and to some condylarths. The occurrence of *Hyracotherium* cf. *H. angustidens* in the late Paleocene does little to delineate the relationships of the major groups (superfamilies) of perissodactyls. Contemporary representatives of these groups are needed before an accurate determination of early perissodactyl evolution can be made.

After the first version of this paper was written and while we were withholding it from publication, in the conservative hope that more samples of Paleocene hyracotheres would be found in the Polecat Bench Formation, we learned that W. J. Morris had made an important discovery of the upper teeth of hyracotheres in rocks near Punta Prieta, Baja California, which he believes to be of late Paleocene (or early Eocene) date (*16*). These specimens were recovered from strata above those yielding representatives of *Esthonyx* (a late Paleocene–early Eocene taxon elsewhere) and below bones of "barylambdids," a family of pantodonts restricted in the United States to rocks of Paleocene age and occurring in Asia in Eocene sediments. Morris assigns the Baja assemblage to the late Paleocene on the basis of the structures of the equid molars and of the tillodont (*Esthonyx*) teeth.

It is impossible at present to make close comparisons of the age of the Mexican Paleocene hyracotheres reported by Morris with that from Wyoming, but each such occurrence of a pre-Eocene equid not only helps validate the obvious fact that perissodactyls had a long evolutionary history before Wasatchian-Sparnacian time, but also increases hope that many more of the earlier eohippids will be found.

GLENN L. JEPSEN
Department of Geological and Geophysical Sciences, Princeton University, Princeton, New Jersey
MICHAEL O. WOODBURNE
Department of Geological Sciences, University of California, Riverside

References and Notes

1. B. Kurten, *Comment. Biol. Soc. Sci. Fennica* **29** (No. 5), 1 (1966).
2. Funds for this research have been supplied mainly by the W. B. Scott Fund and, recently, in part by grant GB-218 from the National Science Foundation.
3. G. L. Jepsen, *Proc. Amer. Phil. Soc.* **69**, 463 (1930).
4. See G. T. MacIntyre, *Bull. Amer. Mus. Nat. Hist.* **131**, 115 (1966); M. C. McKenna, *Colloq. Int. Centre Nat. Rech. Sci.* **163**, 603 (1967); G. G. Simpson, *Bull. Amer. Mus. Nat. Hist.* **85**, 1 (1945); R. E. Sloan and L. Van Valen, *Science* **148**, 220 (1965); L. Van Valen, *Bull. Amer. Mus. Nat. Hist.* **132**, 1 (1966); L. Van Valen, *ibid.* **135**, 217 (1967).
5. D. A. Andrews, W. G. Pierce, D. H. Eargle, "Geologic Map of the Bighorn Basin, Wyoming and Montana," showing terrace deposits and physiographic features [U.S. Geological Survey Oil and Gas Investigation, preliminary map 71 (Denver, Colo., 1947)].
6. G. L. Jepsen, *Proc. Amer. Phil. Soc.* **83**, 236 (1940).
7. W. G. Pierce, "Geologic Map of the Clark Quadrangle, Park County, Wyoming" [U.S. Geological Survey, geology quadrangle map 15'GQ-477 (Denver, Colo., 1965)].
8. When it was found, the specimen was casually examined in the field and labeled "*Ectocion*" because fossil representatives of species within this genus are among the forms most frequently found in the area. Not until the summer's collections were being cataloged, several months later, was the specimen perceived to be an equoid perissodactyl.
9. S. Sisson and J. D. Grossman, *The Anatomy of the Domestic Animals* (Saunders, Philadelphia, 1953), p. 260.
10. D. B. Kitts, *Bull. Amer. Mus. Nat. Hist.* **110**, 1 (1956).
11. W. D. Matthew, *ibid.* **34**, 429 (1915).
12. This specimen was found by W. Ulrich, member of a 1966 field research group of Princeton University.
13. L. A. Radinsky, *Amer. Mus. Novitates No. 2179* (1964).
14. C. A. M. Meszoely, *Copeia* **2**, 346 (1967).
15. G. L. Jepsen, *Proc. Amer. Phil. Soc.* **78**, 291 (1937).
16. W. J. Morris, *Science* **153**, 1376 (1966); *Los Angeles County Museum Contrib. Sci. No. 151* (1968).

