The origin of black magnetic spherules through a study of their chemical, physical and mineralogical characteristics

M. Del Monte (*) – T. Nanni (**) – M. Tagliazucca (**)

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Summary. — The origin of black magnetic spherules sampled in air, and in ancient and recent marine sediments has been investigated.

Experiments were performed reproducing in laboratory the same processes undergone by the cosmic dust during its flight through the atmosphere. Spherules similar in size, shape, chemical and mineralogical characteristics to the natural ones have been obtained. It has been tested that hollow spherules can be also produced in the high atmosphere.

The bubble formed inside some black magnetic spherules by the decrease of solubility of oxygen at the melting point can be sometimes ejected from the rear side of the spherule producing secondary particles less than 10 μm is size.

The volcanic origin of black magnetic spherules has been excluded. In fact ferromagnetic volcanic particulate matter present mineralogic. chemical and structural characteristics different from that of black magnetic spherules.

Also the use of some parameters is suggested to discriminate industrial ferromagnetic spherules from black magnetic spherules of extraterrestrial origin.

Samples from sediments old enough to exclude industrial contamination allow to calculate the earth accretion in cosmic dust.

Riassunto. — E stata svolta un'indagine sull'origine delle "Black Magnetic Spherules" campionate sia in aria che in sedimenti recenti e di età geologica.

(*) Istituto di Geologia e Paleontologia, Via Zamboni 65, Bologna, Italy.

(**) Microfisica dell'Atmosfera – C.N.R., Via Castagnoli 1, Bologna, Italy.

Si sono riprodotti in laboratorio gli stessi processi subiti dalla polvere cosmica durante il passaggio attraverso l'atmosfera. Attraverso queste prove di laboratorio si sono ottenute "spherules" simili a quelle trovate in natura (per dimensioni, forme e caratteristiche chimico-mineralogiche).

È stato inoltre provato che le "spherules" cave si possono essere formate nell'alta atmosfera.

All'interno di alcune b.m.s. si può sviluppare una bolla dovuta alla diminuzione di solubilità dell'ossigeno al punto di fusione. Questa bolla talvolta può venire espulsa dalla parte posteriore della sferula producendo particelle secondarie di diametro inferiore ai 10 μm.

Inoltre è stato possibile escludere l'origine vulcanica delle b.m.s. Infatti la frazione ferromagnetica del materiale vulcanico in particelle presenta caratteristiche mineralogiche, chimiche e morfologiche differenti da quelle delle b.m.s.

Si propone l'impiego di alcuni parametri che permettono di distinguere le sferule ferromagnetiche di origine industriale da quelle di origine extraterrestre.

Dall'indagine svolta su campioni prelevati da sedimenti formati in epoche abbastanza antiche, tali da escludere una contaminazione industriale, si è potuto calcolare l'accrescimento terrestre della polvere cosmica.

Our work is concerned with the origin of the fraction of ferromagnetic particulate matter made up of black magnetic spherules (b.m.s.) less than 100 microns in diameter. Samples were taken from the air, from marine sediments and from topographic highs.

For many years we samples airborne particulate matter on the top of Mt. Cimone (2,170 m) in the Italian Apennines, using an electromagnetic device. We also took samples of ferromagnetic material from sediments old enough to exclude industrial contaminants which are usually present in airborne particulate matter. A careful investigation was carried out on four marine cores in the Mediterranean Sea and eleven samples from condensed successions on ancient and recently formed structural highs (see Table 1).

Chemical, mineralogical and morphological analyses were carried out on both single and multiple particles from all the samples, using an X-ray microanalyser, an X-ray diffractometer, X-ray contact micrography technique, a scanning electron microscope, an atomic absorption spectrometer and a Debye-Scherrer-Gandolfi camera. The particles show the following characteristic (see Table 2):

a) a high iron content, associated with a small quantity of Ni and Co, and traces of Ir; the Mn content is always lower than the detection limit (< 1 p.p.m.);

b) magnetite, wüstite and α-Fe paragenesis with radial distribution;

c) a dendritic surface (see Fig. 1);

d) a polycrystalline structure;

e) the microcrystals are less than 1 μm in size and are randomly oriented;

f) an acentric cavity in about 10% of the b.m.s. in the size range $10 < r < 10^2$ μm, that occupies half of the spherule diameter (see Fig. 2).

