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MAN-MADE Pt–PtAs$_2$ SPHERULES AFTER SPERRYLITE FROM ALLUVIAL DEPOSITS IN FINNISH LAPLAND

YRJÖ VUORELAINEN
Matinkatu 28, SF-02230 Espoo, Finland

RAGNAR TÖRNROOS
Geological Survey of Finland, Stenkarlsvägen 1, SF-02150 Esbo, Finland

Abstract

Besides gold, platinum-group-element nuggets and microspherules have been encountered in heavy-mineral concentrates panned from alluvium in the three rivers Miessijoki, Puskuoja and Sotajoki, and in the Härkäselkä area in northern Finland. We have found abundant composite Pt–PtAs$_2$ spherules or roundish grains. Compositionally, these form a series from pure sperrylite PtAs$_2$ to intergrown As-bearing Pt and PtAs$_2$. Morphologically, with the decrease in As, sperrylite changes from idiomorphic crystals to perfect spherules showing a eutectoid intergrowth of Pt and PtAs$_2$. These spherules and roundish grains form during the drying of the last (heaviest) fraction in the miners' pans.

Keywords: Pt–PtAs$_2$ alloy spherules, "spherulization", sperrylite, placer, Lapland, Finland.

Sommaire

On trouve, en plus de l'or, des pépites et des microsphérules enrichis en éléments du groupe du platine dans les concentrés de minéraux lourds alluvionnaires des trois rivières Miessijoki, Puskuoja et Sotajoki et dans la région de Härkäselkä, dans le Nord de la Finlande (Laponie). Il y a une abondance de sphérules et de grains arrondis. Ils forment une série allant de sperrylite pure (PtAs$_2$) à une intercroissance de platine arsenifère et de sperrylite. A mesure que la teneur en As diminue, la sperrylite change de sa forme idiomorphe originelle à celle d'un sphérule parfait à texture eutectoïde. Ces sphérules et grains arrondis se seraient formés au cours de la dessiccation de la dernière fraction (la plus dense) dans la cuvette des prospecteurs.

(Traduit par la Rédaction)

Mots-clés: sphérules, alliage Pt–PtAs$_2$, "sphérulisation", sperrylite, placer, Laponie, Finlande.

Introduction

Placer gold has been recovered since the last century from river beds in the granulite complex of Finnish Lapland. Heavy-mineral concentrates supplied to us by several miners working deposits of placer gold along the Miessijoki, Puskuoja and Sotajoki rivers and in the Härkäselkä area (localities shown on the map in Fig. 1) represent several thousand tonnes of river gravel.

The granulite complex of northern Finnish Lapland forms an arc that extends north–south from the Norwegian border and intersects the Russian border in an east–west direction (Fig. 1). This arc is bordered in the southwest by Archean greenstones, quartzo feldspathic schists and gneisses.

About 140,000 individual platinum-group-element (*PGE*) grains were separated from the materials by one of us (Y.V.) Approximately 95% of them are sperrylite grains or crystals, whereas the remainder comprise many different platinum-group minerals and alloys. Together with some very dense microspherules, abundant Pt–PtAs$_2$ spherules and rounded Pt–PtAs$_2$ grains have also been encountered; these spherules and grains are the subject of

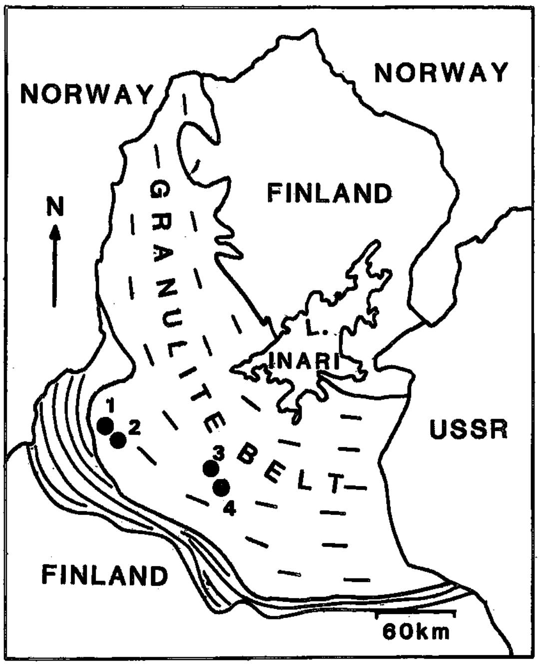

FIG. 1. Map of northern Finnish Lapland showing the alluvial deposits: 1 Miessijoki, 2 Puskuoja, 3 Sotajoki, 4 Härkäselkä area.