16 January 1969

■

Silicate Spherules from Tunguska Impact Area: Electron Microprobe Analysis

Abstract. *The major oxide composition of four silicate spherules from the area of forest devastated by the explosion of the Tunguska meteorite has been determined by electron microprobe analysis. In general, the spherules have compositions similar to that of igneous glass except for the low iron and the high calcium oxide content of the three spherules that have a low content of silicon dioxide. None of the spherules seem to have compositions similar to the silicate portion of any major meteorite group.*

On 30 June 1908, a meteorite flashed through the earth's atmosphere and exploded above a forest in the basin of the Podkamennaya Tunguska River, Central Siberia (60°55'N,101°57'E), devastating an area 20 to 30 km in radius (*1*, *2*).

Soil samples collected from the devastated area yielded magnetic and silicate spherules. Statistical analysis of the distribution of the metallic spherules indicates that the areas of relative enrichment cannot be explained by background variations, thus indicating that the magnetic and silicate spherules are associated with the explosion of the Tunguska meteorite (*3*).

In some cases, the silicate spherules have metallic spherules attached to or included in them. Thus Soviet investigators believe that the siliceous and magnetic spherules were formed simultaneously from parent material of a heterogeneous nature (*4*).

After the discovery of microtektites associated with the Australasian tektite-strewn field (*5*), Glass and Heezen suggested (*6*) that the microtektites (and tektites) might have had an origin similar to that of the Tunguska silicate spherules. Nine samples of these spherules (*7*) were obtained for examination.

All nine of the spherules are about 80 to 100 μ in diameter. They are all spheroidal in shape, but a few are irregular with conical protrusions. The spherules are transparent and colorless. In transmitted light most of them contain dark areas due to numerous small bubble cavities; two of the spherules contain no bubble cavities.

Four of the silicate spherules were randomly selected for microprobe analysis. The spherules were individually mounted in epoxy aluminum cylinders (inside diameter, 0.64 cm). They were ground to expose a section and polished with successively finer abrasives so as to produce a flat, smooth surface. The samples and standards were then vacuum-coated with a thin layer of carbon. Each specimen was analyzed for nine oxides in the following groups of three: Fe-K-Na, Ca-Si-Al, and Mn-Ti-Mg (*8*). In addition, the spectrum was scanned from 1.1 to 9.9 Å and peaks were observed only for those elements listed above (Table 1).

Based on calculations of standard deviations, the precision (at a 90 percent confidence level) for samples 111, 112, and 747 is 1 to 4 percent of the amount present for SiO_2, Al_2O_3, MgO, CaO, TiO_2, and MnO. In sample 753 the precision is 2 to 6 percent of the amount present. The precision for sodium oxide and potassium oxide in sample 111 is about 30 percent of the amount present. In samples 112, 747, and 753 the precision for sodium oxide and potassium oxide is 6 to 9 percent of the amount present. The precision for iron is 4 to 5 percent of the amount present in samples 111 and 112, and 20 percent of the amount present in

Table 1. Chemical composition of Tunguska spherules. Values in parentheses represent the number of determinations.

Oxide	Sample 111		Sample 112*		Sample 747		Sample 753	
	Range (%)	Average (%)	Range (%)	Average (%)	Range (%)	Average (%)	Range (%)	Average (%)
SiO_2	47.2–50.6(12)	49.3	45.3–52.5(10)	50.4	44.0–46.2(10)	44.9	53.9–64.1(12)	60.0
Al_2O_3	12.3–13.9(6)	12.9	12.4–13.6(5)	12.9	11.6–12.6(6)	12.2	15.8–20.2(6)	17.4
FeO†	7.3–9.2(7)	8.4	1.3–1.5(6)	1.4	2.2–4.1(5)	2.8	2.0–4.8(6)	3.4
MgO	5.8–6.8(12)	6.3	6.0–6.9(10)	6.5	7.9–8.7(10)	8.3	1.6–3.4(12)	2.4
CaO	16.4–18.1(12)	17.3	22.3–26.8(10)	23.2	27.1–29.2(10)	28.0	3.2–10.0(12)	5.9
Na_2O	1.4–2.2(7)	1.7	0.8–1.4(6)	1.0	1.1–1.6(5)	1.4	1.3–1.7(6)	1.5
K_2O	1.6–2.5(7)	1.9	2.3–2.6(6)	2.5	0.8–1.0(5)	0.9	7.5–9.4(6)	8.5
TiO_2	1.0–1.1(5)	1.0	0.3–0.4(5)	0.4	0.2(1)	0.2	0.4(1)	0.4
MnO	0.44(5)	0.4	0.5–0.6(5)	0.5	0.5–0.6(5)	0.5	0.2–0.4(6)	0.3
Total		99.2		98.8		99.2		99.8

* The refractive index of this spherule is 1.582 to 1.594. (The refractive indices of two other spherules, not included in this table, were also determined. One had a refractive index of 1.608 ± .002 and the other had a range of refractive index from 1.551 to 1.585.) † Total iron as FeO.

samples 747 and 753. By comparison with the standards, the silicate spherules are somewhat heterogeneous, especially sample 753. Of the elements, K, Fe, and Na seem to be the most heterogeneous, and Mn, Mg, and Ca seem to be the most homogeneous, except in sample 753. Silicon is fairly homogeneous in all four samples and Al is somewhat heterogeneous.