To test the supposed extraterrestrial origin of the b.m.s. some Laboratory investigations were carried out. An attempt was made to reproduce the effect of thermodynamical processes on extraterrestrial ferromagnetic particles during their flight through the atmosphere. In this way we were able to produce artificially hollow and completely solid b.m.s. similar in shape, size, paragenenis and mineralogical distribution to their natural counterparts (Del Monte et al., 1974) (3).

The experiments were performed in a cylindrical pyrex chamber supporting two Fe (or 90% Fe – 10% Ni) electrodes that faced one another. A large number of molten particles of the required size were produced by applying a high frequency current and proper tension to the electrodes. The particles cooled during their fall (their cooling time is some tenths of a second) and were collected on a plate at the bottom of the chamber.

The results indicate that the paragenesis, mineralogical distribution and presence of the cavity are strictly dependent on O_2 partial pressure in the atmosphere in which the particles melt and cool (see Table 3). B.m.s. similar to natural ones were obtained for air pressures of about 20 mm of Hg. In particular, as far as the hollow particles are concerned, we noted that while their number and size of cavity increase as the O_2 partial pressure is raised, they were not produced in atmospheres containing argon or nitrogen.

On the basis of our experiments we propose that the cavity in b.m.s. may be due to the decrease in the solubility of O_2 in iron when the particle cools below melting point. In fact, the solubility of O_2 in molten Fe is high (Smithells, 1967) (14) and the particle is thus able to absorb all the oxygen molecules it meets. Owing to the high oxidation rate at the temperature experienced by b.m.s. (Kubaschewski and Hopkins, 1967) (9) the particle can be completely oxidized before it reaches freezing point. The excess of O_2 inside the particle is freed by

Fig. 1 – Dendritic structure of a natural b.m.s. fragment.

Fig. 2 – The X-ray image of a hollow natural b.m.s. (30 μm in diameter).

diffusion in the form of bubbles (Dushman and Lafferty, 1962) (4) towards the inner part of the spherule which acts as an accumulation region for the released oxygen since it is at a higher temperature than the surface area.

This process has been tested in the Laboratory by reproducing the same dynamic pressure experienced by ferromagnetic particulate matter in the molten state during its flight through the atmosphere (see Fig. 3).

We have also observed artificial b.m.s. which show ragged openings (see Fig. 4) or a protruding dome (see Fig. 5) similar to that observed by several authors and ourselves, both in airborne samples and marine sediments (Bruun et al., 1955; Hodge et al., 1964; Funiciello and Fulchignani, 1969; Rosinski, 1972; Del Monte et al., 1974) (1,8,6,12,3).

The observation of the presence in b.m.s. of acentric cavities, protruding domes or ragged openings indicates that the bubbles are forced to move inside the particles by a force field.

Experiments were performed under different dynamic conditions relative to the particle system, to see whether the shifting of the bubble is due to an inertial force field.

Metallic drops which cooled in the earth's gravity field ($a \sim 1000$ cm/sec^2) showed an acentric cavity, whereas the solidified ones, during their free fall ($a = 0$), contained a perfectly centered cavity.

In fact, as a cosmic dust fragment interacts with the atmosphere, a force field is induced in a coordinate system moving with in the particle, owing to the deceleration. The gas bubble formed during the cooling phase offers a resistance to the force field so different from that of the particle that it causes the bubble to shift inside it or to be ejected from the rear side. Decelerations undergone by b.m.s. are functions of their size and angle of incidence in the atmosphere.

We have calculated that during the solidification phase the particles experience decelerations varying from some thousands to some hundreds of meters per sec^2. By introducing these decelerations and parameters relative to both O_2 and iron in Stokes' equation, we can calculate the rate of movement of the gas bubble inside the molten particle. We obtain a rate of displacement such that the gas bubble can reach the surface of the molten particle in a very short time ($\sim 10^{-6}$ sec). The breaking of the magnetite sheet requires some hundredths of a second. The times we consider are thus comparable to those necessary for a molten particle to cool below melting point by some hundreds of degrees ($\sim 10^{-1} \div 10^{-2}$). Thus, gas bubbles can sometimes escape from