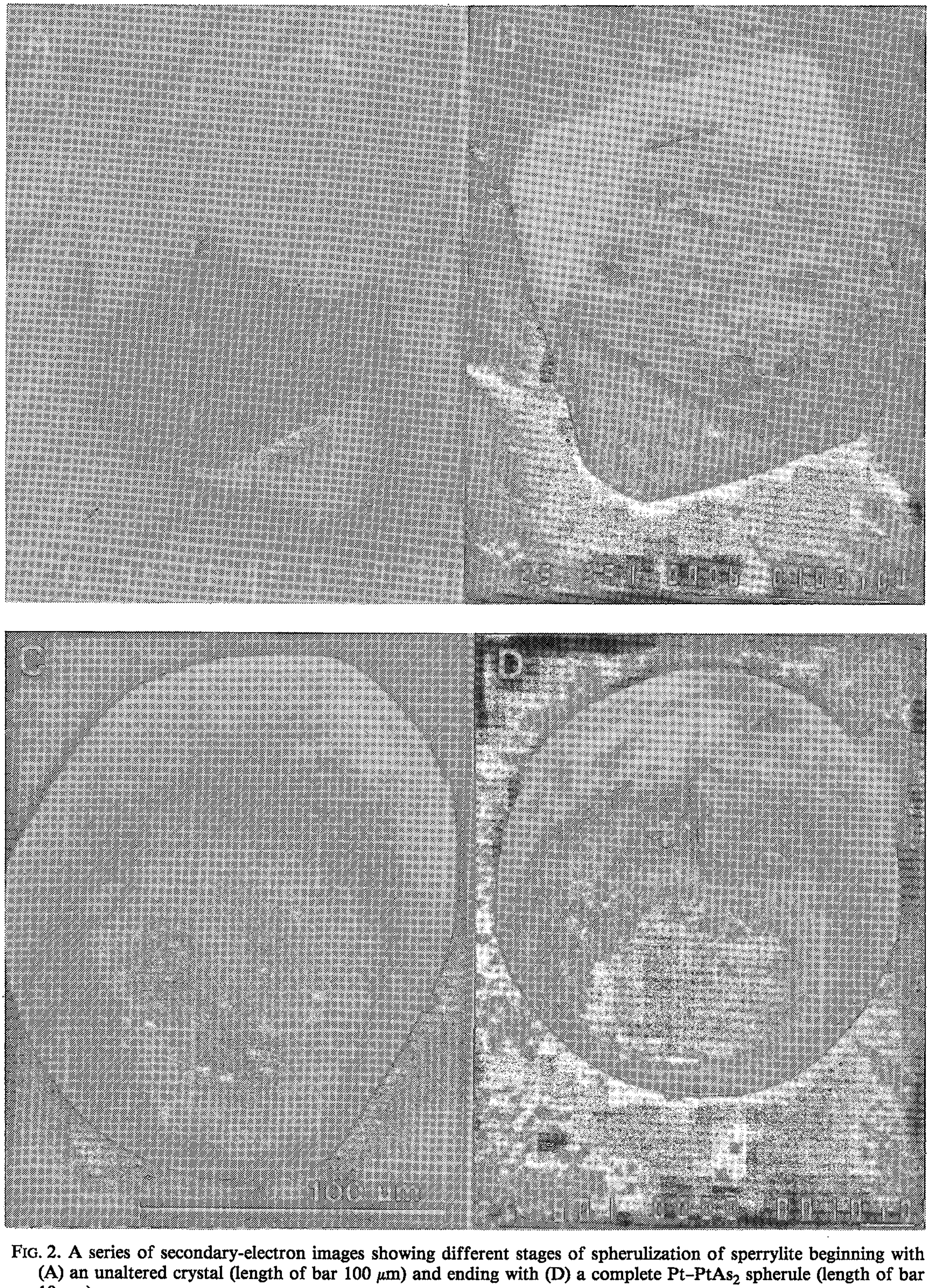

FIG. 2. A series of secondary-electron images showing different stages of spherulization of sperrylite beginning with (A) an unaltered crystal (length of bar 100 μm) and ending with (D) a complete Pt–$PtAs_2$ spherule (length of bar 10 μm).

the present paper. The concentrates also include numerous other artificial spherules (scrap products, welding sparks), which have to be "screened" out. Sperrylite crystals had earlier been described from these areas by Koivisto *et al.* (1980), but no mention was made of As-depleted grains.

