conditions and time scales in Sixiangkou shock veins cannot be explained by accepted shock models and therefore may warrant revision of such models. The relatively long time that the Sixiangkou shock veins remained in the pressure range of 20 to 24 GPa is inconsistent with transformations occurring during rapid decompression after the peak shock pressure was reached.

The conditions required for the formation of ringwoodite (γ) and wadsleyite (β) from olivine during shock events in ordinary chondrites are poorly constrained. Steele and Smith (*24*) and Stöffler *et al.* (*25*) suggest that special conditions, such as elevated temperatures of the target before shock compression, are required to transform olivine to ringwoodite. Such high temperatures were unlikely during the formation of Sixiangkou shock veins because they would have resulted in back transformation to the low-pressure phases after decompression. Scenarios suggesting peak pressures in excess of 50 GPa, as high as 80 GPa, were also developed (*26*). These models cannot be reconciled with our findings in Sixiangkou because there would be insufficient time available for the growth of relatively large ringwoodite and majorite grains with subgrain microstructures during the rapid decompression.

The composition and textural relations of the two high-pressure assemblages studied have important implications for (i) the pressure and temperature conditions that exist during dynamic events that lead to the formation of high-pressure polymorphs in chondritic meteorites, (ii) the duration of shock events in meteorites, and (iii) the crystallization of melts in shock veins. It may appear impossible to retain high pressures and temperatures for up to several seconds on the basis of shock experiments, but one can envisage that collisions of large asteroidal bodies or the passage of multiple shock waves through such bodies during complex collisional events could account for such conditions.

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29. B.W. was supported by NSF grant GER 9023520.

18 August 1995; accepted 27 November 1995

Iridium Metal in Chicxulub Impact Melt: Forensic Chemistry on the K-T Smoking Gun

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Iridium concentrations in successively smaller subsplits of melt rock and melt breccia from the Chicxulub impact basin were tracked to isolate and identify iridium carrier phases. Iridium-rich particles were isolated from two samples, and a micrometer-scale, silicate-enclosed aggregate of subhedral iridium metal grains was identified in one, confirming earlier reports of iridium at ground zero of the impact at the Cretaceous-Tertiary (K-T) boundary. The aggregate may be either a phase formed after the collision or a relict of the Chicxulub basin-forming meteorite. In either case, its presence indicates that even among the largest impact structures on Earth, meteoritic components may be preserved within the crater.

Of all the elements in the periodic table, iridium (Ir) figures most prominently as a chemical fingerprint of meteorite impact events in shock-metamorphosed target rocks and ejecta on the Earth and moon (*1*). Discovery of anomalously high concentrations of Ir coincident with the K-T boundary, the worldwide stratigraphic horizon defined by a major biological mass extinction event 65 million years ago, led to the hypothesis that impact of an Earth-crossing asteroid ~10 km in diameter was responsible for the sudden influx of Ir and the ensuing biological crisis (*2*). All available evidence points to the Chicxulub structure—buried beneath Mexico's Yucatán peninsula, with diameter estimates of 180 to 300 km—as the site of the K-T impact (*3–6*).

Definitive constraints on the nature of the impacting body (whether asteroid or comet), in terms of size, velocity, and possible compositional correlation with other meteorites (*7*), are yet to be determined. Anomalously high Ir concentrations in some Chicxulub samples (*4*, *8*) suggest that melt rocks within the crater may provide additional constraints on the nature and fate of the projectile. To better understand the partitioning of projectile material between crater deposits and ejecta, we began a search for physically identifiable carrier phases of Ir and other siderophile elements within these melt rock samples (*9*, *10*). We discovered an Ir metal particle enclosed in

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silicate, providing additional evidence for fractionation of siderophile elements and for preservation of meteoritic components in impact melt rocks from within one of the largest impact structures on Earth.