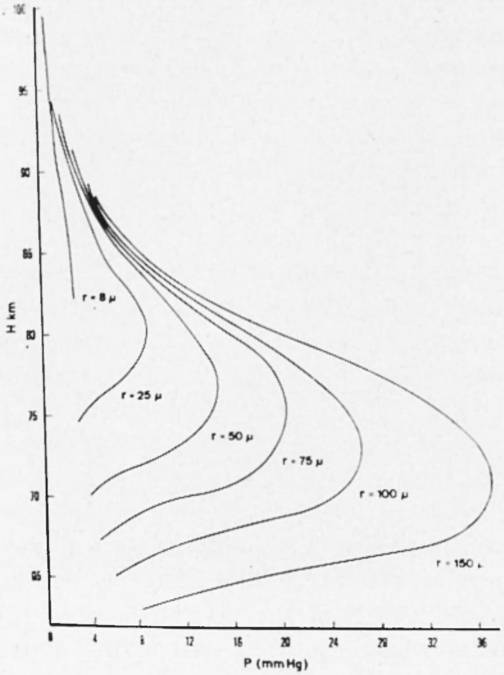


Fig. 3 – Dynamic pressure experienced by natural b.m.s. as a function of height.

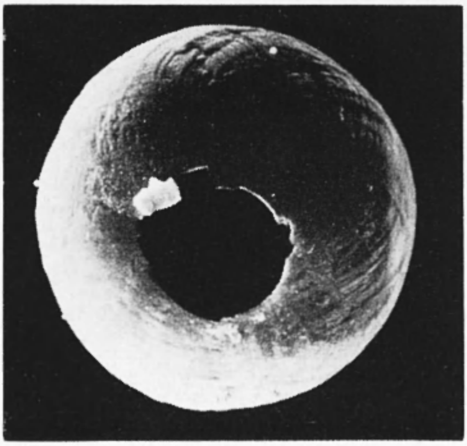


Fig. 4 – Electron microphotograph of a natural b.m.s. with a ragged opening (30 μm in diameter).

the micrometeorite body before a complete crystallization takes place; they sometimes remain trapped at the surface.

We found experimentally that, if the internal O_2 pressure is such as to overcome the pressure due to the surface tension of the molten particles and the bubble's escape time is shorter than that of solidification, numerous secondary spherules, in the micron and submicron range, may be produced as a result of the splashing of the molten surface lamina. In fact, iron powders selected in the size range 64-156 μm were let into O_2 plus H_2 flame at about 2200°K. They melted instantaneously while they were being transported by the gas flux and cooled rapidly. Examination of the melting product with an electron microscope revealed the presence of spherules less than 10 μm in diameter. Since they were absent in the initial distribution, they must have been produced by the splashing of the "black spherules" surface, caused by the escape of the O_2 bubble. The submicron secondary particles ($10^{-2} < r < 10^{-1}$ μm) generally formed chains or a dense mass (see Fig. 6) which resembled the fluffy particles found in the upper atmosphere (Hemenway and Soberman, 1962) (7).

The experimental evidence is in agreement with the results of our calculations and supports the hypothesis that b.m.s. are produced by the interaction of cosmic dust with the upper atmosphere (Opik, 1956; Vittori, 1970) (11,15).

We must, however, take into account alternative hypotheses, that b.m.s. may, for example, be of industrial or volcanic origin.

We first investigated the possibility of volcanic activity as a source of b.m.s. We examined twelve samples of particulate matter collected from the air, from tuffaceous or semi-incoherent ignimbritic levels, and from ash layers of marine core from the Gulf of Pozzuoli (see Table 4). In each sample the ferromagnetic fraction was composed of some thousands of particles whose dimensions were less than 1 mm.

The analyses carried out on the ferromagnetic particulate matter, using the same techniques as those used for the b.m.s. showed:

a) magnetite crystals generally associated with silicate fragments which are usually idiomorphic; their most common shape is octahedron or rhombic dodecahedron (see Fig. 7);

b) a high iron content (60%) is present associated with minor elements typical of magnetic lattice such as Si, Al, Ti, Ca, Mg, Cr, Mn (see Table 2);

c) there are no hollow particles.

