical pits alter contraction cracks indicating that these fissures were aerodynamic stress points with captured vortices in a turbulent airstream. B) Profile of Ala-Tau spherule with stepped flange. The hemispherical pits and meandrine grooves formed at the equatorial boundary and on the posterior probably due to tumbling in turbulent airstreams. Pits are accentuated by oxidized components of soil. Protrusions at the stagnation point of anterior suggest that an efficient surface recession continued after the loss of flight stability. C) Profile of Laurel Hills spherule with stepped flange. U-shaped grooves and pits on the posterior are accentuated by oxidized components of soil. D) Sculpturing of ablation melt, accumulated on flanges of Ala-Tau spherule, suggests that primary flange structure detached in flight before ablation ceased and the projectile subsequently tumbled in turbulent airstreams. E) Conical anterior of oriented Laurel Hills spherule with ridges eccentro-radiating from stagnation point. F) A rounded fragment of button-shaped spherule from Ala-Tau location indicating disintegration in flight before ablation ceased. The polygonal pattern of ridges was likely formed in the secondary quenching process when a thin layer of underlying melt was squeezed through contraction cracks.
does not exclude a possibility for a role of leaching in expanding aerodynamic surface features of tektites.

Experimental works by Johnson (1959) have shown that aerodynamic flow can produce cavities. These experiments also demonstrated severe turbulent distortions in hypervelocity flow around the body containing forward-facing cavities in the surface. Hemispherical pit geometry indicates that a trapped ring-vortex ablates pits at a rate faster than the neighboring surface (Sepri and Chen 1976). If oblique orientation persists long enough
the hemispherical pits elongate into meandrine grooves. Iron silicide spherules show that U-shaped grooves are predominantly connected to aerodynamic stress points such as notches in stepped flanges or internal vesicles exposed through the surface recession (Figs. 3F, 5F, 6E, and 6F). It should also be noted that the sharp edge of the surface boundary, characteristic of U-shaped grooves and pits, requires a solid surface and could not have formed on a molten object.

An abundance of fine fissures (1–10 µm) is characteristic for smooth primary surface retained on posterior of some silicide samples from Ala-Tau and Laurel Hills with stable flight morphology. A polygonal net pattern of distribution on the surface characterizes the fissures as contraction cracks (Figs. 3C and 6B). They are usually overlaid with occasional U-shaped grooves or splashes of melt conveyed from ablated anterior (Fig. 7A). The ablation features alter the original pattern of quench texture. This sequence in the formation process of surface morphology suggests that the initial quenching episode was prior to atmospheric entry and antedates secondary heating in the ablation process. Evidence for a secondary quenching episode is present on ablated anteriors (Figs. 1K,L and 7F). The polygonal net pattern of magnetite flow ridges raised on the anterior surface was likely formed when the lower layer of surface melt was squeezed through contraction cracks developed in secondary quenching.

Dumbbell shapes are usually associated with the rotation of completely molten tektite material in null gravity. Centrifugal forces would be expected to divide the liquid sphere at the rotation axis into two proportionally equal opposing parts of the mass. Variations of dumbbell-shaped silicide objects (see Figs. 8A–D) show that some samples have distinctly unequal proportions of mass partitioned by centrifugal forces. This is not consistent with the formation from completely molten material. Samples illustrating progression steps in the evolution of dumbbell morphology (see Fig. 8) suggest that the observed dumbbell shapes were likely acquired by solid objects. They suggest that observed dumbbell shapes developed in the ablation process when droplets of surface ablation melt accumulated at the posterior of rotating solid objects and shifted the center of gravity.

A few samples have parasitic spherules attached. Extruding melt-stream pattern on these samples originates on a parasitic spherule and proceeds on the surface of the host object (Fig. 1H). The retained shape of the parasitic spherule and prominent melt flow illustrate that both objects remained solid during high-velocity atmospheric passage while surface ablation heating continued after the collision.

Variations in ablation rates of tektites were alternately explained by tumbling, higher vaporization due to turbulence (Chen 1975), and wake conditions due to swarm entry (Sepri et al. 1981). Among iron silicide particles of the same size, the oriented samples with the lowest surface area exposure to heat have the highest rate of surface recession (Figs. 6A–D). This indicates that ablation rates depend on the duration of a stabilized stage in flight or tumbling of the object. Morphological variations of iron silicide particles suggest that rapid rotation and tumbling decreased the ablation rate of some spherules (Figs. 3A and 4A) by reducing exposure time of any surface point to ultrahigh temperatures of the air compressed in front of the projectile. Iron silicide spherules with the least signs of ablation most likely preserved the globular shape by rapid rotation and tumbling accelerated by oncoming airstreams.

Occasionally, the surface recession is pronounced even on the samples with missing signs of heat exposure and melt transfer. These particles have patches of granular microtexture (Figs. 9A and 9B). Similar microtextures of protruding phases exposed in the matrix were produced by direct evaporation phenomenon in arc jet ablation experiments on heterogeneous surfaces (Vignoles et al. 2009; Ogasawara et al. 2011). When patches of microtexture formed by evaporation cross contraction cracks uninterrupted, this indicates that the primary quenching episode preceded ablation (Fig. 9B). Features of this kind are closely similar for Ala-Tau and Laurel Hills samples. Iron silicide particles from both locations retain a similar morphological record of various stages in aerodynamic ablation of surface experienced by a decelerating cold solid object at different velocities and temperatures: direct evaporation, rapid volatilization and frothing, transfer of liquid layer, surface recession, and equatorial accumulation of ablation-melt.

Compositional Evidence for Ablation

The diagram of conditions for the Fe–Si system is characterized by the existence of five stoichiometric phases: Fe₂Si (hapkeite), Fe₃Si (gupeiite), Fe₅Si₃ (xifengite), FeSi (naquite), and FeSi₂ (linzhiite). Other phases of iron silicide fall into the category of instability.

Characteristic iron silicide spherules are typically composed as an intergrowth of gupeiite (Fe₃Si) or xiphengite (Fe₅Si₃) with hapkeite (Fe₂Si) or naquite (FeSi) (Tables 1 and 2). The matrix is enclosing an abundance of small (3–10 µm) inclusions of FeSi, Fe₂Si, or FeSi₂ and occasional TiC, SiC as well as unregistered U and Zr silicides (see Tables 4 and 9). Spherule rims are compositionally more diverse
Typical rims are comprised of exterior magnetite or nonstoichiometric wustite shell (1–3 µm) and substratum (10–400 µm) of underlying nonstoichiometric Fe₃Si₂, Fe₇Si₂, and Fe₇Si phases. They form a distinct zonal structure at the periphery of spherules abundant with dendritic SiC (moissanite), (Ti, V, Fe)C (khamrabaevite), TiC, and C inclusions (see Table 5). Iron-rich rim and substratum matrix with (Fe, Ti)₄Si₅, (Fe, Ca, Ti)₅Si₄, (Fe, Ca, Ti)₇Si₇, and other Ca-, Al-, and Ti-enriched inclusions of small size (<30 µm), oversaturated with Si beyond stoichiometry, suggest unmixing of solid solution. The dendritic structure of inclusions indicates quenching (Fig. 12). It should be noted that abundant SiC and TiC carbides on the surface of the spherule require temperatures >2100 K to form. Observed chemical zoning (Table 3, Figs. 10 and 12) is consistent with progressive stages of Si depletion and Fe oxidation (Table 3) shown in experimental work as stages in the thermal decomposition of iron silicide (Novoselova and Bagdasarov 1979). Reported occurrences of submillimeter silicate glass globules in association with silicide spherules are possible evidence for the efficiency in Si separation and loss in flight during the ablation process.
**Interior Composition and Evidence of Heating Episodes**

The complexity of the interior structure of iron silicide spherules is size dependent. This suggests that the extent of heat exposure and corresponding mineral phase transformations increased with particle size.

