quasars 1510−089 and 1741−038 on the TDRSE-Usuda baseline. Most baselines between TDRSE and Tidbinbilla were less than 1 earth diameter.

We calibrated data from Tidbinbilla and Usuda with a standard technique, using noise diodes to monitor the system temperature and by observing sources of known flux density to measure antenna gain. Calibration of TDRSE was more difficult, because of its limited sensitivity and its automatic gain control. The method for calibrating TDRSE took advantage of the fact that our baselines between the spacecraft and Tidbinbilla were at certain times similar to the spacings on baselines between Australia and Japan, or Australia and California, for the same source. On 19 May and 2 June we conducted 2.3-GHz VLBI observations between Goldstone, California; Tidbinbilla, Australia; and Usuda, Japan. The correlated flux density at these two available "crossing points" was used with measured correlations on baselines to TDRSE to derive the ratio of antenna gain to system temperature. It was assumed that the correlated flux density was constant from May through August and that the gain to system temperature ratio of TDRSE was constant. The preliminary result was a 320 K system temperature, with an aperture efficiency of 0.4; this result was used to derive correlated fluxes. By comparison, the gain to system temperature ratios of the 64-m ground antennas were 4000 to 5000 times that of the TDRSE telescope.

For quasar 1730−130, the correlated flux density dropped rapidly with increasing baseline length, from 1.8 ± 0.2 janskys (Jy) on a 7300-km projected baseline to 0.3 ± 0.1 Jy for a 17,800-km projected baseline (Fig. 2). For quasar 1510−089, the falloff was less dramatic: 0.78 ± 0.1 Jy on a 7300-km projected baseline and 0.32 ± 0.1 Jy on a 15,500-km projected baseline. We did not have a ground baseline on quasar 1741−038, but the correlated flux on a 13,000-km projected baseline was 1.2 ± 0.4 Jy. For any VLBI observations with TDRSS, only a few baseline orientations will be available. Therefore, only rudimentary details of the structure of these radio sources can be determined. For proper mapping, a more sensitive telescope in an optimized orbit is needed.

We have demonstrated that correlation can be achieved in a VLBI experiment, with a free-orbiting satellite used as one of the observing stations in the interferometer. Corrections of the phase and delay variations along the spacecraft-ground link and along the directions to the radio sources were sufficiently accurate to achieve 84% coherence for integrations of 700 seconds in length. Fringes were detected on projected baselines in excess of 1 earth diameter for all three sources. This experiment, which used an operational TDRSS spacecraft as an orbiting VLBI telescope, demonstrates the feasibility and potential of using a dedicated observatory in space.

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Lightning Strike Fusion: Extreme Reduction and Metal-Silicate Liquid Immiscibility

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A glassy fulgurite, formed recently on a morainal ridge in southeastern Michigan, contains micrometer- to centimeter-sized metallic globules rich in native silicon, which unmixed from a silica-rich liquid. The unusual character of these globules and their potential for elucidating conditions of fulgurite formation prompted further study. Thermodynamic calculations indicate that temperatures in excess of 2000 K and reducing conditions approaching those of the SiO_2-Si buffer were needed to form the coexisting metallic and silicate liquids. The phases produced are among the most highly reduced naturally occurring materials known. Some occurrences of other highly reduced minerals may also be due to lightning strike reduction. Extreme reduction and volatilization may also occur during high-temperature events such as lightning strikes in presolar nebulae and impacts of extraterrestrial bodies. As a result of scavenging of platinum-group elements by highly reduced metallic liquids, geochemical anomalies associated with the Cretaceous-Tertiary boundary may have a significant terrestrial component even if produced through bolide impact.

LIGHTNING IS AN EXCEEDINGLY common terrestrial phenomenon, occurring at a rate of 100 sec^{-1} around the earth, with an average energy release of 10^9 J for each flash (*1*). Air temperatures momentarily reach 10,000 K and, in some instances, 30,000 K (*2*). Measured peak currents of 10 kA and as much as 200 kA are reached in microseconds (*3*). Under such conditions, it is not surprising that solids may melt or vaporize, or both, when struck by lightning.