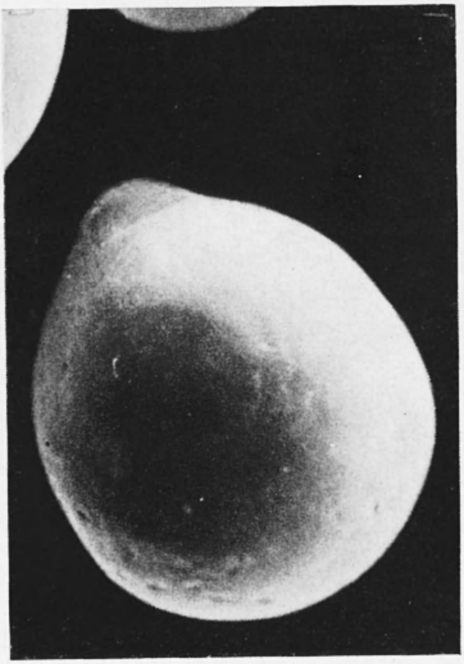


Fig. 5 – Electron microphotograph of a natural b.m.s. showing a protruding dome (42 μm in diameter).

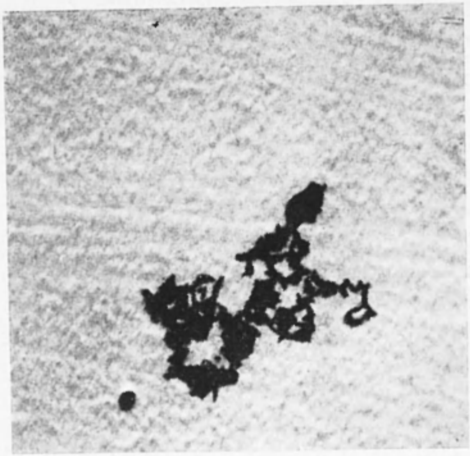


Fig. 6 – Electron microphotograph of artificial secondary particle aggregate.

The features of ferromagnetic particulate volcanic matter appear to be determined by a thermodynamic process of formation. This is neither consistent with the b.m.s. spherical shape nor with their microcrystalline structure. In fact, the b.m.s. and ferromagnetic volcanic particulate matter appear to be of different origin, undergoing processes which are characterized by different maximum temperatures, rates of crystal growth, cooling times and freezing temperatures.

The thermodynamic equations we used to describe the processes of formation of both b.m.s. and ferromagnetic volcanic particulate matter are (Cottrell, 1965) (2):

$$f = n\nu \qquad [1]$$

$$n = N \exp\left(-\Delta F/KT\right) \qquad [2]$$

$$A = a\gamma^3 \left(M T_M/\vartheta L_M\right)^2 \qquad [3]$$

$$a_0 = -4\gamma \left(M T_M/\vartheta L_M\right) \qquad [4]$$

where

f = rate of crystal growth;
n = number of nuclei in the system;
ν = frequency at which a single molecule from the melting matter joins a critical nucleus to make it a stable crystal;
N = number of possible nucleation sites;
ΔF = total free energy change involved in forming the nucleus;
A = critical value of the work of nucleus formation;
γ = surface free energy of unit area of the interface between the nucleus and the parent phase (for Fe_3O_4, $\gamma = 204$ ergs/cm^2);
K = Boltzmann constant;
T = temperature of nucleation;
T_M = melting point (for Fe_3O_4, $T_M = 1811$°K);
ϑ = $T_M - T$;
a_0 = critical size of nucleus;
a = shape parameter (for spherical shape, $16\,\pi/3$);
M = volume of a gram-molecule (for Fe_3O_4, $M = 44.6$ cm^3);
L_M = latent heat per gram-molecule (for Fe_3O_4, $L_M = 1.38 \cdot 10^{12}$ ergs per gram-molecule).

The magnetic crystal can separate from the molten magma only if O_2 partial pressure is sufficiently high and the cooling time of the lava is long enough to allow the growth of crystals in equilibrium conditions until the observed dimensions have been reached (Fenner, 1929) (5). In fact, to reach given dimensions, a monocrystal needs a time expressed by the ratio between the number of molecules of Fe_3O_4 contained in the monocrystal and the rate of growth (equation [1] for $n = 1$). The time is of the order of a few seconds for crystals of some tenths of a micron in size. However, the process of crystallization is retarded by the diffusion of Fe atoms within the molten silicate. The diffusion times are a third order of magnitude greater than that of the crystal. On the other hand, the observed microcrystalline structure of b.m.s. ($< 1\ \mu m$) shows (see Fig. 8) that they underwent rapid crystallization in a supercooled state.

