FURTHER STUDIES ON COSMIC SPHERULES FROM DEEP-SEA SEDIMENTS

By D. W. PARKIN,† R. A. L. SULLIVAN† and J. N. ANDREWS‡
† *School of Physics, University of Bath, Claverton Down, Bath BA2 7AY, U.K.*
‡ *School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.*

(*Communicated by Sir Charles Frank, F.R.S. – Received* 25 *September* 1978
– *Revised* 18 *October* 1979)

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We presume that cosmic spherules are 'sparks' formed by collisions in the asteroidal belt. With other debris they spiral to earth under the Poynting–Robertson effect. During a 10^6 year residence in space, they become saturated with solar-wind gas. These 100 μm diameter spherules will survive a grazing atmospheric flight but on a more plunging flight they may melt. If this happens, the solar-wind gas develops sufficient pressure to explode the spherule.

We support these proposals with (i) a size distribution analysis, which shows that spherules are destroyed if they become molten and also suggests that spherules make up 10 % of the zodiacal cloud, (ii) an examination of the spherules with the scanning electron microscope (s.e.m.), which strongly suggests that they have remained solid during atmospheric flight, (iii) an investigation of grindwheel sparks, which shows that forms resembling iron cosmic spherules can be reproduced, if sparks are quenched close to the wheel.

X-ray diffraction analysis and s.e.m. photography yield convincing evidence that stony cosmic spherules are not ablation droplets from the crust of stony meteorites and, by implication, are not derived from meteors. The magnetite lattice parameter for the spherules is less than that for the meteorite crust. The fayalite fraction of the olivine in the spherules is close to that occurring in the interior of the meteorite and quite distinct from that occurring in its crust. The spherules are coarsely crystalline, whereas the meteorite crust appears 'glassy'.

1. Introduction

Murray & Renard (1891) found that deep-sea red clay contained numerous sub-millimetre black 'stony' and 'iron' magnetic spherules, the so-called 'cosmic spherules'. The stones are mixtures of olivine and magnetite; the irons are oxides of iron often containing a metal globule rich in nickel. Using the new electron probe technique, Castaing & Fredricksson (1958) confirmed an extraterrestrial origin for the irons. Hunter & Parkin (1960) found that approximately equal numbers of stones and irons occurred in three surface sediment samples, one from the Pacific and two from widely distant sites in the Atlantic. This constant global ratio strongly suggests that both types of spherule are extraterrestrial. Recently Ganapathy *et al.* (1978) have shown conclusively that the stony spherule is extraterrestrial. By means of neutron activation analysis, a good match with carbonaceous meteorite composition was obtained for three stony spherules.

Although it is natural to assume that cosmic spherules are merely ablation droplets from meteorites or meteors, Öpik (1951, 1956) proposed an alternative hypothesis. The Van de Hulst (1947) model for the size distribution in the zodiacal cloud (which emphasizes the 100 μm particle) predicts that several hundred tons of particles arrive on Earth per day. According to Öpik, a certain fraction of these particles will melt in the atmosphere and survive evaporation. He estimated a size distribution for these surviving spherules. Hunter and Parkin were unable to fit this distribution by taking stony and iron spherules separately. Instead, they compared the two distributions with each other and argued in favour of Öpik's theory. We will re-examine these size distributions, under the new assumption that cosmic spherules already exist in the zodiacal cloud.

This assumption was advanced in a preliminary report by Parkin *et al.* (1977) on the basis of some scanning electron microscope (s.e.m.) photographs and X-ray work. In this paper, we give more photographic and X-ray evidence and compare the spherules with fusion crust of meteorites. The different stony meteorites have similar fusion crusts, because the bulk chemistry of their refractory materials is much the same. If this same chemistry extends to meteors, then cosmic spherules are not ablated from either meteorites or meteors.

Of course, mass influx to earth should settle this question, but unfortunately all estimates are rather vague. Parkin & Tilles (1968) extrapolated the 'cometary' meteor distribution and found 200 tonne per day; whereas Lovell (1954), including fire-ball sizes, estimates about 18 tonne per day. In the case of meteorites, most authorities choose 1–10 tonne influx to the upper air per day. In the next section, we estimate the cosmic spherule influx at about 14 tonne per day. Therefore it seems unlikely that meteors or meteorites could provide sufficient molten spray to account for cosmic spherules as most of the ablated mass is vaporized away. Recently Brownlee *et al.* (1976) found several 2–30 μm diameter crumb-like particles in the stratosphere that have a composition like heated carbonaceous meteorite. Sulphur and magnetite were both present. About 10 % of these 'chondritic aggregates' were spheres and these lack sulphur; they seem very like stony deep-sea spherules. We prefer to regard these stratospheric particles as coming directly from the zodiacal cloud, rather than from the melting or break-up of larger bodies in the atmosphere. We believe that cosmic spherules are 'sparks' from colliding asteroidal material or cometary matter passing through the asteroidal belt. We follow up this suggestion by an examination of grindwheel sparks.

The spherules now to be described were extracted from the same surface sediments used by Hunter and Parkin; namely Atlantic (24° 30′ N, 64° 47′ W, depth 5949 m) and Pacific (22° 07′ S, 115° 10′ W, depth 3060–3200 m).

2. Spherule extraction and flux estimation

The samples of surface sediment were stored in glass jars, the Atlantic sample still in the moist state, the Pacific sample as dried blocks. Scoops of the moist sample were taken from the middle of the jar; the blocks were brushed clean. With dust-free distilled water, each sample was worked into a thin slurry and passed through a 43 μm sieve. In the wet state, magnetic extraction on both the fine and coarse fraction was carried out with the aid of a powerful hand magnet. Detachable glass plates covered the pole-pieces. Clean-room conditions were maintained throughout the process. A little HCl was added to the slurry (pH > 3) to remove carbonate. This did not affect the spherules.

No carbonate was present in the Atlantic sample and the amount of dried clay was 290 g. Considerable carbonate was present in the Pacific sample; the 224 g blocks yielded 67 g of dried clay. In each sample, the amount of magnetic material was of the order of a few milligrams. The fine magnetic extracts were examined under the s.e.m. Cosmic spherules were located with difficulty and they could be confused with numerous rounded magnetite grains that are probably terrestrial. In plate 1 we show some of these rounded grains. Also shown are bits of vesicular glass which resemble the fusion crust of a meteorite, although they are probably volcanic. The number of cosmic spherules increases with decreasing size, but there is a sharp fall-off for diameters less than 7 μm. In fact only one of diameter 4 μm was found. Brownlee *et al.* (1975) give the diameter of 6 of their stratospheric spherules as 12, 8.5, 7, 7, 6 and 4.5 μm. It seems that a practical cut-off, at about 5 μm diameter, exists.

In the coarse magnetic extract (greater than 43 μm) cosmic spherules are easily found with a stereoscopic microscope at 50–100 times magnification. Rounded magnetite grains with diameters greater than 50 μm are very rare. Several fragmentary grains were examined by X-ray diffraction and electron probe techniques. No extraterrestrial fragmentary material was found, other than a few minor portions of broken spherules. Perhaps most of the large fragmentary zodiacal particles are too fragile to survive atmospheric flight and any metallic iron would not survive under marine conditions.

From the Atlantic sample a crude estimate of the mass influx can be made. Dr D. V. Kent of the Lamont–Doherty Geological Observatory informs us that core V23–133 (22° N, 61° W – close to our Atlantic sample) has been magnetically dated. The rate of sedimentation is about 7 m per 10^6 a. If relative densities for stony spherules and for irons are taken to be 3.2 and 6.0 respectively (see Hunter & Parkin), the mass of spherules with the diameters not less than 50 μm in the Atlantic sample is 199 μg for stones and 68 μg for irons. In the fine magnetic fraction, we estimate a mass of about 7 μg. Hence, down to the 5 μm cut-off, the total mass is 274 μg in 290 g of dried clay. In round numbers, the mass sedimentation rate is taken as 10 g of dry clay per square metre per year. This gives the influx of spherules to earth as 14 tonne per day. For reasons which will become evident in the next section, we note (from the tables given later) that seven stony spherules with diameter not less than 120 μm were found in the clay. In the same Atlantic clay Hunter and Parkin found 20 such spherules in 490 g of dry clay. This gives 0.035 spherule per gram of clay on average. For the irons we shall need numbers of spherules with diameters not less than 40 μm. In the Hunter & Parkin collection there are 19. In the present collection, sieving restricted the count to spherules with diameters not less than 50 μm, but from graphical extrapolation we estimate that there are 29. This gives 0.062 spherule per gram of clay, on average.

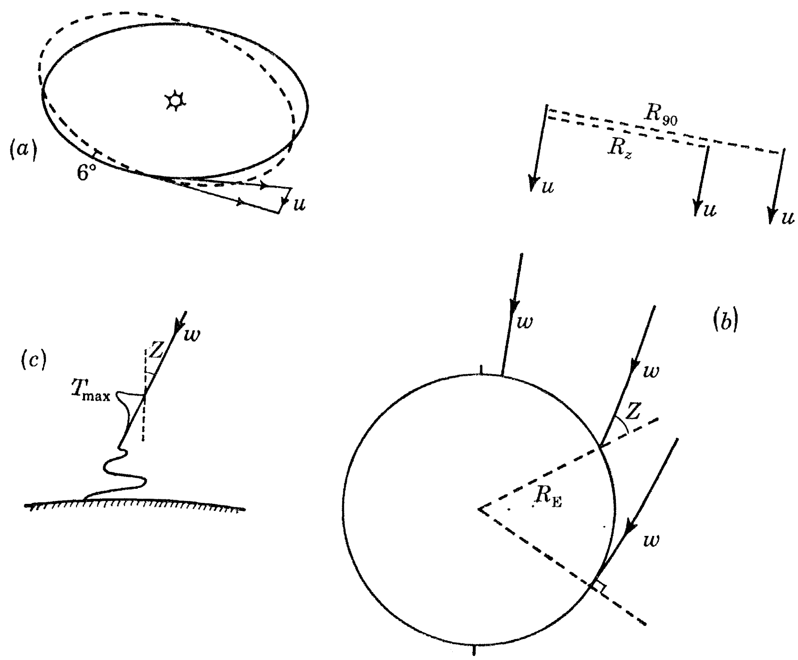

FIGURE 1. (*a*) Direct circular orbits of zodiacal particles (orbital velocity 30 km s^{-1}), resulting in a geocentric velocity u = 3 km s^{-1} for 6° inclinations to the ecliptic. (*b*) Such particles are attracted to the Earth along hyperbolic orbits and impact the upper atmosphere with velocity w = 11.5 km s^{-1}. (*c*) If the particles survive high temperature atmospheric flight (T_{max} at about 90 km altitude), they drift to ground level in a few days.

3. The zodiacal cloud, a discussion

Öpik attempted to reconcile the Van de Hulst size distribution in the zodiacal cloud with the observed size distribution of the deep-sea spherules; figure 1 will clarify the argument. The velocity w ($\approx$ 11.5 km s^{-1}) of a zodiacal particle impacting the upper atmosphere is calculated from $w^2 = u^2 + V^2$, where V (11.1 km s^{-1}) is the Earth's escape velocity and u ($\approx$ 3 km s^{-1}) is a typical velocity relative to Earth for direct, nearly circular orbits of low inclination to the ecliptic. If any latent heats and any heats of combustion are neglected then the maximum temperature achieved by a surviving particle of radius r and density δ in flight through the atmosphere with zenith angle z is given by Öpik's micrometeorite formula (adapted to SI units),

$$T_{max} = \left(\frac{r\,\delta\,w^3 \cos z}{2.77 \times 10^{-6} H}\right)^{\frac{1}{4}}.$$

The numerical factor contains Stefan's constant, and estimated values such as the emissivity of the particle and an accommodation coefficient expressing the fraction of energy given to the particle by the colliding air molecules. Particles will reach maximum temperatures at altitudes approximately 90 km, where the air density increases by a ratio e for a thickness H (≈ 7 km), the so-called scale height. It is clear that large particles would remain solid during a grazing flight, but only those with radii less than a certain small critical radius, r_0, would survive melting at normal incidence, $z = 0°$.

Öpik thought that most of the zodiacal particles would be metallic iron as they would best resist destruction by mutual collisions in space, and naturally he considered fragmentary shapes of equivalent spherical radius r. In order to make droplets of iron, fragments would have to enter the atmosphere at the appropriate zenith angle to cause melting; hence $T_{max} = 1800$ K. At $z = 0°$, r_0 can now be calculated. All particles smaller than r_0, impacting on the atmosphere, will not melt and these will have the same size distribution as the zodiacal particles. This customarily takes the form $dn = K\,dr/r^p$ where dn is the number of particles in the range r to $r+dr$ per m^3 of space near to earth. From brightness measurements, Van de Hulst estimated $p = 2.6$ and $K = 2.2 \times 10^{-17}\ m^{-1.4}$, when r is also in metres. With such a law there must be a maximum particle size; this is taken to be a radius of 350 μm. Now for particles greater than r_0 only a certain fraction will remain solid. By referring to figure 1, their rate of arrival is calculated as follows. If R_{90} is the radius of the Earth's capture crosssection ($z = 90°$), we have from conservation of angular momentum $uR_{90} = wR_E$, where R_E is the Earth's radius. The capture radius R_z for angle of incidence z is $R_z = (wR_E/u)\sin z$. This zenith angle determines a radius, $r > r_0$, of particles that just reach the melting point. However, particles of this size will not melt if they pass through an annulus of area $\pi(R_{90}^2 - R_z^2)$. Hence the rate of arrival of unmelted particles of radii r to $r+dr$ impacting on the Earth from this single direction, shown in the figure, is proportional to $\pi(R_{90}^2 - R_z^2)\,u$ or $\pi(R_E^2\,w^2/u)\cos^2 z$. There are other possible directions. All particles in orbits of low inclination and eccentricity (strictly, those making a 6° angle with the Earth's orbit) will impact the Earth with $w = 11.5$ km s^{-1}. By substituting for $\cos^2 z$ and remembering that $r_0 = 2.77 \times 10^{-6}\,HT_{max}^4/w^3\delta$, where T_{max} is the melting point, the rate of arrival on the earth for unmelted particles with radii greater than r_0 is

$$dF = \frac{\pi R_E^2\,w^2 r_0^2}{u}\,\frac{C\,dr}{r^{p+2}}.$$

Here C is the spatial constant for particles impacting with a velocity of 11.5 km s^{-1}. We introduce the new constant C ($\lesssim K$) to allow for the possibility that all zodiacal particles may not necessarily be in circular or near-circular orbits. Of course, the rate of arrival on earth of unmelted particles of radii less than r_0 is just

$$dF' = \frac{\pi R_E^2\,w^2}{u}\,\frac{C\,dr}{r^p}.$$

Öpik considered that if $T_{max} \approx 2200$ K, some 400 K greater than the melting point, the iron droplet would vaporize away. By using the melting point and vaporization temperatures, he derived a size distribution for surviving molten droplets based on the Van de Hulst model. This can be tested against that observed for the deep-sea spherules. Agreement is reasonable for larger diameters but hopeless for the smaller ones; in fact the theory gives no droplets with diameters less than about 30 μm. To cope with this, Öpik introduced a spread of impacting velocities and allowed w to range up to 16.9 km s^{-1} for 50 % of the particles. In another approach he considered a spread of fragmentary shapes and allowed some evaporation to occur. Here the argument becomes complex and we will not pursue it further.

Now, the observed distributions can easily be interpreted with Öpik's theory if we simply assume that the deep-sea spherules were already round bodies in space and therefore do not need to become molten during passage through the atmosphere. However, it is necessary to assume that they are destroyed if they become molten. Later, we discuss the destruction process, i.e. bursting as a result of internal gas pressure of absorbed solar wind. We first discuss the stony spherules. In figure 2 we show the cumulative numbers of stony spherules with diameters greater

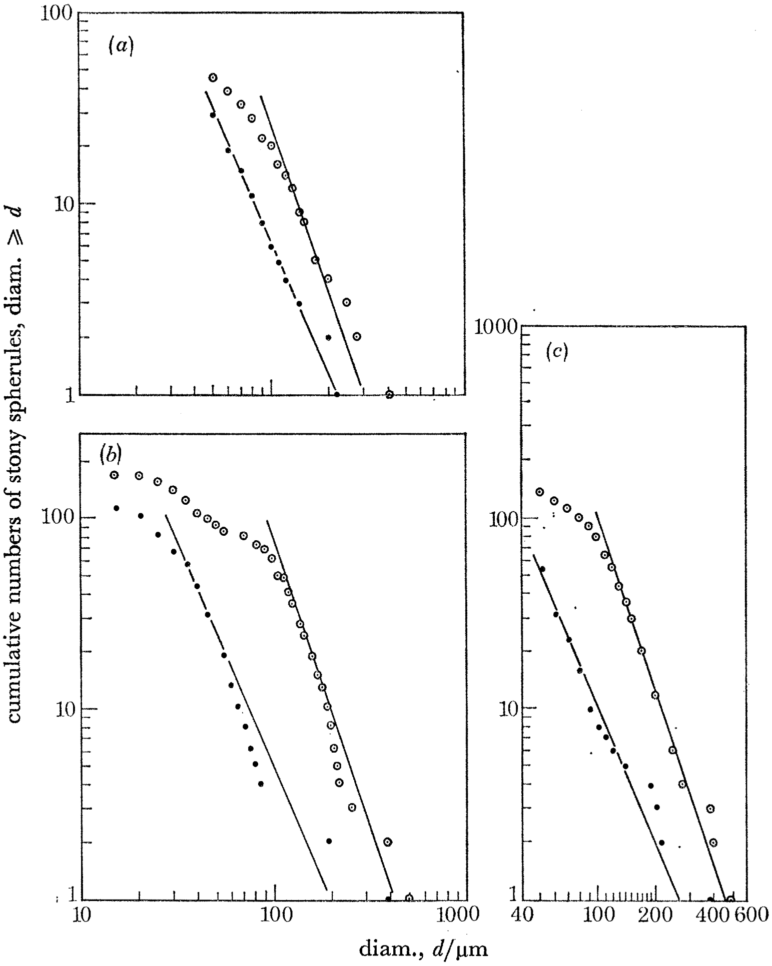

FIGURE 2. Size distributions of the total iron spherules (●) and the total stony spherules (⊙) found in both oceans. (*a*) Present work; (*b*) Hunter & Parkin; (*c*) combined collections. For the Hunter & Parkin collection, spherules from three oceanic sites were used – see their figure 4. Stony–iron or composite spherules have not been treated separately, they are totalled together with the stones. The lines through the iron points in each diagram are parallel, likewise for the stones.

than or equal to diameter d. In the present work, sieving restricted counts to $d \geqslant 50$ µm, but in the Hunter & Parkin collection sieving was not used. The logarithmic plot, obtained by combining the present collection with those from the more numerous Hunter & Parkin collection, is the one used. A distinct kink can be seen at a critical diameter $d_0 \approx 120$ µm. (Microscopic undercounting is hardly possible at these large sizes; in fact it would only become serious at $d < 30$ µm in the Hunter and Parkin collection). We associate this value with the critical radius r_0. Spherules larger than this will melt in atmospheric flight for normal incidence and for $w = 11.5\ \mathrm{km\ s^{-1}}$. Also, we see that a good straight line exists for $d > 120$ μm, where the 'pure' power law $1/r^{p+2}$ should apply. (A straight line on the cumulative logarithmic plot would be expected from the power law, by assuming that the maximum spherule diameter was as large as 700 μm, the assumed spatial cut-off.) From the slope we find $p = 2.0$. Of course, the kink at $r_0 = 60$ μm can now be used to test the theory by estimating the melting point of the stony spherules with $z = 0°$ in the micrometeorite formula. Taking $\delta = 3.2 \times 10^3\,\mathrm{kg\,m^{-3}}$, $w = 11.5\,\mathrm{km\,s^{-1}}$ and $H = 7.0$ km, we find $T_{max} = 1970$ K. From the X-ray results given in table 1, the olivine is, on average, about 22 % fayalite. For

TABLE 1 (*a*). THE STONY SPHERULES: GRANULAR-VUGGY FORM (X-RAY LINES SMOOTH)

spherule	diam. / μm	mole % fayalite in olivine	magnetite a/Å	mass % olivine in spherule	surface appearance and other comments
1A	110	29	8.382	80	fusion crust fully developed; found broken, whitish interior with cavities
2A	130	26	8.346	72	fusion crust fully developed; found broken, brownish interior with vugs and cavities
3A	60	17	8.336	43	perfect crystals (1–5 μm)
4A	90	8	8.342	42	fusion crust fully developed; found broken, whitish interior with cavities
5A	130 oblate	31	8.366	51	completely sintered-looking; cavities and vugs seen on surface
6A	150	27	8.350	83	perfect crystals (5–20 μm)
7A	70 oblate	17	8.318	67	sintered-looking, glazed patch developing on 'frontal' hemisphere.
8P	80	20	8.341	?	perfect crystals (1–10 μm)
9P	130	21	8.328	62	completely sintered-looking with glazed patches; found as a shell; large interior bubble, dark inner wall
10P	150	22	8.327	50	completely sintered-looking with glazed patches; found as a shell; large interior bubble, dark inner wall
11P	60	23	8.356	39	perfect crystals (5–10 μm); some signs of marine corrosion
12P	70	29	8.341	48	perfect crystals (1–5 μm); triangular pits on some crystal faces
13P	80	22	8.330	?	perfect crystals (2–5 μm) – see Parkin *et al.* (1977), their figure 1
14P	50	24	8.345	61	completely glazed
15P	60	25	8.321	48	mainly perfect crystals (2–5 μm), glazing on one patch; trumpet-like crystals in surface vug
16P	120	33	8.355	76	perfect crystals (2–20 μm)
17P	80	21	8.357	66	perfect crystals (5–10 μm); some signs of marine corrosion
average	95	23.2	8.344		

The averages should be compared with those of the dendritic forms.

this composition (ignoring the magnetite), melting commences on the solidus curve of the pure-olivine phase diagram at 1655 °C = 1928 K. This agreement lends credence to our hypothesis, and it seems that the kink at a diameter of 120 μm is real. It is the critical diameter for those spherules (possibly the most) that impact the earth with the minimum velocity of 11.5 km $\mathrm{s^{-1}}$. Clearly, velocities as low as the escape velocity could not exist in the immediate vicinity of the Earth. There is no evidence for a ring of dust around the Earth. It is legitimate to ignore the presence of magnetite in the stony spherules. When heated slowly, olivine–magnetite mixtures partially melt at approximately 1200 °C. But in atmospheric flight there is no time to complete this diffusion reaction. General melting would only occur at the higher temperature of the 'isolated' minerals.