Previous instrumental neutron activation analyses (INAA) (*4*) show that several Chicxulub samples have Ir concentrations (2.5 ± 0.5 to 13.5 ± 0.9 ng per gram of sample) well above those typical of the Earth's crust (*11*). These Ir enrichments can be explained by the admixture of up to ~3% chondritic material into impact melt of granodioritic composition (*12*). The absence of detectable Ir (<1 ng/g) in other samples and an overall lack of siderophile element coherence suggest that Ir and other meteoritic components are concentrated in sparsely disseminated trace phases (*4*, *9*); this hypothesis is corroborated by concentrations and isotopic ratios of Os and Re (*13*). However, these observations are not consistent with widely held views suggesting that impact melts tend to have uniform concentrations of meteoritic elements (*14*) or that, when present at any given impact site, Ir enrichments are generally found in all samples from the same melt body (*15*). With exception of the ~100-km-diameter Popigai structure (*16*), impact melt rocks with Ir concentrations >1 ng/g have been reported only from craters <25 km in diameter [table 1 in (*15*)]. Theoretical models of high-speed impacts show that the masses of melted and vaporized material are proportional to projectile kinetic energy, with the mass of impact melt exceeding that of the vapor by a factor of 6 (*17*). Furthermore, computer simulations indicate that a 10-km-diameter impacting asteroid vaporizes, and virtually all of it would be ejected (*18*), suggesting that any projectile residue in the impact melt of a Chicxulub-size crater may be diluted beyond geochemical detection. Although independent verification of our Ir measurements has been documented through blind analyses of several of our samples (*19*), contamination is a concern. Consequently, identification of the carrier phases for Ir and other siderophile elements is crucial to a better understanding of the Chicxulub basin-forming projectile's distribution.

We performed INAA measurements on splits of previously unirradiated powder from two specimens in which Ir had been measured; specimen locations, petrographic descriptions, and previous chemical analyses are published elsewhere (*4*, *6*, *12*). Results for splits of C1-N10-1 (65.53 mg) and Y6-N19-R (62.62 mg) are indistinguishable at the 2σ level from those of the previous experiment for most elements, including Ir concentrations of 4.1 ± 0.5 and 13.8 ± 0.7 ng/g, respectively (*20*). These powders were split into five subequal fractions and put into polyethylene vials for low-background gamma-ray counting (*21*, *22*). This procedure was repeated several times for both samples (*23*), further subdividing the split with the highest Ir concentration (Fig. 1).

Results show that the mass of Ir in the most Ir-rich subsplit of each generation approaches a constant value (Fig. 1). If all of the Ir in the most Ir-rich third-generation splits of C1-N10-1 and Y6-N19-R were in single, pure Ir metal spheres (22.42 g cm^{-3}), their respective diameters would be ~2.2 and 2.7 μm. Alternatively, Ir could be in any number of smaller particles included in mineral phases that crystallized from the impact melt, possibly alloyed with other platinum group elements (PGE). The maximum dimension of particles in the melt rock powders is ~75 μm, with most particles measuring ≤10 μm. Obviously, typical grinding procedures are incapable of homogenizing such particles to an extent that would ensure a representative sample of Ir at this scale. Thus, when splitting of C1-N10-1 was halted (*23*), even though 99.99% of the starting material had been winnowed, thereby increasing the Ir concentration four orders of magnitude, we were still faced with searching among thousands of particles.

We used scanning electron microscopy to examine particles of C1-N10-1 melt rock on the surface of a polyethylene vial section containing ~1.3×10^{-10} g of Ir (*23*) and found one particle with high backscattered electron intensity and characteristic x-ray lines of Ir (*24*). This section was sliced twice again, and all pieces were counted to confirm that a ~1.0 mm by 0.8 mm section containing the Ir-bearing particle was the sole source of detectable Ir gamma rays. Secondary electron imaging shows the particle as an irregularly shaped lump with approximate dimensions of 4 μm by 2.5 μm by 0.5 μm (Fig. 2A). Backscattered electron imaging (Fig. 2B) reveals that this particle is an aggregate of several smaller grains, some of which exhibit crystal faces consistent with a face-centered-cubic lattice structure. Its surface is coated by a thin, translu-

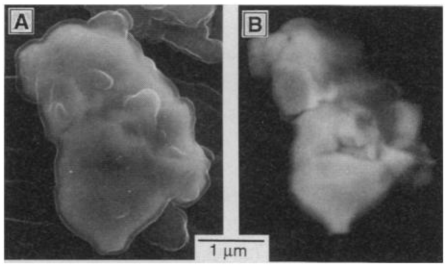

Fig. 2. (**A**) Secondary electron photomicrograph of an Ir metal particle enclosed in silicate material from the C1-N10-1 impact melt rock. (**B**) Backscattered electron photomicrograph of the Ir particle.