Crystallization times as a function of undercooling can be obtained from the ratio between the number of molecules of the particles and the rate of nucleation (equation [1] where n is calculated from equation [2]). These times are of the order of about 10^{-7} sec. B.m.s. crystallization times are found to be very short compared with those of ferromagnetic volcanic crystal formation.

On these grounds we come to the conclusion that the contribution of ferromagnetic volcanic particulate matter to the b.m.s. sampled in the air, in marine sediments or in polar ices must be considered nil.

We would now like to discuss the contribution made by other terrestrial sources such as the iron and steel industry or the combustion of products containing Fe to the deposits of ferromagnetic matter found at Mt. Cimone. In both industrial and urban areas we took samples of ferromagnetic matter and examined them chemically, morphologically and mineralogically. The results of the analyses are as follows:

a) the Fe content is about 50% and a small quantity of Si, C, Ti, Mn, V, Al, Cr may be present; Ni and Co are absent (see Table 2);

b) the mineralogy of the particles is hematite, magnetite and graphite;

c) some particles have a dendritic surface, while others have a polished, shiny surface;

d) all the crystals have a polycrystalline structure;

e) almost all the ferromagnetic particles are spherical and 90% of them are hollow; the cavities are very large or show ragged openings.

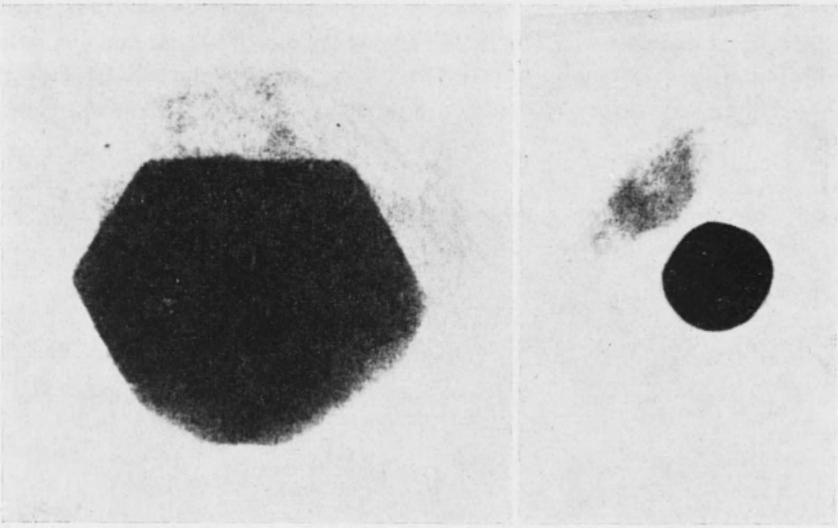
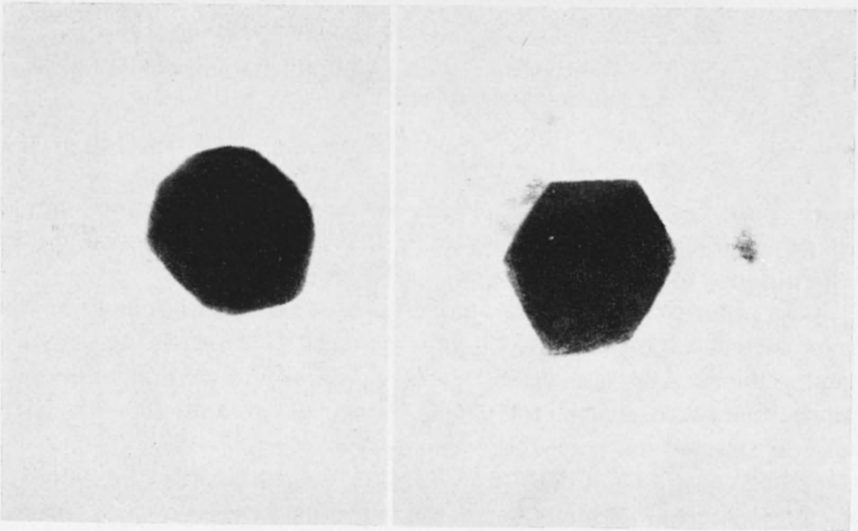


Fig. 7 – X-ray images of ferromagnetic volcanic particles:

(*a*) Magnetite crystals associated with silicate fragments (20-80 μm in diameter);



(*b*) Magnetite simple crystals (50 μm in equivalent diameter).