Spherules, and especially *PGE* alloy spherules, have long interested scientists, and their origin has been a subject of debate (*e.g.*, Bird & Bassett 1980, Blanchard *et al.* 1980, Brownlee *et al.* 1984, Feather 1976). This paper contributes to the discussion by showing that the Pt–$PtAs_2$ spherules and rounded grains found in Finnish Lapland are man-made in origin.

Materials and Microprobe Investigations

The artificial spherules (welding sparks, scrap products) are ~100 μm to 1 mm in diameter, whereas the *PGE* alloy spherules are 85 to 200 μm, and the perfectly spherical Pt–$PtAs_2$ spherules are slightly smaller (50 - 100 μm). The rounded Pt–$PtAs_2$ grains, on the other hand, are somewhat larger (150 - 300 μm).

Chemical analyses were conducted and scanning-electron photographs (SEM) were taken using a JEOL JCXA-733 microprobe equipped with a Princeton Gamma-Tech energy-dispersion spectrometer. The following standards were used: synthetic compounds $Pd_{11}Sb_2As_2$, RhSb, $Pt_{1.0}Fe_{0.64}Cu_{0.36}$ for Pd, Rh, As, Sb, Pt, Fe and Cu, the natural minerals loellingite for As, and laurite for Ru and S. The X-ray lines measured were $K\alpha$ for Fe, Cu and S, and $L\alpha$ for the others. The accelerating voltage was set at 30 kV, and the probe current at 1 nA.

Spherulization of Sperrylite

The roughly 133,000 sperrylite grains include several more-or-less rounded grains with a marked variation in proportion of Pt and As. Idiomorphic crystals have the sperrylite composition $PtAs_2$ or are near to it, but crystals that appear porous on the surface show a deficiency in As content. These crystals are roundish, becoming more so with decreasing content of As. Figure 2 shows such a series from an idiomorphic crystal to a complete As-deficient spherule.

Under the microscope, the As-bearing platinum can be seen to form a eutectoid (vermicular) texture with sperrylite (Fig. 3), beginning at the surface of the crystal. With the continued decrease in As, the Pt and $PtAs_2$ form a eutectoid texture, and the process ends with a spherule. The process is illustrated in Figures 2 and 3. Figure 2 shows a series of SEM photographs depicting different stages in the "spherulization" process, beginning with an idiomorphic crystal of sperrylite and ending with a perfect eutectoid Pt–$PtAs_2$ spherule. The

TABLE 1. CHEMICAL COMPOSITION OF Pt-As PHASES OF "SPHERULIZED" SPERRYLITE FROM ALLUVIAL DEPOSITS IN FINNISH LAPLAND

	1	2	3	4	5	6
Pt wt.%	55.0	80.0	96.9	53.9	53.8	54.6
Fe	0.41	0.46	0.25	nd	nd	nd
Cu	0.46	0.48	0.30	nd	nd	nd
Rh	0.44	1.60	1.26	0.91	0.87	0.93
As	42.9	14.3	0.97	43.2	43.3	43.0
Total	99.21	96.84	99.68	98.01	97.97	98.53
Atomic per cent						
Pt	32.28	64.86	93.54	32.06	31.99	32.46
Fe	0.84	1.30	0.85	-	-	-
Cu	0.82	1.20	0.89	-	-	-
Rh	0.49	2.45	2.30	1.02	0.99	1.04
As	65.57	30.19	2.43	66.91	67.03	66.49

nd = not detected

1) Sperrylite crystal, unaffected, as in Fig. 2A.

2) Intermediate phase, 3) Almost pure Pt phase, 4) Sperrylite remnant. — Correspond to points marked in Fig. 3.

5) Sperrylite crystal from sand dried by gentle heating.

6) Sperrylite remnant after sperrylite crystal from sand dried by intense heating. Corresponds to point in Fig. 5.

backscattered-electron images of polished sections in Figure 3 show various vermicular textures in the altered sperrylite grains and spherules. Results of analyses of the various phases are given in Table 1 (2 - 4).