Fulgurites (products of lightning strike fusion) are abundant and widely distributed on the surface of the earth (*4*) and have attracted scientific interest since the expeditions of von Humboldt and Darwin (*5*). Fulgurites are commonly formed in sand but are also reported in rock and soil (*6*). Most sand fulgurites are tubules only a few centimeters in diameter, but they may extend laterally or vertically for up to 10 m. Rock and soil fulgurites are highly vesicular and show only occasional development of crude tubelike shapes. Only a few workers have systematically analyzed the resultant silicate glasses, which are heterogeneous on a micrometer scale (*6, 7*). Comparison of glass chemistries with initial rock compositions sometimes (*6*), though not always (*7*), reveals differential volatilization of major

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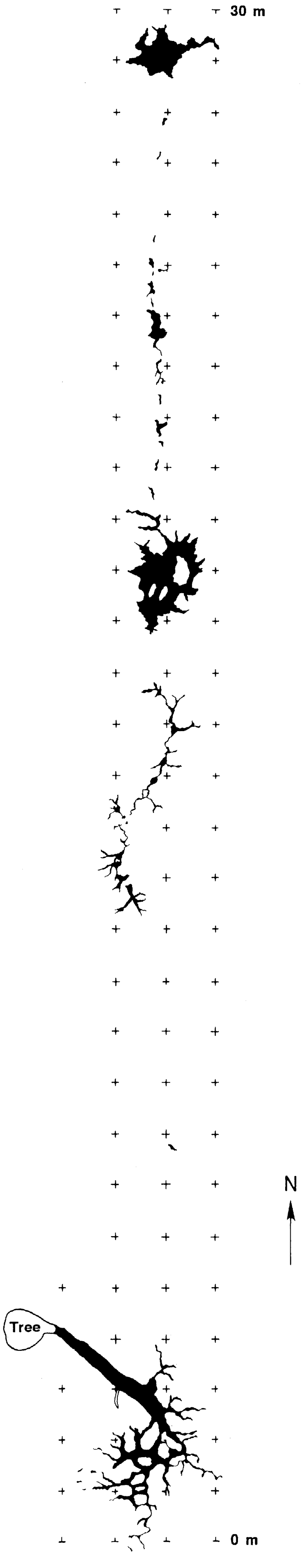


Fig. 1. Map of Winans Lake fulgurite showing distribution of fusion in black. Regularly spaced crosses represent the square meter reference grid.

elements during fusion (*8*). Although melting of quartz and volatilization of rock clearly require extreme temperatures, the physicochemical conditions of fulgurite formation have not, to our knowledge, been quantified.

In late April 1984, we were led to a fulgurite site near Winans Lake, in Livingston County, 20 km north of Ann Arbor, Michigan, by T. Keener and D. Andres. Several fulgurite masses of exceptional size extended for 30 m along a low ridge of soil and Pleistocene glacial till. Charred new growth on surrounding herbaceous vegetation suggested that the lightning strike had occurred within several weeks of this visit. The site was mapped from a north-south baseline by means of a subdivided square meter quadrat (Fig. 1). Fulgurite development was concentrated in three separate loci, but their alignment and the continuity of charred soil and vegetation between loci imply a single event. Areas around the thicker fulgurite masses were concentrically reduced and oxidized as indicated by the transition from white (adjacent to glass) to red to black zones in the normally brown soil. The fulgurites extended laterally rather than vertically and comprised a branching system of subcylindrical structures. The largest fulgurite mass at the south end of the mapped area was excavated and slabbed. With a maximum diameter of 0.3 m and a length of 5 m, this fulgurite appears to be the largest known. The glass varies from white, to light green, to dark gray and is variably vesicular. Quartz cobbles from the till have become fused and deformed during the melting event.

The most surprising aspect of the Winans Lake fulgurite is the occurrence of large metallic spheroids within the dark glass closely associated with a charred tree root in the area of most extensive fusion. The unusually low density and generally nonmagnetic character of the metal prompted further careful study.