It is clear that, at first sight, these particles can be confused with b.m.s. of extraterrestrial origin. The confusion disappears on chemical and mineralogical analysis. In fact, the minor elements present in these particles are typical of cast iron, while Ni and Co, ever present in b.m.s. of extraterrestrial origin, are absent. Their mineralogy is clearly distinguished by the presence of graphite and hematite and by the absence of wüstite and α–Fe (see Table 2).

Fig. 8 – Electron microphotograph of a natural b.m.s. showing a microcrystalline structure (8 μm in diameter).

In order to evaluate the contribution of terrestrial sources to the samples collected from Mt. Cimone, we need to refer to the chemical and mineralogical characteristics of uncontaminated b.m.s. sampled in sediments old enough to exclude industrial contaminants which are usually present in particulate matter.

Therefore, as can be seen in Table 1, we can assume the following to be significant parameters of the airborne extraterrestrial fraction of b.m.s.:

a) the Ni/Fe ratio which is about 10% in the extraterrestrial fraction of b.m.s. (Heide in Rosler and Lange, 1972) (¹³) and about 0.1% in the lithosphere (Taylor in Rosler and Lange, 1972) (¹³);

b) The Ni content, which, by mean's of Link's equation (Link, 1964) (¹⁰), indicates the ratio between the extraterrestrial and the terrestrial components;

c) the percentage of spherical hollow particles;

d) the amount of wüstite and α-Fe.

The Ni/Fe ratio is found to be nil in ferromagnetic particulate matter sampled in urban areas, while it assumes values of about 10% for b.m.s. in uncontaminated sediments (see Table 2). The airborne samples collected from the top of Mt. Cimone are characterized by a strongly variable Ni/Fe ratio. This probably depends on meteorological conditions which may either favour or prevent the rise of terrestrial particulate matter. The mean value found is about $6.3 \cdot 10^{-2}$, while the minimum is about 10^{-2}.

The set of these ratios shows that at certain times a considerable amount (up to 90%) of airborne spherules sampled at the top of Mt. Cimone are of terrestrial origin.

These results are also confirmed by the Ni content in airborne ferromagnetic particulate matter (Link's equation).

The estimate of the annual increase in b.m.s. on the Earth, measured at Mt. Cimone and on the recent and ancient topographic highs, varies between 10^4–10^5 tons per year.

TABLE I

Description of samples from marine sediments and topographic highs.

Sample occurrence	Location		Age	Composition	Thick-ness cm.	Ni	Ni/Fe	$\frac{N_{\text{b.m.s.}}}{\text{g dry sed}}$
	Lat.	Long.						
M_1 Marine core	41°13′57″N	17°48′55″E	Holocene–Recent	Clays	—	0.002	0.13	167
M_2 » »	43°19′41″N	15°05′32″E	»	»	—	0.002	0.14	243
M_3 » »	44°18′05″N	13°25′41″E	»	»	—	0.002	0.14	310
A_1 Baronie sea mount	40°50′00″N	10°15′05″E	Recent	Carbonatic with b.m.s.	—	0.003	0.16	10^3
T_1 Torbe	45°33′15″N	10°56′06″E	Cretaceous	Carbonatic with metallic films and b.m.s.	—	0.019	0.60	—
T_2 »	»	»	»	»	16	0.021	0.65	$3\cdot10^4$
T_3 »	»	»	»	»	—	0.009	0.47	—
P_1 Prun	45°34′45″N	10°57′01″E	»	»	—	0.018	0.69	—
P_2 »	»	»	»	»	—	0.035	0.68	—
P_3 »	»	»	»	»	12	0.046	0.70	$4\cdot10^4$
P_4 »	»	»	»	»	—	0.022	0.69	—
P_5 »	»	»	»	»	—	0.026	0.67	—
C_1 Pannone	45°51′46″N	10°56′50″E	Paleocene	»	14	0.033	0.69	$3.5\cdot10^4$
C_2 Ronzo	45°54′24″N	10°57′01″E	Cretaceous	»	10	0.052	0.90	$5\cdot10^4$

TABLE 2

Chemical and mineralogic composition of b.m.s. samples at Mt. Cimone, in marine sediments, in urban areas and of ferromagnetic particulate matter sampled in volcanic areas.