The typical submillimeter spherules of a most primitive structure are characterized by monosilicide FeSi matrix, alternatively by gupeite (Fe$_3$Si) or xifengite (Fe$_5$Si$_3$), dominating in the assemblage. The spherules are represented as an agglomerate of 3–5 μm globular grains that retain the characteristics of quenched material (Figs. 11A and 11B). A likely process of accretion for this aggregate may be the coalescence of droplets of metallic liquid. With an increase of spherule size (>2 mm), the grains become larger (Fig. 11C; Table 1, #1). The spherules appear as an agglomerate of elongated globules—ichtioglypts (sized 5–30 μm) with interspace filled with abundant micropores (1–3 μm) (Fig. 11D). The difference of coefficients of thermal expansion between cubic and hexagonal phases is likely responsible. The ichtioglypts have a zonal structure. They are composed of Fe$_5$Si or Fe$_5$Si$_3$ core, which encloses poorly individualized white micro-inclusions of monosilicide FeSi enriched with calcium and titanium. The gray peripheral shell of ichtioglypts does not differ compositionally from the latter.

Decomposition of the solid solution increases with spherule size. Chains of small (3–5 μm or 10–20 μm) rounded grains of cubic phase, radiating at a 60° angle, are characteristic for these objects (Figs. 10C, 10F, 11E, and 11F). Along with the increase in spherule size, a partition of the initially homogeneous matrix into iron-rich (Fe$_5$Si or Fe$_5$Si$_3$) and silicon-rich (FeSi) component phases may be observed. By features of stoichiometry, they are consistent with two eutectic phases: hexagonal (Fe$_5$Si$_3$) and cubic (FeSi). The evolution of the droplet agglomerate, as the result of the decomposition of solid solution and recrystallization, may be observed in progression. The sequence of phase transformations is shown in Fig. 11 corresponding to Tables 1 and 2.

a. A chain of trigonal crystals (3–5 μm) with indications of skeletal growth probably inherits the size and composition of the inclusions in the precursor droplets (Fig. 11E; Table 1, #2).

b. Ca- and Ti-rich monosilicides enclosed in the initial droplets are enlarged and pushed to the periphery forming edgings on elongated lens-like inclusions (100–200 μm) (Fig. 11F; Table 1, #3). Meanwhile, their composition experiences variations between the iron-rich (Fe, Ca, Ti)$_4$Si$_4$ and the silicon-rich (Fe, Ca, Ti)$_9$Si$_7$. The difference of coefficients of thermal expansion between cubic and hexagonal phases is likely responsible for micropores. Subsequent structural transformations continue in the following sequence:

c. Needle-shaped phases (30 × 500 μm) (Fig. 11G; Table 2, #1).

d. Large elongated inclusions with elements of rhythmic crystallization (one edge is relatively even while the second edge presents a complex morphology) (Fig. 11H; Table 2, #2).

e. Large skeletal crystals of arrow shape (Fig. 11I; Table 2, #3).

The interior structure of silicide spherules indicates that the subsequent heating conditions for phase transformations, skeletal growth, and recrystallization existed after the original mineral phases were quenched.

The compounds of the quadruple system Fe-Ca-Ti-Si present evidence for the second heating episode. They play a more visible role in the composition of peripheral phases and large particles with extensive signs of melt. Their matrix, oversaturated with silicon beyond stoichiometry, encloses two types of inclusions (Table 3,
The first type is represented by a nonstoichiometric Ca-Si phase with a low iron content (black inclusions of irregular shape). The second type is represented by a triple compound (Fe, Ti)$_4$Si$_5$ (gray phase with micrographic intergrowths). Both types belong to higher silicides, while their compositions fall into an area of instability on the diagram of state. The abundance of nonstoichiometric phases as well as
dendritic SiC, TiC, and (Ti,V, Fe)C carbides, localized in the peripheral zone and on the rim (Fig. 12), suggest that the secondary heating event in the thermal history of the spherules was also interrupted by a subsequent quenching episode.

An association of stoichiometric and nonstoichiometric phases is consistent with complex and extreme conditions of formation. Occasional clusters of concentric or curved fibrous phases (Figs. 10F and 11H) indicate the unequilibrated conditions of crystallization and are similar to morphologies observed in tektites and glass spherules from nuclear test sites (O’Keefe 1966).

The internal structure of spherules suggests that iron silicide objects had experienced two heating events and both were interrupted by quenching. The sequence

| Sample | ATU-02<sup>a</sup> | ATU-03 | LHH-03 |
|--------|---------------------|--------|--------|
| Test   | Inclusion ~Fe<sub>2</sub>Si | Matrix ~Fe<sub>3</sub>Si | Inclusion ~Fe<sub>3</sub>Si<sub>3</sub> | Inclusion ~FeSi | Inclusion ~Fe<sub>3</sub>Si | Matrix ~Fe<sub>3</sub>Si<sub>3</sub> |
| K      | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Al     | 1.09 | 1.85 | 0.41 | 0.73 | 0.14 | 0.24 |
| Si     | 20.09 | 32.4 | 16.3 | 27.3 | 23.7 | 37.9 |
| Ti     | 0.41 | 0.39 | 0.02 | 0.02 | 2.43 | 2.28 |
| Ca     | n.d. | n.d. | n.d. | n.d. | 0.19 | 0.22 |
| Mn     | 0.06 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Fe     | 80.1 | 65.08 | 85.1 | 71.7 | 73.4 | 59.05 |

| Sample | ATU-04 | LHH-04 | ATU-05 |
|--------|--------|--------|--------|
| Test   | Matrix ~Fe<sub>3</sub>Si | Inclusion ~FeSi | Matrix ~Fe<sub>3</sub>Si | Inclusion ~FeSi | Matrix ~Fe<sub>3</sub>Si | Inclusion ~FeSi |
| K      | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Al     | 0.63 | 1.06 | 1.36 | 2.07 | 0.70 | 1.22 |
| Si     | 15.8 | 27.8 | 34.02 | 49.2 | 16.3 | 27.1 |
| Ti     | 0.02 | n.d. | 0.05 | 0.02 | 0.02 | 0.04 |
| Ca     | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Mn     | 0.02 | n.d. | 0.05 | 0.05 | 0.05 | 0.05 |
| Fe     | 85.1 | 70.9 | 66.3 | 48.2 | 85.2 | 71.4 |
| Cr     | 0.13 | 0.12 | 0.56 | 0.47 | 0.10 | 0.09 |
| Zr     | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| U      | 0.05 | 0.01 | n.d. | n.d. | 0.05 | 0.01 |
| Cu     | 0.03 | 0.02 | 0.01 | 0.01 | 0.03 | 0.02 |
| P      | 0.02 | 0.03 | 0.01 | 0.02 | 0.01 | 0.02 |

Mineral-forming major elemental abundances are emphasized in bold.

*Analyses in Table 1 correspond to the following photomicrographs: #1—Fig. 11C; #2—Fig. 11E; #3—Fig. 11F.

*Analyses in Table 2 correspond to photomicrographs: #1—Fig. 11G; #2—Fig. 11H; #3—Fig. 11I.
Table 3. Electron microprobe analyses of peripheral phases in iron silicide spherules.

| Sample | ATU-9 | LHH-08 | ATU-09 | LHH-09 | ATU-10 | ATU-11 | LHH-10 | LHH-11 | ATU-13 | ATU-14 | LHH-12 |
|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| wt%    | 1     | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     | 11     |
| Fe     | 93.67 | 94.37  | 93.27  | 93.98  | 62.86  | 63.76  | 40.42  | 65.45  | 66.87  |        |        |
| Si     | 6.72  | 6.02   | 11.65  | 10.74  | 66.18  | 11.37  | 6.0    | 36.82  | 0.01   | 34.57  | 0.01   |
| Cr     | 0.15  | 0.12   | 0.07   | 0.13   | 0.03   | 0.07   | 0.11   | 0.14   | 0.01   | 0.24   | 0.02   |
| Ti     | n.d.  | n.d.   | 0.04   | 0.05   | 0.02   | 0.06   | 0.02   | 0.15   | n.d.   | 24.83  | n.d.   |
| Ca     | n.d.  | n.d.   | n.d.   | n.d.   | 32.08  | n.d.   | n.d.   | 0.03   | 0.02   | n.d.   | 0.01   |
| Total* | 100.54| 100.51 | 101.09 | 100.19 | 100.0  | 99.59  | 100.11 | 100.0  | 63.8   | 100.0  | 65.49  |

Mineral-forming major elemental abundances are emphasized in bold.