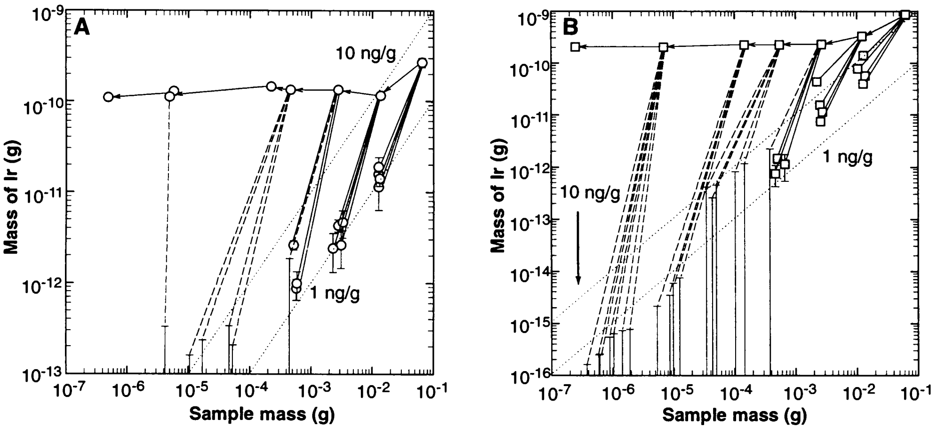

Fig. 1. "Family tree" depicting the mass of Ir in respective subsplits of melt rock samples (**A**) C1-N10-1 and (**B**) Y6-N19-R from the Chicxulub impact basin. From right to left, lines project from parent to descendent splits for each subsequent generation. Vertical bars show analytical uncertainties (±1σ) of measured abundances and upper limits (2σ) for abundances below detection (denoted by dashed lines). Isopleths for constant Ir concentrations of 1 and 10 ng/g are shown by dotted lines.

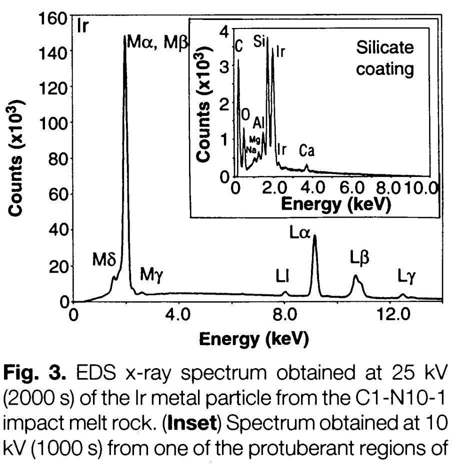

Fig. 3. EDS x-ray spectrum obtained at 25 kV (2000 s) of the Ir metal particle from the C1-N10-1 impact melt rock. (**Inset**) Spectrum obtained at 10 kV (1000 s) from one of the protuberant regions of the silicate coating surrounding the Ir particle; the carbon peak and a portion of the counts in the oxygen peak are due to x-rays from the polyethylene substrate.

cent veneer of nearly uniform thickness ($\sim$0.05 μm) but forming bulbous protrusions up to $\sim$0.4 μm thick in several places (Fig. 2A). Where the coating is relatively thin, energy-dispersive x-ray spectrometry (EDS) analyses at 25 kV (*24*) indicated that the grains consist of pure Ir metal (Fig. 3). On the basis of comparisons with standard spectra (*24*), we can state with reasonable confidence that the Ir is not alloyed with any other PGE at concentrations $\geq$1%. Analyses of protuberant regions of the coating (*24*) show a silicate with relative proportions of major element constituents similar to those of the bulk C1-N10-1 host rock (Fig. 3, inset).