Examination of polished sections of the Winans Lake fulgurite reveals abundant opaque spherules in the glass matrix. Viewing these with backscattered electron imaging in an electron microprobe provides strong contrast due to variations in the average atomic number of the phases (Fig. 2). The spheroidal shape of the metallic globules and their distribution throughout the dark glass (Fig. 2A) imply unmixing of a metallic liquid from a silicate liquid. Indeed, laboratory reduction of rhyolite and tektite by heating to between 1900 and 2000 K with carbon has yielded remarkably similar textures of immiscible molten iron in molten silicate (*9, 10*). Our direct observation of spheroidal metals in the Winans Lake fulgurite confirms previous inferences of submicroscopic spheroids of silicon-bearing iron in sand fulgurites, based on electron magnetic resonance spectroscopy (*11*).

Examination of the larger metallic globules reveals complex and diverse intergrowths of metals, silicides, and phosphides that can be distinguished with the electron microprobe. In one sample (Fig. 2B), laths of Fe_3Si_7 are intergrown with irregular FeSi grains and long laths of TiP and $FeTiSi_2$. The average composition of this globule is $Si_{0.6}Fe_{0.4}P_{0.01}Ti_{0.01}$. In another sample (Fig. 2C), a globule containing subhedral silicon and anhedral Fe_3Si_7 is enclosed within a matrix of siliceous glass. The average composition of this globule is $Si_{0.9}Fe_{0.1}$. Skeletal silicon is also found encasing submicrometer-sized blebs of gold (Fig. 2D). Some metal samples are magnetic and are composed dominantly of iron, containing accessory Fe_3P or FeS without silicides.

The identity of the phases in the metal globules has been confirmed by quantitative microprobe analyses (Table 1). The metallic silicon phase has >99.5 atom percent silicon with minor amounts of titanium, iron, and phosphorus. The TiP, FeSi, and Fe_3Si_7 are nearly stoichiometric, while $FeTiSi_2$ has significant solid solution of phosphorus substituting for silicon. Although iron, Fe_3P, FeSi, Fe_3Si_7, and silicon have been reported as terrestrial minerals, TiP and $FeTiSi_2$ represent new mineral species and need further study. The fulgurite glass contains crystals of graphite, quartz, and rare ZrO_2. Graphite occurs as subhedral crystals and was presumably derived by reduction of organic matter in the soil. Detrital quartz grains are preserved as rounded relicts or were totally melted to form silica glass. In addition, detrital zircon ($ZrSiO_4$) is found partially decomposed to ZrO_2 and SiO_2, which can only take place at temperatures above 1950 K (*12*). The fulgurite glass is heterogeneous and has 85 to 99% SiO_2 by weight (Table 2). The adjacent (Table 2, till analysis) is also siliceous and resembles the fulgurite glass except for possible depletion of sodium in the fulgurite. Some parts of the Winans Lake fulgurite contained silicon-rich liquid while others contained iron-rich liquid, but both metallic liquids coexisted with SiO_2-rich silicate liquid. For thermodynamic calculations, the metal may be treated as a Fe_xSi_{1-x} liquid.

A phase diagram for an iron-silicon metal coexisting with SiO_2 may be calculated from available thermodynamic data for SiO_2 combined with activity-composition data for iron-silicon liquid and the liquidus curve for the iron-silicon system (*12*). This diagram has been calculated with intensive variables of oxygen fugacity ($f[O_2]$, which equals the partial pressure of oxygen for a 1-bar standard state) and temperature, T, in kelvins (Fig. 3). For the reaction $SiO_2 = Si + O_2$, the equation $-\Delta G_T = RT\ \ln(a[Si] \cdot f[O_2]/a[SiO_2])$ allows calculation of $f[O_2]$ from the activities, a, of silicon in metal and SiO_2 in silicate for a given free energy of silica (R is the Boltzmann constant). Liquid SiO_2 will coexist with silicon-rich metallic liquid ($X[Si] = 0.9$) at $T > 2000$ K for $f[O_2]$ slightly higher than that for the SiO_2-Si buffer. Correcting for the reduction of $a[SiO_2]$ in the silicate liquid ($a[SiO_2] = X[SiO_2] = 0.85$ to 0.99) will shift the $f[O_2]$ down to values overlapping with those for the SiO_2-Si buffer. On the other hand, iron-rich metal with $X[Fe] = 0.9$ will coexist with SiO_2 within a few logarithmic units of the FeO-Fe buffer (Fig. 3). It is evident that strong gradients of some ten orders of magnitude in $f[O_2]$ were maintained during fulgurite formation.