Three of the spherules (samples 111, 112, and 747) are characterized by low silicon dioxide (45 to 50 percent) and high calcium oxide (17 to 28 percent) content (Table 1). Sample 753 has a fairly high silicon dioxide content (~ 60 percent) and an anomalously high K_2O content (8.5 percent).

Since the silicate spherules were found in an isolated region of Central Siberia, it is unlikely that they are industrial contaminants (however, such a possibility cannot be entirely dismissed). They contain more silicon dioxide and iron and less calcium oxide than most iron slags from blast furnaces (*9*). No trace of any other common base metal was found during microprobe analysis which would indicate that the glass is slag from some other base metal, such as Cu, Zn, or Pb. Likewise, no trace of sulfur was found which would be indicative of slag from a sulfide ore. It is unlikely that the spherules are a common artificial glass, since most ordinary synthetic glasses contain less aluminum oxide and more silicon dioxide and sodium oxide (*10*). We cannot, however, rule out the possibility that the spherules are fly ash produced from the burning of powdered coal, since spherules produced in this manner exhibit a wide range in composition (*11*).

A glass with high silicon dioxide content can be formed by the burning of straw or wood; it is unlikely that the Tunguska spherules were produced in this manner, since such a glass would probably have a much lower aluminum oxide content (*12*). According to Baker and Gaskin (*12*), soil or rock can be fused by a forest fire. The composition of the resulting spherules would depend upon the composition of the rock.

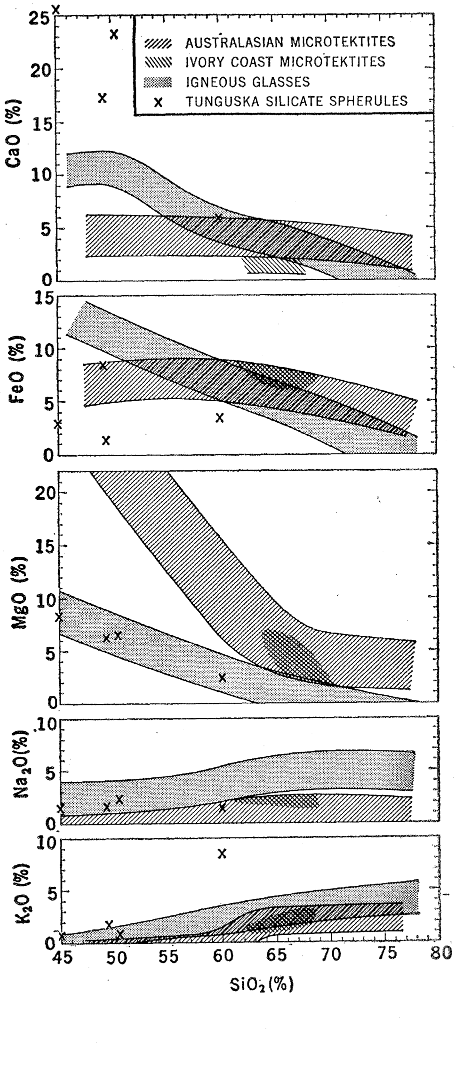

Fig. 1. Relation of Tunguska spherules to microtektites and igneous glass. Data on Australasian microtektites from Cassidy *et al.* (*18*). Composition of igneous glasses is based on published analyses of over 120 igneous glasses. Greater than 90 percent of the analyses fall within the range indicated. FeO represents total iron.

All four of the spherules (except sample 753) have a content of K_2O, MgO, and Na_2O similar to that of igneous glasses (Fig. 1). Although not shown in Fig. 1, their Al_2O_3 content is also similar to that of igneous glass. However, they differ from igneous glasses in their high calcium oxide and low iron content (Fig. 1). Furthermore, there has been no recent volcanism in Central Siberia and it is unlikely that spherules of this size could have been carried far by winds (*13*). On the other hand, their association with magnetic spherules which have an iron-nickel ratio indicative of a cosmogenic origin (*4*) and their occurrence in the forest area devastated by the explosion of the Tunguska meteorite suggest that the silicate spherules are cosmic in origin and that they are, in fact, a residue from the Tunguska meteorite (*2*). Since no traces of cratering or destruction of the ground could be connected with the explosion of the Tunguska meteorite (*2*), it is unlikely that the silicate spherules are impactites.

