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## On the origin of cavities in extraterrestrial magnetic spherules<sup>(\*)</sup>

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*This contribution is dedicated to the  
memory of the late Clarence T. Nagamoto*

**Summary.** — It was discovered that extraterrestrial magnetic spherules larger than  $10\ \mu\text{m}$  in diameter contain internal cavities. The possible origin of cavities is discussed. It is suggested that the primary particles contain ferrous carbonate or ferric hydroxide that upon heating during entry of micrometeorite releases carbon dioxide or water vapor that produces cavity in the molten spherule. The chemical composition of magnetic spherules is similar to that of the crust of the Earth.

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Sampling of aerosol particles in the southern hemisphere during October and November of 1967 and in 1969 revealed the presence of extraterrestrial particles [1-7]. These particles, called spherules, were magnetic, mostly round and were associated with what was thought to be an unknown meteor stream.

Under that hypothesis these particles, during entry into the atmosphere, at about 80 km altitude above the Earth, would be heated, through collisions with atoms and molecules present at this altitude, to the temperature at the melting points of the chemical compounds they were made of. The particles would, upon entry into the atmosphere, become molten spheres that would subsequently cool down to the temperature of the environment [8, 9].

Particles between  $2\ \mu\text{m}$  and  $5\ \mu\text{m}$  in diameter were solid spherules. X-ray photographs of the spherules larger than about  $10\ \mu\text{m}$  in diameter (fig. 1, from [6]) have shown the presence of internal cavities. The first X-ray photograph of an extraterrestrial particle (spherule) with an internal cavity was made by F. Prodi in 1968. The largest hollow spherule that was found was  $25\ \mu\text{m}$  in diameter with a skin thickness of  $1\ \mu\text{m}$ . The

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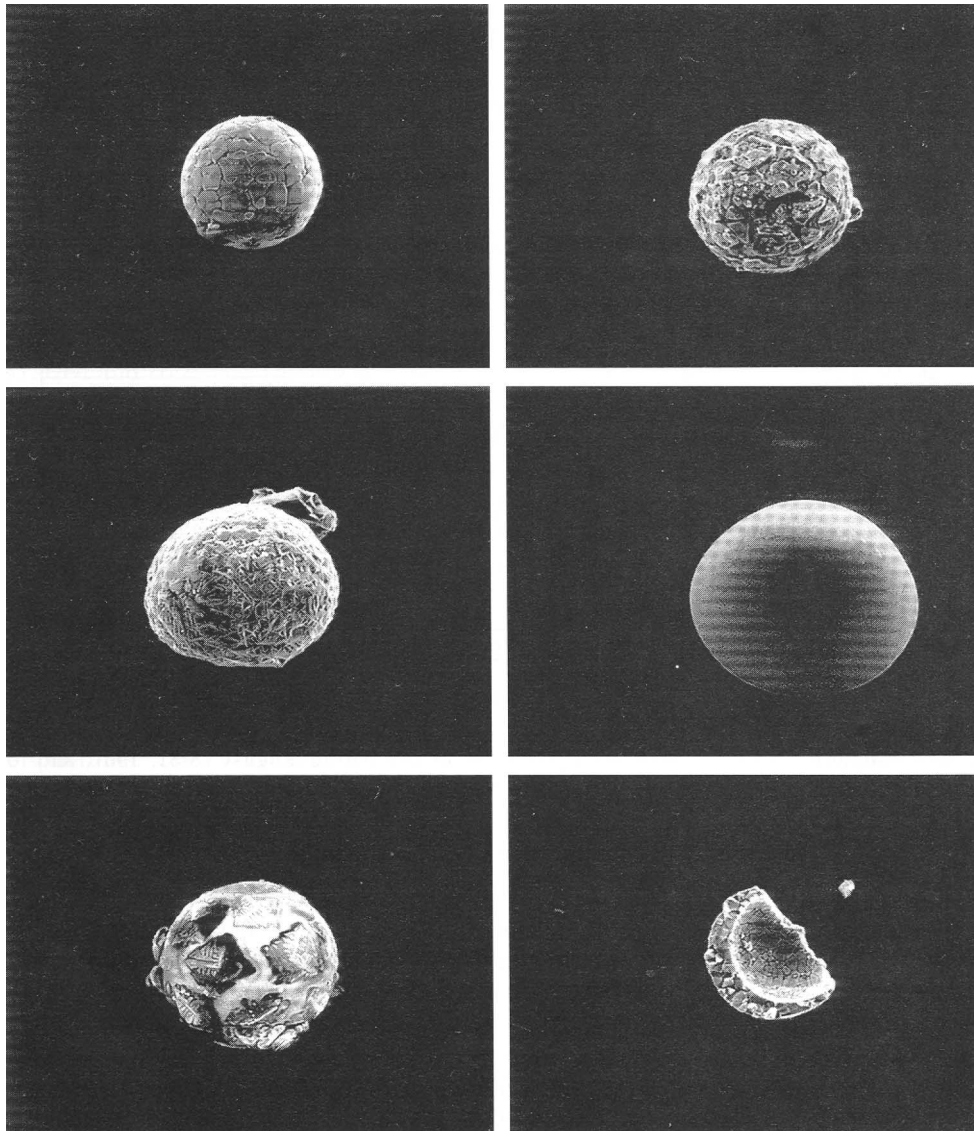