Abundant carbon compounds were available in the form of roots and plant detritus in the soil hosting the Winans Lake fulgurite. At high temperatures, oxidation of carbon will smelt the till to form metallic liquids by the reduction of silicates, as in an iron-refining process. However, other mechanisms, such as degassing of oxygen or formation of nitrogen oxide gases, might also aid or dominate in the reduction process. Boiling has produced vesicles and open axial canals in the fulgurite. Vaporization of oxygen during the boiling process may provide an effective reducing mechanism at high enough temperatures. The driving force for this process may involve the flow of electrons through the melt, which could cause local reduction and nearby loss of oxygen as in electrolysis. Alternatively, nitrous oxides, which form in microseconds from air at high temperatures (>5000 K) during the passage of lightning (*1*), may be effective in scavenging oxygen from the fulgurite. The importance of these alternative processes for fulgurite reduction cannot presently be evaluated.

The reduction levels of the Winans Lake fulgurite may be compared with the most reduced meteorites (the enstatite chondrites, enstatite achondrites, pallasites, and ureilites), which contain iron with $X[Si] = 0.01$–0.25 (*13*). If equilibrated at high levels of $a[SiO_2]$, these require $f[O_2]$ intermediate between that of the FeO-Fe and SiO_2-Si buffers (Fig. 3). Thus, the Winans Lake fulgurite appears to have been locally far more reduced than the most oxygen-poor meteorites known.

Table 1. Analyses of fulgurite metal phases from Winans Lake fulgurite obtained at 15 kV with an electron microprobe (CAMECA Camebax) and elemental standards except for phosphorus, where apatite was used.

Phase	Composition of metal (% by weight)							Formula
	Si	P	Ti	Al	Fe	Mn	Sum	
Si	99.7	0.1	0.0	0.1	0.2	0.0	100.6	$Si_{99.7}P_{0.1}Al_{0.1}Fe_{0.1}$
Fe_3Si_7	54.9	0.1	0.0	0.1	45.9	0.7	101.7	$[Fe_{29.4}Mn_{0.5}][Si_{69.9}P_{0.1}Al_{0.1}]$
FeSi	34.6	0.1	0.0	66.0	0.1	0.1	100.9	$[Fe_{48.8}Mn_{0.1}Ti_{0.1}][Si_{50.9}P_{0.1}]$
$FeTiSi_2$	31.4	6.4	29.8	0.0	33.3	0.4	101.3	$[Fe_{24.2}Mn_{0.3}]Ti_{25.3}[Si_{45.4}P_{4.7}]$

Reports of other highly reduced phases in geological settings [for example, silicon (*14, 15*), SiC (*15, 16*), aluminum (*17*)] provide inadequate characterizations and have often been ignored or questioned as descriptions of minerals (*18*). In light of our documentation of highly reducing conditions in a terrestrial fulgurite, reports of these minerals should not be rejected a priori as requiring impossible geological conditions. Calculations of phase equilibria show that SiC is stable only 1 to 2 logarithmic units above SiO_2-Si and can form by reaction of SiO_2 equilibrated with carbon at $T > 1790$ K (Fig. 4). On the other hand, aluminum requires much higher T (>2310 K) before it can form from Al_2O_3 by oxidation of carbon (Fig. 4). Reports of aluminum closely associated with quartz or silicates seem exceedingly unlikely, as silicon (with or without refractory oxides) will form at much more oxidizing conditions than those needed for aluminum. Another reducing mechanism should be found before aluminum can be regarded as other than a man-made contaminant. Electrolysis may provide a possible mechanism, although its viability in natural settings is yet to be demonstrated. Several other models have been proposed to explain highly reduced minerals. Percolation of dry, highly reduced hydrogen gas from the mantle into the crust has repeatedly been proposed by many Soviet scientists to explain some of their observations of reduced minerals (*16, 17, 19*). Unfortunately for this hypothesis, dry hydrogen will rapidly react with the oxygenated mantle and crust to form far less reduced H_2O-rich fluid, and it cannot remain reduced at high levels in the earth's crust. Ablation or spalling of reduced materials from meteorites during passage through the atmosphere has also been proposed (*15*), but no known extraterrestrial solids are sufficiently reduced to yield metallic silicon or aluminum. Bird and Weathers