If all stony spherules had orbits of low inclination and eccentricity, all those smaller than 120 μm would show unglazed surfaces. From the photographs we see that this is not so. However, it is very reasonable to assume impacting velocities greater than 11.5 km s^{-1}, i.e. contributions from eccentric orbits in the plane of the ecliptic. But as we do not know how to apportion the spherules

Table 1 (*b*). The stony spherules: dendritic form (X-ray lines spotty or streaky); mass % olivine uncertain

spherule	diam. / μm	mole % fayalite in olivine	magnetite a/Å	mass % olivine in spherule	surface appearance and other comments
18A	410 egg	24	8.374	50	parts of crust removed, exposing crystals with pitted ends – could be marine corrosion
19A	200	34	8.364	50	parts of crust removed, exposing crystals with pitted ends – could be marine corrosion; cupule hemispherical
20A	280	21	8.343	30	parts of crust removed
21A	70	19	8.369	40	completely sintered-looking with glazed patches; segmented form
22A	60	18	8.358	50	completely sintered-looking; lumpy form, giving spherical polyhedron appearance
23A	170 prolate	36	8.370	70	no fusion crust; a stack of 2 μm thick plates, could be single crystal; floor of dished cupule, black
24P	120	21	8.367	50	parts of crust removed; could be spherical polyhedron
25P	140 egg	20	8.356	60	completely sintered-looking, with glazed patches; hemispherical cupule near sharp pole – see Parkin *et al.* 1977, their figure 2
26P	90	13	8.356	50	completely sintered-looking with glazed patches; segmented form
27P	80 prolate	14	8.360	50	parts of crust removed; broken on mounting for s.e.m.
28P	110 egg	18	8.368	40	parts of crust removed from 'frontal nose'
29P	100	33	8.348	30	completely sintered-looking; cupule, hemispherical
30P	70 prolate	24	8.349	?	partly sintered-looking; flat ends, could be stack of plates like 23A and near single crystal.

Table 1 (*b′*). The stony spherules: dendritic form (X-ray lines smooth)

spherule	diam. / μm	mole % fayalite in olivine	magnetite a/Å	mass % olivine in spherule	surface appearance and other comments
31P	100 prolate	22	8.377	?	completely sintered-looking; dished cupule at one pole, with associated splintering
32P	100 egg	19	8.355	25	completely sintered-looking, with glazing at sharp pole; crust is 'brushed back' from pole
33P	50	7	8.359	?	slightly sintered-looking
34P	80	no data			completely sintered-looking; broken on mounting for s.e.m.
35P	70				completely sintered-looking; broken on mounting for s.e.m.
average	128	21.4	8.361		

(The only crystalline phases are magnetite and olivine. The Fe content of olivine $(Mg, Fe)_2 SiO_4$ is expressed as mole % fayalite Fe_2SiO_4 in the olivine. It is accurate to a few parts per cent. Mass % olivine in spherule ignores the presence of glass, as glass is very rare.)

in the various directions, it is impossible to analyse the distribution for radii less than r_0. For instance, to estimate the total rate of arrival on Earth we might write C_0, C_1, C_2 etc. for the spatial constants appropriate to the stepwise increasing velocities u_0, u_1, u_2, etc., for particles coming from all reasonable directions. Velocity $u_0 = 3\ \mathrm{km\,s^{-1}}$ applies to all particles with typically low inclination and eccentricity, whereas $u_1 < u_2$, etc., applies to all other particles with increasing inclination and eccentricity; presumably $C_0 > C_1 > C_2$ etc.

For $r > r_0$, $$\mathrm{d}F_0 = \pi R_\mathrm{E}^2 \left[\frac{w_0^2}{u_0} r_0^2 C_0 + \frac{w_1^2}{u_1} r_1^2 C_1 + \frac{w_2^2}{u_2} r_2^2 C_2 + \dots\right] \frac{\mathrm{d}r}{r^{p+2}},$$

where r_0, r_1, r_2 etc. are the appropriate critical radii for w_0, w_1, w_2 etc.

For $r_0 > r > r_1$, $$\mathrm{d}F_1 = \pi R_\mathrm{E}^2 \frac{w_0^2}{u_0} C_0 \frac{\mathrm{d}r}{r^p} + \pi R_\mathrm{E}^2 \left[\frac{w_1^2}{u_1} r_1^2 C_1 + \frac{w_2^2}{u_2} r_2^2 C_2 + \dots\right] \frac{\mathrm{d}r}{r^{p+2}}.$$

For $r_1 > r > r_2$, $$\mathrm{d}F_2 = \pi R_\mathrm{E}^2 \left[\frac{w_0^2}{u_0} C_0 + \frac{w_1^2}{u_1} C_1\right] \frac{\mathrm{d}r}{r^p} + \pi R_\mathrm{E}^2 \left[\frac{w_2^2}{u_2} r_2^2 C_2 + \dots\right] \frac{\mathrm{d}r}{r^{p+2}}$$

and so on. Clearly, we can only properly discover p in the range $r > r_0$ where a 'pure' power law $1/r^{p+2}$ exists. If w did not range too high it might be possible to guess p from a distribution of the smallest spherules; here the distribution would approach another 'pure' power law $1/r^p$.

A crude estimation of C_0 for the stony spherules can be made. From the micrometeorite formula, $r_0 w_0^3 = r_1 w_1^3 = r_2 w_2^3 = \dots =$ constant. Hence

$$\mathrm{d}F_0 = \pi R_\mathrm{E}^2 \frac{w_0^2}{u_0} r_0^2 C_0 \frac{\mathrm{d}r}{r^{p+2}} \left[1 + \frac{C_1}{C_0}\left(\frac{u_0}{u_1}\right)\left(\frac{w_0}{w_1}\right)^4 + \frac{C_2}{C_0}\left(\frac{u_0}{u_2}\right)\left(\frac{w_0}{w_2}\right)^4 + \dots\right].$$

The value of the factor in the square bracket is most likely to be of order unity. From the previous section we found that on average 0.035 Atlantic stony spherules with $d_0 \geqslant 120\ \mu\mathrm{m}$ were present in 1 g of clay that deposits at $10\ \mathrm{g\,m^{-2}}$ per year. Hence the number to Earth per second is 1.1×10^{-8} $4\pi R_\mathrm{E}^2$, where R_E is in metres. By cancelling πR_E^2, we obtain the equation

$$4.4 \times 10^{-8} = \frac{w_0^2}{u_0} r_0^2 C_0 \int_\infty^{r_0} \frac{\mathrm{d}r}{r^{p+2}} = \frac{w_0^2 C_0}{u_0} \frac{1}{3r_0},$$

where $p = 2$, for stones. We find $C_0 = 1.8 \times 10^{-16}\ \mathrm{m^{-2}}$.

For the irons, we now repeat the analysis. Unfortunately the present collection was restricted by the sieving technique to diameters not less than 50 μm, but no kink is evident in this range. By assuming no microscopic under-counting for $d > 30\ \mu\mathrm{m}$, the Hunter & Parkin collection seems to show the critical diameter is approximately 40 μm. Taking $r_0 = 20\ \mu\mathrm{m}$ and $\delta = 6.0 \times 10^3\ \mathrm{kg\,m^{-3}}$ (Hunter & Parkin), we find $T_\mathrm{max} = 1747$ K, which is in the melting range for magnetite (see figure 3). The combined collections do not give a very convincing straight line and it is tempting to impose $p = 2$ on the irons; but it seems $p = 1.36$ is a better value. Taking 0.062 as the average concentration in the Atlantic clay for diameters not less than 40 μm, we equate

$$7.9 \times 10^{-8} = \frac{w_0^2}{u_0} r_0^2 C_0 \int_\infty^{r_0} \frac{\mathrm{d}r}{r^{p+2}} = \frac{w_0^2 C_0}{u_0} \frac{1}{2.36\, r_0^{0.36}},$$

where $p = 1.36$. We find $C_0 = 8.6 \times 10^{-14}\ \mathrm{m^{-2.64}}$.

Let us now compare the total volume of the spherules in $1\ \mathrm{m^3}$ of space with that estimated from the values given by Van de Hulst, i.e. $p = 2.6$ and $K = 2.2 \times 10^{-17}\ \mathrm{m^{-1.4}}$. With $(\frac{4}{3}\pi r^3)\ \mathrm{d}n$ for the volume of spherules in the range r to $r+\mathrm{d}r$, the lower limit of particle size can be taken as zero because $p < 3$. With 350 μm as maximum radius, the volume concentration of stony spherules is 4.6×10^{-23} and that of iron spherules is 10×10^{-23} m^3 per m^3. The total volume concentration compares favourably with the Van de Hulst concentration which is 96×10^{-23} m^3 per m^3. It is interesting to recalculate the Van de Hulst concentration with change of p, under the condition of keeping the total particle crosssectional area constant; zodiacal brightness depends mainly on particle area. By changing p to 2.0, K becomes 6.5×10^{-15} m^{-2} and the concentration becomes 167×10^{-23} m^3 per m^3, which is not a large change. By allowing for a further contribution from eccentric orbits, it seems that an appreciable fraction (no less than about 10 %) of the zodiacal particles are spherical.

4. Cosmic spherules, fusion crust of meteorites and grindwheel sparks

The large spherules retained on the sieve were cleaned of clay particles in a viscous oil and washed in benzene. They were then photographed with the s.e.m. and subsequently exposed to Co Kα radiation in an X-ray powder camera. The lattice parameters were corrected for the effects of absorption if spherule diameters exceeded 100 μm. Errors are in the range $\pm$ 0.004 Å†, but in the case of a few faint metal lines the error could be $\pm$ 0.01 Å. These results are listed in tables 1, 3, 4 and 5. Note that no pyroxene was found in the stony spherules. From X-ray films of known olivine/magnetite mixtures, it is possible to estimate the percentage of olivine in a spherule if the lines are smooth. For spherules which have spotty lines, only crude estimates can be made.

The tables and the selected photographs are organised according to chemical type and physical form. Each spherule is given a number and an A or P denotes the ocean. Most spherules, particularly the irons, are spherical. If slight departures occur, oblate, prolate or egg-shapes are indicated after the listed average diameter. By using the s.e.m. photographs, the appearance of the other spherules can be visualized from the comments in the tables.

Stony spherules are corroded by prolonged burial and are rarely found in deep-sea cores. Iron spherules are unaffected by such burial and are plentiful in the cores. The metallic globule is usually well protected by a film of oxide. However, rusting sometimes occurs in surface sediment and a blood-red excrescence partly surrounds a hollow shell of magnetite. We call these infrequent forms 'red-heads'. Some spherules show etching around grain boundaries and pitting in the centre of grains and a few show more extensive corrosion. For most spherules however, the 'varying appearance' of the surface is probably produced by varying degrees of atmospheric damage, rather than by varying amounts of corrosion. If this is accepted, then the spherules are likely to have remained solid during atmospheric flight and so it follows that they are already spherical bodies in space. It is not easy to explain the 'varying appearances' if they were sprayed from the surface of either meteorites or meteors. Such sprayed droplets should freeze to a 'standard appearance', like grindwheel sparks. Furthermore, all stony spherules should be blackened throughout, like the upper layer on meteorite fusion crust.

† Å = 10^{-10} m.

(a) *Stony spherules*

Two textural forms occur; a granular–vuggy form and a dendritic form. Table 1 (*a*) lists the granular form – the X-ray lines are smooth. In plate 2 the spherules 6A and 16P show no sign of damage and we maintain that this was their appearance in space, whereas 7A and 14P (stereopair) show the progressive development of a fusion crust. Spherule 10P was found broken and is part of a thick-walled bubble. In plate 3 we show more spherules that were found broken, 1A and 2A having whitish interiors with black outer coats. If the spherules in plate 2 were to be deliberately crushed, they would show whitish interiors. A good example appears in Hunter & Parkin (their figure 8 (*a*)). The stereopair of 1A shows interior spherical cavities with smooth walls. These cavities should be distinguished from the irregular rough walled holes or vugs occurring on the surface. Observations on grindwheel sparks lead us to believe that the cavity could at one time have contained a globule of another phase. The stereopair of 15P shows peculiar trumpet-ended crystals protruding from the wall of a vug on the surface of the spherule (for a view of other protruding crystals see 13P, Parkin *et al.* (1977) – their figure 1). It seems clear that volatiles were present during the formation stage of these vuggy spherules.

In space the outgassed spherule would become saturated with solar-wind gas and, if it melted or partly melted in atmospheric flight, sufficient pressure would develop to burst the spherule by bubble formation. We believe that 9P and 10P formed in this way. Certainly the star-like explosions in the trails of grindwheel sparks are caused by gas pressure resulting from carbon burning.

In the dendritic form, the X-ray lines are spotty or streaky for spherules in table 1 (*b*) and smooth for those in table 1 (*b'*). Plates 4 and 5 show some of these forms. Cupules are often present in the surface and again it seems certain that at one time such a spherule was host to a globule of another phase. Spherule 19A was found broken and shows signs of marine corrosion, but this must be very slight as the cupule is perfectly preserved. In expelling the globule, 31P (stereopair) has suffered partial cracking and the cracking of 23A reveals a stack of very uniform 2 μm thick plates. The lumpy polyhedral form of 22A suggests that it was never fully molten at its formation stage. The two spherules 28P and 32P suggest aligned flight through the atmosphere, a superficial layer has been brushed back from the frontal nose. Portions of a 1 μm thick fusion crust on 24P (stereopair) have cracked away, revealing the dendritic crystals in the interior. In contrast to granular-vugs, the interiors of the dendritic forms are dark and nearly black.

(b) *Fusion crusts of stony meteorites*

We now compare, in some detail, stony spherules with the fusion crusts of stony meteorites. This provides further evidence that spherules are not ablation droplets. Brownlee *et al.* (1975) have given complete descriptions of the crust on carbonaceous meteorites, but descriptions of the crust on ordinary meteorites are rather vague. Actually, we find that these different types of meteorite have very similar crusts. The molten layer, about 100 μm thick, freezes into a black mass of 1 μm diameter crystals of olivine and magnetite, cemented together with thin films of glass. This black layer is opaque; it is difficult to transmit light through fragments with thickness as small as 5 μm. No pyroxene exists and no extensive areas of glass are found. Below the layer, the crystals are similar to those in the interior, with diameters of the order of millimetres and sintered together. The whole structure, some 4 mm thick, is easily prised away from the less cohesive interior.

Dr R. Hutchison (British Museum) kindly supplied us with pieces of crust from:

ordinary chondrites:	Barwell	(L5–6 hypersthene)	off 1966, 59
	Kernouve	(H6 bronzite)	off 43400
	Parnallee	(LL3 amphoterite)	off 33792
	Appley Bridge	(LL6 amphoterite)	off 1920, 40
carbonaceous chondrites:	Orgueil	(CI1)	off 36104
	Murchison	(CM2)	off 1970, 6

Scrapings, no more than 10 μm deep, were removed from the outer layer and a few crystals from the underside of the piece were crushed. The X-ray results are given in table 2. Meteorites of petrographic type 5 or 6 are well metamorphosed and a sample anywhere in the interior ought to be representative. For the poorly equilibrated carbonaceous meteorites of type 1 and 2, this is not so; but in comparing black layer with interior we assume that the layer is likely to be derived from material close to the underside of the given piece.

Table 2. The stony meteorites

meteorite	mole % fayalite in olivine of: interior	crust	crust magnetite a/Å	crust mass % olivine	other minerals identified in interior and comments
Barwell	24	12	8.378	55	pyroxene; no magnetite
Kernouve	18	10	8.376	30	pyroxene; no magnetite
Parnallee	23	11	8.377	35	pyroxene; no magnetite
Appley Bridge	30	13	8.376	60	pyroxene; no magnetite
Murchison A	24	14	8.381	45	pyroxene; some magnetite;
Murchison B	13	20	8.373	75	also clay (kaolinite?)
Orgueil	no olivine	13	8.381	45	mostly magnetite (a = 8.393 Å)*; some altered epsomite;
blob from surface of Orgueil		16	8.382	45	also clay (montmorillonite?)

* The lattice parameter of the magnetite in the interior of *Orgueil* is close to that of pure magnetite – see Kerridge (1970).

(Only glass, magnetite and olivine are present in the black crustal layer which is about 100 μm thick. All X-ray lines are smooth. Mole % fayalite in olivine is accurate to a few parts per cent. Mass % olivine in crust ignores the presence of glass. Glass exists as very thin films surrounding the tiny magnetite and olivine grains.)

The results clearly show that the fayalite content of the crustal olivine is about half that of the interior olivine. If stony spherules (on average 22 % fayalite) were derived from the black outer layer, not only would they be black throughout and very turbid, but the meteorite parent bodies would be expected to contain an average of 44 % fayalite. This is much in excess of what is commonly observed. In fact, the spread in fayalite content of the spherules is very similar to that in the interior of the meteorites (Mason 1962, p. 81; Keil & Fredriksson 1964 and Fredriksson *et al.* 1968). Furthermore, the magnetite lattice parameter is much greater in the crusts than in the spherules.

As all the fusion crusts appear similar, we only show a few of them in plate 6. At low magnification, the top surface of Barwell shows the blistered nature of the black layer and general views of the fracture section of Murchison and Orgueil show the structure of the fusion crust as a whole. High magnification views of the top surface and a fresh fracture section of Barwell show the black layer to be deceptively glassy-looking and broken pieces would resemble the glass fragments seen in plate 1. The only sign of a possible spraying event was a blob seen on the surface of Orgueil. This was chipped during removal. The fracture shows the same vesicular glassy texture as elsewhere. Ball-like forms (some with smaller balls growing out of larger balls) have been found on protected parts of the hot surface of Orgueil. The middle photograph in plate 7 shows a group of them protected by the ropy flow of the viscous black layer and the lower photograph shows them in high magnification. The upper photograph shows a ball not on the surface but located some way down a fracture section. This must have grown in a natural crack. Even if the blob and these ball-like forms were to be detached from the surface, they would not be recognized as cosmic spherules.

All the X-ray lines from the black layer are smooth, not because of the numerous scrapings used but because of the random orientation of the myriads of tiny grains within each scraping. Soaking these scrapings in concentrated HCl for 2 h has no effect on their turbidity. They remain dark brown and barely translucent under intense illumination. On stony cosmic spherules acid has an immediate bleaching effect, and on broken fragments it is possible to see 3 μm 'cubes' of magnetite attached to the olivine crystals whose outlines remain well preserved. These grains must have co-precipitated with the olivine during the original formation stage as there is evidence of crystallographic alignment from the X-ray pattern – spots on neighbouring olivine and magnetite lines often coincided. From a phase diagram given by Speidel & Nafziger (1968), it is possible to select a cooling path that avoids the pyroxene field. First, olivine precipitates from the melt. Then olivine and magnetite co-precipitate. Finally, the remaining melt would freeze as a 3-phase mix of olivine, magnetite and silica. In plate 8, we show fragments of the crushed spherule 35P. Many of the large slabs of olivine are a translucent amber colour. Parts are obscured by attached turbid clumps of a dark brown colour – spot A is a good example. We associate such clumps with the 3-phase mix. They are very like the meteorite scrapings; however, they immediately decolourize in acid. Wedges of clear glass have been seen in some crushed fragments but glass is very rare in both the dendritic and granular forms.

The dark surfaces of 6A and 16P (plate 2) are likely to result from oxidation during low temperature atmospheric flight. We carried out a heating experiment on magnetically clean powdered olivine (20 % fayalite) in 4×10^{-5} atm† oxygen for 15 min. A temperature gradient existed through the 2 mm thick powder, 1100 °C at the top and 1400 °C at the bottom. The powder was mostly unchanged. A few crystals at the top were stained red (haematite?) but underneath a few black sintered clumps were found. Only the surfaces of the crystals were darkened. These clumps were magnetic and one was X-rayed. Smooth faint lines of magnetite (8.384 Å) appeared on the film together with strong spotty lines of olivine (still 20 % fayalite). There is no doubt that surface blackening of stony spherules could occur in the atmosphere at temperatures below the melting point.

The thick walled spherules 9P and 10P (plates 3 and 2 respectively) are likely to have broken up in high temperature atmospheric flight. If a whole piece of meteorite crust is soaked in acid, the black layer stands out with startling clarity – within minutes the dark sintered crystals beneath are decolorized. Both 9P and 10P had black inner and outer surfaces; they were crushed to produce a fresh fracture section. Soaking in acid immediately decolourized the middle of the section but two black layers, about 5 μm thick, remained on either side. Therefore bursting must have occurred in the atmosphere, exposing the inner surface to oxidation. Both inner and outer surfaces resemble the high temperature texture of the surface of the blob on Orgueil.

† atm = 101 kPa.

(c) *Chemical analysis by X-ray microprobes (e.d.s. and w.d.s)*

Exploratory analysis was performed on a few spherules, specifically to search for Ni and S. No S was found and in this respect they resemble the stratospheric spherules found by Brownlee *et al.* (1976). It was generally not possible to isolate individual magnetite grains as the width of the beam was about 3 μm. However, by using e.d.s., a pure magnetite grain was located on the glazed surface of the hemispherical portion of a deliberately crushed spherule 27 P shown in plate 8. The ratio, Ni:Fe, found in the grain was approximately 0.1, but a similar ratio was found on the olivine dendrites in the interior; details of these long dendrites are also shown.

The dendritic spherule 25 P (an s.e.m. photograph showing the surface cupule appears in Parkin *et al.* (1977) their figure 2) was polished to a section passing through the cupule. By using w.d.s. and a Ni standard, a concentration of 0.84 % Ni was found to be uniform over the section except for a higher concentration, 2.4 %, around the cupule. This Ni distribution is shown in plate 8. Probing the surface of other cupule-bearing spherules, we often found Ni enhancement over the floor of the cupule. We conclude that the lost globule is metallic, in most cases.

On one of the fragments of the crushed spherule 35 P, the turbid clump (spot A) was analysed with e.d.s. The concentration of Fe was very high and we suspect much magnetite among the tiny olivine grains, but no Ni was detected. On the olivine slab (spot B), the ratio, Ni:Fe, was approximately 0.02 and Ca, Mn, Cr, and Cu were also present in noticeable amounts, but these were probably less than 1%. The stereopair shows interesting detail of pits and steps on these fragments of olivine.

The suspected presence of Ni in the olivine distinguishes it from olivine in meteorites where Allen & Mason (1973) find the concentration of Ni to be less than $300/10^6$. Actually, the magnetite will be a solid solution containing magnesioferrite (MgO, Fe_2O_3) which, in the pure state, has a parameter a = 8.375Å. The small observed parameter, a = 8.35Å, might be achieved by the addition of Ni, as trevorite (NiO, Fe_2O_3) has a parameter a = 8.339Å. Free magnetite particles are present in Orgueil, but Kerridge (1970) finds the concentration of Ni to be less than 0.1 %. Perhaps stony spherules form from a melt that is rich in Fe – probably with variable amounts of free metal involved. In cooling, variable amounts of Ni enter both the olivine and magnetite co-precipitating phases. The three stony spherules, analysed with neutron activation by Ganapathy *et al.* (1978) show this variability in Ni. They had bulk Fe contents 30.4, 38.6 and 41.8 %; the Ni content was 2.92, not greater than 0.02 and 1.02 % respectively. These Fe concentrations are higher than those occurring in any type of stony meteorite. However, this fact is of doubtful value as there may have been preferential loss of SiO_2 from the melt.