This particle accounts for about half of the Ir measured in the $\sim$65-mg original split of C1-N10-1. The other half of the Ir is distributed in the different splits at concentrations of about 1 ng/g (Fig. 1A), indicating that it is either evenly disseminated in smaller particles or is homogeneously dissolved in the melt rock. To date, three analyses of C1-N10-1 melt rock powder, using masses of $\sim$40 to 65 mg, have all yielded Ir concentrations of 5 ± 1 ng/g. Thus, it is conceivable that the $\sim$0.5-g fragment of melt rock ground for analysis contained on the order of 10 such Ir particles. Assuming a Poisson distribution, the probability of sampling one such particle in any given 40-mg split is only about 0.37, while the probabilities of finding zero, two, three, or four are 0.37, 0.18, 0.06, and 0.015, respectively. The subsplit data (Fig. 1) demonstrate that Ir-rich particles exist in C1-N10-1 and Y6-N19-R, and we infer that similar particles occur in the other Y6-N19 subsamples in which Ir was detected (*4, 9, 12*).

Failure to detect Ir in other samples [table 1 in (*12*)] may result from problems of obtaining representative samples in splits of a few tens of milligrams, as discussed above, or from a sampling problem on a much larger scale. Sparsely distributed projectile residuum, existing as coherent masses with $\sim$1 ng of Ir per gram or more of melt rock, might also explain the chance detection of Ir in our samples. If such residuum were included in millimeter-size clasts containing discrete PGE metals and alloys, then grinding could disaggregate and partially homogenize them, yielding a bulk rock powder with relative abundances of refractory siderophile elements in roughly meteoritic proportions. This would explain the paradox of pure Ir metal and the apparent correlation among Os, Re, and Ir concentrations between different melt rock fragments from the same core interval (*13*). This Ir particle is not the first evidence for essentially pure PGE metals at the K-T boundary: micrometer-size grains of almost pure Pt with <1% Fe were reported in K-T boundary marl at Zumaya, Spain (*25, 26*).

We are unaware of any documented analyses of naturally occurring Ir metal of the purity described here, although grains of other almost pure PGE metals (for example, Ru, Re, and Pt) have been found within calcium- and aluminum-rich inclusions in some meteorites (*27*). A terrestrial Ir source seems unlikely (*28*). We consider three general categories of working hypotheses to encompass any plausible natural origin of Ir-rich particles in our Chicxulub samples: (i) condensation directly from impact-derived vapor, (ii) formation during melt rock solidification or metamorphism, and (iii) incorporation of relict projectile fragments that escaped annihilation. We note that the only meteorites currently known to contain micrometer-size nuggets of highly fractionated PGE metals are C2 and C3 carbonaceous chondrites (*29–31*).

This Ir metal particle enclosed in silicate (Fig. 2A) establishes beyond reasonable doubt that the Ir measured in our melt rock samples is not the result of any conceivable anthropogenic contaminant and provides compelling evidence for an extraterrestrial component in Chicxulub impact melt. As such, it confirms earlier Ir measurements (*4, 12*) demonstrating that even among the most highly energetic impact events known, some chemical trace of the projectile may be preserved within the crater.

Note added in proof: A second particle of Ir metal with adhering silicate, approximately 5 μm by 4 μm by 1 μm, has now been identified in the most Ir-rich, sixth-generation split of the Y6-N19-R melt breccia sample (*23*).