Table 4. Electron microprobe analyses of U inclusions in iron silicide particles

| Sample | ATU-02 | LHH-07 | ATU-08 | LHH-06 |
|--------|--------|--------|--------|--------|
| Test  1 |        |        |        |        |
| ~ (Fe, U, Al, Zr)₅Si₃ | (Fe, Al, U)Si | ~Fe(U, Al)₂Si | ~Fe(U, Zr)₅(Si, P)₂ |
| wt%    | atom%  | wt%    | atom%  | wt%    | atom%  |
| K      | 0.01   | 0.02   | 0.03   | 0.04   | 0.02   | 0.03   |
| Al     | 0.86   | 1.65   | 9.32   | 15.8   | 0.06   | 0.12   |
| Si     | 21.69  | 39.72  | 30.83  | 50.8   | 19.51  | 36.51  |
| Ti     | 0.32   | 0.36   | 0.2    | 0.18   | 0.03   | 0.03   |
| Ca     | 0.03   | 0.06   | 0.58   | 0.65   | 0.01   | 0.01   |
| Mn     | n.d.   | n.d.   | 0.02   | 0.2    | n.d.   | n.d.   |
| Fe     | 57.21  | 52.69  | 31.42  | 26.08  | 62.14  | 58.48  |
| Cr     | 0.03   | 0.03   | 0.04   | 0.04   | 0.06   | 0.07   |
| Zr     | 2.62   | 1.48   | 0.97   | 0.49   | 0.20   | 0.13   |
| U      | 17.28  | 3.73   | 29.28  | 5.7    | 19.05  | 4.21   |
| Cu     | 0.05   | 0.04   | 0.02   | 0.02   | 0.05   | 0.04   |
| P      | 0.13   | 0.22   | n.d.   | n.d.   | 0.22   | 0.37   |
| Total  | 100.23 | 100.0  | 102.71 | 100.0  | 101.35 | 100.0  |

Mineral-forming major elemental abundances are emphasized in bold.

Table 5. Electron microprobe analyses of carbide inclusions in iron silicide particles.

| Sample | ATU-10 | LHH-13 | LHH-11 | ATU-03 | ATU-10 | ATU-11 | ATU-11 | ATU-09 | LHH-07 |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| wt%    | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      |
| K      | n.d.   | n.d.   | 0.69   | 0.07   | 0.01   | n.d.   | 3.11   | n.d.   |
| Al     | n.d.   | 0.07   | 1.38   | 0.74   | 0.33   | 0.45   | 8.60   | 0.05   |
| Si     | 70.0   | 0.94   | 17.29  | 0.23   | 4.98   | 13.27  | 32.98  | n.d.   |
| Ti     | n.d.   | 68.40  | 0.31   | 48.83  | 7.63   | n.d.   | 0.97   | 0.01   |
| Ca     | n.d.   | 0.04   | 0.16   | 0.02   | 0.02   | 36.27  | 1.17   | n.d.   |
| Mn     | n.d.   | n.d.   | n.d.   | n.d.   | 0.01   | 0.02   | 0.02   | n.d.   |
| Fe     | 0.21   | 5.79   | 1.37   | 0.80   | 24.83  | 0.01   | 2.18   | 66.66  |
| Cr     | n.d.   | 0.29   | 0.07   | 0.33   | 0.17   | 0.17   | 0.03   | n.d.   |
| Zr     | n.d.   | 0.52   | 32.34  | 0.16   | 44.50  | 0.02   | 0.02   | 0.03   |
| U      | n.d.   | 0.01   | 0.24   | n.d.   | 3.17   | n.d.   | n.d.   | 0.03   |
| Cu     | n.d.   | n.d.   | 0.02   | 0.03   | 0.04   | n.d.   | 0.01   | 0.03   |
| P      | n.d.   | n.d.   | n.d.   | n.d.   | n.d.   | n.d.   | 0.02   | n.d.   |
| Total* | 70.21  | 76.06  | 53.87  | 51.21  | 85.68  | 50.22  | 48.11  | 66.83  |

Mineral-forming major elemental abundances are emphasized in bold.

*Analyses in Table 4 correspond to photomicrographs: #1—Fig. 11C; #3—Fig. 10C; #4—Fig. 10F.

*Carbon was not analyzed.
of events reflected in the internal structure is consistent with the processes of formation in impact ejecta followed by hypervelocity atmospheric reentry of solid objects quenched in space.

**Assemblage and Associated Minerals**

Besides the described phases of iron silicide, other inclusions would be similarly problematic for geological processes and some of them represent new minerals (Tables 4 and 5). Unregistered minerals are represented by several versions of uranium-bearing silicides (Tables 4 and 9, Fig. 13): (Fe, Al,U)Si, (Fe,U, Al)2Si, (Fe,U, Zr)3(Si,P)2, (Fe,U)4(Si,P), (Fe,U)2Si, and (Fe,U, Al, Zr)2Si3. Unfamiliar minerals are also presented as silicon-rich carbides of aluminum, zirconium, or calcium composition (Table 5, #3, 5, 6, 7 and Table 9). For an object with aerodynamic features, the abundances of U, Zr, and other refractory elements in these mineral phases may seem strange. The composition of some inclusions may seem implausible. However, the accuracy of microprobe identification is demonstrated by X-Ray fluorescence spectrometry.

Fig. 10. Comparison of internal features characteristic for iron silicide spherules. The internal composition of iron silicide spherules from Ala-Tau and Laurel Hills locations reflects a similar metamorphic sequence in unmixing of solid solution. Here the internal phase structure is demonstrated on backscattered electron photomicrographs of samples from both locations and compared at two stages of recrystallization. A) Ala-Tau silicide spherule (ATU-06)* with Fe3Si3 dendritic phases in FeSi matrix. The zonal composition is visible at the edges of the sphere. Large phases of non-stoichiometric (Fe, Ti)2Si4 and Fe3Si2 are bordering edges and are elongated perpendicular to the surface rim composed of FeSi saturated with iron beyond stoichiometry. B) ATU-07 sample demonstrates under increased magnification the internal structure of the core of a sphere similar to ATU-06: dendritic Fe3Si phases in FeSi matrix. The matrix is structured as an agglomerate of 3–5 μm globular phases with occasional 5–10 μm Fe–inclusions, TiC, SiC, and abundant 1–2 μm micropores. Small vesicles at the edges of larger voids of irregular shape suggest that both types of vesiculation were due to the quenching process. C) ATU-08 sample (Table 4, #3) with ~(Fe,U, Al)2Si inclusions and chains of small Fe3Si phases in FeSi matrix belong to an earlier stage in the unmixing of the solid solution than ATU-06 and ATU-07 spherules. D) Structure of the LHH-05 spherule is similar to sample ATU-06. Dendritic Fe3Si phases in FeSi matrix of Laurel Hills sample demonstrate decomposition of an initially homogeneous matrix into iron-rich and silicon-rich components. The zonal composition is emphasized by enlarged non-stoichiometric (Fe, Ca, Ti)2Si4 and Fe3Si2 phases bordering edges perpendicular to the Fe3Si2 rim. Profile of U-shaped meandrine grooves on the surface edges of LHH-05 and ATU-06 shows a similar zonal structure of substratum. E) Dendritic Fe3Si phases and agglomerate of FeSi matrix at the core of the LHH-05 spherule are closely similar to the internal structure observed in the ATU-07 sample. F) LHH-06 sample (Table 4, #4) is similar to the internal structure observed in the ATU-08 spherule. However, a chain of Fe3Si in the FeSi matrix shows phases of smaller size, fibrous silicide phases are thinner and uranium silicide phases ~(Fe,U, Zr)3(Si,P)2 retain dendritic structure suggesting that LHH-06 spherule reflects an earlier stage of decomposition of the solid solution than ATU-08. *Abbreviation in the sample numbering refers to the location: ATU—Ala-Tau, Urals; LHH—Laurel Hills, Holmdel. 