(d) *Composite spherules*

These stony spherules have been given a separate grouping as extra phases are present and in some of them free metal in globular form is found. They are listed in table 3 and shown in plate 9. The kamacite globule in 36 A has a diameter half that of the whole. The similar shape of spherule 37 A suggests the presence of a large globule but the only extra phase is wüstite. The tiny globule embedded in 43 P gives a clear indication of how cupules in some of the other stony spherules could be formed. The globule could be kamacite.

Extensive marine corrosion is evident on 45 P. It is a 'red-head' and must have possessed a metal globule. Very large olivine blocks have survived; they are yellow and lack a black coating. This spherule is reminiscent of a similar looking spherule found by Hunter & Parkin (their figure 8(*c*)). There, a small metallic globule was embedded just beneath the surface of transparent green olivine.

The vesicular glassy spherule 39A, silvery-looking and dusted with orange powder, is very odd; no olivine lines appear on the X-ray film. This is the only spherule showing glass as a noticeable phase. Perhaps the smooth material smearing the surface of 44P is not a glass. No elements heavier than Na were detected under e.d.s. analysis; perhaps it is dried marine slime, in which case 44P is an ordinary stone.

Table 3. The composite stony spherules

spherule	diam. / μm	mole % fayalite in olivine	magnetite *a*/Å	wüstite *a*/Å	kamacite *a*/Å	surface appearance and other comments
36A	55 egg	23 spotty	8.350 spotty	4.272 spotty	2.871 smooth	some perfect crystals; large eccentrically placed globule (containing kamacite, about 6% Ni) partly hidden
37A	55	22 streaky	8.337 streaky	present v. faint	absent	perfect crystals; suspected globule (containing wüstite) eccentrically placed but completely hidden
38A	50	19 smooth	8.343 smooth	4.261 smooth	absent	partly sintered-looking; surface covered with very fine dendrites
39A	60	absent	?	?	2.857 v. faint	silvery gleam; surface coated with orange powder; vesicular glass prominent; kamacite phase uncertain
40P	250	35 smooth	8.373 smooth	4.276 smooth	absent	parts of crust removed; fine dendritic structure; hemispherical cupule, 20 μm diam.
41P	100	32 smooth	8.364 smooth	4.274 smooth	absent	completely glazed; very large hemispherical cupule, 60 μm diam; particle appears as a thick walled bowl, suggesting metal globule was ejected
42P	50	34 smooth	8.363 smooth	4.272 smooth	absent	partly sintered-looking; large cupule, 30 μm diam. – nearly hemispherical, suggesting metal globule was ejected
43P	50	10 streaky	8.321 streaky	absent	present v. faint	some perfect crystals; small 10 μm diam. globule (containing kamacite?) protruding at surface; partly dendritic
44P	60	14 spotty	8.370 spotty	absent	absent	seems sintered-looking; surface partly covered with smooth layer which may be marine slime; spherule could be a true stone
45P	150 prolate	24 spotty	8.357 spotty	4.287 spotty	absent	no sign of fusion crust; definite marine corrosion; yellow crystals are single crystal (50 μm) blocks; whole particle could be single crystal; original metal globule rusted away, leaving red material capping one side
46P	80	present v. faint	8.384 streaky	4.285 streaky	? v. faint	perfect crystals, almost completely covered with red material, overall size 140 μm; spherule appears dendritic
47P	40	present v. faint	? v. faint	4.285 faint	absent	perhaps perfect crystals, almost completely covered with red material, overall size 80 μm

The quality of the X-ray lines is given in the appropriate column.

(*e*) *Iron spherules*

These have rough or shiny surfaces and can occur in two forms; those with an eccentric globule of metal in a shell of magnetite and wüstite and those which are just solid oxides. In table 4 (*a*) we list the forms where the globule is taenite but it is not possible to give a unique Ni content for the globule when the lattice parameter of taenite is high. In the table, we list the two possible values. The photographs in plate 10 show a sequence of atmospheric damage. The hummocky magnetite on the 'pristine' spherule 48A shows no sign of glazing and the globule shows no sign of melting. In 49A the dished globule has suffered some melting and a liquid film has glazed the 'frontal' hemisphere. The stereopair of 50A shows that a deep bowl has been formed in the globule. There is extensive glazing even to the rear of the spherule. A good example of a completely shiny spherule is shown by the stereopair of 52A. Appreciable metal remains but it is capped by a layer of oxide. This spherule is in the first stages of what we call 'ballooning', i.e. conversion of the metallic globule to oxide scale during atmospheric flight.

The fully ballooned forms, 58A, 59P, and 60P are listed in table 4 (*a*′). Their photographs in plate 11 show a small hole leading into a small bubble in the ballooned scale. This suggests gas evolution in a semi-plastic state, contributing to an internal pressure caused by expansion as the

TABLE 4 (*a*). THE IRON SPHERULES: METALLIC GLOBULAR FORM – TAENITE GLOBULE FORM (X-RAY LINES OF OXIDES SPOTTY, METAL LINES SMOOTH)

spherule	diam. μm	metal *a*/Å	metal %Ni	wüstite *a*/Å	magnetite *a*/Å	surface appearance and other comments
48A	90	3.592	45 (32)	4.284	8.382	hummocky; globule visible and undamaged
49A	70	3.573	61	4.286	8.385	'rear' hemisphere hummocky, 'front' hemisphere glazed; globule visible and dished
50A	100	3.584	51 (29)	4.285	8.400	completely glazed; globule visible, with deep hemispherical bowl
51A	50	3.585	50 (30)	4.287	8.411	completely glazed; globule not visible; small hole, suggesting blow-out
52A	70	3.581	54 (28)	4.284	8.394	completely glazed, very shiny; globule capped with oxide
53A	220	very faint	?	4.274	8.380	partly glazed; crystals flush with surface; globule not visible
54P	50	faint	≈ 80	4.278 smooth	8.384 smooth	crystals flush with surface; globule not visible
55P	50	3.516 faint	≈ 100	4.303	8.389	hummocky; half coated with red material, suggesting rusted globule; typical 'red-head'
56P	80	no data, lost before X-ray				hummocky with glazed patch
57P	50	no data, acid soaked				completely glazed, very shiny; globule believed present, but had dissolved

TABLE 4 (*a*′). THE IRON SPHERULES: METALLIC GLOBULAR FORM – BALLOONED FORM (GLOBULE OXIDIZES TO NON-MOLTEN SCALE)

spherule	diam. μm	metal *a*/Å	metal %Ni	wüstite *a*/Å	magnetite *a*/Å	surface appearance and other comments
58A	110	3.546	82	4.280	8.390	hummocky; found broken as hemisphere, see Parkin *et al.*, their figure 4
59P	60	3.545	83	4.286	8.396	completely glazed; spherule cracking apart
60P	60	not found		4.278	8.389	glazed

globule converts to scale. This pressure must have cracked 58 A which was found as a hemisphere. Parkin *et al.* (their figure 4) show a polished section of this spherule with the section passing through the ballooned scale. All that remains of the metal globule is a crescent whose arms enclose the scale. Probe analysis (w.d.s.) gave Ni concentrations of 30 % in the scale, 80 % in the

TABLE 4(*b*). THE IRON SPHERULES: METALLIC GLOBULAR FORM – KAMACITE GLOBULE FORM (X-RAY LINES OF OXIDES SPOTTY, METAL SMOOTH)

spherule	diam. µm	metal a/Å	metal %Ni	wüstite a/Å	magnetite a/Å	surface appearance and other comments
61 A	90 egg	2.871	?	4.290	8.397	completely glazed; sharp pole dished; 'front' hemisphere has fine long crack; globule not visible
62 A	80	2.865	?	4.283	8.378	hummocky; globule not visible

TABLE 4(*c*). THE IRON SPHERULES: METALLIC GLOBULAR FORM – RUSTED GLOBULE FORM, 'RED-HEADS' (PARTLY ENCASED IN RED MATERIAL, NO METAL FOUND)

spherule	diam. µm	wüstite a/Å	magnetite a/Å	surface appearance and other comments
63 A	60	4.284	v. faint	hummocky; hollow visible
64 A	40	4.284	v. faint	hummocky; hollow not visible
65 A	30	no data, not X-rayed		hummocky; hollow not visible
66 A	40			hummocky; hollow not visible
67 A	30			hummocky; large hollow visible
68 P	30			hummocky; hollow not visible
69 P	50			completely glazed, very shiny; large hollow, rust filled
70 P	40			hummocky; hollow not visible

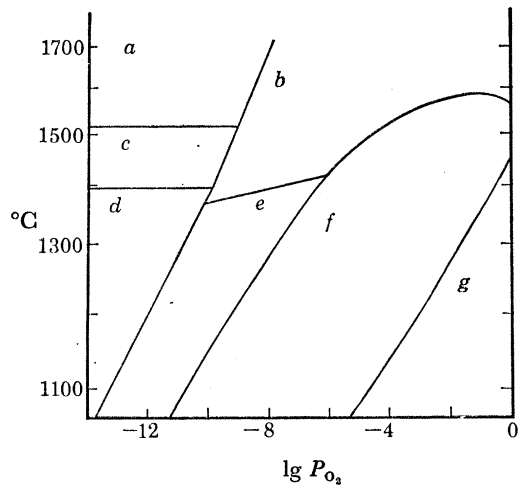

FIGURE 3. The phase diagram of the Fe–O_2 system. The oxygen partial pressure P_{O_2} is in atmospheres. *a*, Liquid–iron; *b*, liquid–oxide; *c*, δ–iron; *d*, γ–iron; *e*, wüstite; *f*, magnetite; *g*, haematite.

crescent, but only 1 % in the oxide shell. A similar section was made on 60 P but no metal was visible under microscopic inspection. E.d.s. probing gave equal amounts of Ni and Fe over the scale but a ratio, Ni:Fe, of only 0.02 over the shell.

In space we assume that all these spherules were like 48 A. Their 'varying appearances' can be described with the aid of the phase diagram given by Darken & Gurry (1953) and reproduced in figure 3. At a height of about 100 km the air density ρ is about 10^{-6} kg m^{-3}. For a velocity v of about 11 km s^{-1} the pressure, P, on the nose of the spherule is 10^{-3} atm, where $P = \rho v^2$. Hence, the spherule is in an average oxygen partial pressure of about 10^{-4} atm. This fixes the melting point of magnetite at 1510 °C. Just below this temperature, say for a moderately plunging flight, the metal globule melts and produces liquid oxide. If time allows, a glazing film spreads around the magnetite shell which remains completely solid. No Ni should exist in this film as Ni would readily diffuse to the remaining metal. For temperatures falling below 1370 °C, the globule ceases to produce liquid that could flow away. Instead a plastic wüstite scale develops, trapping much of the Ni. Possibly 58 A was on a grazing flight and never achieved melting temperatures, as there is no sign of glazing.

Table 5 (*a*). The iron spherules: pure oxide form – wüstite–magnetic form (X-ray lines spotty)

spherule	diam. / μm	wüstite *a*/Å	magnetite *a*/Å	surface appearance and other comments
71 A	120	4.283	8.399	hummocky; found broken as hemisphere
72 A	50	4.277	8.387	hummocky; glazed patch
73 A	50	4.287	8.391	glazed; irregular hole, suggesting blow-out

Table 5 (*a*′). The iron spherules: pure oxide form – wüstite–magnetite form (X-ray lines smooth)

spherule	diam. / μm	wüstite *a*/Å	magnetite *a*/Å	surface appearance and other comments
74 A	140	4.273	8.395	hummocky; petal-like formation
75 P	60	4.297	8.393	perfect crystals; pitting in centre of grains, perhaps etching at grain boundaries

Table 5 (*b*). the iron spherules: pure oxide form – magnetite form (X-ray lines spotty or smooth)

spherule	diam. / μm	wüstite *a*/Å	magnetite *a*/Å	surface appearance and other comments
76 A	50	absent	8.382	completely glazed, very shiny; irregular hole or pipe; suggesting blow-out
77 A	80	absent	8.389	glazed; large crystals 10–20 μm
78 A	80	absent	8.392 spotty	glazed; large crystals 20–30 μm
79 A	40 prolate	absent	8.406	glazed; perhaps pure Ni present
80 P	70	absent	8.353 spotty	completely glazed, very shiny; irregular hole or pipe, suggesting blow-out; note low magnetite parameter

Table 5 (*c*). The iron spherules: pure oxide form – magnetite–haematite form (X-ray lines of haematite smooth but very faint)

spherule	diam. / μm	wüstite *a*/Å	magnetite *a*/Å	surface appearance and other comments
81 A	60	absent	8.384 spotty	hummocky – fine grains; light grey colour
82 P	200	absent	8.392	glazed; large crystals 20 μm; irregular hole, suggesting blow-out
83 P	50 egg	no data, broken on mounting		hummocky; light grey colour, dusted with orange powder haematite suspected but not confirmed

The spread of a glazing film is demonstrated on the cracked spherule 57 P. This shiny spherule was soaked in 2 M HNO_3 for 64 h to see if the film would etch. It did not, but the metal globule had dissolved and the shell fell to pieces. A 1 μm thick film is clearly seen, spreading roof-like over the outer surface of the shell. No Ni could be found anywhere on this piece, but e.d.s. probing at several points on the surface and the fracture section found Mg, Al, Si, Cl and Cu in detectable amounts.

Although most globules are taenite, two kamacite spherules are listed in table 4 (*b*). The egg-shaped one, 61 A, is shown in plate 11 and the ordinary sphere, 62 A, appears in plate 12. We doubt that 61 A is a case of ballooning, because polishing down to a diameter revealed a perfectly round 45 μm diameter globule of metal at the 'frontal' nose – however, note the fine long crack on the frontal hemisphere that suggests internal pressure. Perhaps initially, the globule was well inside the oxide shell and aligned flight has shaped the spherule. The 'pristine' spherule 48 A (plate 10) was polished to a diameter. The taenite globule was perfectly round and had a diameter half that of the whole. Specks and streamers of metal were seen in the oxide, close to the globule.

In a few cases such as 51 A, 54 P and 62 A (plate 12) the globule is not visible at the surface. Spherule 54 P is most peculiar, the 'flat-faced' grains lie strangely flush with the surface of the spherule. Spherules 55 P and 63 A are 'red-heads'. Some metal that could be pure Ni remains in 55 P – but the X-ray lines are faint. Other 'red-heads' are listed in table 4 (*c*).

Finally, some of the iron forms which lack the metal globule are shown in plates 13 and 14 and all of them are listed in Table 5 (*a*, *a'*, *b* and *c*), according to oxide composition and quality of the X-ray lines. We note that two spherules show faint haematite lines. Spherule 71 A was found as a broken hemisphere. It is solid throughout. In fact, all the iron forms that we have either cracked open, polished down or found broken are solid. Hollows at the surface can be seen on a few spherules, without red attachment, but it is clear that these are cases where the globule has been expelled rather than rusted out. It is difficult to account for the fracture of the solid oxide spherules, as ballooning could not have occurred. Grindwheel sparks are never found as broken spheres. We think it unlikely that fracture could have occurred during residence in the sediment or during extraction. Perhaps collisions in space are the cause of fracture in these solid oxide forms.

Some of the glazed and many of the thoroughly glazed or shiny spherules show ragged holes leading into deep pipes. The stereopair of 76 A (plate 13) shows that the pipe walls are quite smooth, although irregular. Perhaps high temperature (near to the melting point) atmospheric flight causes semi-molten plugs to be expelled by evolving gas pressure. A further rise in temperature, above the melting point, could explode the whole spherule. This certainly occurs in grindwheel sparks.

The presence of Ni confirms an extraterrestrial origin for these solid oxide forms. By using e.d.s. on the polished section of 74 A, the ratio Ni : Fe was found to be 0.04. Also traces of Si, Mg, and Ca were suspected. The large spherule 53 A (not shown) was polished down. No metal could be seen, even though X-ray diffraction detected a faint taenite line. By using w.d.s., the Ni content was found to be uniform over the section, at 3 %. The low magnetite lattice parameter of 80 P also suggests an appreciable Ni content.

(*f*) *Iron meteorites and grindwheel sparks*

According to Krinov (1964) droplets of magnetite are swept from the surface of iron meteorites. He found them in the soil around the site of Sikhote-Alin, but they differ from deep-sea iron spherules in several respects. No metallic globule forms are reported. Although spheres predominate, oval shapes (some with tails) and hollow flasks occur. Many of the droplets are hollow.

However, metallic globular spherules, very similar to cosmic spherules, can be reproduced by quenching grindwheel sparks about 5 cm from the wheel. Here, tapes of bright metal are stripped off the steel bar and they are hot enough to start burning at one end, the tape being drawn into a molten ball of wüstite and magnetite. These round quenched sparks have diameters ranging down from 100 μm and have the same hummocky surface as the 'pristine' cosmic spherule, but the globule is not visible by surface inspection. If burning is allowed to continue, gas pressure bursts the spark and produces the familiar star-like forking along the trails. Even low carbon steels develop tens of atmospheres pressure and destruction by fine spraying is the fate of most sparks. However, some survive as pure magnetite spheres but always with a large oval hollow in their interior. It is not clear how this oval hollow forms inside a perfect sphere. The presence of the hollow is not usually visible by surface inspection. Although some hollow egg-shapes are found, with openings at the sharp pole, most are perfect spheres. All the surfaces have the smooth hummocky 'standard appearance', irrespective of whether they have been quenched or not. No glazing or ballooning is seen. No broken hemispheres are found. Very rarely, thin perforated shells (like colanders) are collected at the end of the trails, which indicates the violence of the star-like gassy explosion.

The sparks are helpful in the interpretation of cupules, interior cavities and vugs seen on stony spherules. If a quenched spark is broken, the globule readily rolls out of the shell. Its surface is quite smooth and the cavity wall in the shell is also smooth. If a hollow form is broken, the wall of the hollow is covered with short fingers of magnetite protruding into the void, rather like the protruding crystals in the wall of a vug.

5. Concluding remarks

(i) The size distribution analysis demands that some mechanism be found for destroying the spherules, if general melting occurs in high temperature atmospheric flight. Break-up by internal gas pressure has been suggested and this is clearly demonstrated on grindwheel sparks. Presumably, during formation in space, the spherule will rid itself of any volatiles by a thorough outgassing. However, during its residence in space it will become saturated with solar-wind gases. If these 100 μm diameter spherules are formed as 'sparks' in the asteroidal belt, they would take about 10^6a to spiral in circular orbits to the earth under the action of the Poynting–Robertson effect. Lovell (1954) gives a brief account of this effect.

Lunar soil grains are exceptionally rich in solar-wind gases and Kirsten *et al.* (1970) estimate that, by diffusion, a 100 μm diameter soil grain would fill with ^{4}He to the extent of about 10^{-4} mol per g, if it was exposed for about 10^3a on the surface of the moon. Let us take this value for the spherule and assume that a bubble of comparable size is formed when atmospheric temperatures rapidly reach 2000 °C during a plunging flight. In a spherule of diameter 100 μm (mass, 1 μg), a gas pressure of 16 atm would result. This is more than adequate to burst a molten spherule against its surface tension. Hence, a mechanism is at hand to explain the kink in the size distribution at the critical spherule size.

(ii) There is mutual collision among zodiacal particles, but clearly the deep-sea spherules have escaped, unless we assume that some of the broken hemispheres are formed in this way. From articles by Hartung (1976) and Morrison & Zinner (1976), there is still controversy over micrometeorite flux estimates based on pit concentrations seen on lunar rocks. Generally, exposures of 10^4–10^6a are assumed and concentrations range from 8×10^4–6×10^6 m^{-2}, for pit diameters not less than 10 μm. If we assume that the higher value can be applied to the 10^6a residence of a 100 μm diameter spherule, the chance of destructive collision (pit diameter not less than 10 μm) is about 5%.

It is interesting to use our derived spatial spherule concentration to estimate the pit concentration on the lunar rocks, i.e. only those that have been caused by cosmic spherule impact. High velocity (approximately 1 km s^{-1}) impact experiments show that pit diameters are 1–3 times the diameter of the projectile, depending on materials used and kinetic energy. If we assume that the 5 μm diameter cut-off really exists, then 10 μm diameter lunar pits are the smallest produced by 'classical' zodiacal spherules. An integration between spherule radii 350–2.5 μm gives the number of stones and irons per m^3 of space as 7.2×10^{-11} and 2.0×10^{-11} respectively. By neglecting gravitational focusing and taking the lunar impact velocity as 3 km s^{-1}, the number of pits with diameters not less than 10 μm produced in 10^6a is 9×10^6 m^{-2}. Agreement with the observed value must be fortuitous as spherules could hardly make a 100% contribution to the zodiacal cloud. For instance, although we have failed to locate extraterrestrial fragmentary material, the finding of stratospheric crumbs shows that it does exist. We recall that the crumbs contain sulphur. Therefore they cannot be fragments from the break-up of zodiacal spherules.

For smaller pit diameters, the concentration on the lunar rocks suddenly increases rapidly. Fechtig (1976) consideres this to be due to a new zodiacal component, the so-called β-particles. These 0.1 μm diameter particles are thought to be created from colliding 'classical' zodiacal particles in the inner Solar system. They reach the moon with speeds of 20–50 km s^{-1}, being expelled by radiation pressure. Such β-particles might produce one or two 1 μm diameter pits on a cosmic spherule. We have examined high magnification views of some of the 'perfect' crystals on the 'pristine' spherules but failed to find evidence of space erosion. Perhaps such small pits would anneal out during hot atmospheric flight.

(iii) It is difficult to describe the collisional formation stage of cosmic spherules with any precision. Obviously a hot oxidizing atmosphere was present, probably derived from hydrated minerals. Even ice in the 'sparking' materials can be suggested, as cometary matter may collide with asteroids. The phase diagrams are not helpful in fixing the oxygen partial pressure as conditions are far from equilibrium. Free metal is actually present or seems to have been present in many stony spherules. Speidel & Nafziger (1968) find that there is no value of oxygen fugacity that will allow free metal and magnetite to grow together from a cooling silicate melt under equilibrium conditions. It seems reasonable to suppose that free metal was added to the molten silicate and complete oxidation of the metal was arrested soon after the spherule was formed. Likewise, complete combustion of the metal in the iron spherules must have been prevented by a rapid quenching; but note the large magnetite grains in some of the spherules, for instance 78A. The presence of pure magnetite spherules suggests a fairly high oxygen pressure, we never find pure wüstite spherules.

The commonly occurring granular-vuggy form presents a problem. If freezing from a melt occurred, one would expect the surface to have the usual smooth hummocky appearance, like the iron form. Instead, the spherule is an aggregate, with crystals randomly projecting out of the surface. Such an arrangement could arise if the crystals were already present in a volatile liquid drop and evaporation brought them together. The dendritic form is more readily explained. The crystals form from the freezing of an outgassed supercooled melt, although details remain obscure.

For example, it is not clear how the near-single crystal 23A could form as a uniform stack of plates.