Fig. 1. – Scanning electron microscope photographs of five magnetic spherules and one spherule fragment. Diameters range from 15 to 20  $\mu\text{m}$ . The photograph of the fragment shows that larger spherules may contain cavities.

particles were analyzed by means of a scanning electron microscope and an ion probe microanalyzer. The chemical analysis of the solid part of magnetic spherules has shown that they consisted of a mixture of iron oxides with traces of: Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, and Ni. Chemical analysis of interiors of magnetic spherules revealed the presence of methane, ethane, carbon dioxide, water vapor and in some, nitrogen and oxygen only. The outer layer of the spherules consisted of FeO 1.3 and the layer below was FeO 1.1. The melting point of FeO is 1420 °C, and Fe<sub>2</sub>O<sub>3</sub> is 1560 °C. These

molten spherules must have, therefore, probably been at temperatures higher than the temperatures of their melting points at some time in their lifetimes. When a spherule was molten, there was mixing of oxides in the outer layer, evaporation and dissociation of oxides (oxygen leaving the surface) and later, mixing of the still molten interior with the sub-surface of the shell. The whole process probably took place in less than one second (0.1 to 0.3 s [9]).

If one takes a molten metal or molten iron oxide and pours it into some colder substance (*e.g.*, water), it will solidify into solid globules, *i.e.* they would not produce cavities. In 1939, the first author of the present paper was preparing chemically pure copper sulfate. To speed up the dissolution of copper in hot, concentrated sulfuric acid, he was melting copper in a crucible and adding sulfur to the molten metal. This caused the boiling of the crucible contents and the copper began to boil. The copper was then poured into a diluted solution of sulfuric acid. The solidified product consisted of large copper bubbles, some of which were 2 cm in diameter, with a skin thickness of about 100  $\mu\text{m}$ . In an analogous way, some gas or vapor, therefore, must have been present in the extraterrestrial particles to produce cavities.

The chemical compound that should be considered in production of cavities containing carbon dioxide is ferrous carbonate. It decomposes upon heating and releases carbon dioxide. When carbon dioxide leaves that compound it releases ferrous oxide, FeO. The volume of 22  $\mu\text{m}$  diameter spherule (diameter of the cavity is 20  $\mu\text{m}$ ) is about 4000 ( $\mu\text{m}$ )<sup>3</sup>. The volume of the released gas is a thousand times more. Most of the carbon dioxide will be released from the surface into the atmosphere upon heating of the entering particle. A cavity will be formed when the interior of the entering particle is still hot (maybe even molten) and the surface of the particle is still liquid. A candidate for the production of a cavity containing water vapor is ferric hydroxide, Fe(OH)<sub>3</sub>. This compound, upon heating, releases 1.5 molecules of water per molecule of hydroxide, and leaves Fe<sub>2</sub>O<sub>3</sub> (ferric oxide).