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Fig. 11. The sequence of iron silicide phase metamorphism. Backscattered electron photomicrographs of samples from Ala-Tau and Laurel Hills locations demonstrate the internal structure of iron silicide spherules characterized by unmixing of solid solution and recrystallization. The observed sequence of phase transformations is similar for silicide samples from both locations. Stages in the evolution of silicide phases are shown in progression. A) Primitively structured Ala-Tau spherule (ATU-01) is composed as an agglomerate of 3–5 μm globular FeSi grains with occasional FeSi inclusions and phases of dendritic TiC and SiC in mostly homogeneous FeSi matrix. B) Higher magnification of similar Laurel Hills spherule (LHH-01) reveals the dendritic structure of TiC inclusions indicative of primary quenching. C) Chains of FeSi gray phases in FeSi matrix (Table 1, #1) and white uranium inclusions (Fe, U, Al, Zr)₅Si₃ (Table 4, #1) in Ala-Tau spherule sample ATU-02. Orientation at three directions under 60° angle to each other is characteristic for chains of silicide phases. D) Ca- and Ti-enriched Fe₃Si dendritic phases, isolated in FeSi matrix of 3–5 μm droplet agglomerate with abundant 1–2 μm micropores in Laurel Hills spherule sample LHH-02. The difference of coefficients of thermal expansion between cubic (Fe₃Si) and hexagonal (FeSi) phases is likely responsible for micropores. E) Gray chains of “trigonal” FeSi phases with signs of skeletal crystal growth in Fe₃Si matrix (Table 1, #2) with black rectangular SiC inclusions and dendritic TiC (Table 5, #4) in Ala-Tau spherule sample ATU-03. F) FeSi ichthyoliths with black TiC-, Ca-, and Ti-enriched silicide inclusions and elongated protrusions on uneven edges in Fe₃Si matrix (Table 1, #3) of Laurel Hills spherule sample LHH-03. G) Needle-shaped FeSi phases in Fe₃Si matrix (Table 2, #1) and black TiC inclusions in Ala-Tau spherule sample ATU-04. H) Large elongated FeSi phase in Fe₃Si matrix (Table 2, #2) and fibrous Ti and Si carbide inclusions in a broken fragment of a large Laurel Hills sample LHH-04. I) Large skeletal crystals of FeSi in Fe₃Si matrix (Table 2, #3) with 10–20 μm TiC and SiC inclusions in Ala-Tau spherule sample ATU-05. *Abbreviation in the sample numbering refers to the location: ATU—Ala-Tau, Urals; LHH—Laurel Hills, Holmdel.

(Table 6), analysis of associated minerals (Table 7), consistent X-ray diffraction data (Table 8), repeated test results in various facilities (Table 9), and the close similarity with the data on iron silicide spherules that has been previously reported in mineralogical literature. Ala-Tau samples are in close agreement with spherules from Laurel Hills (Tables 1 and 2; Figs. 3 and 4) and other reported finds. Similarities include such unique features as previously
unknown uranium-bearing silicides and fibrous silicide phases. Common disagreement with thermodynamics should also be noted. TiC and SiC thermodynamically may not coexist with metallic Al (Essene and Fisher 1984). Aluminum would oxidize at temperatures required to form TiC or SiC, while TiC and SiC would decompose at temperatures required to form metallic Al. Identical peculiarities in composition and morphology of iron silicide spherules, found in various geographical locations as well as different geological and stratigraphic settings, suggest that similar and unusual processing is responsible. This will be addressed further in the discussion of formation processes.

The paragenetic mineral complex of iron silicides includes other petrological materials (Tables 6, 7). Limonite nodules (0.2–3 cm) enclosing globules of iron silicide, spinel, alumina, and silicate glass (Fig. 2D) are occasionally found in association with Ala-Tau iron silicide particles. Typical specimens enclose well-defined spherules. Some contain silicide grains with a diffused boundary of high-iron phases indicating partial melt (Figs. 14A and 14C). A possibility of shock-induced heating is supported by the occurrence of samples enclosing brecciated and fragmented grains.

The gradual variation of oxygen depletion between alumina, spinel, and silicate glass is not dependent on the location of phases in the matrix (Table 7). Also noteworthy is a gradual variation in abundances of minor refractory elements between the inclusions. Alumina and spinel are depleted in U, Th, V, Zr, and Ti, unlike enriched silicide grains. Along with the increase in oxidation levels of the inclusions, the grains of alumina, spinel, and silicate glass demonstrate the gradual enrichment in moderate temperature elements, such as Na and K, non-measurable in silicides. Affinities of spinel may only partially explain this pattern since its minor element composition is closely correlated with trace elements in alumina, which does not share these affinities. The minor element trend suggests that iron silicide spherules were formed at much higher temperatures than alumina and spinel, contrary to what may be expected given the thermodynamics of these minerals.

Magnetite in globular and splash forms represents another type of associated material. This type is an aggregate of magnetite, hercynite (iron spinelid), and a fine dispersion mixture of iron silicides, silicate glass, spinel, and alumina (Table 7, Fig. 14D). Phases of the magnetite matrix correspond to the transitional member of an isomorphic series: magnetite (FeFe₂O₄)—hercynite (FeAl₂O₄). Silicate glass spherules with dendritic iron phases in the matrix of magnetite-spinelid are likely a melt product of iron silicide. The splash-form spinelid samples suggest a shock-melt version of the silicide-bearing assemblage.

The assemblage of the iron silicide mineral complex is indicative of the extreme conditions of formation in an ultrahigh-temperature event. It is also consistent with the common paragenetic conditions of an unusual formation process, which is likely responsible for all iron silicide spherules with aerodynamic features that were reported occurring in various stratigraphy.

Isotopic and Chemical Evidence for a Shock Event

The analyses of U/Pb isotopic composition have shown that the Ala-Tau samples of iron silicide spherules are characterized by unusually high uranium abundances (up to 129 ppm), low radiogenic lead concentrations (0.5–6.8 ppm), and age values of 1.21 (±0.16)–3.14 (±0.2) × 10⁹ years (Table 10). The tests had revealed that the isotopic composition of Pb is heterogeneous (Fig. 15). A comparative analysis of leach step fractions has shown that the isotopic composition of Pb is substantially different in HBr and HNO₃ solutions with values far exceeding the margin of error. The measurements of leach step fractions differ from the bulk composition and are far more radiogenic. A more concise assessment of Pb isotopic composition was not accomplished, considering that the radiogenic lead represents 8 (±4)% to 12(±8)% of Pb, which constitutes approximately 0.06% total wt% of Pb in the sample. Attempts to establish further details of the U/Pb isotopic history of specimens had failed so far due to low abundances of relict Pb (44.4 ppb) and the relatively small size of particles subjected to acid treatment. However, initial measurements of Pb isotopic composition in solid residue, remaining after stepwise acid treatment, have revealed values on the mixing line of the Canyon Diablo troilite—a standard for meteoritic Pb (Fig. 15).

Although incomplete, the assessments of U/Pb isotopic composition are consistent with an ultrahigh-temperature heating event reflected in the composition of the gas. The gas release tests of iron silicide particles, carried out at the preliminary stage of noble gas analysis at the Vernadsky Institute, have established that the atmospheric component is not manifested in the composition of volatiles: H₂—22.53, H₂O—41.94, C₂—C₃H₄=0.72, CO—32.54, CO₂—0.43, N₂—1.07, O₂—0.01, H₂S—0.0, SO₂—0.01; H/C = 3.8, N/C = 0.060. The gas composition reflects highly reducing conditions. The concentration of volatiles, abnormally low by any standard (1.71 ncm⁻³ g⁻¹), suggests that the particles have experienced an episode of severe degassing. Very low abundances of noble gases (He—4.1 × 10⁻⁶ cm³ g⁻¹; Ar—3.4 × 10⁻⁷ cm³ g⁻¹) are particularly notable.
Fig. 12. Backscattered electron photomicrographs of peripheral zoning of iron silicide spherules from Ala-Tau and Laurel Hills locations. High iron nonstoichiometric silicide matrix, dendritic phases of khamrabaevite, graphite, TiC and SiC carbides, magnetite and cohenite rim. A–D) Ala-Tau samples. E, F) Laurel Hills samples.

Fig. 13. Variations of U-enriched inclusions in silicide spherules. Backscattered electron photomicrographs correspond to test results 1–5 in Table 9: A—ATU-12; B—ATU-13; C—ATU-14; D—LHH-08.