(iv) It might be argued that the X-ray evidence used in differentiating the stony spherules from the fusion crusts of stony meteorites is weakened because the crusts on museum meteorites were formed during the last stages of ablation, when they were at low altitude. Any ablation droplets would be shed at all altitudes and droplets shed at high altitude may be different from crusts formed at low altitude, because of varying atmospheric oxygen partial pressures. The pattern and intensity of the magnetite lines on the X-ray films suggest magnetite and not cation deficient maghemite ($\gamma - Fe_2O_3$, a = 8.350 Å). However, some cation vacancies may have been introduced into the magnetite lattice, thereby contributing to a lowering of the parameter. A high oxygen pressure would favour such a lowering. Therefore, if anything, any droplets shed at high altitude should have a higher parameter than that observed on museum meteorites (a = 8.38 Å). The magnetite parameter for the stony spherules (a = 8.35 Å) is well below that of the lowest value for the meteorites. Clearly, the low parameter in the stony spherules must be due to other causes, for example Ni impurity.

Actually, it is not clear how atmospheric oxygen partial pressure enters directly into any detailed consideration of the oxidation state of ablated droplets. Obviously, in order to survive, droplets must be shed into the vacuum wake at the rear of the meteorite and this zero pressure condition exists at all altitudes. Furthermore, up to the moment of spraying, the liquid layer always stays in intimate contact with the interior of the meteorite. Irrespective of pressure due to hypersonic flow, the oxidation state could be much the same at all altitudes.

It is conceivable that some of the 'varying appearances' seen on cosmic spherules could arise on the surfaces of meteoritic droplets; provided the droplets were in the solid state prior to any further atmospheric damage. Clearly 32P could not have been pointed whilst still in the completely molten state. It is likely that a meteorite will be tumbling during its passage through the atmosphere. The liquid layer, created at the front, will be carried round to the rear where sustained boiling may eject droplets into the wake. After freezing to a 'standard appearance', the droplets would now have to leave the wake at a rather critical distance behind the meteorite in order to suffer only superficial damage. Only a negligible fraction would survive in this way as most would leave too soon and boil away or leave too late and remain unaffected. This would make the mass balance problem even more acute and an unreasonably high influx of meteorites would be needed to account for the number of deep-sea spherules. If forced to find a meteoritic droplet amongst our collection, the odd spherule 39A seems a possible choice – perhaps it was reduced to glass and metal in the vacuum wake and later rusted in the marine environment. By comparison with these contrived processes, we believe that our hypothesis offers a more plausible explanation for the 'varying appearances' of the spherules and the hypothesis is supported by the size-distribution analysis. It seems inconceivable that black coated, white interior, granular-vuggy spherules could ever arise in complete atmospheric melting processes, either from meteorites, meteors, or from melting zodiacal fragments.

(v) Some independent support for our hypothesis may come from the analysis of inert gases released from the bulk magnetic fraction of deep-sea red clays (Merrihue 1964). The results are inconclusive with regard to ^{4}He:^{3}He ratio, but it does seem that there is an enrichment of ^{4}He. The ^{40}Ar:^{36}Ar ratio, for argon released at 1400 °C was 172 compared with 296 for atmospheric argon. Because of the presence of these gases, some portion of this magnetic fraction is extraterrestrial and this portion is not meteoric or meteoritic molten debris. Merrihue concluded, from the isotopic compositions, that the gases were of solar flare or solar wind origin. They were implanted into free dust grains in space. The dust could have been circulating around the Sun for some 10^5a. Of course, the finding of inert gases of non-terrestrial origin in cosmic spherules would provide conclusive proof that they had existed in space as rounded bodies.

We are very grateful to our colleagues in the School of Materials Science: Dr F. J. Hazlewood for carrying out the heating experiment on olivine and for continuous helpful discussion, Dr V. D. Scott for providing the electron optical facilities and Mr H. R. Perrott and Dr G. Love for technical assistance. Mr B. Chapman of the School of Physics undertook the X-ray exposures and we thank him for his services. We must also thank Mr K. Topp of the Metallurgy Department, Royal Military College of Science, Shrivenham, for the e.d.s. analysis. Two undergraduate students of the School of Physics, Miss S. Holmes and Mr M. Folkard, made the observations on the grindwheel sparks and we are pleased to acknowledge their contribution to this work.

We are obliged to Dr R. Hutchison of the British Museum (Natural History) for supplying the pieces of fusion crust of the meteorites and also to Dr D. V. Kent of the Lamont–Doherty Geological Observatory for information on Atlantic red-clay sedimentation rates. We must record our indebtedness to the late Dr W. H. Morton of the Geology Department, University of Addis Ababa, for much general information in the early stages of this work, and to Sir Charles Frank, F.R.S., of the Physics Department, University of Bristol, for his interest throughout the course of this work.

Also, we mention the discussion with Dr G. P. Jones and Dr T. I. Barry of the National Physical Laboratory, Teddington, which prompted us to consider the evolution of gases as the reason for spherule break-up in the atmosphere. Finally, we thank Mr R. A. Parkin, the father of one of the authors, for his assistance in the photographic reproductions.

Note added in proof, 17 *March* 1980. Iron spherules have been extracted from the upper 250 cm length of the Lamont–Doherty core RC 10–158. This central north Pacific core had been magnetically dated. The known sedimentation rate (1.5 mm per 10^3a for the top portion and 1.2 mm per 10^3a for the bottom portion) allows a uniform time scale to be attached to the depth horizons.

If our hypothesis is correct, then the time Δt (in 10^6a) for a spherule to spiral to Earth from a collision event in the asteroidal belt is given by the Poynting–Robertson formula

$$\Delta t = 3.5 \times 10^{-7}\, \delta d(a^2 - 1),$$

where δ(kg m^{-3}) and d(μm) are the density and diameter of the spherule respectively; and a (astronomical units) is the distance of the collision from the Sun. Therefore, if the diameters of the spherules found in each horizon are plotted against time down the core, a series of sloping lines should be evident, if the collisions have not been too frequent. In the array of points obtained, a few sloping lines can be discerned and statistical analysis (recently completed in the School of Mathematics, University of Bath) strongly suggests that the whole array has a sloping 'texture'. These slopes place the events in the asteroidal belt – i.e. $a = 2$–3 astronomical units.

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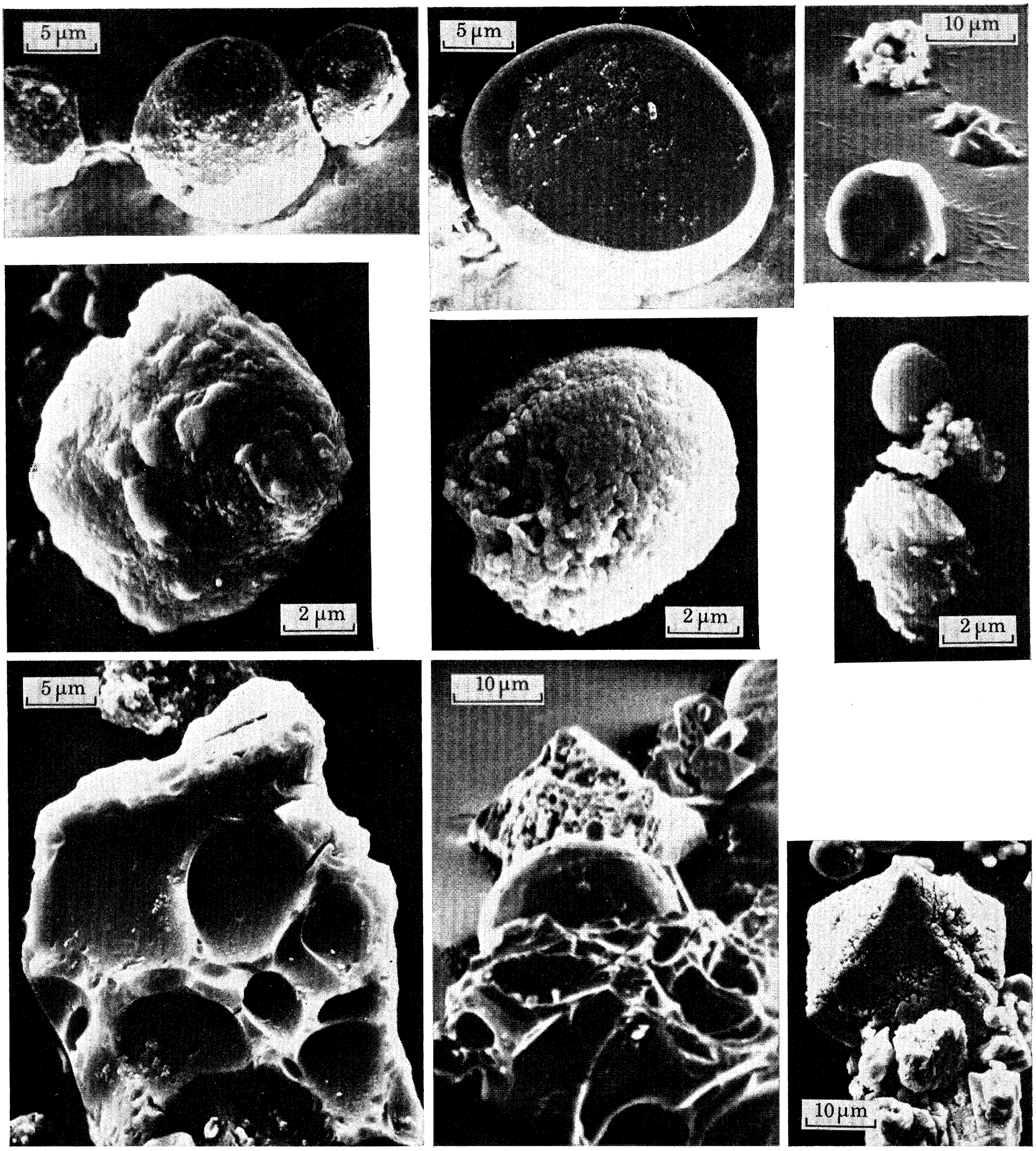


PLATE 1. Rounded objects of doubtful origin in the fine magnetic fraction from the Pacific sample. The faceted-objects seem to be rounded magnetite crystals that have grown on the sea-bed. The vesicular glass could be volcanic, but it does resemble fusion crust of stony meteorite. A few small cosmic spherules are seen in the lower photographs.

(*Facing p.* 518)

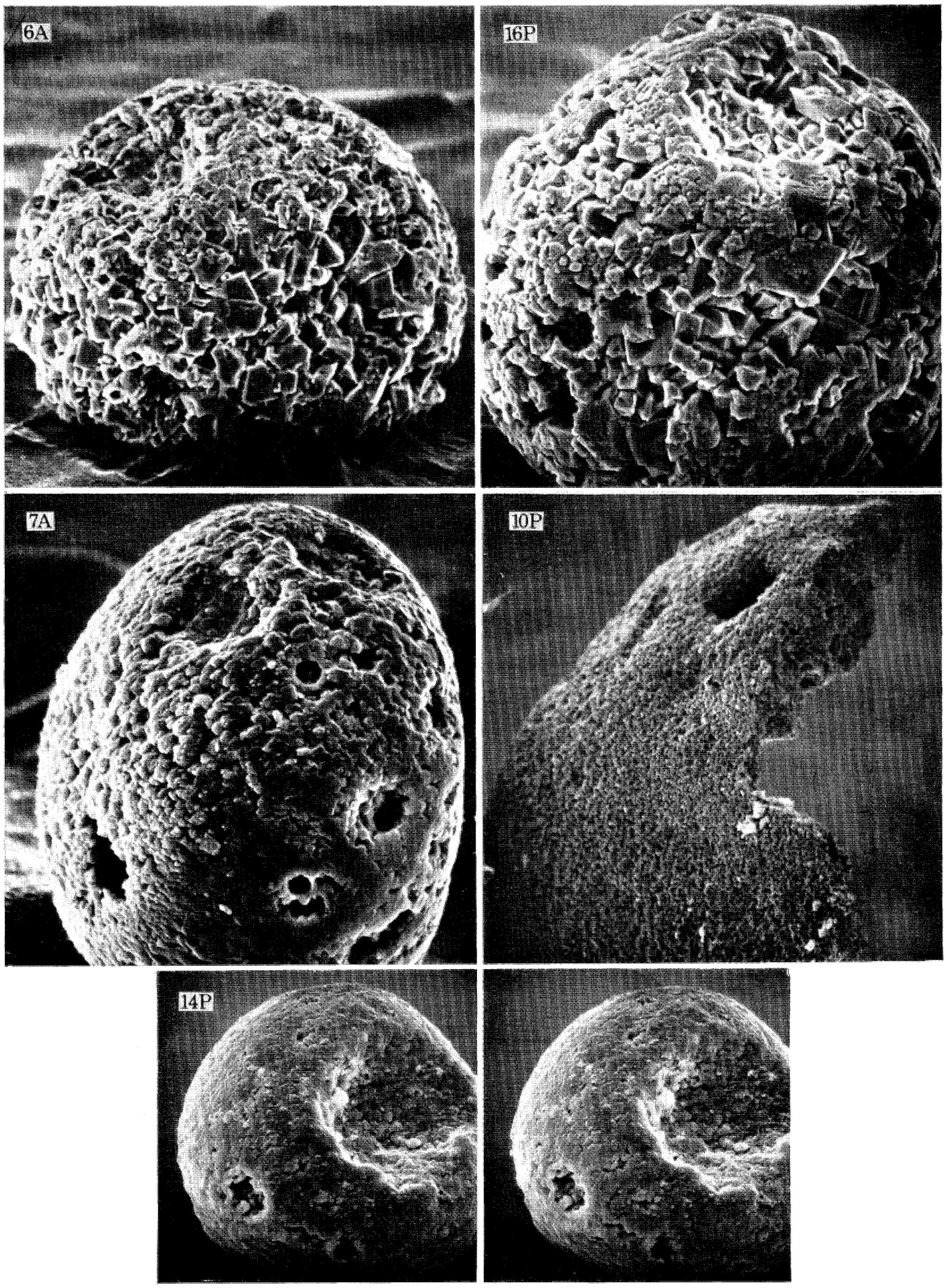


PLATE 2. Stony spherules, granular–vuggy form: surface details.

	6A	16P	7A	10P	14P
Diam./μm	150	120	70	150	50

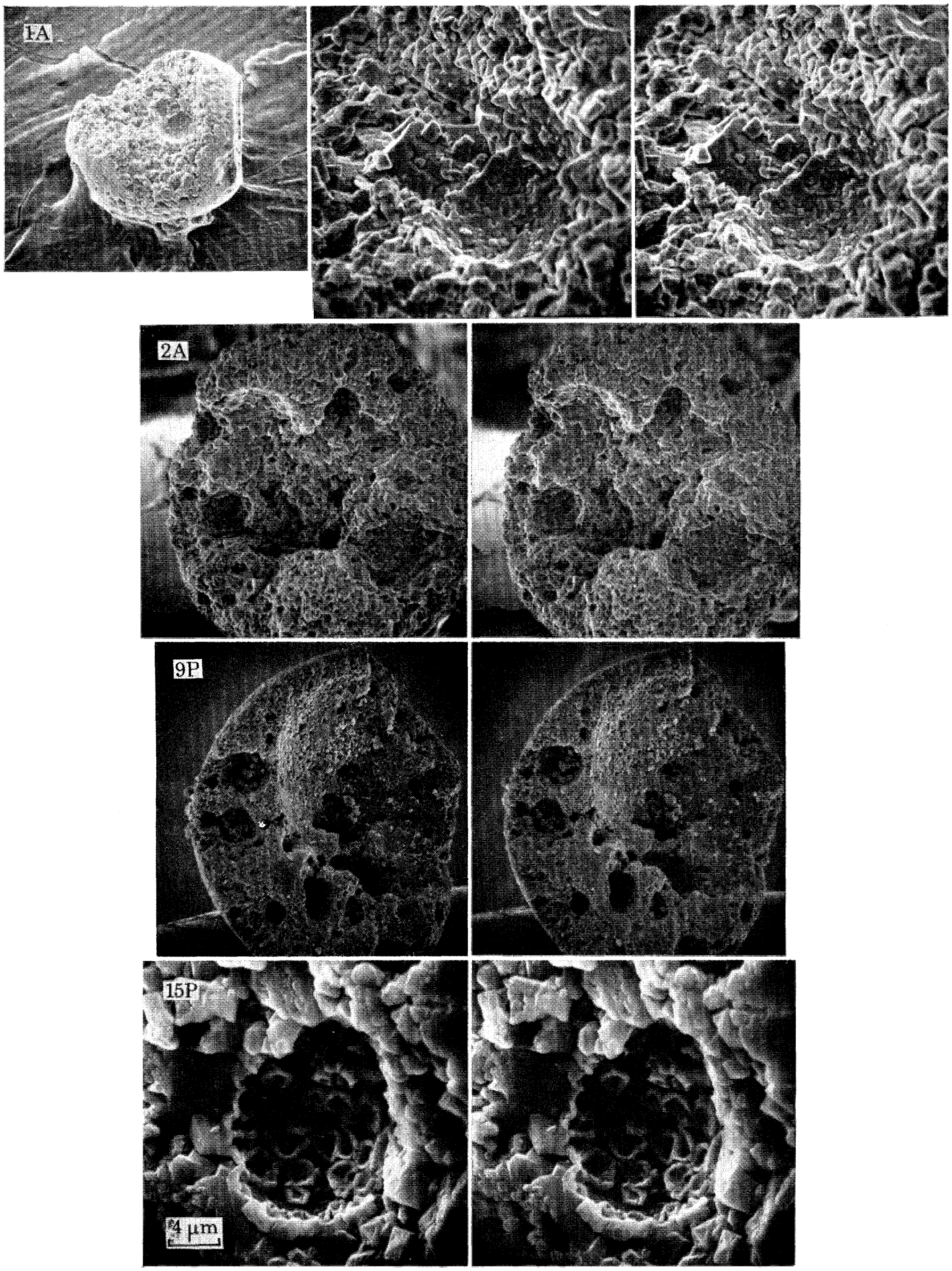


PLATE 3. Stony spherules, granular–vuggy form: interior details.

	1A	2A	9P
Diam./µm	110	130	130

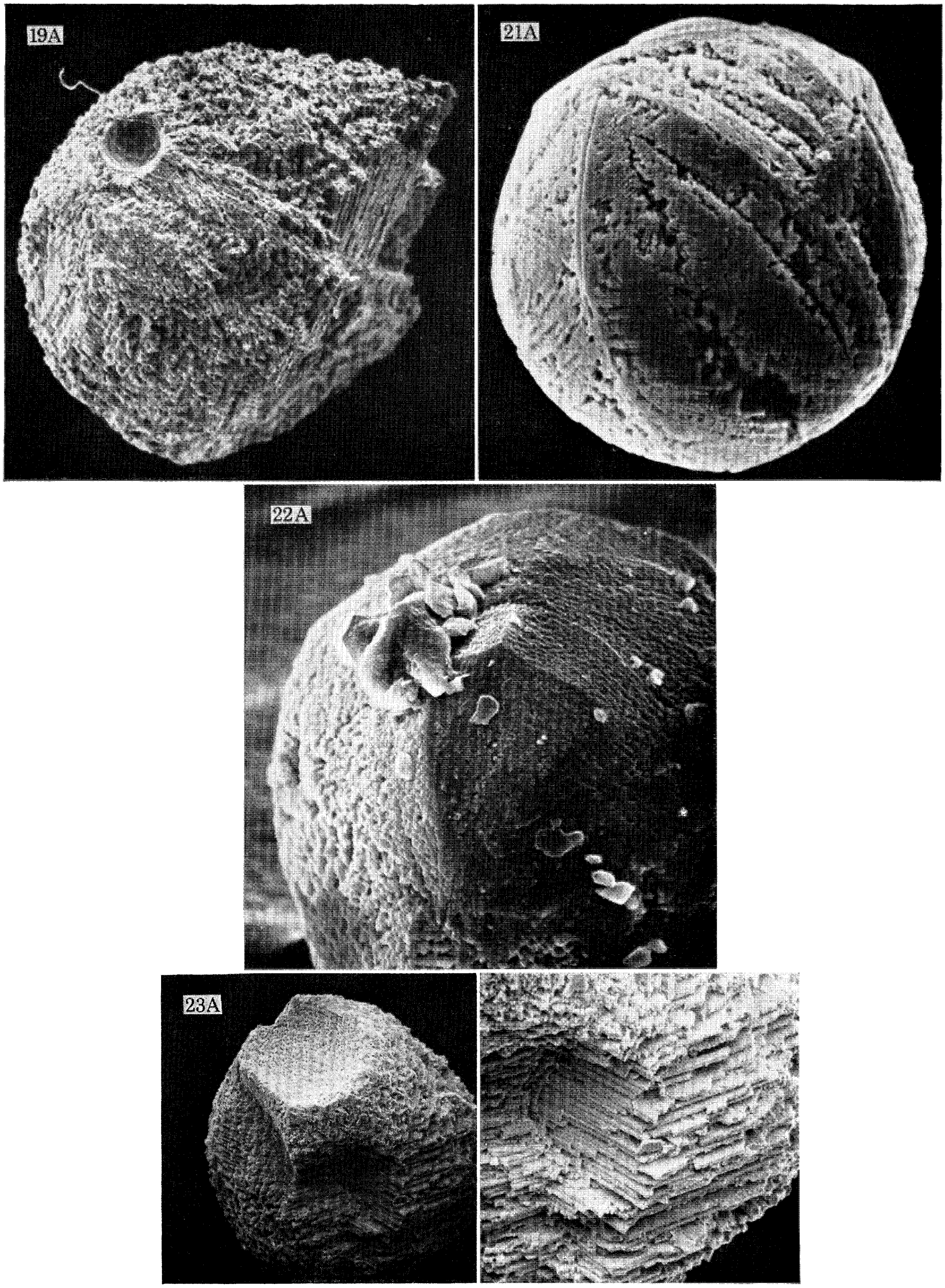


PLATE 4. Stony spherules, dendritic form: surface details.