One process that could conceivably release arsenic and produce alterations such as those shown in Figure 2 and the textures in Figure 3 is heating in air. The variable degrees of rounding imply that the grains have been exposed to a range of either high temperatures or heating times, or both. The questions are: could heating possibly produce spherules from sperrylite grains by the release of arsenic, and what has caused the heating?

One answer might be a forest fire, but because the material is recovered by panning several thousand tonnes of gravel, this can hardly be the main explanation. In fact, the panning and procedures used by the miners suggest a more plausible one: the last, very heavy fraction in the pan has to be dried, and to hasten this, miners commonly use a blow torch. Could this heating release arsenic and also be responsible for the textures?

We checked the possibility with some experiments. First, DTA experiments ($\Delta T = 5°/\text{min}$) conducted on sperrylite crystals give a very strong exothermic reaction at 408–572°C. In the temperature range 350–900°C, simultaneous thermogravimetric determination gave a total weight loss of 42.25%, which takes place in three steps. In the temperature interval 350–408°C, the weight loss was 0.85%, in the interval 572–900°C, 0.40%, and during the strong exothermic reaction it was 41.00%. The total loss in weight is equivalent to the As content in sperrylite. Thus a blow torch certainly can produce enough heat to release arsenic.

Electron-microprobe examination of the grains after the DTA–TG experiments revealed that As was no longer present; only Pt was detected. Thus in this