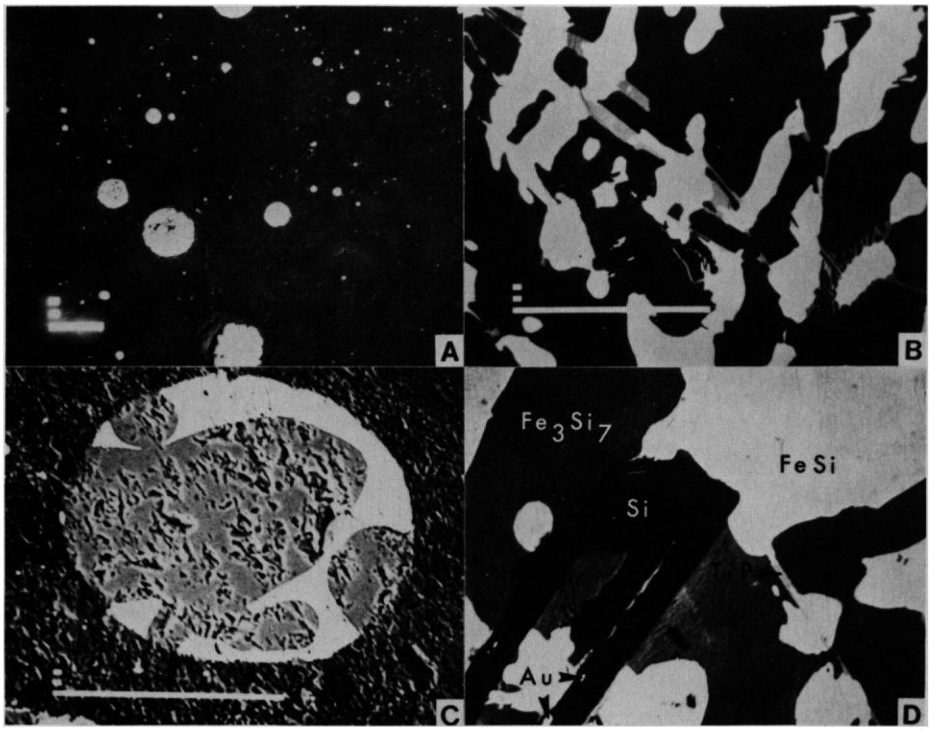


Fig. 2. Backscattered electron photographs of Winans Lake fulgurite. Long scale bar, 100 μm (A, B, and C). (A) Spheroidal globules unmixed from silicate glass. (B) Intergrowths of FeSi (white), Fe_3Si_7 (dark gray), and laths of TiP and $FeTiSi_2$ (light gray). (C) Globule containing subhedral Si (dark) and Fe_3Si_7 (light). (D) Skeletal silicon (5 μm wide) encasing submicrometer-sized blebs of gold and encased in a matrix of FeSi, Fe_3Si_7, and TiP.

Table 2. Analyses of Winans Lake fulgurite and till. Analyses of glasses were obtained with different samples at 12 kV on the electron microprobe with silicate standards, and special care was taken to avoid alkali migration. Till analysis was obtained with an x-ray fluorescence unit (Philips PW 1400) and rock standards. ND, not determined.

Oxide	Proportion of oxide (% by weight)					
	Fulgurite glass					Till
	1	2	3	4	5	
SiO_2	81.8	85.0	88.2	96.7	98.9	87.76
TiO_2	0.2	0.4	0.5	1.1	0.0	0.33
Al_2O_3	10.3	5.6	7.4	1.6	0.0	6.14
FeO	1.9	1.8	2.3	0.5	0.2	1.85
MnO	ND	ND	ND	ND	ND	0.03
MgO	1.2	0.4	0.6	0.1	0.0	1.15
CaO	1.8	0.9	1.4	0.2	0.0	0.91
Na_2O	1.5	0.8	0.8	0.3	0.0	1.72
K_2O	2.4	1.4	2.1	0.6	0.0	1.34
P_2O_5	0.0	0.1	0.1	0.1	0.0	0.06
Sum	101.1	99.6	100.2	101.2	99.1	101.29