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22. Subsplits of the melt rock powders, as well as those of the standards, were weighed to an accuracy of ±0.02 mg and counted in the low-background Radiation Counting Laboratory at Johnson Space Center (*32*). In addition to Ir, abundances were obtained for Fe, Sc, Cr, Co, Ni, Sr, Ce, Eu, Tb, Hf, Th, and Zn. Because of uncertainties inherent in weighing small amounts of powder, particularly beyond the third-generation splits (*23*), subsplit masses from the second generation onward were back-calculated by mass-balance normalization of the apparent Sc abundance for each subsplit to the mean Sc abundance of the five first-generation subsplits. The subsplit masses were then used to convert all elemental masses into concentrations (*32*).
23. When we attempted the fourth-generation split of C1-N10-1, a considerable fraction of material ($\sim$75% or $\sim$0.2 mg) adhered to the inside surface of the vial. We further split the sample by sectioning the vial with a stainless steel razor blade. Sectioning was halted when the prospect of losing the yet to be identified Ir host was felt to be too risky; the inner surface area of a triangular section containing an estimated 1.29×10^{-10} g of Ir in 5.7 μg of C1-N10-1 powder was $\sim$4.3 mm^2. After the fourth-generation split of Y6-N19-R, Ir was tracked through two subsequent generations with glass slides and convex covers rather than polyethylene vials. The powder in one of these sandwiches had an estimated mass of 0.25 μg and contained $\sim 2 \times 10^{-10}$ g of Ir (Fig. 1B).
24. A JEOL 35CF scanning electron microscope was used for secondary and backscattered electron im-

aging. We performed EDS analyses with a PGT System IV equipped with Be and thin organic windows. Analyses of the Ir particle were obtained at 25 kV for 2000 s with a Be window. Other EDS analyses with better sensitivity for oxygen were performed at 10 kV for 1000 s with the thin organic window, to determine if the Ir particle was oxide or metal and to evaluate the composition of the silicate coating. Using the same respective instrument conditions, we obtained spectra from polished standard blocks for pure metals of Ru, Re, Os, and Pt and for a Pt-Ir (9:1) alloy, and from a polished fused glass bead from a split of the C1-N10-1 whole rock powder (*4, 12*). After discovery of the particle, IrO_2 and Ir metal standards were obtained and analyzed. Comparisons of spectra from the particle to those of the above standards, as well as to "composite standards" [J. T. Armstrong, A. El Goresy, G. J. Wasserburg, *Geochim. Cosmochim. Acta* **49**, 1001 (1985)] for $Ir_{99}Os_1$ and $Ir_{99}Pt_1$, clearly show that other PGEs are not present in the particle to within EDS detection limits.

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16 October 1995; accepted 16 February 1996

Exchange of Carbon Dioxide by a Deciduous Forest: Response to Interannual Climate Variability

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The annual net uptake of CO_2 by a deciduous forest in New England varied from 1.4 to 2.8 metric tons of carbon per hectare between 1991 and 1995. Carbon sequestration was higher than average in 1991 because of increased photosynthesis and in 1995 because of decreased respiration. Interannual shifts in photosynthesis were associated with the timing of leaf expansion and senescence. Shifts in annual respiration were associated with anomalies in soil temperature, deep snow in winter, and drought in summer. If this ecosystem is typical of northern biomes, interannual climate variations on seasonal time scales may modify annual CO_2 exchange in the Northern Hemisphere by 1 gigaton of carbon or more each year.

Observations of atmospheric CO_2 indicate that the carbon balance [net ecosystem production (NEP)] of the Earth's terrestrial biosphere varies by 1 gigaton of carbon per year (Gt C $year^{-1}$) (1 Gt = 10^9 metric tons) or more from year to year (*1*). Many ecosystem processes are sensitive to weather (*2*), and the fluctuations in global NEP are probably a consequence of interannual climate variability. However, direct observations of the effects of climate variability on the CO_2 exchange of whole ecosystems are required before the causes of global NEP variation can be assessed reliably.

We used a 5-year record of the turbulent exchange of CO_2 between the atmosphere and a deciduous forest in New England [net ecosystem exchange (NEE)] (*3–5*) to evaluate the magnitude and causes of interannual variations in net production (NEP), respiration (*R*) (*6*), and gross ecosystem exchange (GEE) (*7*). The eddy-covariance technique (*8, 9*) was used to measure hourly NEE from 28 October 1990 to 27 October 1995 (*10*) at Harvard Forest in central Massachusetts. Ecosystem respiration was measured directly during dark periods and estimated as a function of soil temperature during light periods (*8*). Hourly GEE was inferred by subtracting *R* from NEE.