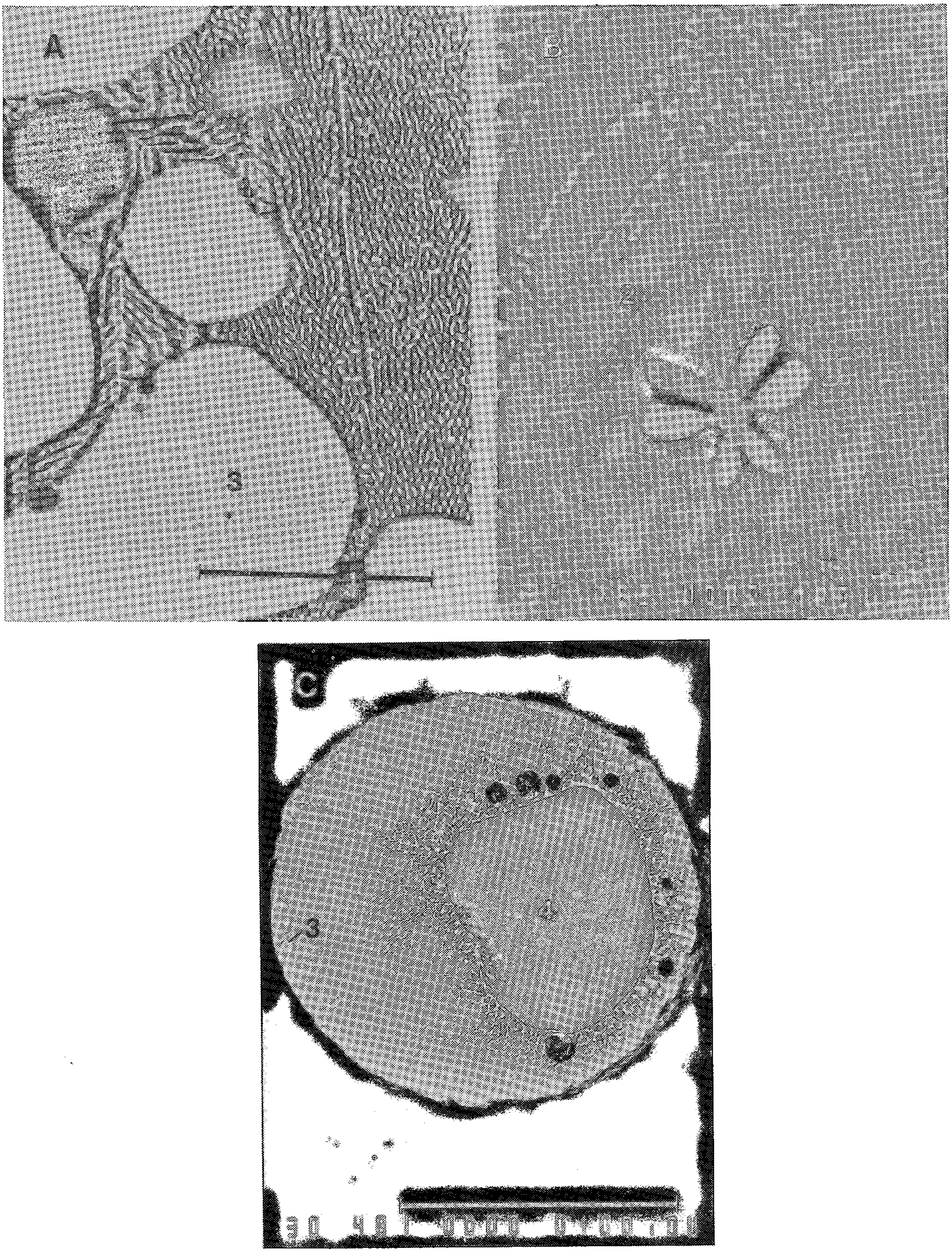

FIG. 3. A) and B) show backscattered-electron images of various eutectoid (vermicular) textures in altered sperrylite grains. C) backscattered-electron image of a section through a Pt–$PtAs_2$ spherule. A small domain of unaltered sperrylite still remains. Numbers correspond to compositions in Table 1. 2) intermediate phase, 3) almost pure Pt phase after sperrylite, 4) relict sperrylite.

temperature interval all the arsenic is released from sperrylite. A backscattered-electron image of a polished section of such a grain is seen in Figure 4. The grains reveal their original morphology, with only a slight rounding of the edges. The interior of the grains, however, is full of cavities as a result of the loss of As. No spherules were found!

The next experiment was performed to reproduce the procedure used by the miners. Some sperrylite crystals were mixed with wet sand, and the mixture was then dried with a blow torch. In the first attempt, when the sand was heated until it was just dry, only a slight reaction was visible on the surface of the sperrylite crystals. The second drying was prolonged until the pan was glowing red (~500°C). Now the sperrylite crystals all became more or less round. Figure 5A shows a secondary-electron image of one of these spherules, and Figure 5B a backscattered-electron image of a section through one of them. The vermicular texture seen is similar to that in Figure 3C. We conclude, therefore, that the $Pt-PtAs_2$ spherules are man-made and were formed during the drying of the last (heaviest) fractions.

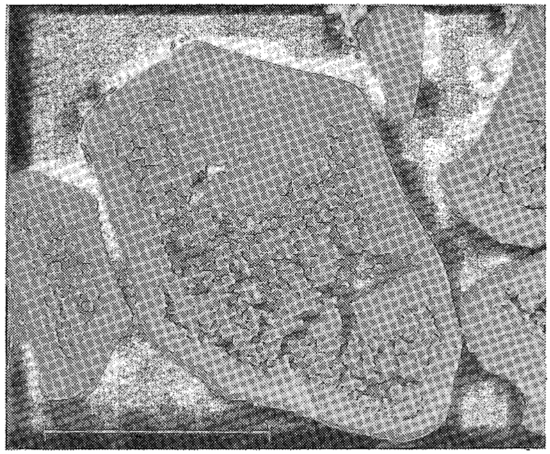

FIG. 4. Backscattered-electron image of polished section through sperrylite crystals after DTA experiment, showing a central part full of cavities surrounded by an outer unbroken rim. In no part of the remainder is any As detected. Length of bar 100 μm.

DISCUSSION

An interesting finding in our experiments was that sperrylite crystals form spherules when heated together with sand using a blow torch, but remain morphologically more or less intact when heated (without sand) more slowly in a DTA–TG appara-