Ferric oxide was never found in the spherules. There was always less oxygen in those mixtures of oxides. Oxygen was lost when the particle was molten at a high temperature at an altitude between 80 and 70 km. What was left, therefore, was a mixture of iron oxides, as has been shown by chemical analysis. When the surface of a molten particle solidifies, water molecules are still released from Fe(OH)<sub>3</sub> present in a still molten interior of a particle, and a cavity is formed. Particles made of ferrous oxide, when heated to the boiling point produced a bubble of FeO vapor. This vapor condensed on the interior of the cavity and produced a spherule with a vacuum inside.

Such may be the mechanism of formation of spherules with internal cavities. If this is the case, then ferric hydroxide or ferrous carbonate must exist in the primary particles in the meteor stream, which produces magnetic spherules. As an example, we can take a 22 micrometer diameter spherule with a cavity of 20 micrometer diameter. The volume of the cavity is  $4 \times 10^3$  ( $\mu\text{m}$ )<sup>3</sup>, and the volume of water vapor available from the whole particle is  $6.3 \times 10^6$  ( $\mu\text{m}$ )<sup>3</sup>, at STP; more than enough to form the cavity. Most of the water vapor released from Fe(OH)<sub>3</sub> is left at high altitudes during the entry of the micrometeorites into the atmosphere.

Rosinski *et al.* [4] found carbon dioxide, water vapor and methane, in three spherules. These chemical compounds indicate that those particular particles contained some organic compounds that, during the heating and formation of spherules, were decomposed. Carbon was oxidized to carbon dioxide, hydrogen was released from water vapor and produced some methane with carbon. Water vapor was released from ferric hydroxide. All these chemical reactions took place in a fraction of a second, and those reactions,

therefore, could not reach chemical equilibrium.

Discovery of a meteor stream that contains magnetic particles consisting of spherules with cavities was made at ground level in the southern hemisphere. Attempts to observe these meteoritic particles entering the Earth's atmosphere in subsequent years failed and therefore those particles must enter our atmosphere at very low velocities. They are not heated probably to the melting point because they are not visible and therefore the mechanism of formation of cavities in those spherules must be different than described earlier.

Kerrigan [10] suggested that those spherules might be premade (in some other event) and that they enter the atmosphere already formed. If that is the case, then authors suggest that 65 million years ago, when a collision took place between an asteroid and the Earth in the Yucatan Peninsula, vapors (because material of the asteroid and the soil with which it collided were vaporized) were thrown into an orbit which should be very similar to that of the Earth [11-13]. It is also possible that some undocumented collisions took place at some later times. These recondensed into particles, and it may be that those particles which ended up as magnetic spherules were formed during this process. This cloud which was vapor of the Earth's material and of the asteroid, recondensed and formed particles which were not spherical particles with cavities but were slightly magnetic particles which were thrown into an orbit similar to the Earth's orbit. These particles are floating in the orbit around the Sun.

Microscopic particles are attracted by the Sun. Some are attracted and some are repulsed. In any case, they almost certainly were removed from the Earth's orbit in 65 million years. This may be the origin of the magnetic particles, which were collected. We collected magnetic spherules with cavities plus large numbers of some particles, which were maybe coagulation products of vapors. The coagulation products, called Rosinski secondary particles (Rosinski and Snow, 1961) are left at high altitudes. The source of magnetic spherules and slightly magnetic particles, which we discovered, is still a mystery.

The authors are now making the suggestion that material ejected into orbit after the collision of an asteroid with the Earth is the source of magnetic particles collected in the southern hemisphere. The orbit would be that of the Earth, plus a displacement by the jet which ejected these materials into space.

The suggestion that methane could be formed in the spherule is difficult to accept, because the atmosphere in a spherule is oxidizing, that is,  $\text{FeO}_x$  and would prevent the formation of methane, because hydrogen and carbon would be oxidized to carbon dioxide and water. This would support this hypothesis, and what we analyzed might be the atmosphere present on Earth 65 million years ago. At the time of this collision with the asteroid, the Earth was covered with vegetation.

This is all that can be done at this time because further study would require sampling. The samples originally collected were destroyed in an accident at the Max Planck Institute in Germany (about 1980) and the only way to look further is to start sampling again (in the southern hemisphere in October for about one hundred days and then also in April in the northern hemisphere, perhaps in Alaska).

Very remote possibilities exist that the presence of methane discovered in cavities of three spherules indicate the existence of extraterrestrial life in the solar system.

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