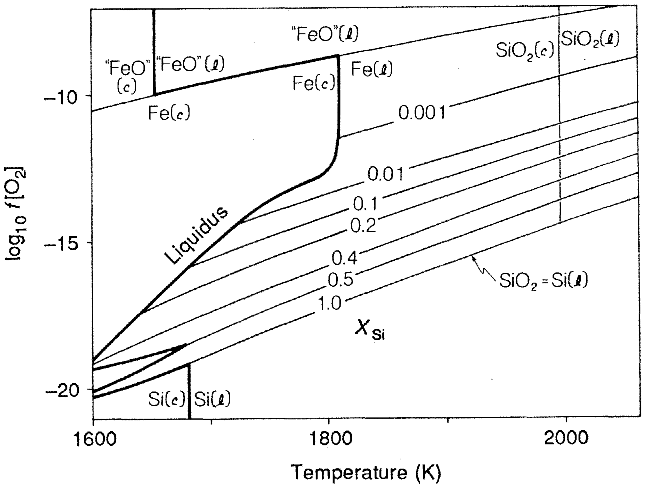
(*14*) have proposed that metallic silicon was transported from highly reduced areas in the core or deep mantle, but this phase is grossly out of equilibrium with its host rock, the Josephine peridotite. If these highly reduced phases are convincingly shown to be natural minerals and unrelated to lightning strikes or other transient ultrahigh-temperature events, additional attention must be paid to their formation mechanisms.

Any of the metals (chromium, iron, or silicon), carbides (Cr_3C_2, Cr_2C, SiC, TaC, TiC, or WC), and silicides (Fe_3Si, Fe_5Si_3, Fe_2Si, FeSi, $FeSi_2$, or Fe_3Si_7) that have been reported as minerals (*14–19*) may form by reaction with carbon at $T > 2000$ K. These phases are generally resistant to corrosion and may survive weathering, so that their detritus is to be expected in young sediments, but on a geological time scale their fate is unclear.

Fulgurite formation is common on the surface of the earth, and extraterrestrial lightning strikes (*20*) may produce similar melts. Indeed, Whipple (*21*) speculated that this mechanism was involved in the formation of chondrules through melting of homogeneous nebular condensates in the presolar nebula. For geochemical reasons, current models of chondrule formation involve melting of preexisting heterogeneous condensates in the nebula, but there is no consensus on the mechanism (*10, 22*). However, one possibility is that lightning could have melted and volatilized already-formed chondritic materials in the nebula. Processes involving extreme reduction and metal-silicate liquid immiscibility might also have occurred in carbon-rich targets such as carbonaceous chondrites.

Other ultrahigh-temperature processes might also produce marked reduction. For example, large meteoritic or cometary impacts on extraterrestrial or terrestrial surfaces may lead to unmixing of highly reduced metallic liquids. If the reducing mechanism involves oxidation of carbon, then sufficient quantities of carbon compounds would have to be available in silicate targets. Metallic iron spheroids in impactites and tektites have often been interpreted to be derived from the impacting body (*23*), although Grossman and Wasson (*24*) have concluded that iron-rich metal globules found in some chondrules are derived by reduction and liquid immiscibility. Reduction, volatilization and recondensation, and variable oxidation by involvement with the atmosphere have also been inferred in some terrestrial impactites (*25*). Thus, several competing processes may determine whether or not metallic iron would be present in impact glasses. In any case, it is clear that the occurrence of iron metal in tektites and impactites should not be taken as conclusive evidence of their origin by impact fusion of an iron meteorite (*26*).

The possibility that metals in impactites are derived from highly reduced target materials rather than from the projectile itself has important implications for understanding the geochemical anomalies that have been widely reported from near the Cretaceous-Tertiary (K/T) boundary and elsewhere in the geological record. Once an immiscible metallic liquid forms within a silicate melt, it will certainly scavenge iridium and other platinum-group metals from the surrounding liquid on account of their strong siderophile affinities. This should lead to local enrichment of iridium by several orders of magnitude over its average concentration in target materials. Although the kinetics of this process need further study, it may have operated even within the relatively brief interval of melting, vaporization, and recondensation associated with a meteoritic or cometary impact. This is borne out by simi-