Fig. 14. Backscattered electron photomicrographs of materials associated with Ala-Tau iron silicide spherules. A) Silicide spherule (white phase) enclosed in limonite relict of the matrix displaying features of possible shock metamorphism. B) Silicate glass spherule with phases of spinel, enclosed in limonite matrix. C) Silicide inclusion (white phase) with features of shock metamorphism in limonite matrix. D) Silicate glass spherule with dendritic iron phases in the matrix of magnetite/spinelid particle, which is likely a metamorphic product of silicide-bearing material.
Departures from Terrestrial Isotopic Norms

The examined Ala-Tau iron silicide spherule with a mass of 184.65 mg has yielded a composition of helium isotopes as $^{3}$He/$^{4}$He = 7.57 ± 1.1 × 10⁻⁶ and concentration of $^{4}$He = 4.06 ± 0.19 × 10⁻⁸ cm⁻³ g⁻¹ (Table 11). Unlike siliceous material of terrestrial impact origin, such as tektites and impact glasses, the $^{3}$He/$^{4}$He ratio for silicide sample ($7.57 ± 1.1 × 10⁻⁶$) is substantially higher than expected for terrestrial atmosphere (1.3–1.4 × 10⁻⁶; Clarke et al. 1976). $^{3}$He/$^{4}$He ratio of silicide sample is also significantly distinct from the range for IDPs (2.5–3.5 × 10⁻⁴; Nier and Schlutter 1992) and from the variety of He patterns for extraterrestrial materials of any kind. An estimate of feasible accumulation of radiogenic $^{4}$He in situ ($1.355 × 10⁻⁸$ cm⁻³ g⁻¹) shows that U and Th decay would be insignificant to account for the concentration of radiogenic $^{4}$He (4.06 ± 0.19 × 10⁻⁸ cm⁻³ g⁻¹) considering the young U/Pb age of the sample and U abundance (59 ppm). A contribution from an extraterrestrial component may not be excluded. However, a complex fractionation of precursor material in an ultrahigh-temperature heating event is a more likely explanation.

Departure from atmospheric norms is also evident in Ar isotopic composition (Table 12). The value of $^{40}$Ar/$^{36}$Ar—325.92 does not support extraterrestrial origins. Yet, the Ar pattern of silicide spherules exceeds the atmospheric norm ($^{40}$Ar/$^{36}$Ar = 295.5; Nier 1950). This may not exclude an admixture of a component with high radiogenic $^{40}$Ar. It should be noted that meteorites have demonstrated a high concentration of radiogenic $^{40}$Ar due to their age and accumulations as the result of K decay. Neither the young age of silicides nor the lack of K in the composition is consistent with excess in the accumulations of $^{40}$Ar. Whether or not the departure from atmospheric norms in the $^{40}$Ar/$^{36}$Ar ratio can be considered to reflect a contribution from an extraterrestrial component may not be excluded. However, a complex fractionation of precursor material in an ultrahigh-temperature heating event is a more likely explanation.

Table 6. X-ray fluorescence spectrometry.

| wt% | 1       | 2       | 3       | 4       | 5       | 6       |
|-----|---------|---------|---------|---------|---------|---------|
| Si  | >10     | >10     | >10     | >10     | >10     | 2.5     |
| Al  | 0.3     | 0.3     | 0.3     | 0.3     | 0.3     | 0.2     |
| Mg  | 0.02    | 0.015   | 0.02    | 0.015   | 0.02    | 0.01    |
| Fe  | >10     | >10     | >10     | >10     | >10     | >10     |
| Ti  | 0.1     | 0.2     | 0.15    | 0.1     | 0.6     | 0.1     |
| Mn  | 0.08    | 0.03    | 0.1     | 0.08    | 0.2     | 0.01    |
| ppm | V       | 2000    | 600     | 500     | 150     | 2000    |
|     | Cr      | 1000    | 800     | 500     | 600     | 800     |
|     | Co      | 80      | 60      | 60      | 60      | 100     |
|     | Ni      | 500     | 500     | 600     | 500     | 800     |
|     | Zr      | 250     | 150     | 200     | 200     | 250     |
|     | Mo      | 15      | 25      | 25      | 30      | 40      |
|     | Pb      | 8       | 8       | 10      | 6       | 10      |
|     | Cu      | 30      | 60      | 100     | 100     | 500     |
|     | Ge      | 30      | 10      | 3       | 20      | 25      |
|     | Ga      | 6       | 2       | 5       | 5       | 5       |
|     | Ni/Co   | 6.25    | 8.3     | 10      | 8.3     | 8       |
|     | Ge/Ga   | 5       | 10      | 5       | 5       | 5       |

Table 7. Electron microprobe analyses of magnetite and limonite particles associated with Ala-Tau iron silicide spherules.

| wt% | Na   | K   | Ca  | Mg   | Al   | Si   | Ti   | Fe   | Mn   | Cr   | Oa  | Total |
|-----|------|-----|-----|------|------|------|------|------|------|------|-----|--------|
| 1   | 0.06 | 1.50| 3.10| 0.95 | 7.48 | 56.82| 0.16 | 14.14| 0.13 | n.d. | 15.67| 100.0 |
| 2   | 0.06 | 1.18| 2.10| 0.93 | 7.25 | 44.06| 0.13 | 27.19| 0.12 | 0.08 | 16.90| 100.0 |
| 3   | n.d. | 0.01| 0.02| 0.73 | 5.91 | 0.16 | 0.23 | 64.38| 0.09 | n.d. | 28.47| 100.0 |
| 4   | 0.07 | 0.01| 0.02| 1.24 | 5.47 | 0.13 | 0.20 | 64.20| 0.12 | n.d. | 28.55| 100.0 |
| 5   | 0.04 | n.d. | n.d. | 0.35 | 3.15 | 0.30 | 0.19 | 67.57| 0.02 | 0.02 | 28.36| 100.0 |
| 6   | 2.67 | 3.43| 0.70| 0.08 | 6.18 | 65.19| 0.17 | 10.51| 0.01 | n.d. | 11.76| 100.7 |
| 7   | 0.10 | 0.04| 0.01| 0.03 | 32.62| 25.23| 0.30 | 8.11 | n.d. | n.d. | 33.36| 100.0 |
| 8b  | 0.71 | 3.55| 0.32| 0.29 | 7.89 | 53.62| 0.73 | 6.74 | 0.02 | n.d. | 26.14| 100.0 |
| 9b  | 0.63 | 3.25| 0.34| 0.37 | 7.78 | 57.64| 0.71 | 6.12 | 0.02 | n.d. | 23.16| 100.0 |
| 10  | n.d. | 0.05| n.d. | 1.34 | 9.08 | 0.13 | 0.71 | 58.28| 0.06 | 0.05 | 30.31| 100.0 |
| 11  | n.d. | 0.02| n.d. | 1.28 | 9.53 | 0.09 | 0.66 | 59.03| 0.03 | 0.03 | 29.33| 100.0 |
| 12  | n.d. | 0.02| n.d. | 1.20 | 8.30 | 0.11 | 0.68 | 59.65| 0.05 | 0.05 | 29.94| 100.0 |
| 13  | n.d. | n.d. | n.d. | 5.90 | 29.59| 0.19 | 0.14 | 30.69| 0.43 | 0.14 | 32.93| 100.0 |
| 14  | n.d. | 0.02| n.d. | 1.79 | 17.59| 0.24 | 0.88 | 47.96| 0.37 | 0.07 | 31.08| 100.0 |

Mineral-forming major elemental abundances are emphasized in bold.

*Matrix with fine dispersion mixture of silicate glass and iron silicides.

O2 Matrix is computational (was not analyzed).
### Table 8. Interplanar distances.

| I   | d/n | Pascual 1989 | Novoselova 1979* | FeSi (ASTM, 1966) | Fe$_2$Si$_3$ (ASTM, 1966) |
|-----|-----|--------------|------------------|-------------------|--------------------------|
| 6   | 3.34| –            | –                | –                 | –                        |
| 24  | 3.17| 23           | 3.17             | 15                | 3.16                     |
| 20  | 2.59| 14           | 2.59             | 10                | 2.59                     |
| 6   | 2.36| 2            | 2.36             | –                 | –                        |
| 6   | 2.32| 3            | 2.31             | –                 | –                        |
| 15  | 2.24| 10           | 2.24             | 5(8)              | 2.24 (2.25)              |
| 5(12)| 2.18| –            | –                | –                 | 60                        |
| 5   | 2.13| 3            | 2.13             | (30)              | 2.14                     |
| 7   | 2.05| 9            | 2.03             | –                 | –                        |
| 100 | 2.01| 100          | 2.00             | 100               | 2.00                     |
| 20(46)| 1.994| –            | –                | –                 | 90                        |
| 8(15)| 1.938| 3            | 1.94             | (25)              | 1.94                     |
| 52  | 1.834| 56           | 1.83             | 60                | 1.83                     |
| 6   | 1.496| 3            | 1.49             | –                 | –                        |
| 10  | 1.355| 7            | 1.35             | 15 (10)           | 1.35 (1.37)              |

*Data of the authors are for Ala-Tau samples. Asterisked columns present combined data for magnetic and non-magnetic fractions. Data for magnetic fraction is in the parenthesis. Characteristic lines are in bold.