	19A	21A	22A	23A
Diam./μm	200	70	60	170

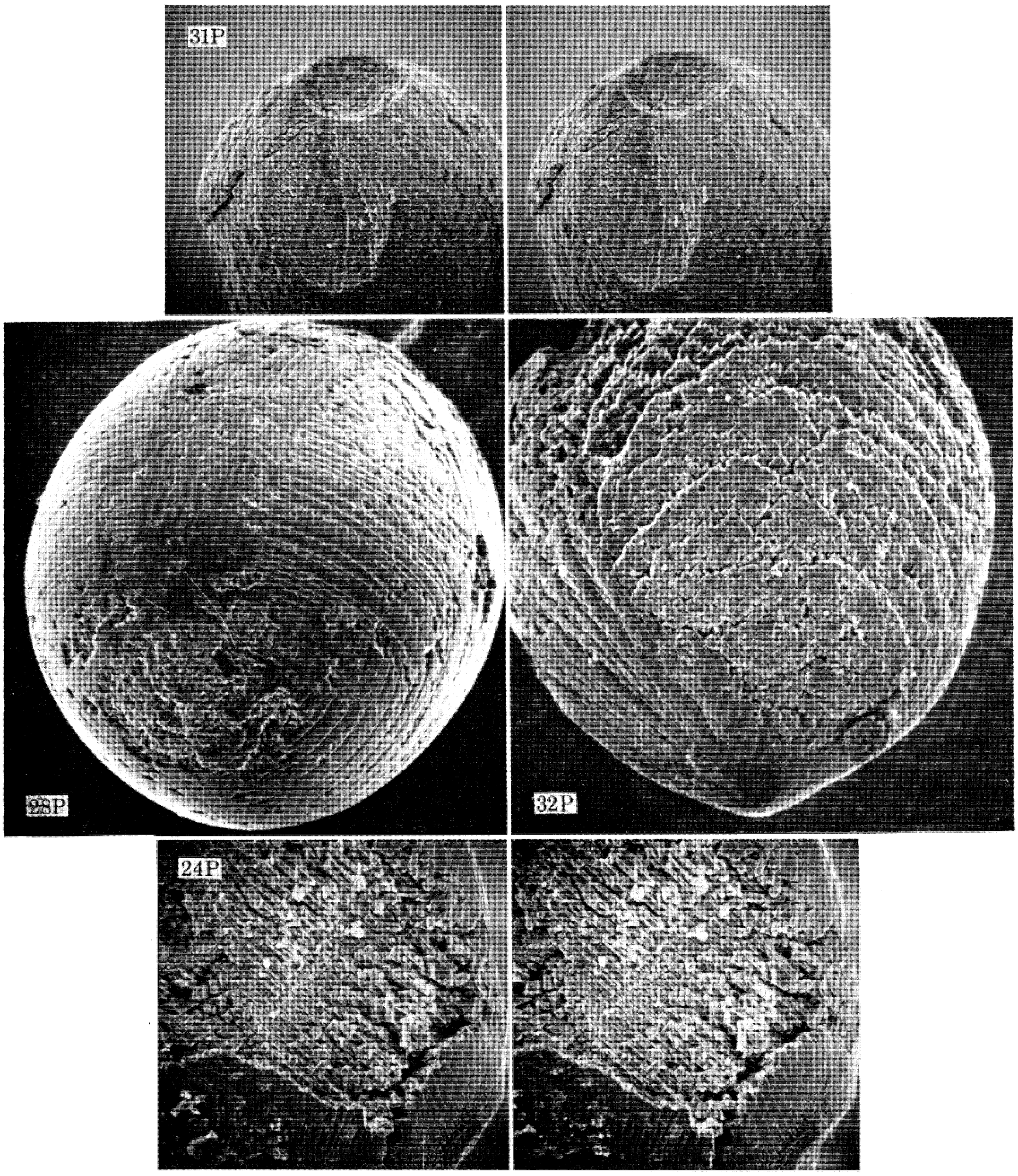


PLATE 5. Stony spherules, dendritic form: surface details.

	31P	28P	32P	24P
Diam./µm	100	110	100	120

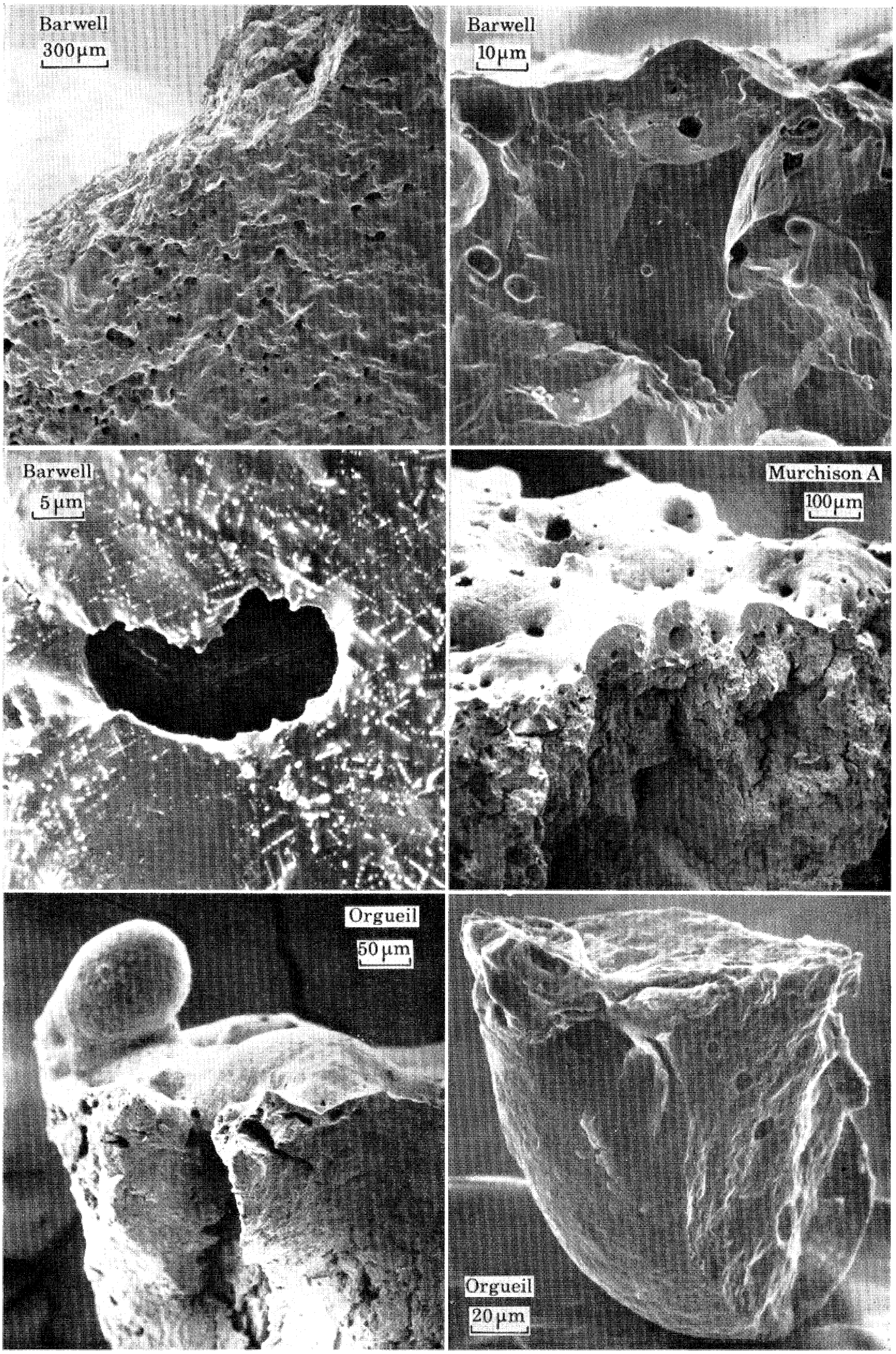


PLATE 6. Fusion crust of meteorites: surface details and fracture sections.

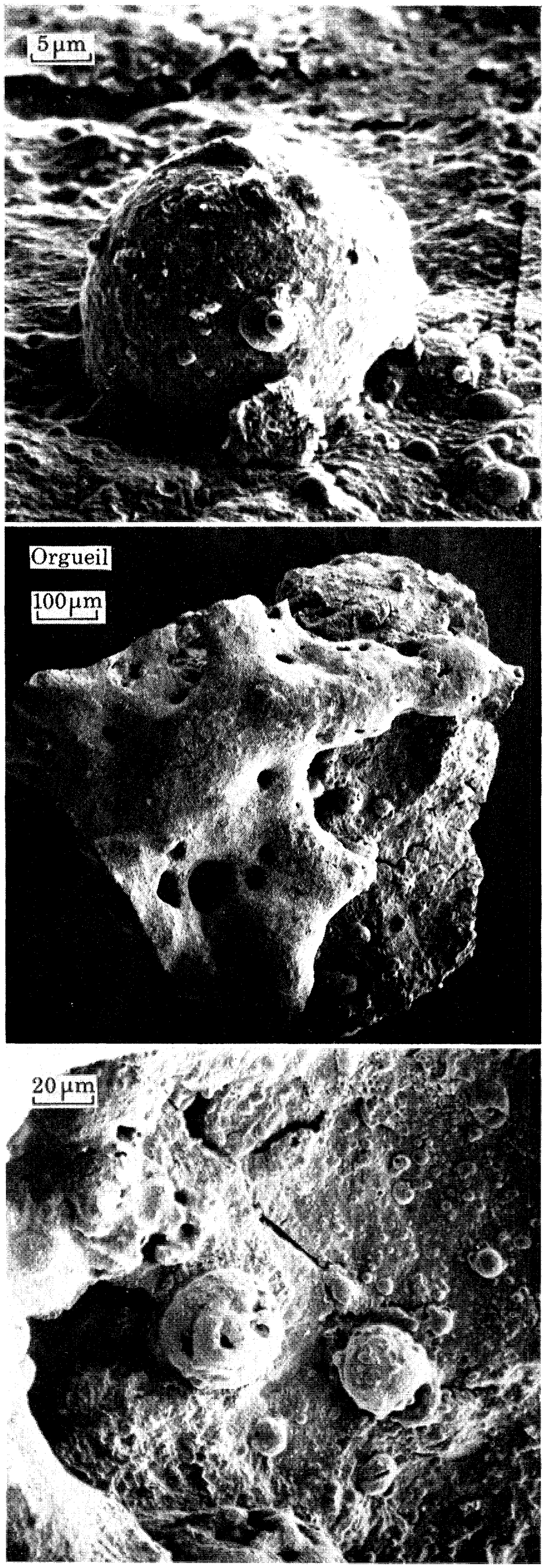


PLATE 7. Fusion crust of Orgueil, showing ball-like forms on or near the surface. See the text for details.

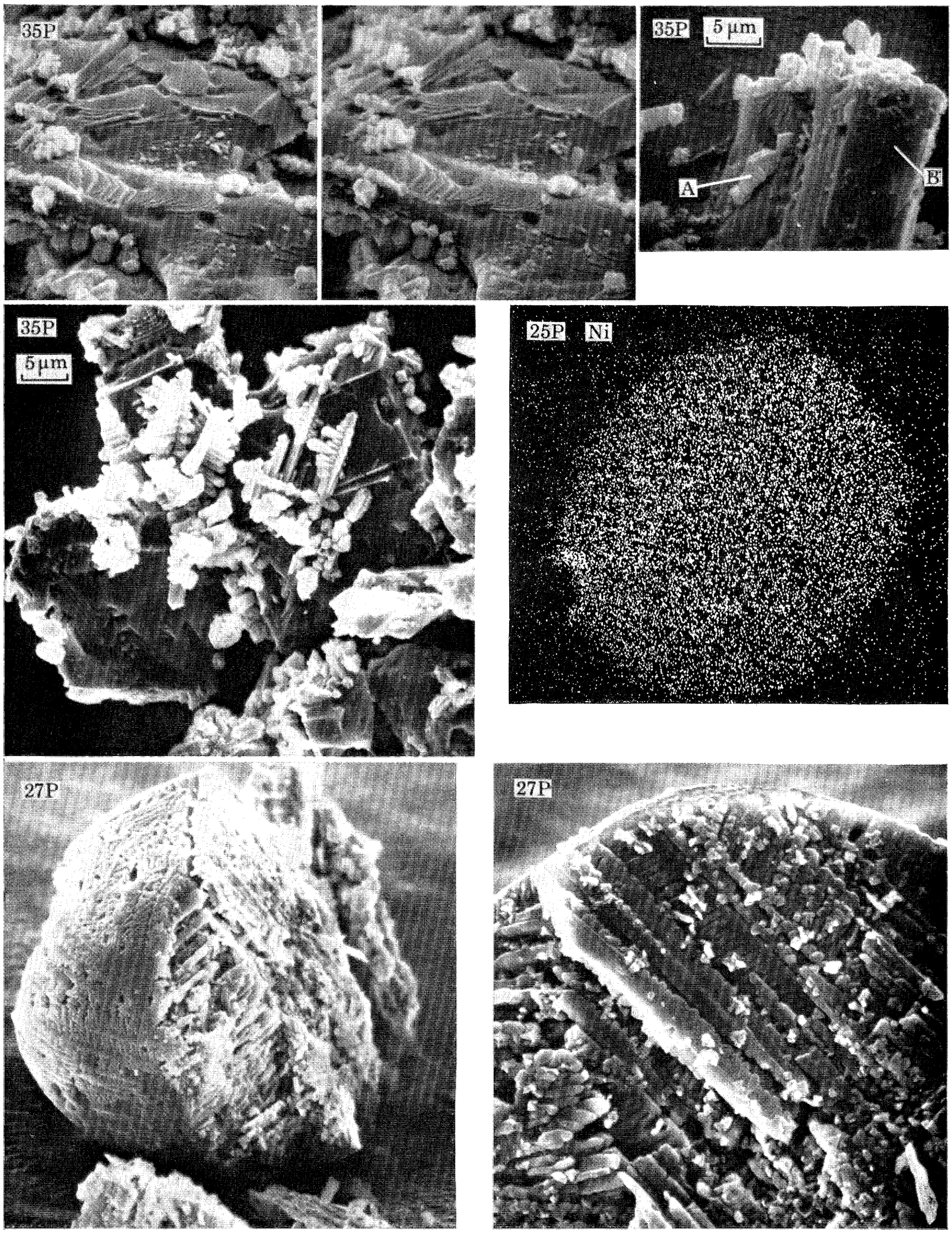


PLATE 8. Stony spherules, dendritic form: interior details.

	25P	27P
Diam./µm	140	80

The Ni distribution over the polished section of 25P is uniform at 0.84 %, except around the cupule where it is 2.4 %.

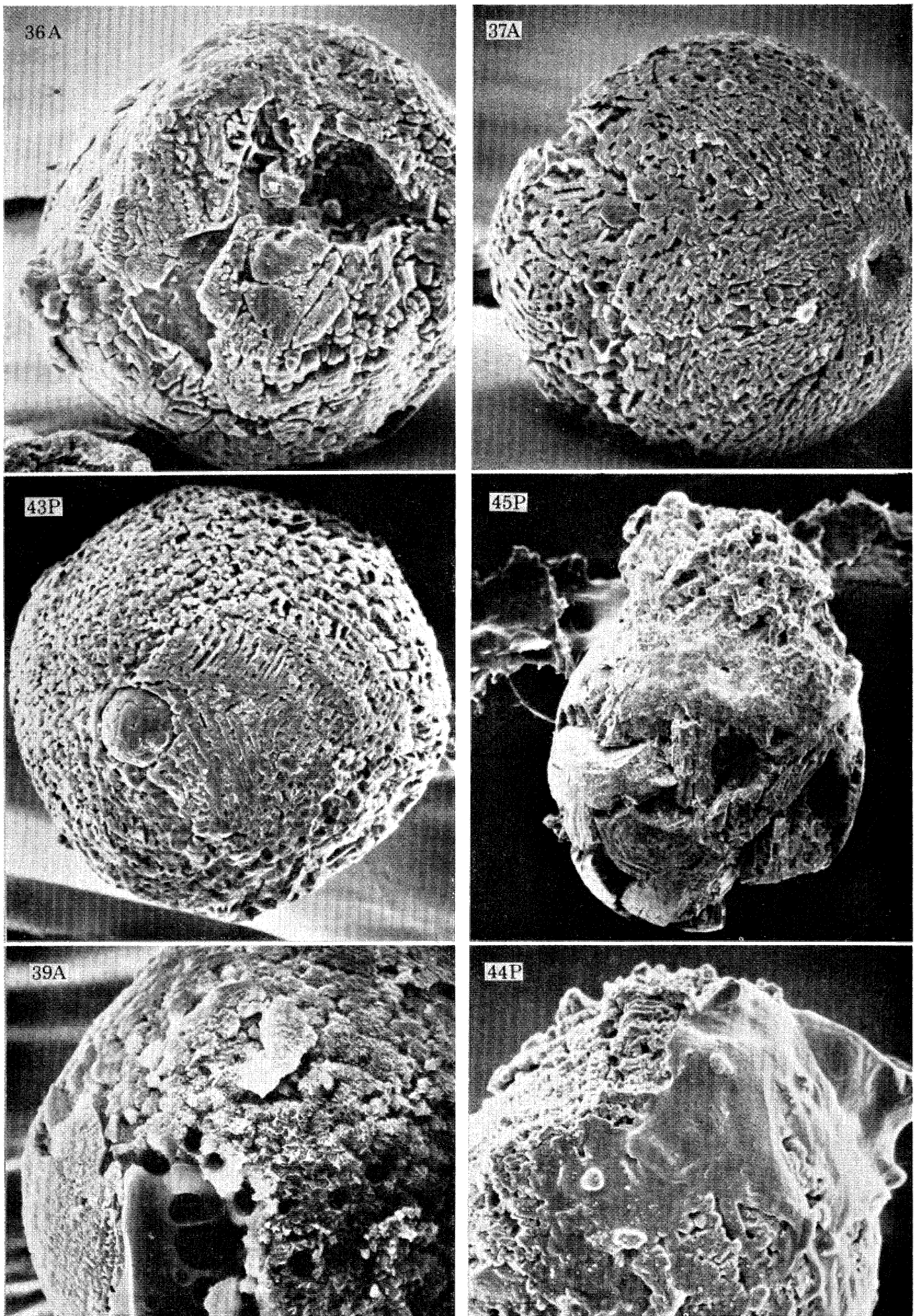
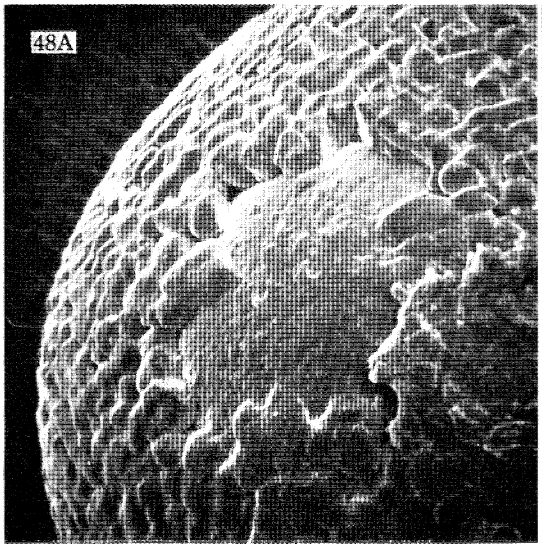
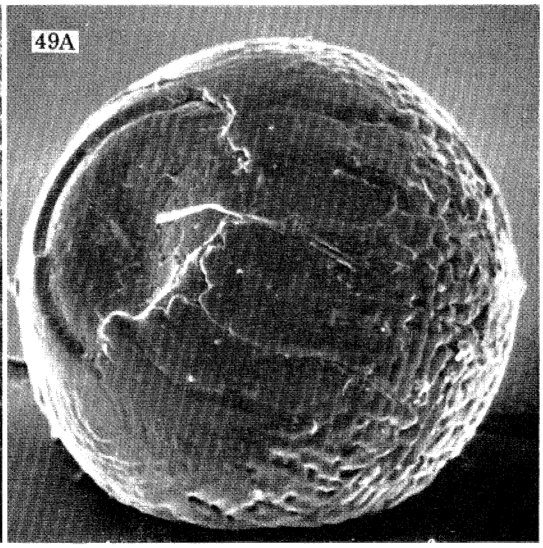
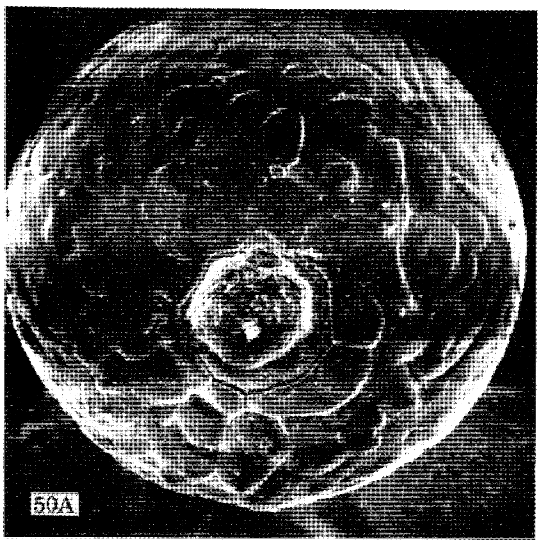


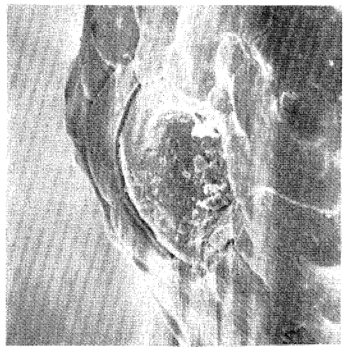
Plate 9. Composite spherules: surface details.

	36A	37A	43P	45P	39A	44P
Diam./μm	55	55	50	150	60	60

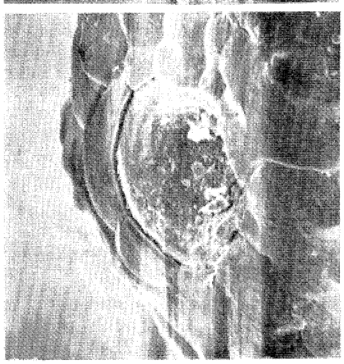




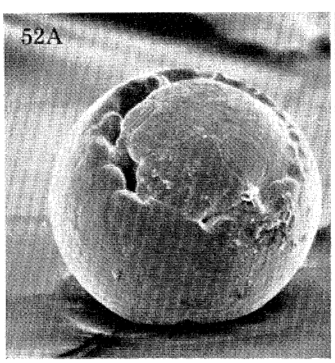




(*a*)



(*b*)



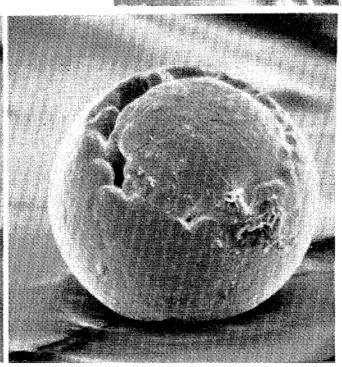


PLATE 10. Iron spherules, metallic globular form: surface details.