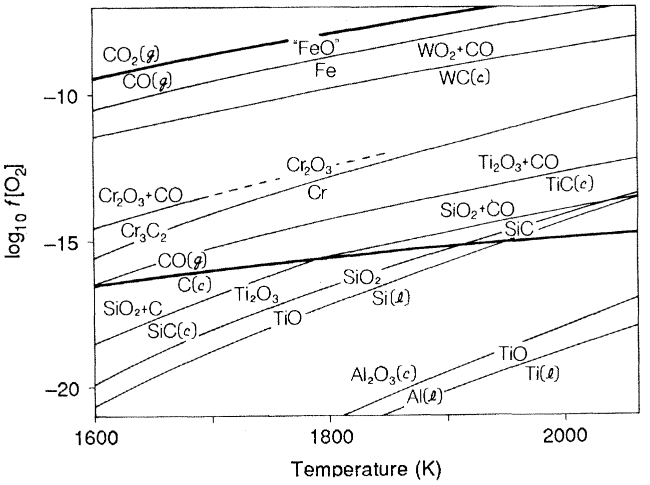


Fig. 3 (left). Calculated $f[O_2]$ versus temperature diagram for the system Fe-Si-O at a total pressure of 1 bar with available nonideal mixing of liquid Fe-Si. The phase "FeO" is $Fe_{0.947}O$. Thermodynamic data from (*12*). Fig. 4 (right). Calculated $f[O_2]$ versus temperature diagram showing the upper $f[O_2]$ stability limit for iron, WC, TaC, Cr_7C_3, Cr_3C_2, chromium, TiC, SiC, TiO, silicon, and aluminum compared to the C/CO and the CO/CO_2 (where $X[CO_2] = X[CO]$) buffers at 1-bar total pressure. The curves for Cr_7C_3 and TaC nearly coincide with that for Cr_3C_2 and are omitted for clarity. Thermodynamic data from (*36*).

lar processes operating in the Winans Lake fulgurite, which concentrated gold from the till in the very brief fulgurite fusion event.

In a large-scale impact such as that interpreted as having occurred at the K/T boundary (27), both silicate and metallic phases would have been explosively dispersed into the atmosphere soon after their formation. While certain aspects of the dynamics of impact ejecta have been studied (28), the existence of two liquid phases with contrasting physical properties would add a new level of complexity. In particular, the far greater viscosity of the silicate, relative to the metallic, phase (29, 30) and the consequent preferential retention of the former within the larger size classes of ejecta material may bias the dispersal process toward broader geographic distribution of the metals. This same pattern may have been enhanced by the greater susceptibility of the metallic liquid to vaporization (30). The smaller size fractions of each phase, including material that was vaporized and recondensed, could have been widely distributed, but the greater density of the metallic phase could have led to its enhanced representation in the earliest "fallout" and thus its contribution to the iridium anomaly. Estimates of the mass of target material incorporated in the impact ejecta (28) imply that the process we are proposing could supply sufficient terrestrial iridium to contribute significantly to the K/T iridium anomaly, even if the only target materials involved were continental crust (31). Even greater amounts of terrestrial iridium would be available if the target location were oceanic (32) and if mantle materials (31) contributed to the ejecta mass.

If iridium anomalies represent, even in part, enrichment in a metallic phase formed by reduction rather than simply addition of iridium from an impacting body, then the total mass of iridium involved in the K/T anomaly provides a less satisfactory basis for estimating the size and nature of the projectile than has been assumed heretofore (27). With regard to both elemental (31) and isotopic composition (33, 34), the anomaly might bear a terrestrial signature (more or less modified by vapor fractionation or adulterated by admixture of projectile material) even if produced by impact of an extraterrestrial object. This scenario allows for regional variation in the character of an anomaly derived from a single impact, rather than implying that regional differences indicate separate impact events (34). It also accommodates variation in the geochemical expression of different impact events due to differences in available target materials (possibly including carbon compounds to aid in reduction) as well as differences in projectile size and composition. Perhaps most important, this revised impact scenario and its implications for the phases expected to accompany iridium in an impact-generated anomaly should provide additional tests for the impact hypothesis itself relative to alternative explanations such as those involving volcanism (35). Adequate tests of these interpretations will require much additional analysis, but the observations discussed here broaden considerably the range of models that should be considered in investigating the origin and implications of the observed iridium anomalies.

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