### Table 9. Variations of U- and Zr-enriched inclusions of iron silicide spherules (wt%).

| Sample  | ATU-12 Fe(U)$_4$(Si,P) | ATU-13 Fe(U)$_5$Si | ATU-14 Fe(Zr)$_3$Si | ATU-14 Fe(U)$_2$Si | LHH-08 Fe(U)$_2$Si$_2$ | LHH-09 Fe(Zr)$_3$Si$_2$ | LHH-09 Fe(Zr)$_6$Si | LHH-10 Fe(U)$_2$Si$_2$ |
|---------|------------------------|---------------------|---------------------|---------------------|------------------------|------------------------|----------------------|------------------------|
| Si      | 5.95                   | 11.74               | 20.67               | 11.19               | 4.72                   | 16.27                  | 7.91                 | 8.28                   |
| Ti      | n.d.                   | n.d.                | 1.17                | n.d.                | 6.92                   | 1.22                   | 9.7                  | n.d.                   |
| Al      | n.d.                   | n.d.                | 0.45                | n.d.                | 0.18                   | 0.05                   | 0.46                 | n.d.                   |
| Cr      | n.d.                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| Fe      | 44.27                  | 47.97               | 51.98               | 36.51               | 31.57                  | 62.74                  | 54.37                | 35.45                  |
| Ca      | n.d.                   | n.d.                | 1.35                | n.d.                | n.d.                   | 0.67                   | n.d.                 | n.d.                   |
| P       | 1.56                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| C       | n.d.                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| S       | n.d.                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| V       | n.d.                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| Zr      | n.d.                   | 1.49                | 15.62               | n.d.                | 23.98                  | 17.23                  | 23.23                | n.d.                   |
| Nb      | n.d.                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| Ce      | n.d.                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | 3.2                    |
| Nd      | 1.8                    | n.d.                | 0.98                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| W       | n.d.                   | n.d.                | n.d.                | n.d.                | n.d.                   | n.d.                   | n.d.                 | n.d.                   |
| U       | 48.22                  | 37.4                | 4.43                | 48.63               | 4.64                   | 1.82                   | 4.06                 | 53.07                  |

Mineral-forming major elemental abundances are emphasized in bold.
distinct from typical values for trapped argon in meteorites, this ratio may not be useful for identification. In contrast to measurements obtained for noble gases, test results representative for Rb/Sr isotopic composition of Ala-Tau iron silicide spherules are clearly distinct from terrestrial norms (Table 13). The concentrations of Rb—0.0266 ppm and Sr—4.44 ppm are very low. The $^{87}$Rb/$^{86}$Sr—0.0174 ratio is substantially lower than may be expected for crustal or igneous terrestrial material. Although this should not be taken as an indication of extraterrestrial origin, the present-day $^{87}$Sr/$^{86}$Sr—0.700181 ratio is comparable to meteoritic values, particularly characteristic for achondrite. A contribution to Rb/Sr composition from precursor material with an inherited link to an extraterrestrial reservoir may not be excluded. More likely, the isotopic ratios may have been disturbed by selective volatilization. The abundances of Rb, very low by any standard, indicate thermal fractionation. The selectivity of chemical differentiation in an ultrahigh-temperature heating event and highly reducing conditions may be responsible for Rb/Sr isotopic

Table 10. U/Pb isotopic composition of Ala-Tau iron silicide spherules.

| Analyses  | Pb (ppm) | U (ppm) | $^{207}$Pb/ $^{206}$Pb | $^{206}$Pb/ $^{204}$Pb | $^{208}$Pb/ $^{204}$Pb | Age (10$^3$y) | K |
|-----------|----------|---------|------------------------|-----------------------|-----------------------|----------------|---|
| ATU-15    | 6.84     | 59.7    | 550                    | 18.262                | 15.620                | 314            | 9.88 |
| ATU-16    | 0.52     | 126.1   | 15313                  | 18.554                | 15.65                 | 38.389         | 158 |
| ATU-17    | 1.58     | 81.3    | 3279                   | 18.567                | 15.669                | 38.465         | 188 |
| ATU-18    | 1.19     | 61.1    | 3254                   | 18.564                | 15.636                | 38.366         | 121 |

Table 11. He isotopic composition of Ala-Tau iron silicide spherule ATU-19.

| $^3$He, cm$^3$ $\times 10^{-14}$ | $^4$He, cm$^3$ $\times 10^{-9}$ | $^3$He, cm$^3$ g$^{-1}$ $\times 10^{-13}$ | $^4$He, cm$^3$ g$^{-1}$ $\times 10^{-18}$ | $^3$He/$^4$He $\times 10^{-6}$ |
|-------------------------------|-----------------------------|---------------------------------|--------------------------------------|----------------------------|
| 5.67 ± 1.06                   | 7.49 ± 0.36                 | 3.07 ± 0.57                     | 4.06 ± 0.19                          | 7.57 ± 1.1                |

Blank at $t = 1500 ^\circ C$: $^4$He = $4.6 \times 10^{-10}$ ± 1.4; $^3$He/$^4$He = $1.25 \times 10^{-6}$ ± 0.21.

Fig. 15. Pb isotopic composition of iron silicide particles. The curves of Pb evolution: CHUR—chondrite model, DM—depleted mantle, Crust—terrestrial crust. The composition of Pb in HBr and HNO$_3$ leach steps is indicated. The slopes of the straight lines correspond to mixing lines of the initial composition of chondrites and Canyon Diablo standard for meteoritic Pb. The obtained values of Pb composition in solid residue are shown on the mixing line of meteoritic standard. An ellipse around the Restite indication shows the margin of error. Abundances: HBr: Pb = 1450 ppb; HNO$_3$: Pb = 3.9 ppb; Bulk: U = 59,670 ppb, Pb = 6840 ppb; Solid residue: U = 3160 ppb, Pb = 44.7 ppb.
composition due to the significant difference in thermodynamics and temperatures of volatilization for rubidium and strontium.

Contrary to the $^{87}$Sr/$^{86}$Sr ratio for silicide spherules, their Nd isotopic composition with the value of $\epsilon_{\text{Nd}} - 11.8$ is a clear signature of a precursor in the continental crust (Table 14). The $^{143}$Nd/$^{144}$Nd test results (0.512034–0.5124; Voitkevich 1983). However, neither the young sediments nor conventional tektites have a $^{147}$Sm/$^{144}$Nd ratio as low (0.06357). Sm/Nd system is a sensitive indicator of fractionation in the light lanthanide elements. A very low $^{147}$Sm/$^{144}$Nd ratio is indicative of the system being strongly fractionated and disturbed, likely in an impact event.

Since the outer electron shells of rare earth elements have an identical configuration, they may be expected to behave quite similarly. Lack of uniformity in REE composition between samples of iron silicide spherules and a wide range between patterns of REE abundances are consistent with strong fractionation (Table 15). Contents of light lanthanide elements of samples ATU-24 and ATU-25 are closely similar to expected for sandstone and are significantly more depleted in heavy lanthanides. REE composition of sample ATU-26 is far more depleted in Ce, Nd and approach chondrite norms in depletion of La, Sm, Eu, Gd, Dy, Er, Yb, and Lu. Negative Eu anomaly in all silicide samples (0.033–0.009) is more pronounced than Knorm (0.05802) — REE contents in chondrites (Evensen et al. 1978). Such variability in REE composition is indicative of extreme conditions of formation.