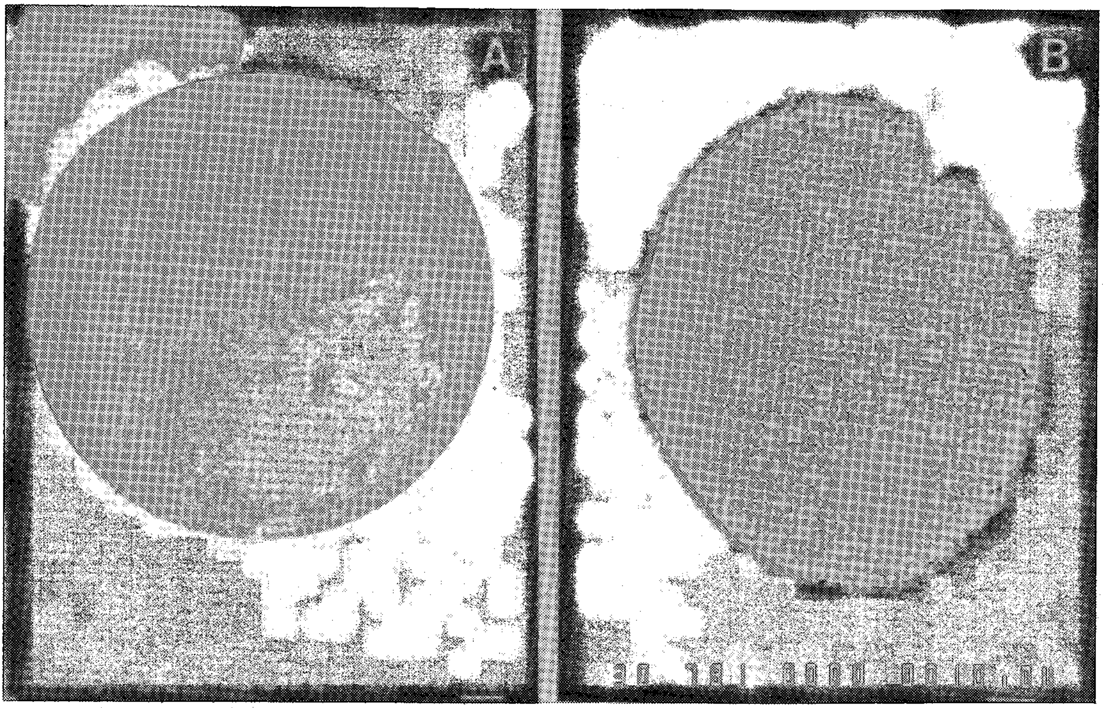

FIG. 5. Scanning-electron photographs of $Pt-PtAs_2$ spherules formed by heating with a blow torch in the laboratory. A) Secondary-electron image of spherule, B) backscattered-electron image of a section through a spherule. The eutectoid texture corresponds to that illustrated in Figure 3. The composition of the relict sperrylite (6) is given in Table 1. Length of bar 10 μm.

tus, developing, however, cavities inside the single-crystal grains. This may be due to the heating rate, which is low ($\Delta T = 5°/min$) in the DTA–TG experiment but high and very sudden with a blow torch.

The Pt–$PtAs_2$ spherules are smaller than the rounded grains probably because the heating did not last long enough to totally "spherulize" the larger crystals; only the small ones were transformed. In the laboratory experiments, "large" (> 200 μm in diameter) crystals of sperrylite were also used, and the heating had to be prolonged to totally "spherulize" all of them.

Many scientists have pondered the origin of *PGE*-alloy microspherules. Some have proposed an extraterrestrial origin (ablation droplets: *e.g.*, Brownlee *et al.* 1984), whereas others favored desulfurization (reduction) of *PGE* sulfides (Stockman & Hlava 1984). Feather (1976) described the texture of *PGE* microspherules from the Witwatersrand; he showed that Os–Ir–Ru alloys may alter into sulfarsenides, which would begin at the grain surfaces, and thus may acquire a vermicular texture.

The outcome of the process described by Feather is the reverse of that seen in the Pt–$PtAs_2$ spherules from Finnish Lapland. Ablation droplets should not show any eutectoid (vermicular) texture, and hence this mode of origin is not applicable to our spherules.

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References

Bird, J.M. & Bassett, W.A. (1980): Evidence of a deep mantle history in terrestrial osmium–iridium–ruthenium alloys. *J. Geophys. Res.* **85**, 5461-5470.

Blanchard, M.B., Brownlee, D.E., Bunch, T.E., Hodge, P.W. & Kyte, F.T. (1980): Meteoroid ablation spheres from deep-sea sediments. *Earth Planet. Sci. Lett.* **46**, 178-190.

Brownlee, D.E., Bates, B.A. & Wheelock, M.M. (1984): Extraterrestrial platinum group nuggets in deep-sea sediments. *Nature* **309**, 693-695.

Feather, C.E. (1976): Mineralogy of platinum-group minerals in the Witwatersrand, South Africa. *Econ. Geol.* **71**, 1399-1428.

Koivisto, H., Vuorelainen, Y. & Sahama, T.G. (1980): Alluvial sperrylite from Finnish Lapland. *Mineral. Record* **11**, 303-305.

Stockman, H.W. & Hlava, P.F. (1984): Platinum-group minerals in alpine chromitites from southwestern Oregon. *Econ. Geol.* **79**, 491-508.

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