The silicate spherules are not similar to any major group of stony meteorites including carbonaceous chondrites. Spherule sample 753 is distinguished from stony meteorites by its high content of silicon dioxide (60 percent) and aluminum oxide (~ 17 percent). The spherules low in silicon dioxide differ from most stony meteorites in their high content of Al_2O_3 (> 12 percent) and CaO (17 to 28 percent) and low MgO (< 8.3 percent) content. I am aware of only one stony meteorite with a comparable content of Al_2O_3 and CaO. This is the Angra dos Reis meteorite which fell near Rio de Janeiro, Brazil, in 1869 (*14*).

Since the number of silicate spherules recovered from the Tunguska impact area is only a small fraction of the number of metallic spherules (*15*), the silicate spherules should probably be compared to the silicate portion of stony-irons or to the silicate inclusions in iron meteorites. However, the mineralogy of the stony-irons suggests that they also contain more MgO and less CaO and Al_2O_3 than the Tunguska spherules. According to Mason, the composition of silicate inclusions in iron meteorites resembles that of the chondritic meteorites (*16*). Thus, the Tunguska spherules do not seem to resemble silicate inclusions in iron meteorites.

A comparison with microtektites shows that only one of the spherules (sample 753) has a composition similar to that of the microtektites of Australasia or the Ivory Coast; this spherule has an anomalously high K_2O content (Table 1, Fig. 1).

The possibility that the silicate spherules are an industrial contaminant, such as fly ash, or are soil or rock fused by a forest fire cannot be completely disregarded. However, their association with magnetic spherules, whose pattern of distribution suggests that they were produced by the explosion of the Tunguska meteorite, suggests that the silicate spherules are also residue from the Tunguska meteorite. Some authors believe that the Tunguska event was the result of the explosion of a small comet in the atmosphere (*2, 17*). If this is true, then the data reported here may constitute the first analyses of the siliceous residue of a comet.

BILLY P. GLASS*

Planetology Branch, Goddard Space Flight Center, Greenbelt, Maryland

References and Notes

1. E. L. Krinov, *Giant Meteorites* (Pergamon, New York, 1966), pp. 125–265.
2. K. P. Florenskiy, V. I. Vronskiy, Yu. M. Yemel'yanov, I. T. Zotkin, O. A. Kirova, *Meteoritika* **18**, 103 (1960).
3. O. A. Kirova and N. I. Zaslavskaya, *ibid.* **27**, 119 (1966).
4. O. A. Kirova, *Ann. N.Y. Acad. Sci.* **119**, 235 (1964).
5. B. Glass, *Nature* **214**, 372 (1967).
6. ——— and B. C. Heezen, *ibid.*, p. 372.
7. Five of the Tunguska silicate spherules were obtained from the Committee on Meteorites of the Soviet Academy of Sciences through the assistance of Drs. E. L. Krinov and O. A. Kirova. Four additional silicate spherules from the Tunguska impact area were obtained from Dr. W. A. Cassidy, who had previously obtained them from the same source.
8. The analyses were performed with an electron microprobe x-ray analyzer (Applied Research Laboratories). The measurements were made at 20 kv and 0.03 μa. The methods, standards, and instrument are the same as those used by L. S. Walter [*Geochim. Cosmochim. Acta* **31**, 2043 (1967)]. The analyses given in Table 1 are corrected for background and instrument drift.
9. The chemical composition of commercial slags varies within relatively narrow limits. Analyses of the slags from most American blast-furnaces (based upon examination of hundreds of analyses) fall within the following percentage range: SiO_2, 33 to 42; Al_2O_3, 10 to 16; CaO, 36 to 45; MgO, 3 to 12; S, 1 to 3; FeO, 0.3 to 2; MnO, 0.2 to 1.5 [G. W. Josephson, F. Sillers, Jr., D. G. Runner, *U.S. Bur. Mines Bull. 479* (1949)].
10. G. W. Morey, *The Properties of Glass* (Reinhold, New York, 1960).
11. W. A. Selvig and F. H. Gibson, *U.S. Bur. Mines Tech. Pap. 679* (1945); W. I. Luke, *Technical Report No. 6-583* (U.S. Army Engineer Waterways Experiment Station, Corps of Engineers, Vicksburg, Mississippi, November 1961).
12. G. Baker, *Mem. Nat. Mus. Victoria No. 23* (1959); ——— and A. J. Gaskin, *J. Geol.* **54**, 88 (1946).
13. According to Glasstone, it would take an 80-μ particle (with a density of 2.5 g/cm^3) only about 6 hours to fall from an altitude of 36,600 m; the larger silicate spherules (350 μ) would take less than an hour to fall from that height. Thus it is unlikely that the silicate spherules could have been carried very far by winds [S. Glasstone, *The Effects of Nuclear Weapons* (U.S. Atomic Energy Commission, Oak Ridge, Tennessee, 1962)].
14. The percentage chemical composition of the Angra dos Reis meteorite is: SiO_2, 43.94; Al_2O_3, 8.73; FeO, 8.28; Fe_2O_3, 0.31; MgO, 10.05; CaO, 24.51; Na_2O, O.26; K_2O, 0.19; TiO_2, 2.39; and P_2O_5, 0.13 [E. Ludwig and G. Tschermak, *Mineral. Petrogr. Mitt.* **28**, 110 (1909)].
15. According to Kirova and Zaslavskaya (*3*), approximately 1000 to 2000 metallic spherules were recovered from the soil samples collected in the Tunguska impact area as compared to a few dozen silicate spherules of the same diameter.
16. B. Mason, *Mineral. Mag.* **36**, 120 (1967).
17. V. G. Fesenkov, *Meteoritika* **20**, 27 (1961).
18. W. A. Cassidy, B. Glass, B. C. Heezen, *J. Geophys. Res.*, in press.
19. I am grateful to Dr. B. C. Heezen whose ideas and encouragement led to this investigation. I thank Dr. L. S. Walter and F. Wood for help with the microprobe analyses. Discussions with D. W. Lewis of the National Slag Association and Drs. J. A. O'Keefe, C. C. Schnetzler, B. French, and B. Mason were helpful. J. A. Glass helped prepare the manuscript. I am indebted to Drs. E. L. Krinov and O. A. Kirova for sending me five of the Tunguska silicate samples.