Source	Si %	Al %	C %	Ca %	V %	Mg %	Ti %	Mn %	Cr %	Fe %	Co %	Ni %	Ir %	Equival. Diameter μm	Mineralogy
Mt. Cimone	—	—	—	—	—	—	—	—	—	63.20	0.21	4.12	tr	20–30	Magnetite-wüstite-α-Fe
» »	—	—	—	—	—	—	—	—	—	60.07	0.12	6.01	tr	10–35	»
» »	—	—	—	—	—	—	—	—	—	71.00	tr	1.02	tr	30–50	»
» »	—	—	—	—	—	—	—	—	—	65.30	0.05	5.17	tr	< 30	»
Marine sediments	—	—	—	—	—	—	—	tr	—	69.60	0.21	5.07	tr	3–60	Magnetite-wüstite-α-Fe
»	—	—	—	—	—	—	—	tr	—	65.62	0.19	7.09	tr	3–60	»
»	—	—	—	—	—	—	—	tr	—	68.87	0.20	5.08	tr	3–60	»
»	—	—	—	—	—	—	—	tr	—	69.00	0.27	7.31	tr	3–60	»
Volcanic areas	0.23	0.10	—	tr	—	tr	tr	—	—	72.05	—	—	—	30–100	Magnetite
»	0.15	0.09	—	tr	—	tr	tr	—	—	71.91	—	—	—	30–100	»
»	0.07	0.05	—	tr	—	tr	tr	—	tr	72.10	—	—	—	30–100	»
»	0.25	0.16	—	tr	—	tr	tr	0.05	tr	71.01	—	—	—	30–100	»
Urban areas	1.3	0.3	5.6	tr	tr	tr	1.2	0.7	0.1	54.5	—	—	—	< 150	Hematite-graphite
»	1.7	0.7	6.1	tr	tr	tr	0.3	0.5	tr	49.3	—	—	—	< 150	Hematite-graphite-magnetite
»	0.9	0.9	8.7	tr	tr	tr	0.2	0.4	tr	45.7	—	—	—	< 150	»
»	5.1	1.5	10.1	tr	tr	tr	0.5	0.1	0.3	43.1	—	—	—	< 150	»

TABLE 3

Thermodynamic and mineralogic data set for artificial and natural b.m.s.

Black magnetic spherules	Atmospheres	Total pressure mm Hg	O_2 partial pressure mm Hg	T_{MAX} °K	Hollow particles %	Paragenesis
Artificial	Ar	760	0	2000	0	*a*–iron
	N	760	0	2000	0	*a*–iron
	Air	760–350	150–70	2200	90	Magnetite, hematite
	Air	60–20	12–4	2200	10	Magnetite, wüstite, *a*–iron
Natural	Air	* Variable as function of radius between some mm Hg and 35 mm Hg	* Variable as function of radius between 1 mm Hg and 7 mm Hg	2200	10	Magnetite, wüstite, *a*–iron

* Dynamic pressure calculated on the basis of Fasano-Vittori model.

TABLE 4

Sites of volcanic samples

Volcano	Location Lat.	Long.	Elevation m	Remarks
ETNA	37° 44′ N	15° 00′ E	3223	air collected 3/6/67
»	»	»	»	» 9/8/69
»	»	»	»	» 8/12/71
SALINA	38° 33′ N	14° 51′ E	962	Pleistocene/Holocene
VULCANO	38° 23′ N	14° 59′ E	499	
LIPARI	38° 29′ N	14° 57′ E	603	
VICO	42° 18′ N	12° 10′ E	507	Pleistocene inf.
BRACCIANO	42° 08′ N	12° 10′ E	200	
HAWAII	19° 58′ N	150° 30′ W	3058	Recent
GALAPAGOS (Isabela)	4° 04′ S	90° 58′ W	20	Recent
VESUVIUS	40° 50′ N	14° 25′ E	1277	Recent
POZZUOLI AREA	40° 49′ N	14° 06′ E	—	Recent (Marine core)

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