Isotopic compositions of iron silicide objects and tektites are distinct. While the isotopic values for silicate glass tektites are indistinguishable from the norms for the upper crust sediments, the isotopic compositions of iron silicide objects demonstrate varied departures from the terrestrial norms. However, the principle chemical and petrological distinctions suggest that in view of the differences in the conditions of processing any greater isotopic similarity should not be expected. Among the major differences in processing between the iron silicide objects and tektites may be their formation under reducing conditions of the substantially higher temperatures, which involve processes of thermal fractionation that may reflect in the isotopic compositions.

**Origin**

The reported finds provide hardly any reason to question IMA approval of silicide spherules as natural minerals, considering predominant occurrence in hard sediments, significant burial depths, remote locations, and undisturbed geological settings of identical specimens with aerodynamic characteristics. Their geological settings mostly as inclusions in the solid matrix of sedimentary rocks reliably exclude technogenic origin. In particular, occurrences of silicide spherules as hard rock inclusions in Lower Cambrian limestone of Sayan Mountains—at a depth of 330 m, in Miocene gypsum of Koshava mine—at a depth of 290 m, in Ordovician silstone of Manitard ridge—at a depth of 82 m, in Miocene limestone of Crimea—at a...
depth of 64 m, in Devonian sandstone of the Chusovaya River basin—at a depth of 71 m, in Permian red shale of Fore-Sudetic monocline—at depths in excess of 657 m are hardly examples in favor of technogenic provenance. A probability of contamination is excluded by the recovery of the specimens from the matrix of solid drill cores and the rock samples obtained from the sidewalls of the mine galleries. Identical composition and aerodynamic ablation morphology of iron silicide spherules, found in alluvial placer deposits, indicate that they share similar origins despite different geological settings. The silicide distribution area of 2 × 4 km at a 90 m burial depth in Eocene sandy-clay sediments of North Azov coastland, or 50 km range of silicide deposits in Cretaceous alluvial sediments of the Isfara River basin exclude technogenic origin by considerations of burial depth and geographic scale alone. Close compositional and morphological similarities of Ala-Tau or Laurel Hills iron silicide spherules with other reported finds suggest similar origin. Recovery of Ala-Tau samples in the undisturbed natural environment of a remote unpopulated region does not set this find apart from other reported occurrences of silicide spherules.

Characteristic ablation morphologies of iron silicide spherules are hardly consistent with conditions of an industrial oxidation-reduction exchange process. Aerodynamic ablation features cannot be reproduced on the molten droplets of a metallurgical product or slag. Formation of equatorial flanges, ring waves, or eccentro-radiating flow lines can unambiguously be ascribed to atmospheric entry only. Metallurgical processes cannot be responsible for the selective loss of surface mass observed on silicide spherules or account for the equatorial flange sculpturing. Besides a specific set of extreme conditions, exclusive for hypervelocity atmospheric entry, the formation of ablation morphologies requires a solid surface of a cold projectile for prerequisite melt-flow transfer and heat removal. Chemically inert properties of iron silicide confirm that the observed meandrine grooves, hemispherical pits, and surface rim belong to a list of ablation features as well. Ablation textures, associated with turbulent atmospheric deceleration, are among aerodynamic features that require a solid surface to form and cannot be mimicked on melt droplets, whether the latter are technogenic or natural.

Do iron silicide spherules bear any resemblance to technogenic artifacts at all? Silicide finds in the pre-industrial age do not qualify as industrial products. Particularly, before the introduction of an electric arc furnace, producing silicides of a grade higher than Si–15 wt% in a blast furnace was impossible (Greiner et al. 1933). Impurities in the production of calcium carbide (CaS, Ca₃P₂, Al₂O₃, SiO₂, SiC), invoked by Spencer (1935) to explain silicide occurrences without due examination, have not included iron silicide and were removed by technological requirements during the production process (White 1928; Gasik 2013). Synthetic iron silicides, manufactured widely since the 1950s, are homogeneous equilibrated materials distinct from heterogeneous composition and complex petrology of iron silicide spherules occurring in natural settings. The differences encompass broad assemblage of silicide and carbide mineral species, zonal structure, and association of stoichiometric with non-stoichiometric phases—compositional characteristics alien to synthetic silicide products. Considering that atmospheric entry heating promotes kinetically controlled metamorphic reactions and melting far removed from equilibrium, principal compositional differences between synthetic and naturally occurring silicides are inevitable. Heating and cooling rates of aerodynamic ablation are far more extreme than conditions for thermal metamorphism in synthetic silicide production. A variety of previously unknown U-silicides as well as Al and Zr carbides, characteristic for iron silicide spherules, are not included in the composition of any technogenic ferrosilicon or synthetic uranium silicides. Production of synthetic reduced materials of any kind cannot account for departures from terrestrial isotopic norms (⁸⁷Rb/⁸⁶Sr—0.0174; ³⁷Sr/³⁶Sr—0.700181; ⁳⁷He/⁴He—7.57 × 10⁻⁶; ⁴⁰Ar/³⁶Ar—325.9) observed in iron silicides with aerodynamic morphological features. U/Pb isotopic dating of Ala-Tau specimens (1.21±0.16–3.14 ±0.2) × 10⁵ yr) as well as stratigraphic ages of identical samples from hard rock sediments in other locations contradict anthropogenic origin.

Four decades after iron silicide spherules found in alluvial sediments of Yunshan River were examined by the IMA CNMMN and were registered as new minerals, there are still no particular reasons to disagree with the IMA opinion on the natural origins of iron silicide spherules with aerodynamic ablation features.

Can silicide particles represent endogenic products? Upper crustal REE composition excludes endogenic origin for iron silicide spherules. Isotopic composition of ⁱ⁴³Nd/ⁱ⁴⁴Nd (0.512034) and ¹⁴⁷Sm/¹⁴⁴Nd (0.06357) does not support magmatic provenance, and neither do departures from terrestrial isotopic norms in Rb, Sr, He, and Ar composition. Igneous processing cannot account for the close similarity in high-U abundances between samples from different locations. Crustal U/Pb composition and isotopic dating also do not offer support to an endogenic origin. Aerodynamic ablation morphologies contradict endogenic origin as well. Igneous melt products cannot mimic aerodynamic
ablation features for reasons already mentioned. Besides, atmospheric entry heating is characterized by ultrahigh heating and cooling rates in a much more severe regime of thermal metamorphism compared to volcanic rocks.

However, luobusaite (Fe$_{0.83}$Si$_2$) aggregates found in ophiolitic rocks of Luobusa mine (Qusong county, Tibet) suggest that occasionally highly reduced minerals of magmatic provenance may include silicides. These 0.1–0.2 mm irregular-shaped interstitial inclusions in chromitite compose an intergrowth with sulfides, arsenides, and alloys of Ir-Fe, W-Co, Ni-Fe, Cr-C, Ti-N (Bai et al. 2006). Associations of this kind indicate that Tibetan luobusaite experienced distinctly different processing than iron silicide spherules occurring in sedimentary rocks. Significant compositional, morphological, and petrological differences between iron silicide spherules with aerodynamic ablation features and singular finds of silicide in igneous rocks place these minerals in separate genetic categories and characterize their provenance as distinct and mutually exclusive.

The close similarity in chemical composition, morphology, petrology, and mineral associations clearly indicates a paragenetic link between all iron silicide spherules and meteorite inclusions or concentric fibrous phases of Ti and Si carbides, confirm their interrelation. Correspondence in these and other idiosyncratic properties certifies that iron silicide spherules were formed by similar processing under analogous conditions and were repeatedly deposited in different geographic regions during various geological times.

A variety of aerodynamic morphologies and surface textures indicate that iron silicide spherules have experienced ablation in the atmospheric deceleration process. The ablation heating is confirmed by the quenched interior structure with the zonal composition of periphery retaining sequences of metamorphic stages in the thermal decomposition of solid solution. Interior phase transformations and exterior surface features characterize silicide spherules as hypervelocity projectiles. In particular, the presence of flanged button-shaped morphology, ring waves, and eccentric-radiating ridges provides unequivocal evidence that iron silicide spherules are a distal ejecta product of meteoritic impact. These aerodynamic ablation morphologies, previously examined in arc jet ablation experiments on australite tektite and meteorite models (Chapman et al. 1962; Shepard et al. 1965), are generally accepted as conclusive evidence for hypervelocity atmospheric entry from space.