	48A	49A	50A	52A
Diam./μm	90	70	100	70

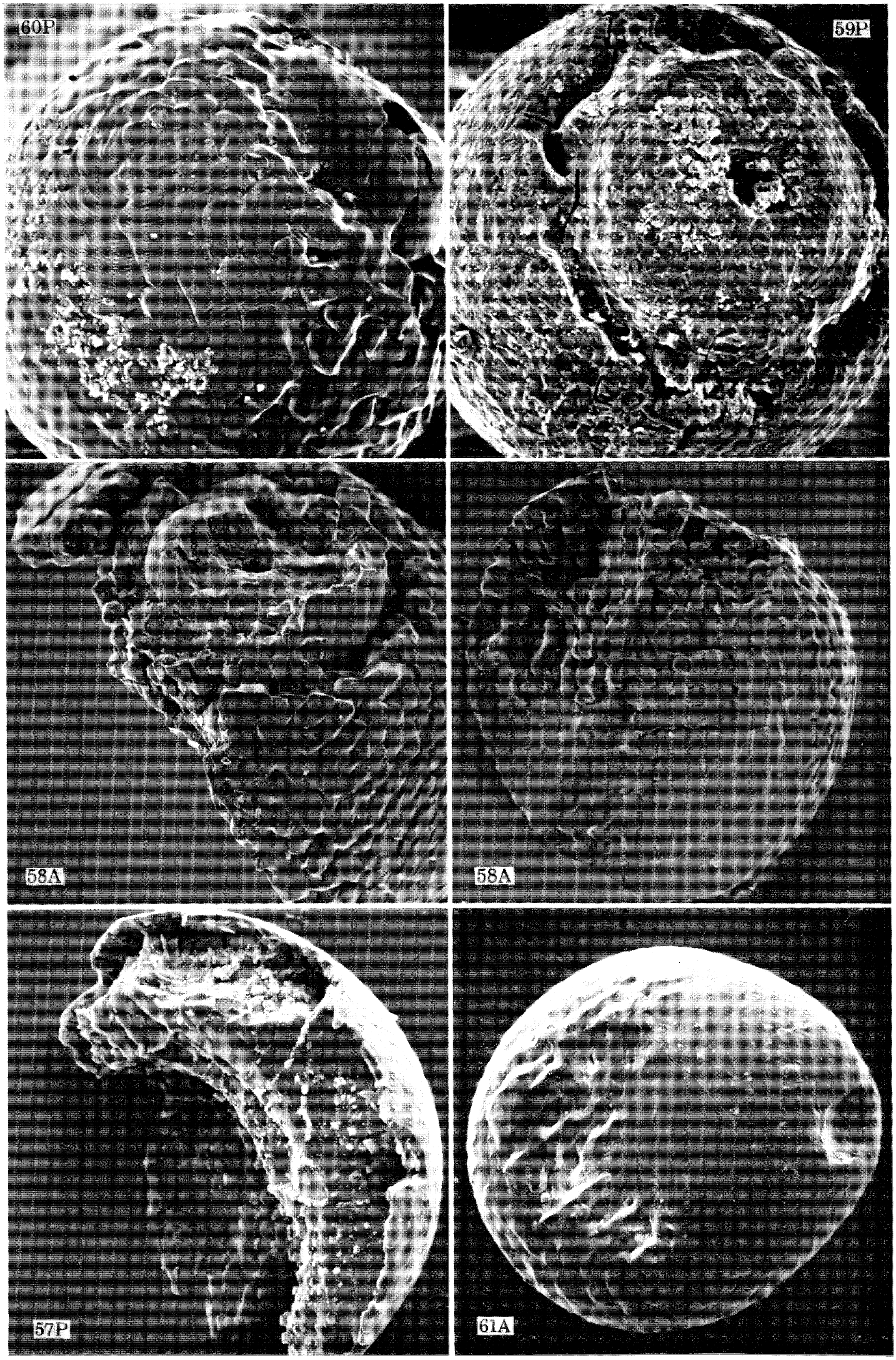


PLATE 11. Iron spherules, ballooned forms and other globular forms.

	60P	59P	58A	57P	61A
Diam./μm	60	60	110	50	90

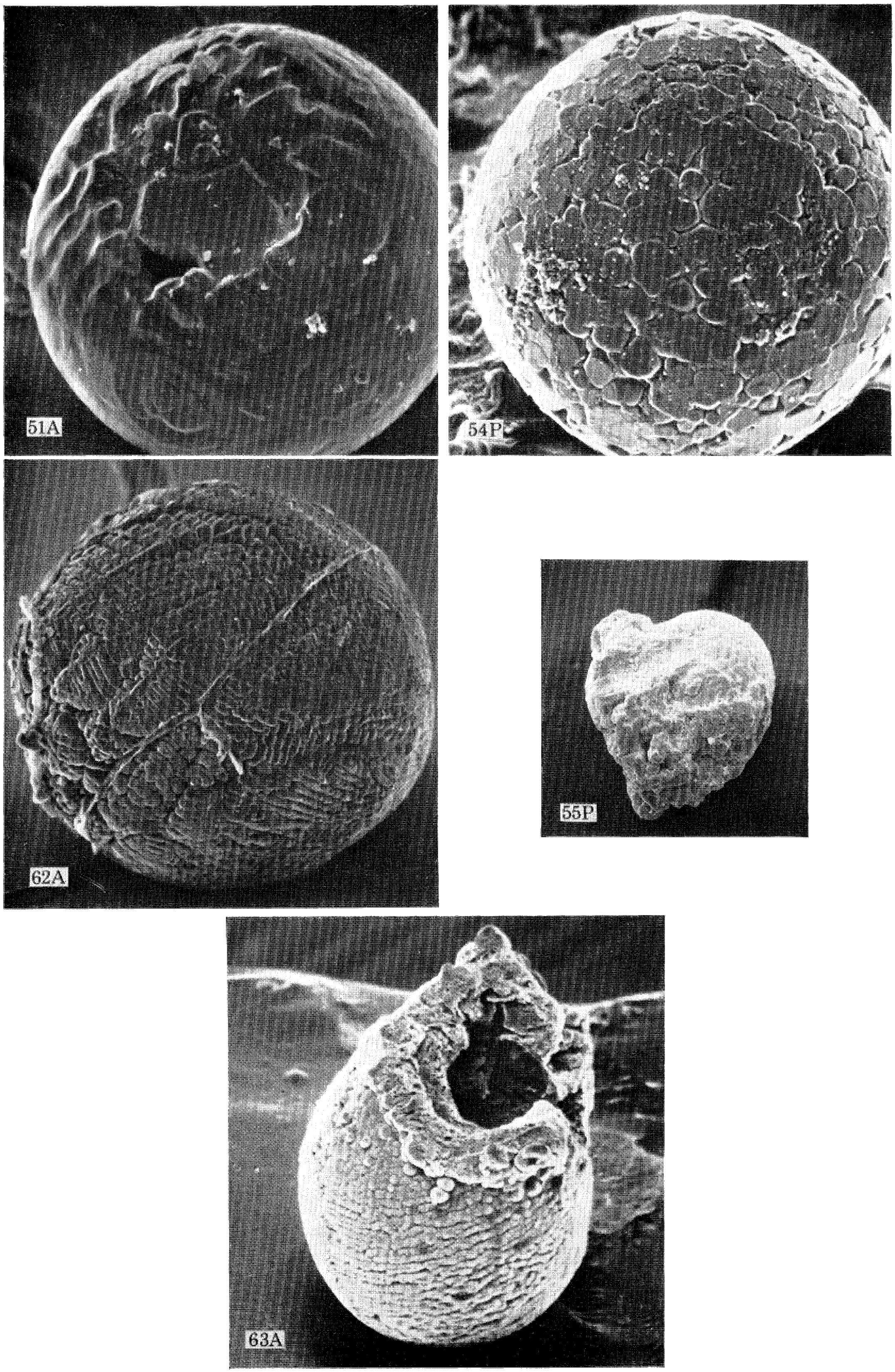


PLATE 12. Iron spherules, globule present but not visible; also the rusted forms or 'red-heads'.

	51 A	54 P	62 A	55 P	63 A
Diam./μm	50	50	80	50	60

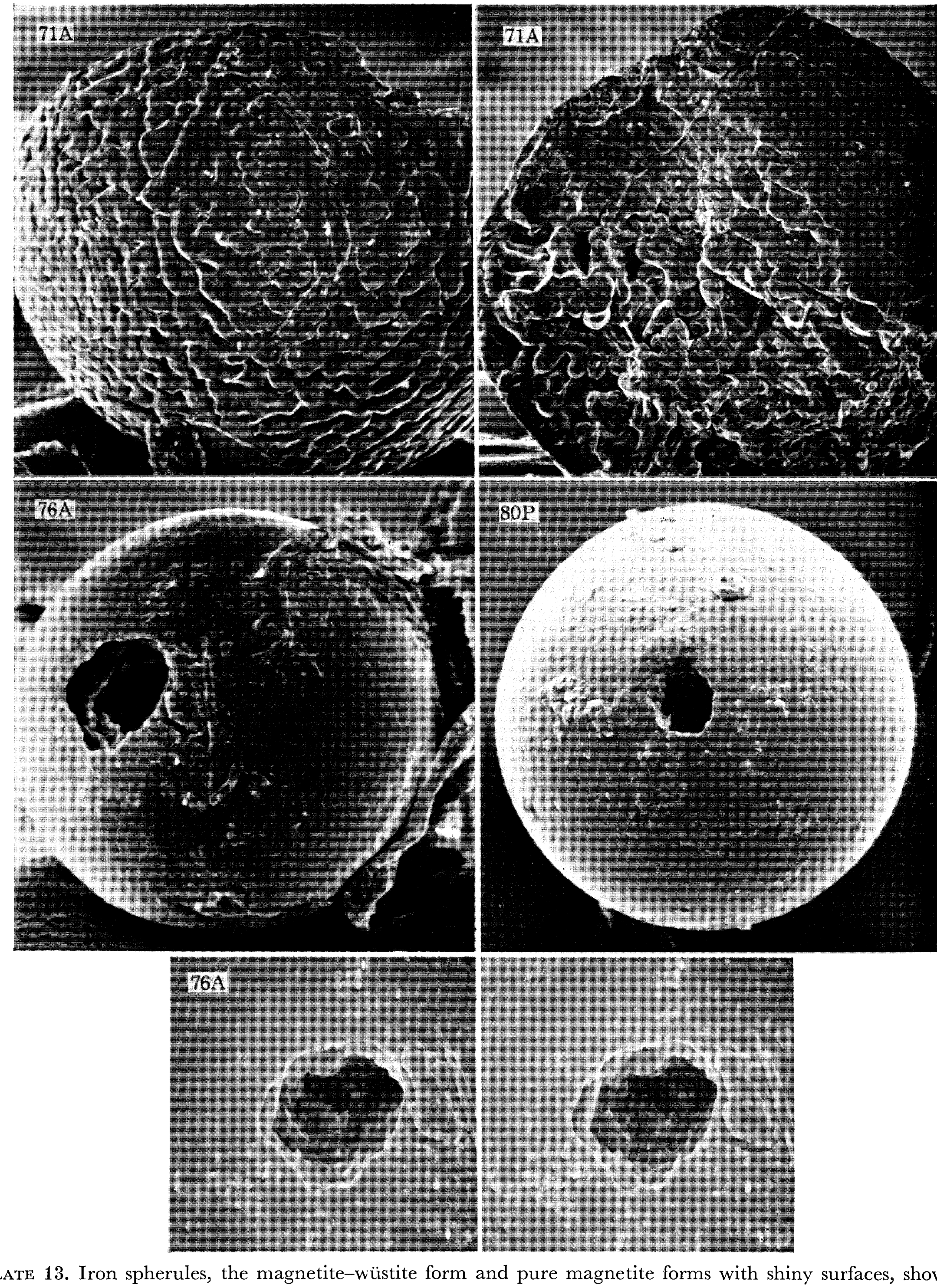


PLATE 13. Iron spherules, the magnetite–wüstite form and pure magnetite forms with shiny surfaces, showing holes.

	71A	76A	80P
Diam./µm	120	50	70

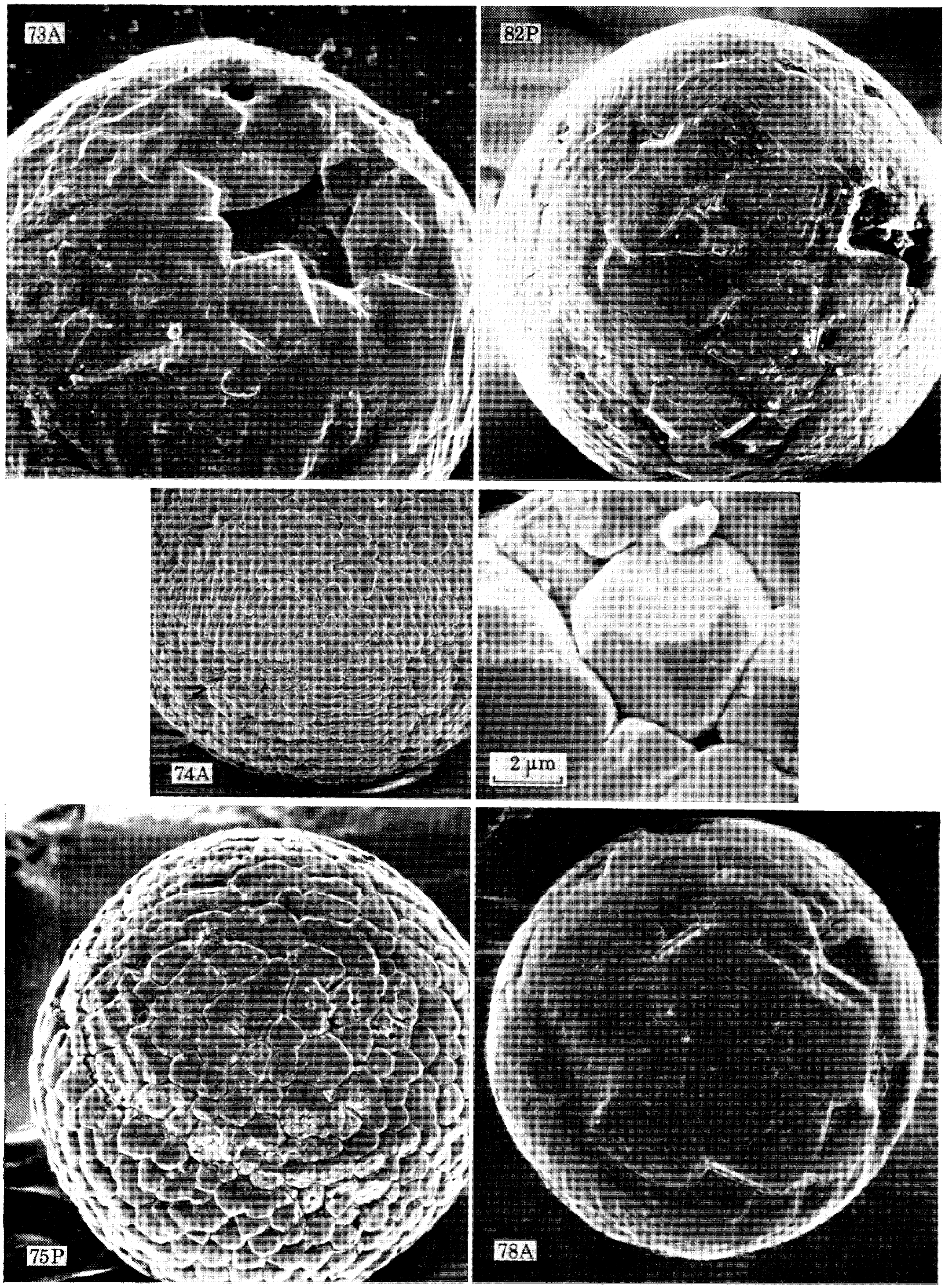


PLATE 14. Iron spherules, the magnetite–wüstite and pure magnetite forms showing large crystals.

	73A	82P	74A	75P	78A
Diam./μm	50	200	140	60	80

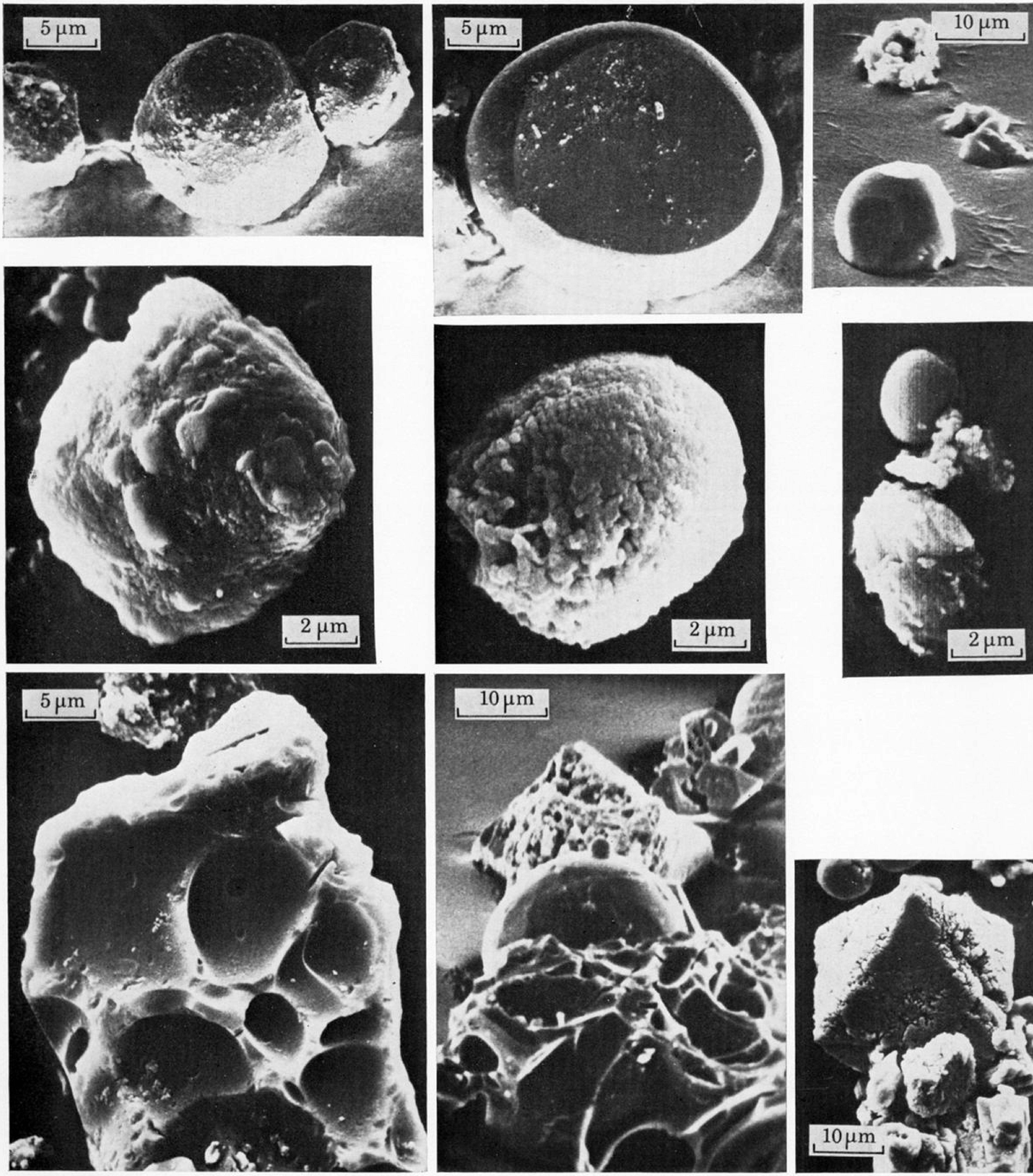


PLATE 1. Rounded objects of doubtful origin in the fine magnetic fraction from the Pacific sample. The faceted-objects seem to be rounded magnetite crystals that have grown on the sea-bed. The vesicular glass could be volcanic, but it does resemble fusion crust of stony meteorite. A few small cosmic spherules are seen in the lower photographs.

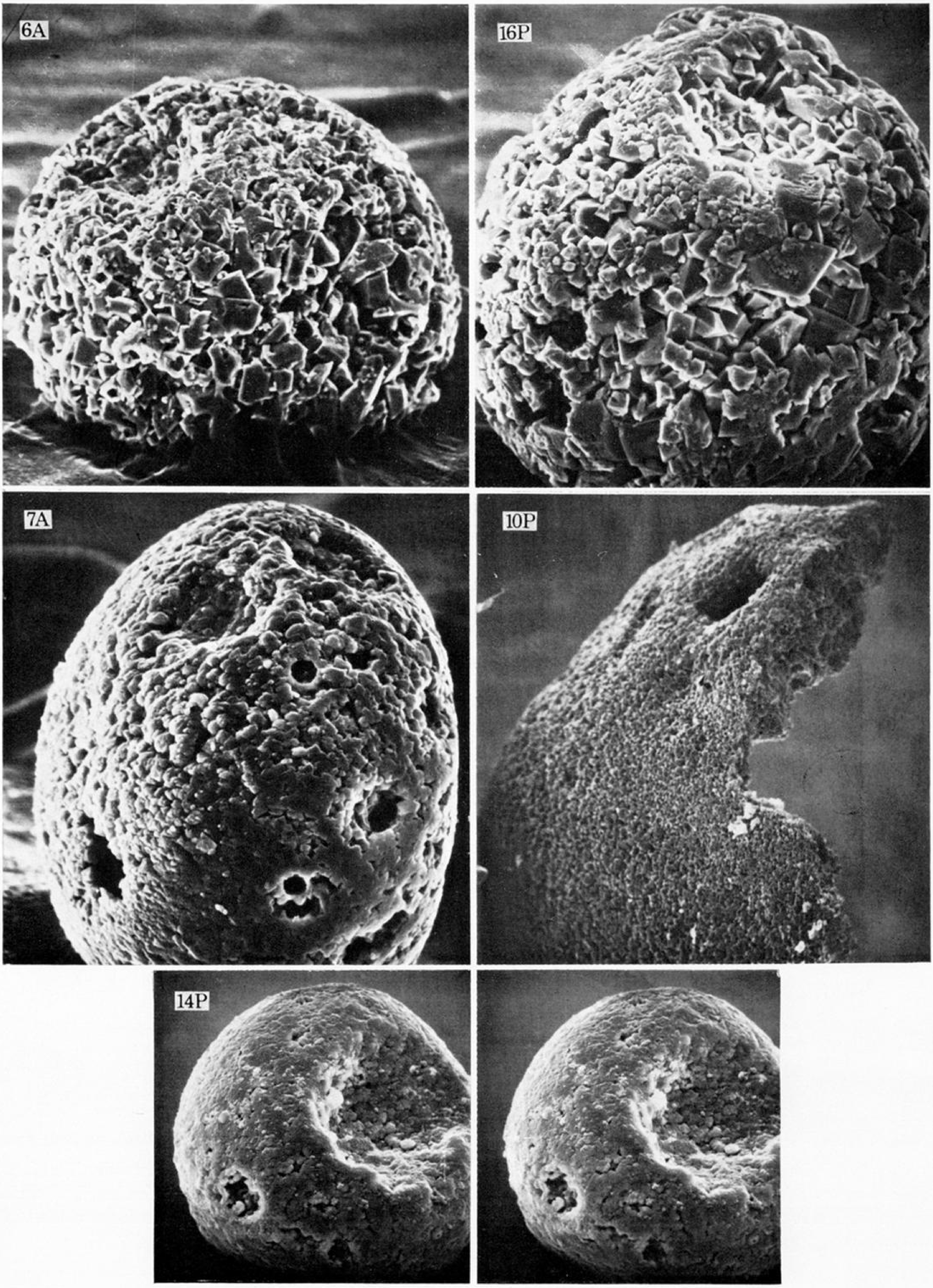


PLATE 2. Stony spherules, granular–vuggy form: surface details.