Measurements of NEE were obtained during 27,000 of 44,000 hours, with gaps for calibration, data transfer, maintenance, equipment failure, rain, and stable nocturnal periods. The study included warm (1990–1991, the 2nd warmest year out of 32), cold (1991–1992, the 2nd coldest; 1993–1994, the 4th coldest), and moderate (1992–1993, the 14th coldest; 1994–1995, the 19th coldest) years (*10, 11*), mild (1991 and 1995, among the four warmest) and cold (1993 and 1994, among the eight coldest) winters, cool (1992, the 3rd coldest) and hot (1993, 1994, and 1995, among the six hottest) summers, and dry (1995, the 6th driest) and wet (1991, 1992, and 1994, among the seven wettest) summers.

The forest gained 30 to 60 kg C ha^{-1} day^{-1} in the growing seasons and lost 10 to 20 kg C ha^{-1} day^{-1} in the dormant periods (Fig. 1). Annual net CO_2 uptake ranged from 1.4 to 2.8 metric tons C ha^{-1} (Table 1) (*12, 13*), with above-average uptake in 1990–1991 and 1994–1995 (*14*). The rise in sequestration during 1990–1991 was caused by increased annual gross production, and the rise during 1994–1995 was caused by decreased annual *R*. Annual GEE and *R* varied as the result of 1- to 2-month-long episodes of anomalous activity (Fig. 2). For example, lower than average annual net production in 1993–1994 (Table 1) was a consequence of both higher than average respiration (Fig. 2) and lower than average gross production (Figs. 2 and 3) in spring.

Large changes in annual GEE were associated with modest changes in the length of the growing season (Figs. 2 and 3). The leaves emerged 6 to 10 days later

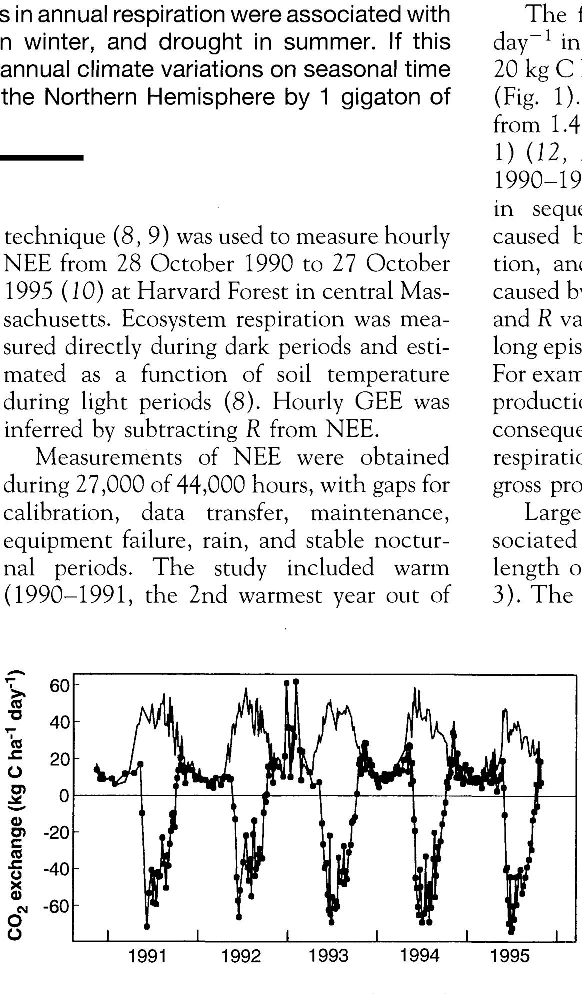

Fig. 1. Daily net CO_2 exchange (NEE) (filled symbols connected by lines) and daily respiration (*R*) (solid line) during 5 years at Harvard Forest. Observations are means for 4 days (*8*).

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