Possible Formation Processes

Several feasible formation processes have to be considered. (1) Silicides may form by reaction with carbon at $T > 2100$ K. (2) An oxidation–reduction exchange process can form iron silicide in the absence of reducing agents, provided pressure ($>75$ GPa) and ultrahigh temperatures ($>3700$ K) (Yakovlev et al. 1992). (3) Condensation of iron from vapor stage with a C/O abundance ratio higher than unity would produce silicides (Lattimer 1982).

If carbon could have been a reducing agent that defined the composition in impact interaction, then iron silicide spherules from various geographic locations would display considerable regional compositional differences. In the absence of these differences, the process is unlikely. The similarity in idiosyncratic features of silicides, including common U abundances that would be aberrant to any local conditions, makes this process even less likely.

The experimental works on impact interaction have demonstrated serious constraints for silicide formation in a shock-melt (Yakovlev et al. 1992). These experiments have shown that an impact of an iron projectile with a siliceous target at a velocity ~6 km s$^{-1}$, shock compression $>75$ GPa, and $T > 3700$ K vaporizes only 1.3% of the combined mass. The oxidation–reduction process in the shock-melt at these conditions was limited to trace amounts of material in the zone of immediate contact between the target and the projectile. It was also revealed that the exchange reaction in the shock-melt releases oxygen from the siliceous target and promotes oxidation of the metallic projectile. For example, $2\text{Fe} + \text{SiO}_2 = 2\text{FeO} + [\text{Si}]$ or $4\text{Al} + 3\text{SiO}_2 = 2\text{Al}_2\text{O}_3 + 3\text{Si}$ (Jammes et al. 1983; Lavrukhina et al. 1984; Schultz and Crawford 1987; Yakovlev et al. 1991).

This implies that an impact melt with negligible volatilization of the target material could not have produced iron silicide. It is even less probable that the close compositional similarities between iron silicide spherules from different geographic locations and of various geological ages could have formed under these conditions. Ultrahigh-temperature fractionation is most likely responsible to account for the observed idiosyncratic elemental accumulations and departures from isotopic norms (Badjukov and Petrova 1993). The processes, which would provide the necessary chemical fractionation, require selective vaporization and recondensation of the volatilized target material.

It should be noted that impact ejecta is not a closed system and no compositional similarity to precursor material should be expected (Nagel et al. 1975). Formation from terrestrial sediments through impact and recondensation is supported by a report of iron
The study of the unique ultrahigh-temperature lightning strike fusion material demonstrated the feasibility for considerable scavenging of refractory elements from highly reduced target materials in a hyperthermal event. Major and minor element composition did not inherit any traceable characteristics from its source in local material due to selective volatilization and ultrahigh-temperature fractionation.

The studies of ejecta from nuclear explosions may provide an approximation of conditions in the ejecta from explosive meteoritic impacts (Jones and Sanford 1976). Explosion at $2.1 \times 10^{25}$ erg produces a fireball with low-density gas ($\sim 4 \times 10^{-5}$ g cm$^{-3}$). This cloud with temperatures exceeding 3500K reaches an altitude of 40 km in 60 s. The ejected material is present in the cloud as vapor, rapidly vaporizing liquid in fine dispersion-state and melting solid fragments up to 7 cm in diameter. Selective volatilization of low and moderate temperature fraction continues while subsequent cooling of the cloud leads to selective recondensation of high-temperature components (Yakovlev and Parfenova 1982). Two variations of impactites enriched in high-temperature elements are accordingly produced at this stage. For products of meteoritic impact ejecta, similar processing would suggest a probability for additional complexity of isotopic composition. Considering the presence of solid residual particles of precursor material in the impact ejecta cloud, neither selective vaporization nor thermal fractionation can totally exclude a possibility for the admixture of an isotopic component from extraterrestrial precursor to impactite. Large impact event capable of ejecting material beyond the atmosphere would correspondingly present more complex and extreme conditions.

The internal structure of iron silicide spherules, indicative of accretion through the coalescence of 3–5 μm droplets, is consistent with recondensation processing. Their observed compositional contradictions to expected thermodynamics would be reconciled and are strongly in favor of C-type recondensation (Lattimer 1982). Some samples are layered in a condensation sequence expected for C-rich gas. For example, moissanite globules, found in association with silicide spherules in Fergana, have SiC core, C mantle, and Fe$_3$C shell (Nikolayeva and Shabanin 1971). All other samples are an aggregate of minerals consistent with a much longer temperature range of C-type condensation.

It should be noted that the condensation sequence depends strongly on the state of oxidation of the initial gas. Condensation sequences for gas with a C/O abundance ratio higher than unity (C/O = 1.2, $p = 10^{-3}$) predict the formation of minerals in the following order: TiC (1893 K), SiC (1742 K), C (1732 K), Fe$_3$C (1463 K), AlN (1390 K), CaS (1385 K), FeSi (1326 K), Al$_2$O$_3$ (1235 K), MgAl$_2$O$_4$ (1229 K; Lattimer 1982). Major and minor element composition of iron silicide mineral complex is in close agreement with the 1893–1154 K range of uninterrupted condensation sequences for carbon-dominated vapor. For example, Ti and Si carbides predicted to condense first, have the highest concentrations of V and Zr in the assemblage, while the lowest concentrations are in the Al$_2$O$_3$ and MgAl$_2$O$_4$ phases. Alumina and spinel demonstrate gradual enrichment in moderate temperature elements, such as Na and K, non-measurable in silicide phases. Fe and Al minerals, which are predicted to cross the condensation range of uranium, have unusually high U abundances. However, U enrichment of these silicide phases is consistent with the expected condensation sequence for FeSi and Al. The shape and size of the original 1–3 μm globular U-silicide phases are not in contradiction to condensation rate or to origin in the gas plume of upper crustal ejecta. Essene and Fisher have shown that due to recondensation, the enrichment of refractory elements in the examined products of a unique ultrahigh-temperature lightning strike was elevated in the abundances by orders of magnitude, compared to the source material (Essene and Fisher 1984).

Compared to minerals expected to form at higher temperatures, FeSi phases show much higher abundances of Al and Ca, as predicted by proximity to condensation temperatures for these elements (Al-1390K, Ca-1385K). The difference in Fe and Ni condensation temperatures for high carbon gas may account for low Ni in silicides. Condensation rate of iron and abundance of kamacite during accretion at lower temperatures would result in iron matrix enclosing globules of the minerals formed earlier. The petrology of limonite nodules associated with iron silicide spherules is consistent with this order of condensation and accretion. C/O abundance ratio shown by the gas release tests of iron silicide spherules is also in agreement with expected conditions.

Formation through recondensation of ejecta vapors is possible and is closely corresponding with the observed characteristics. Consistency with the thermodynamic pattern of C-type condensation on a long range of expected condensation sequences can hardly be explained by any other process.

**CONCLUSIONS**

The support from new data on silicides for the IMA CNMMN opinion regarding gupeite and xifengite is limited. Principal compositional and isotopic
inconsistencies with known extraterrestrial materials do not agree with an extraterrestrial origin. Isotopic composition and REE content suggest that the precursor material of iron silicide spherules is of terrestrial provenance in upper crust sediments.

Reliable morphological evidence for atmospheric entry from space constrains the origins of iron silicide spherules to the formation in distal ejecta from a meteoritic impact. The composition of the silicide mineral complex was likely defined by selective vaporization and ultrahigh-temperature fractionation. The possibility that silicide assemblage may be a product of recondensation of carbon-dominated vapor ejected beyond the atmosphere will be tested in further studies.

Multiple similar finds of silicide spherules in various chronostratification indicate that large-scale impacts capable of delivering ejecta to space are more frequent in geological history than suggested by known evidence of cratering. Despite remaining uncertainties regarding the particular formation processes of iron silicide spherules, the constraints on their origins in meteoritic impact ejecta clearly suggest that further study requires the expertise of meteoriticists rather than geologists, who have persistently excluded since 19th century the possibility of the geological formation for iron silicides with aerodynamic features.

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DATA AVAILABILITY STATEMENT—Data openly available in a public repository that issues data sets with DOIs.

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