	6A	16P	7A	10P	14P
Diam./μm	150	120	70	150	50

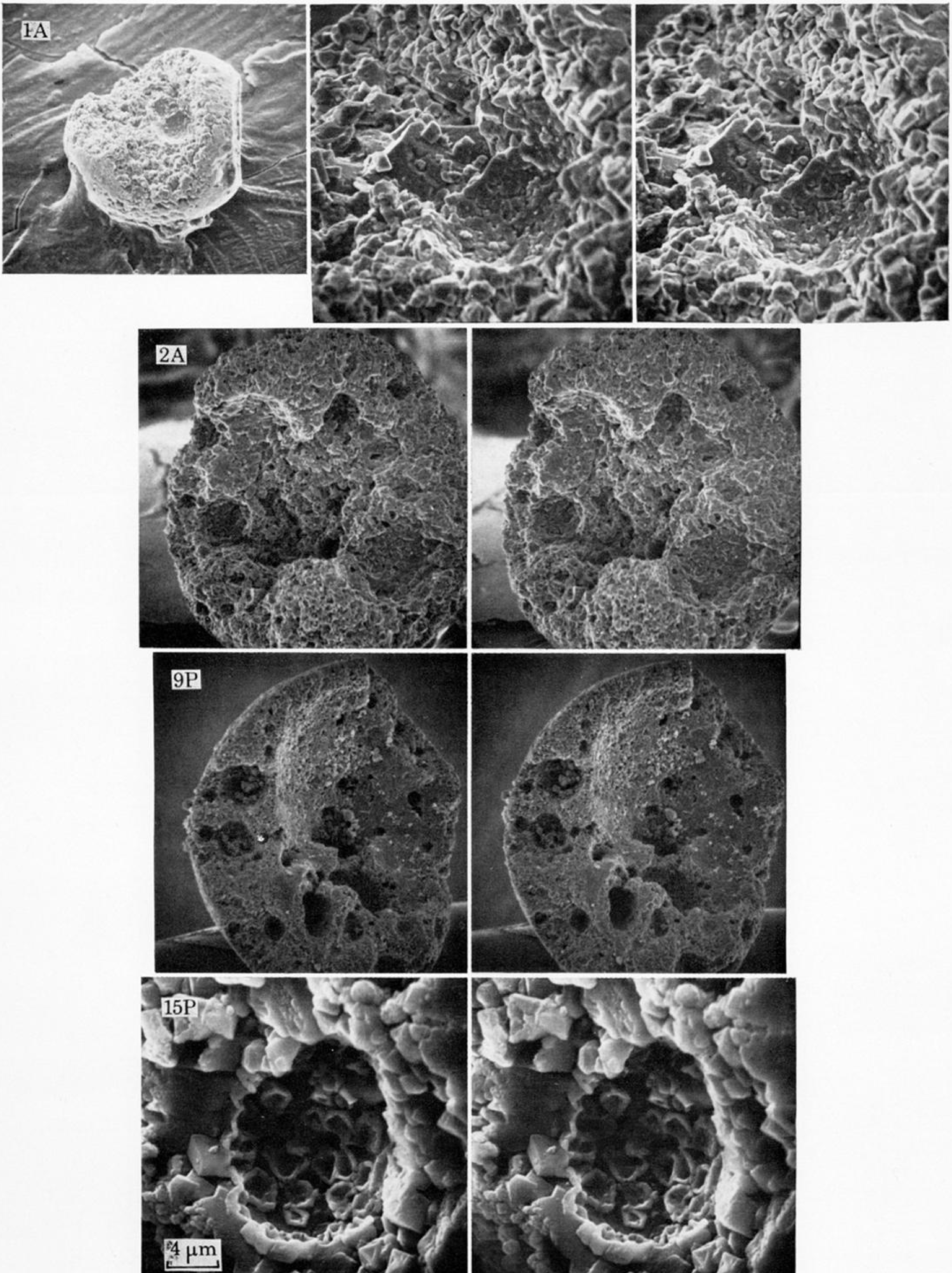


PLATE 3. Stony spherules, granular–vuggy form: interior details.

	1A	2A	9P
Diam./μm	110	130	130

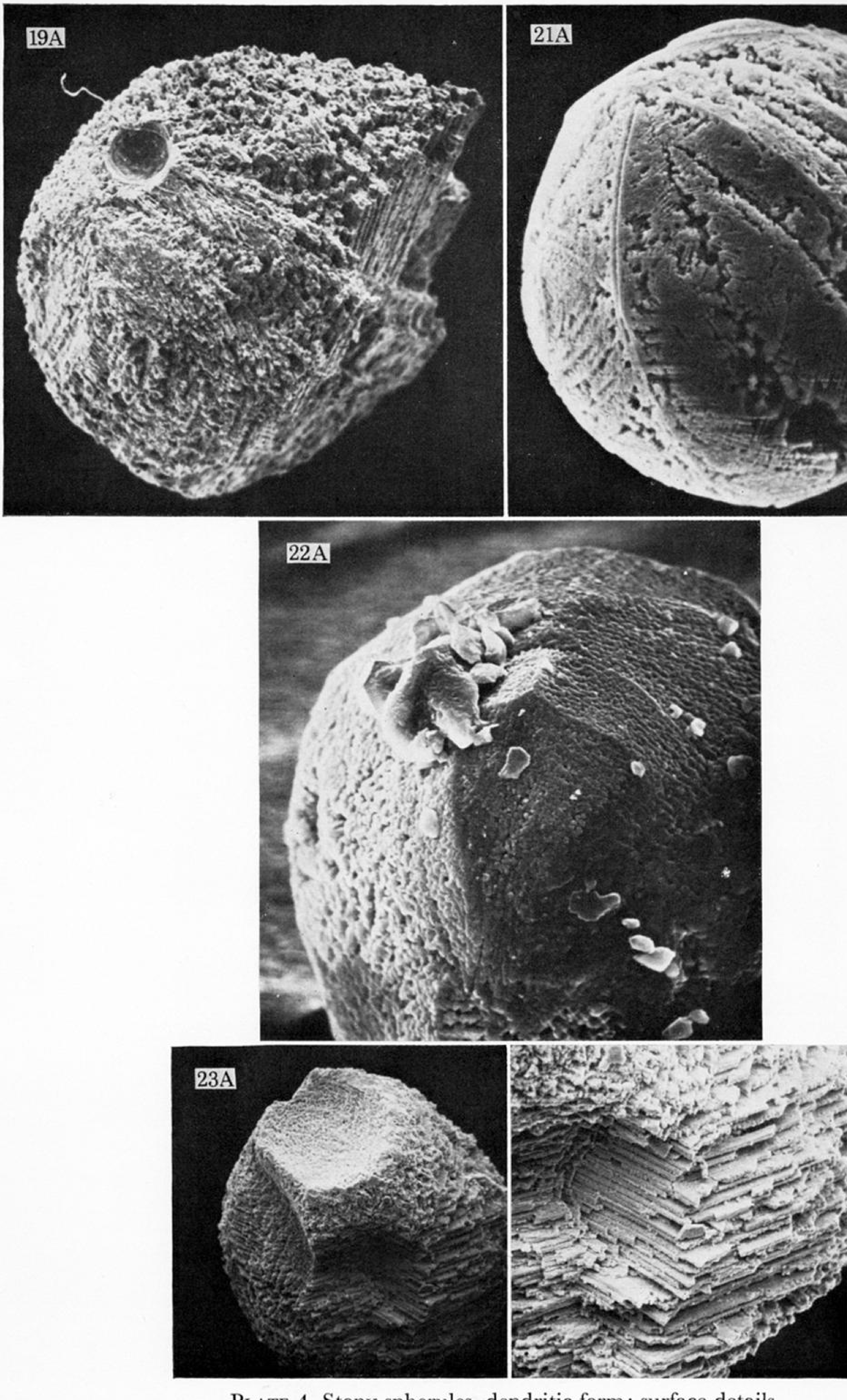


PLATE 4. Stony spherules, dendritic form: surface details.

	19 A	21 A	22 A	23 A
Diam./μm	200	70	60	170

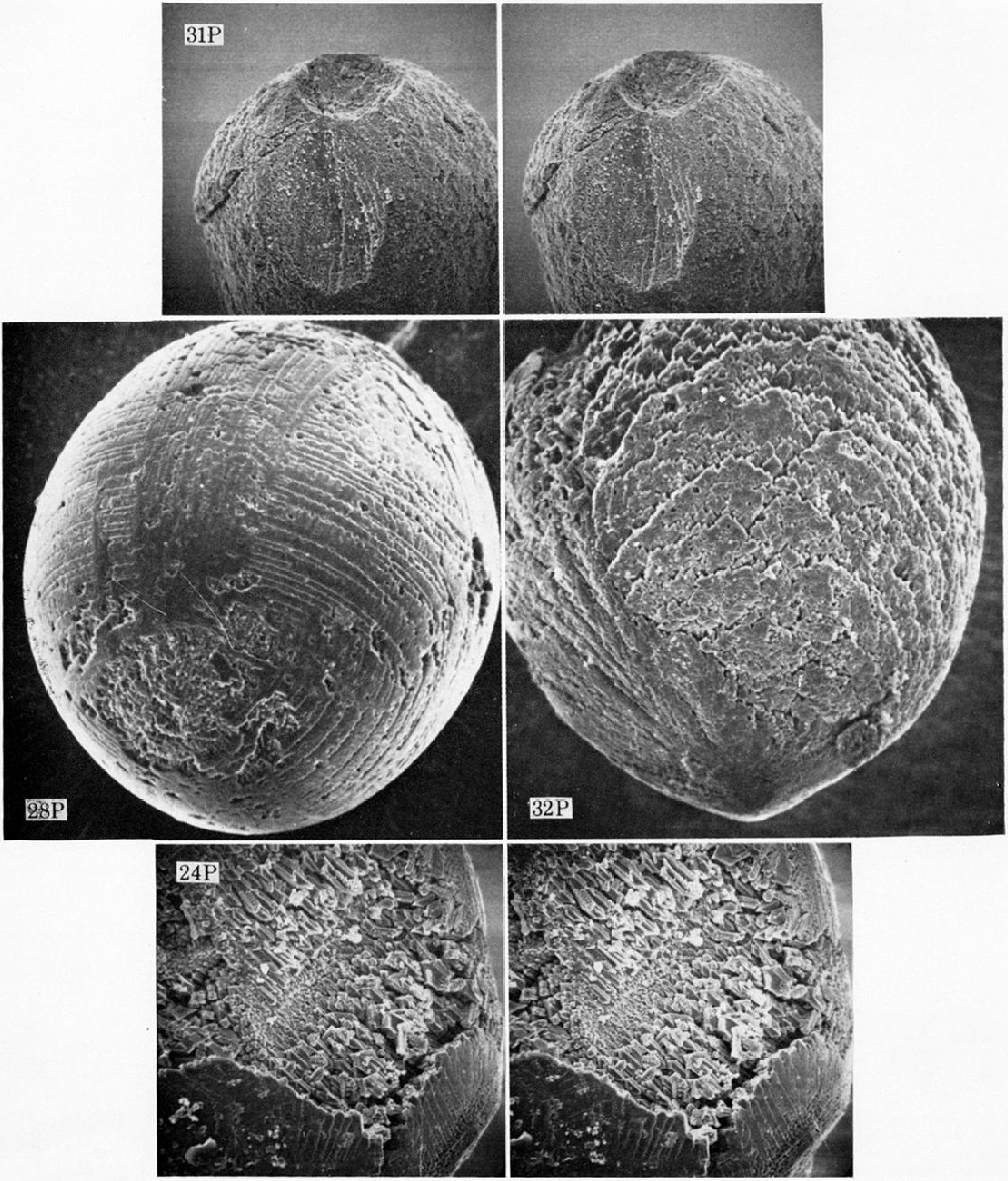


PLATE 5. Stony spherules, dendritic form: surface details.

	31 P	28 P	32 P	24 P
Diam./μm	100	110	100	120

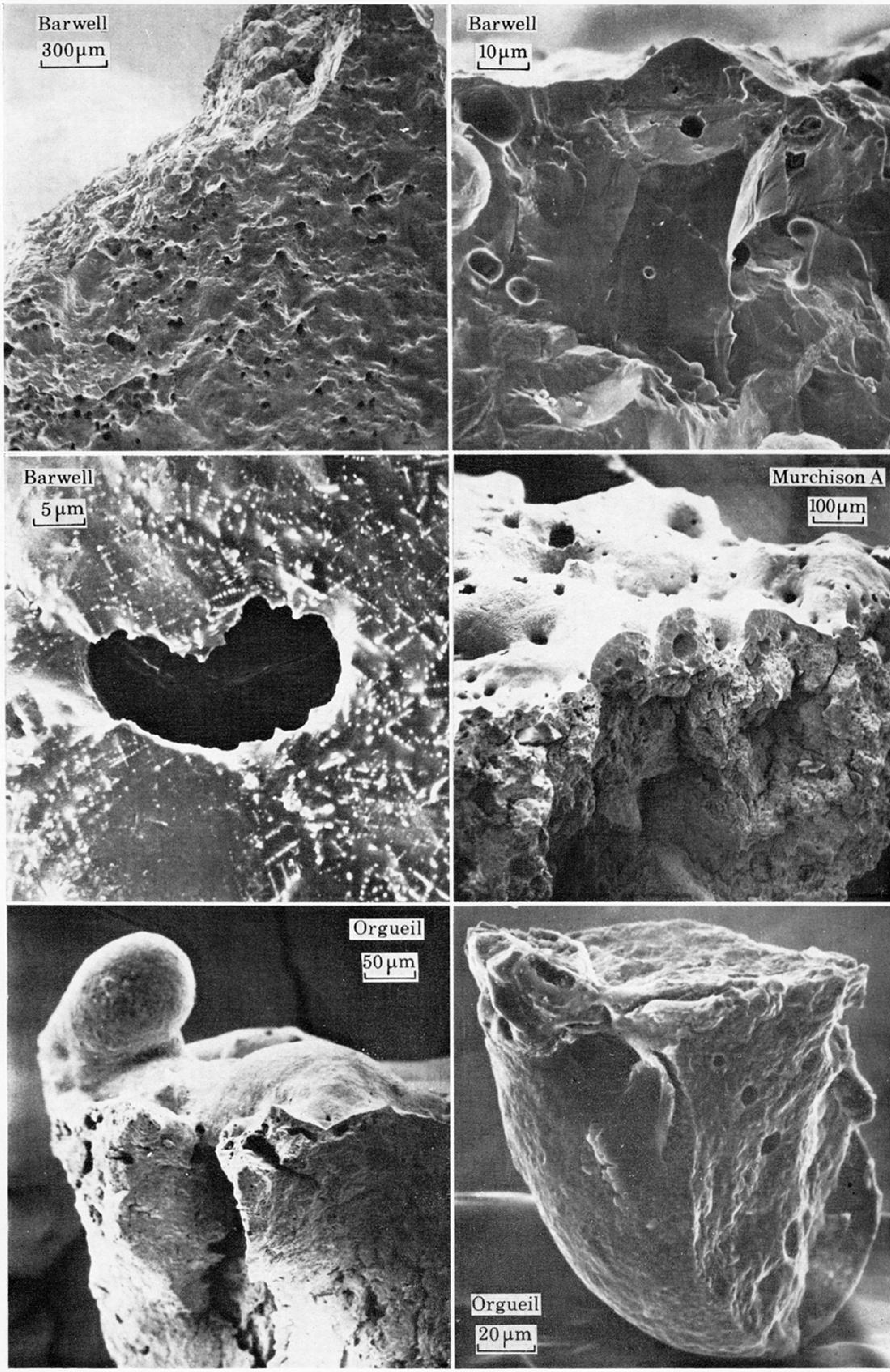


Plate 6. Fusion crust of meteorites: surface details and fracture sections.

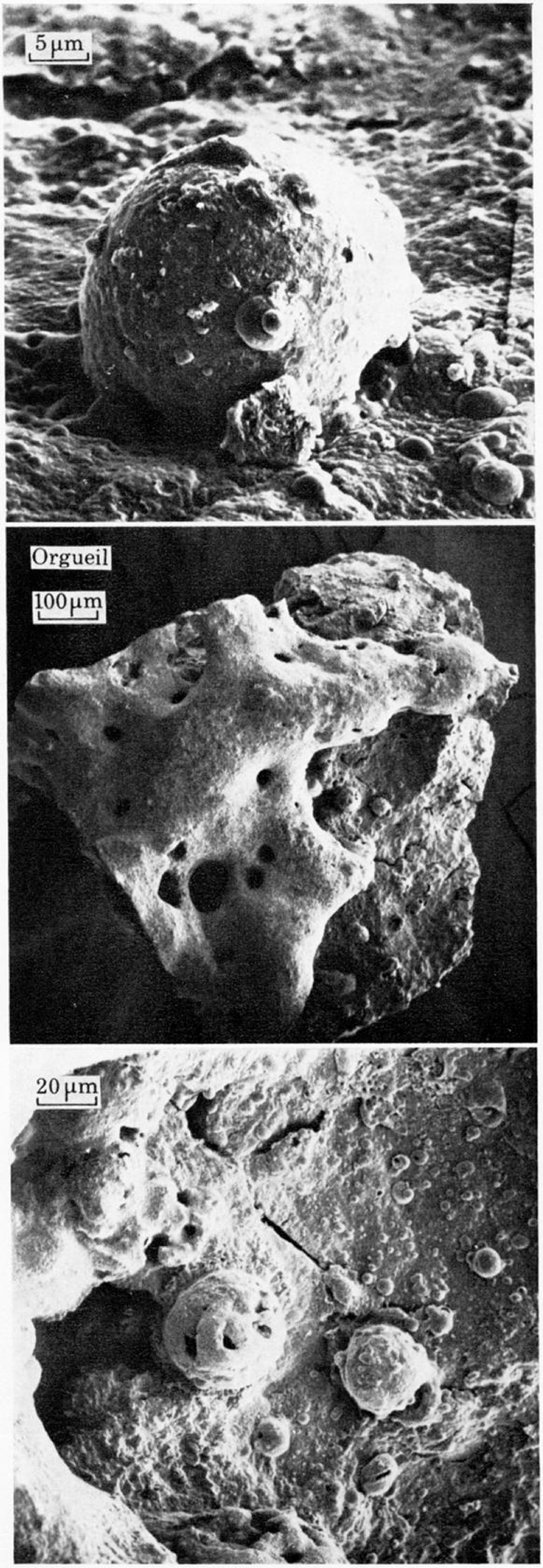


PLATE 7. Fusion crust of Orgueil, showing ball-like forms on or near the surface. See the text for details.

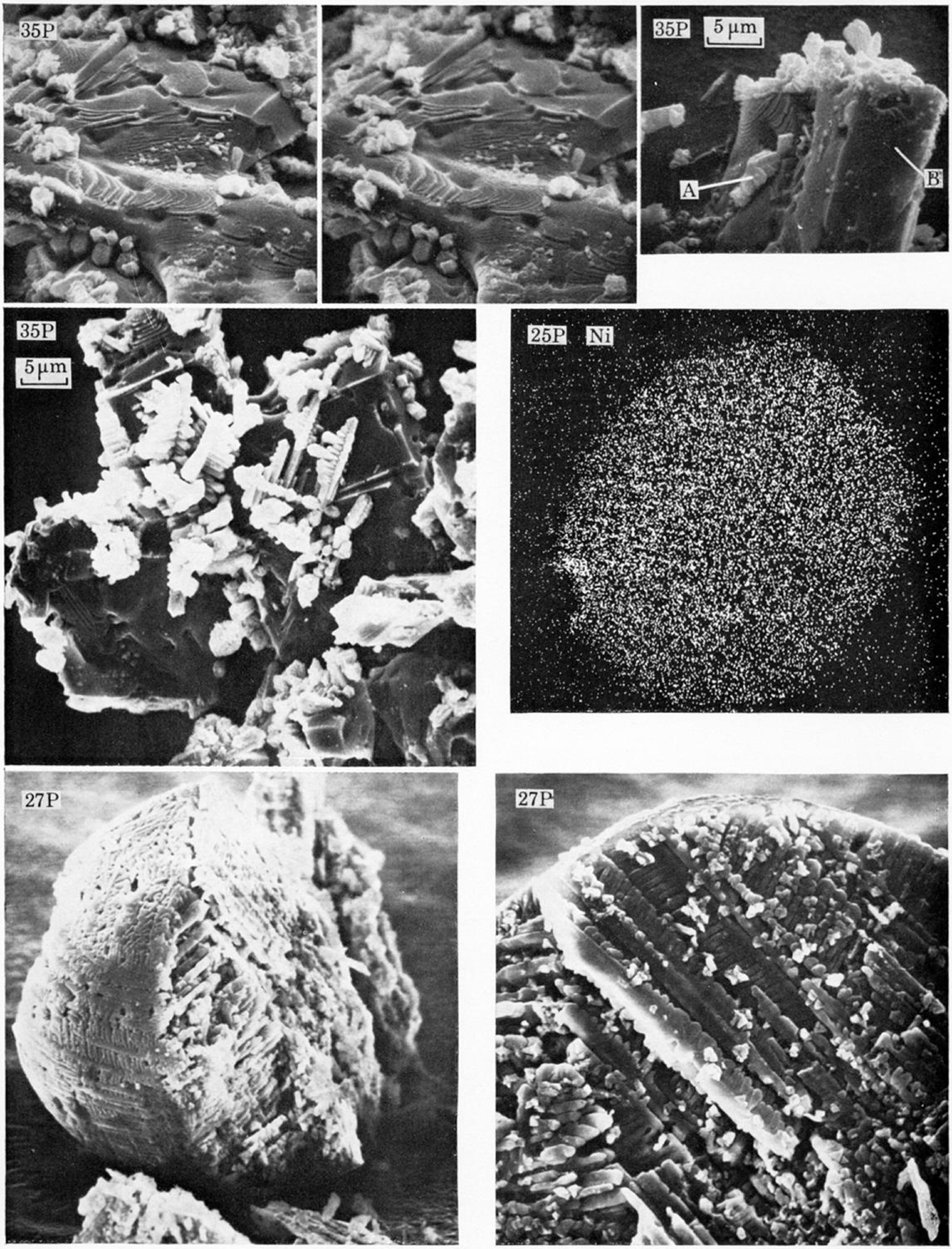


Plate 8. Stony spherules, dendritic form: interior details.

	25P	27P
Diam./μm	140	80

The Ni distribution over the polished section of 25P is uniform at 0.84 %, except around the cupule where it is 2.4 %.