* U.S. Army Corps of Engineers, assigned to Goddard Space Flight Center, Greenbelt, Maryland.

10 February 1969

■

Portland Cement: Pseudomorphs of Original Cement Grains Observed in Hardened Pastes

Abstract. *Scanning electron micrographs show that a hydration product forms inside the anhydrous cement grains and forms a pseudomorph of the original cement grain. The originally water-filled space between the grains is partially filled with calcium hydroxide crystals that appear to be responsible for the strength of the cement paste.*

The hydration of portland cement occurs by either a dissolution of the cement grains and precipitation of the hydration products, or by a surface chemical reaction on or in the cement grains. Despite controversy over the relative importance of these two modes of hydration (*1*), it is known from optical studies under dilute conditions that both reactions occur simultaneously (*2, 3*) on the inside and the outside of the cement grain. Taplin (*2*) formulated a model consisting of an inner and an outer product to derive equations to represent the hydration of portland cement; however, until recently, no microscopic evidence has been found to support this model for cement pastes with a low ratio of water to cement.

Investigations of hardened cement pastes confirm Taplin's model. The pseudomorphs of the original cement grains are preserved in the hardened cement pastes (Figs. 1 and 2) and there are differences in hydration products deposited within and between the original grain boundaries.

Anhydrous portland cement contains four principal compounds: tricalcium silicate ($3\ CaO \cdot SiO_2$), β-dicalcium silicate, tricalcium aluminate, and a ferrite phase belonging to the $2\ CaCO \cdot Fe_2O_3$–$6\ CaO \cdot 2\ Al_2O_3 \cdot Fe_2O_3$ solid solution series. Small amounts of MgO, CaO, and alkali sulfates also occur in many cements. Portland cement is usually manufactured in a rotary kiln where the material coheres into small rounded lumps (cement clinker) which after cooling are ground to a fine powder.

The reaction of portland cement with water is usually described as a hydration process, although it involves more than the formation of hydrates for each of the four starting compounds. The reaction of $3\ CaO \cdot SiO_2$ and water yields $Ca(OH)_2$, which is easily detected by optical microscopy or x-ray diffraction, and a calcium silicate hydrate (sometimes called cement gel or tobermorite gel). The calcium silicate hydrate is isotropic; its x-ray powder pattern consists of three broad bands. In cement $3\ CaO \cdot SiO_2$ is largely hydrated in 28 days, and hydration approaches completion in 1 year. The