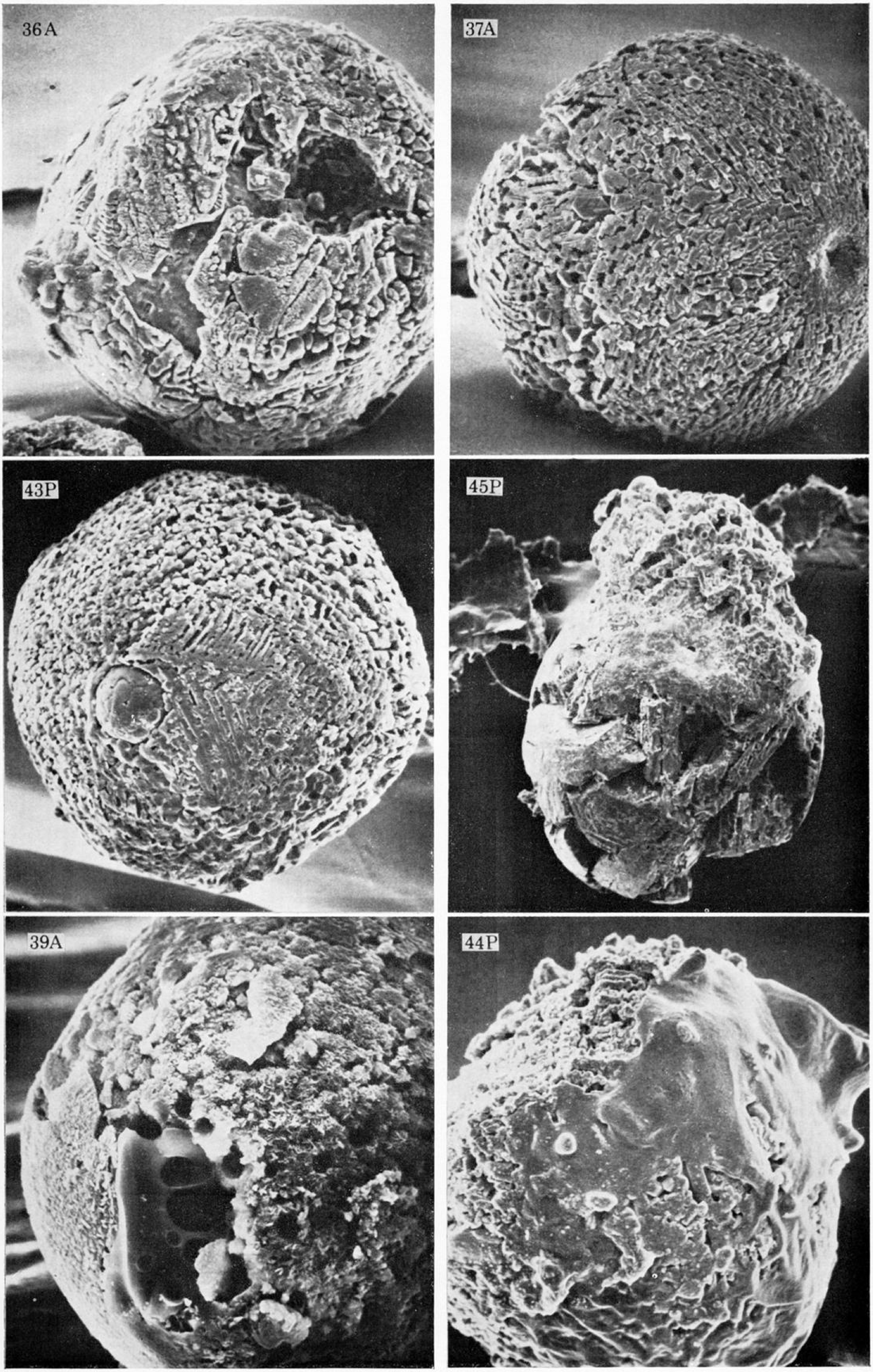


Plate 9. Composite spherules: surface details.

	36A	37A	43P	45P	39A	44P
Diam./μm	55	55	50	150	60	60

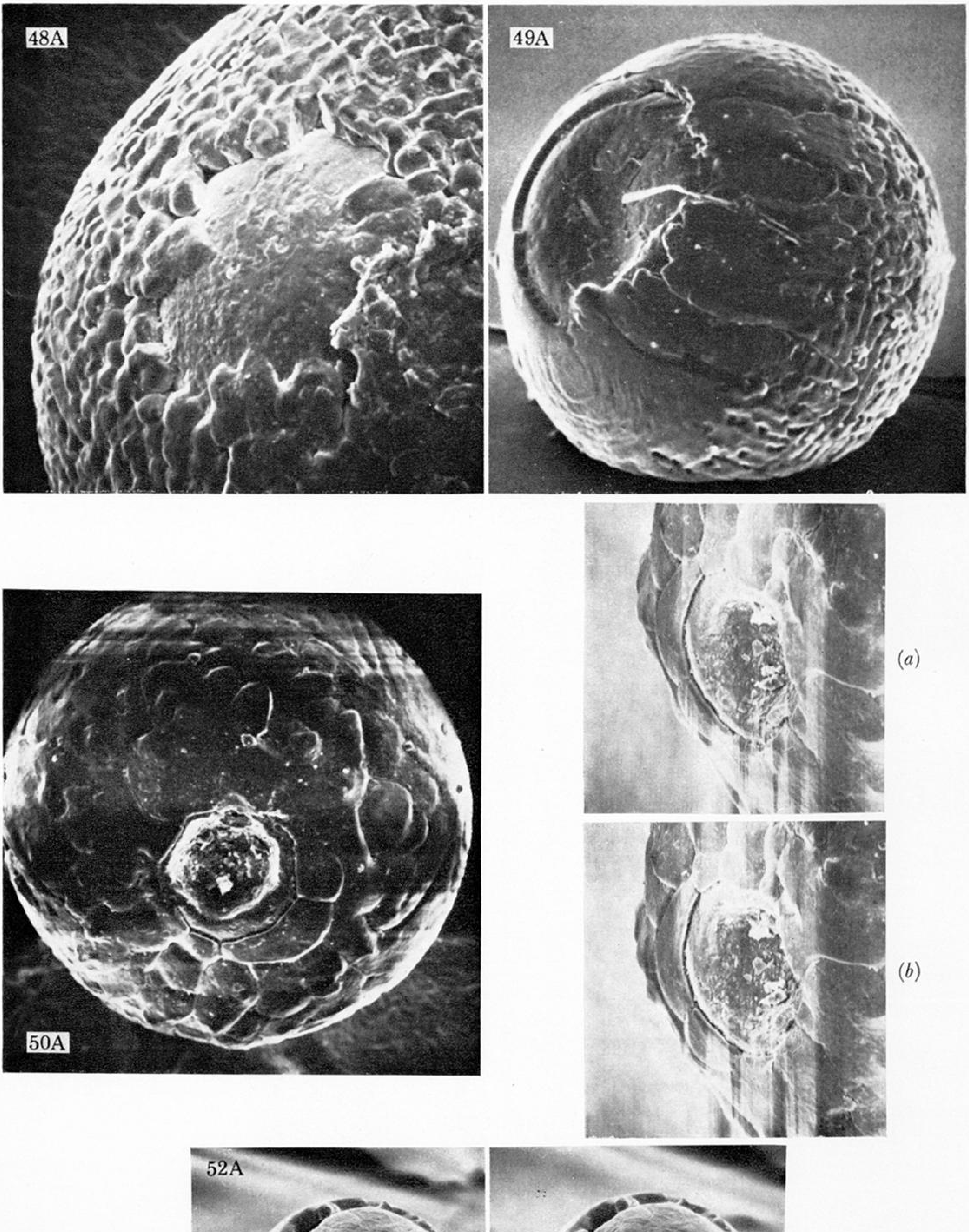


Plate 10. Iron spherules, metallic globular form: surface details.

	48 A	49 A	50 A	52 A
Diam./μm	90	70	100	70

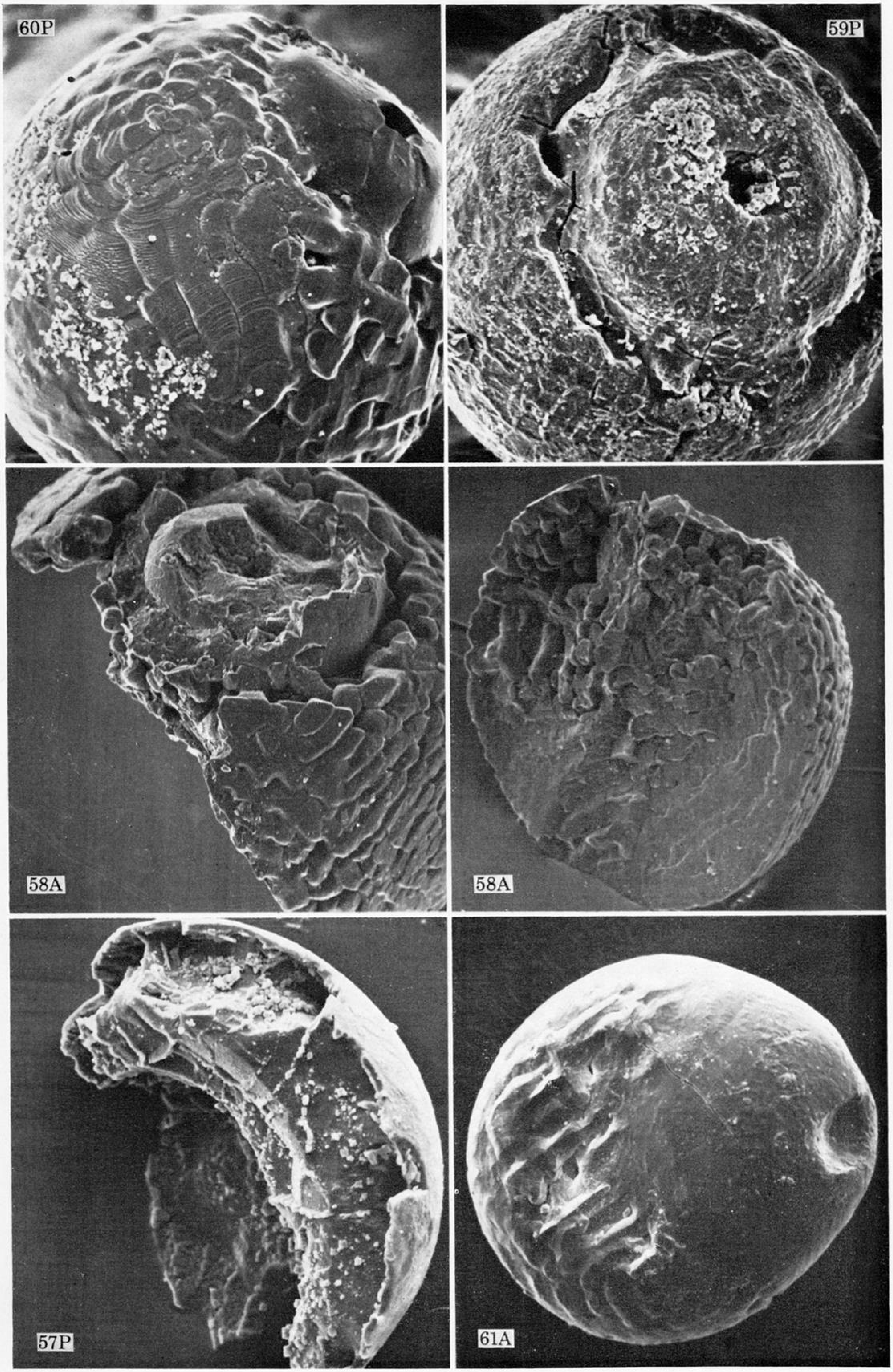


PLATE 11. Iron spherules, ballooned forms and other globular forms.

	60 P	59 P	58 A	57 P	61 A
Diam./μm	60	60	110	50	90

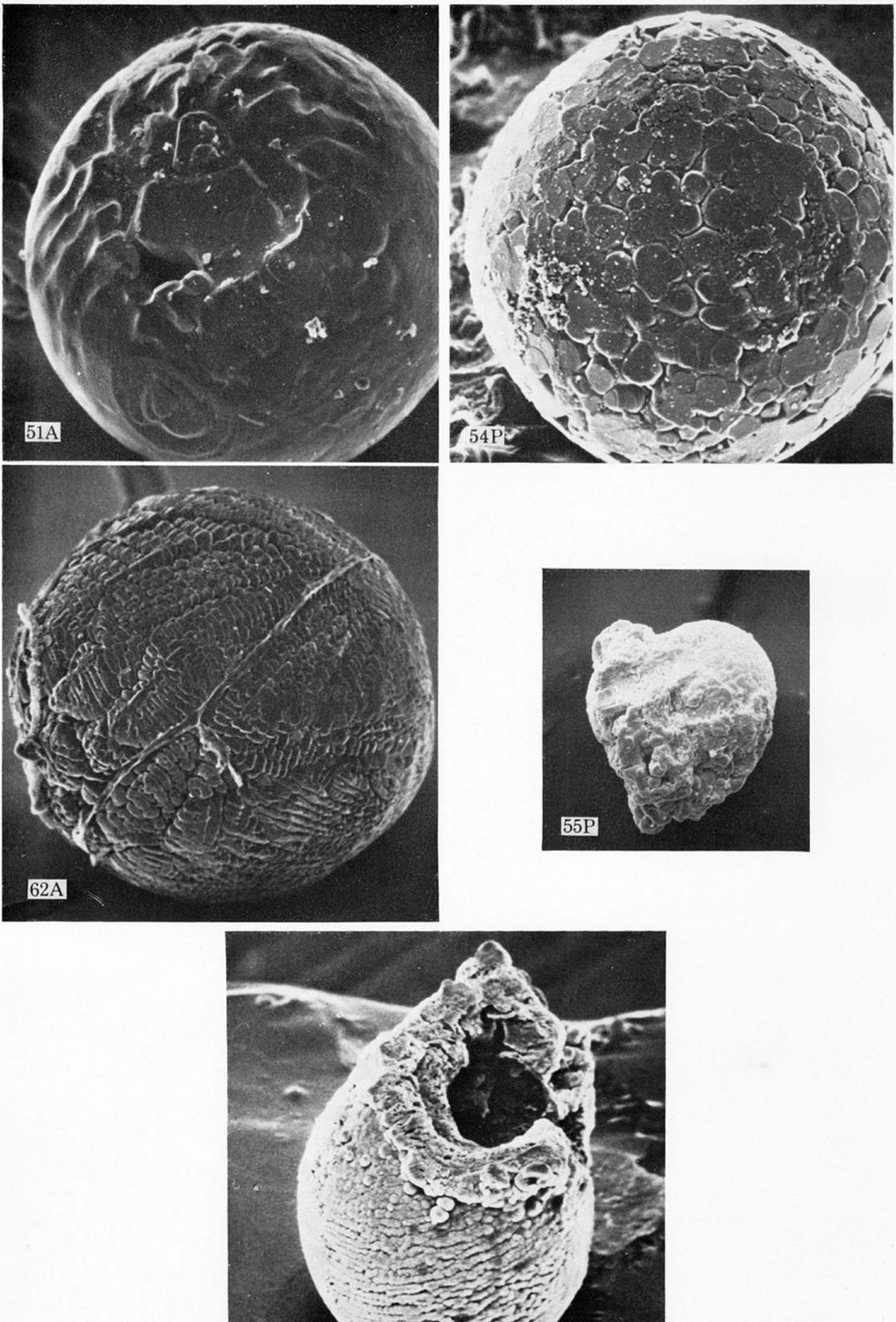


Plate 12. Iron spherules, globule present but not visible; also the rusted forms or 'red-heads'.

	51A	54P	62A	55P	63A
Diam./μm	50	50	80	50	60

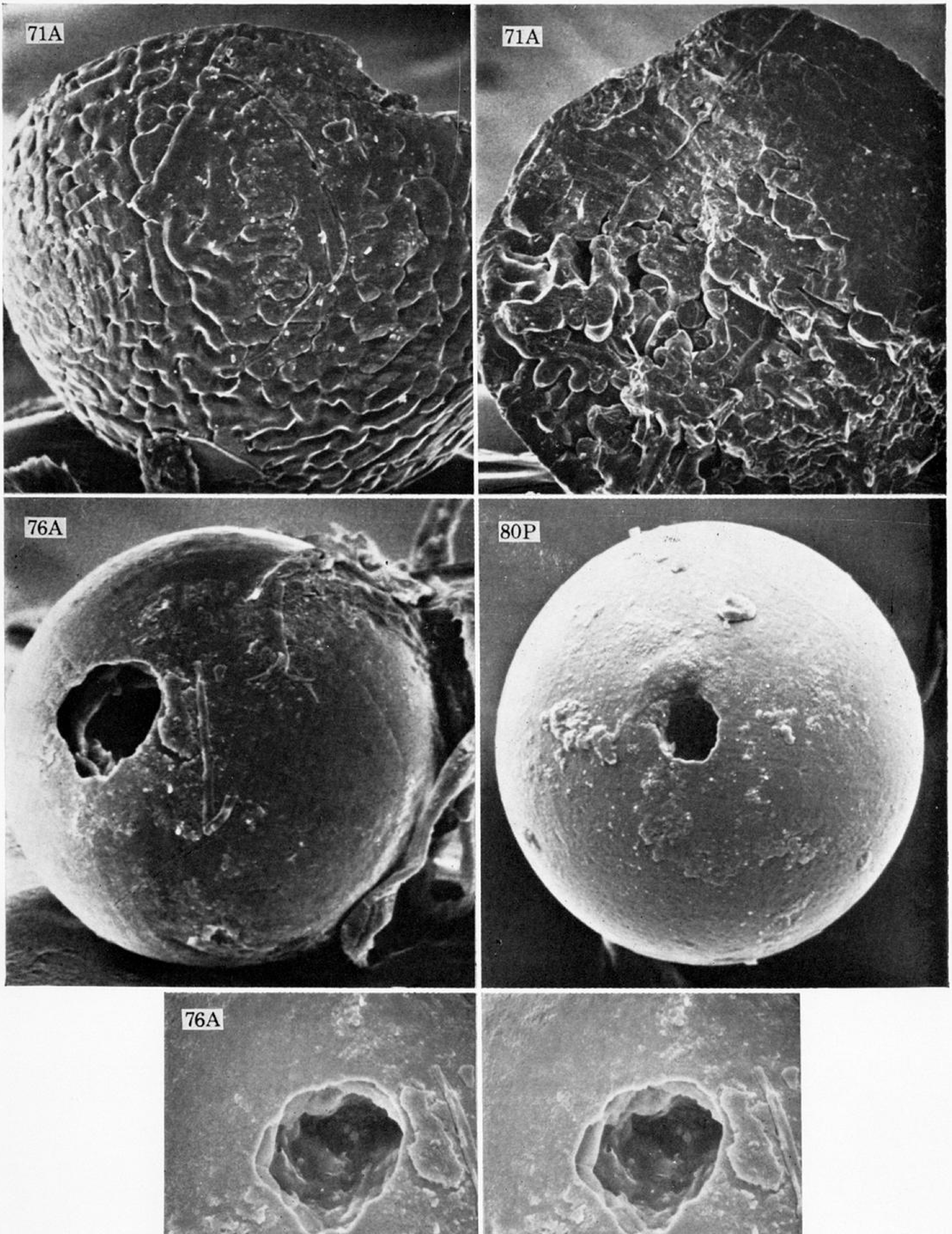


Plate 13. Iron spherules, the magnetite–wüstite form and pure magnetite forms with shiny surfaces, showing holes.

	71 A	76 A	80 P
Diam./μm	120	50	70

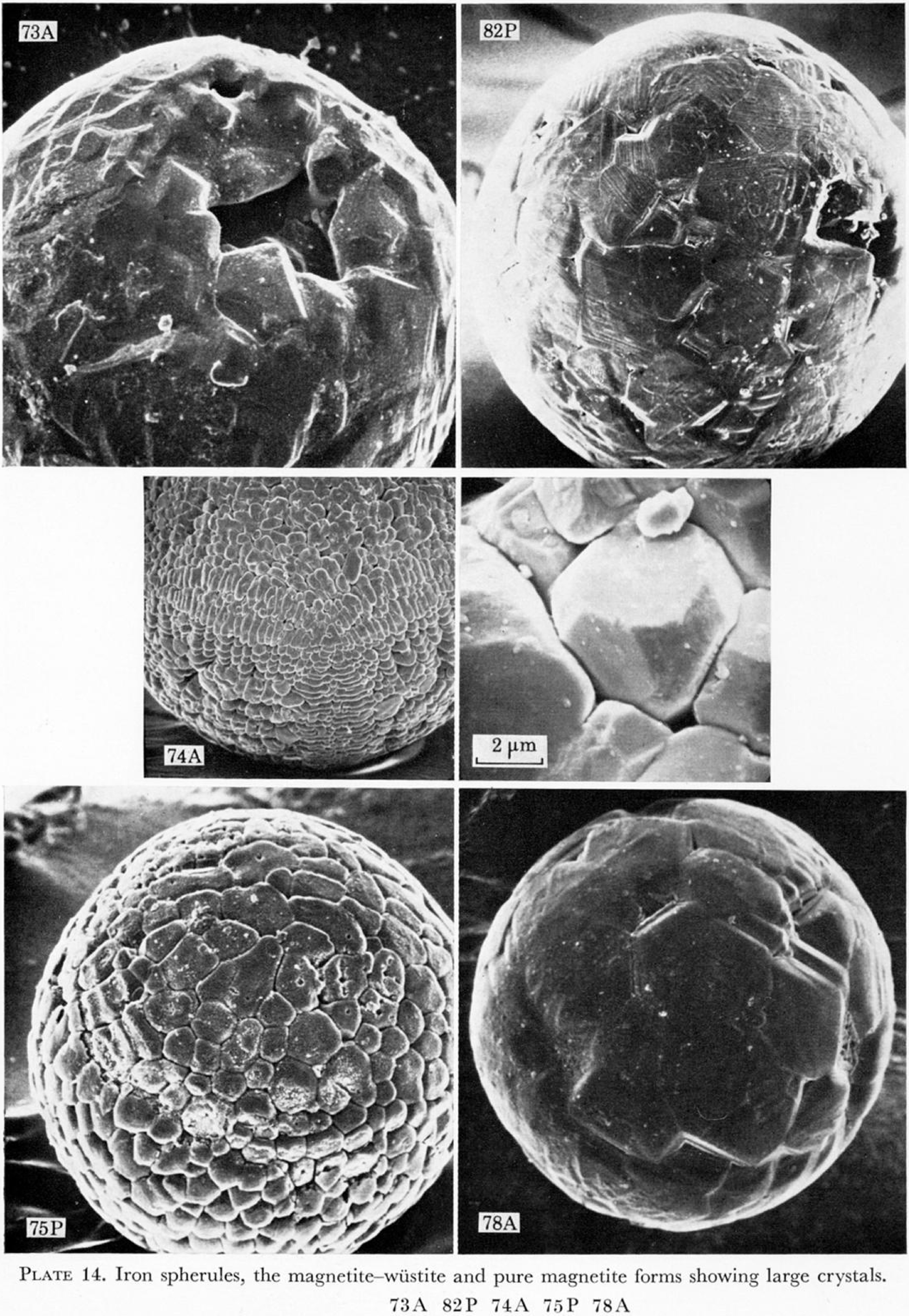


PLATE 14. Iron spherules, the magnetite–wüstite and pure magnetite forms showing large crystals.

	73A	82P	74A	75P	78A
Diam./μm	50	200	140	60	80