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YURIY BORODAEV* — NADEZDA MOZGOVA** — NINA OZEROVA** —
— VLADIMIR SLUSAREV*** — POUNU OIVANEN**** — VEIJO YLETYINEN****

TYPOMORPHIC MINERAL ASSOCIATIONS OF ANTIMONY DEPOSITS WITH NATIVE ANTIMONY IN THE BALTIC SHIELD

(Figs. 4, Tabs. 3)

Abstract: Two antimony deposits with native antimony are described — Seinäjoki (Finland) and Stepanova Guba (Karelia). Ores of these deposits are very similar both with respect to the mineral and chemical composition and as regards paragenetic associations. These are two typomorphic mineral association: quartz-antimony and antimony-sulphide. The data obtained suggest that ores were formed in the deposits under specific conditions: at relatively high temperatures for antimony deposition, and at extremely low sulphur fugacity for the hydrothermal process.

Резюме: Описано два сурьмяных месторождения с самородной сурьмой — Сейняйоки (Финляндия) и Степанова Губа (Карелия). Руды месторождений очень сходны как по минеральному и химическому составу, так и по парагенетическим ассоциациям. Выделяются две типоморфных минеральных ассоциации — кварцево-сурьмяная и сурьмяно-сульфидная. Полученные данные свидетельствуют о том, что руды месторождений образовались в специфических условиях: при относительно высоких для сурьмяного рудоотложения температурах и при крайне низкой для гидротермального процесса фугитивности серы.

As is known, the main type of commercial antimony deposits are antimonite deposits where antimony is present in the sulphide form and which are formed at rather low temperatures and high values of sulphur fugacity. The discovery in the past decades at the Baltic shield of deposits where antimony is present predominantly in the native form significantly broadens our concepts of antimony ore formation. Classed with type is the group of deposits of the Seinäjoki ore region in Finland and an ore mineralization Stepanova Guba in Karelia, which occur in Proterozoic metamorphic schists. In Seinäjoki these are veins and stockworks. Ore minerals form nests, veinlets and impregnations. The main types of host rocks alterations are silicification and sericitization. Mineralization is principally confined to the silicification zones, occasionally definitely gravitates towards graphitized schists. It has been traced in depth to 100 m. In contrast in Karelia there has been located only one surface outcrop of mica crystalline schists with a zone of fine ore impregnation.

The study of Finnish and Karelian ores by means of the mineragraphic, microprobe and other methods has revealed them to be very similar both with respect to the mineral and chemical composition and as regards para-

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* Dr. Yu. Borodaev, Department of Geology, Moscow University, Moscow.

** Dr. N. Mozgova, Dr. N. Ozerova, Institute of Ore Deposit Geology, Petrology, Mineralogy and Geochemistry of the USSR Academy of Sciences, Staromonetny per. 35, 109 017 Moscow.

*** Dr. V. Slusarev, Geological Institute, Karelian filial of the Academy of Sciences, Petrozavodsk.

**** Dr. P. Oivanen, Dr. V. Yletyinen, Geological Survey Finland, SF-02150, Espoo 15.

genetic association. As seen from the Tab. 1, with respect to the set of minerals the ores from either place are, in effect, identical, being different solely in the presence or absence of certain rare mineral species, of which seinäjokite and pääkkönenite are new minerals (Mozgova et al., 1976; 1977; Borodaev et al., 1981). The two principal ore minerals — native antimony and pyrrhotite — are irregularly distributed. If one of them dominates, the other one is either absent or present in a subordinated quantity, the two minerals never contacting with each other. Inside the ore zones, antimony is concentrated in quartz veins and in the intensively silicified rocks. Pyrrhotite, on the other hand, occurs in less altered rocks. The majority of other ore minerals are observed to associate both with native antimony and with pyrrhotite, but in different quantitative relations. Accordingly, at the Seinäjoki deposits we have identified two paragenetic mineral associations (Borodaev et al., 1982, 1983). The same associations have been established also at the Karelian ore mineralization. These are the quartz-antimony and antimony-sulphide associations (Tab. 2).

Table 1

Distribution of ore minerals

Mineral	Formula	Seinäjoki (Finland)	Stepanova Guba (Karelia)
Antimony, native	Sb	+	+
Pyrrhotite	$Fe_{0.86}S$–$Fe_{0.90}S$	+	+
Marcasite	FeS_2	+	+
Arsenopyrite	$FeAsS$	+	+
Sb-arsenopyrite	$Fe(As, Sb)S$	+	+
Loellingite	$(Fe, Ni)As_2$	+	+
Gudmundite	$FeSbS$	+	+
Berthierite	$FeSb_2S_4$	+	+
Stibnite	Sb_2S_3	+	+
Chalcopyrite	$CuFeS_2$	+	+
Sphalerite	$(Zn, Fe)S$	+	+
Tetrahedrite	$Cu_{10}(Fe, Zn)_2Sb_4S_{13}$	+	+
Breithauptite	$NiSb$	+	
Pararammelsbergite	$Ni(As, Sb)_2$		+
Seinäjokite	$(Fe_{0.8}Ni_{0.2})(Sb_{1.7}As_{0.3})_2$	+	
Pääkkönenite	Sb_2AsS_2	+	
Sb-westerveldite	$Fe(AS_{0.95}Sb_{0.05})$	+	
Stibarsen	$SbAs$	+	
Aurostibite	$AuSb_2$	+	
Mineral Y	$Pb_2Sb_{20}As_8S_{19}$	+	
Mineral Z	$PbSb_6As_2S_6$	+	

In the first association the main mineral is native antimony and among the subordinate ones there have been recorded antimonite and antimony and iron sulphides (gudmundite and berthierite). In the second associations these sulphides, alongside with pyrrhotite, become dominant minerals and native antimony a secondary one.

A specific feature of the quartz-antimony association is, on the one hand, a constant arsenic admixture in native antimony (from 7 to 11 % in Seinäjoki and 0.2—0.8 % in Karelia) and, on the other hand, a rather high antimony content in such minerals as arsenopyrite, loellingite, as well as marcasite. In large arsenopyrite crystals there is often observed a zonal distribution of antimony: in interior zones 2 % Sb, in the exterior zone up to 12.0 % (Seinäjoki) and up to 18 % (Karelia). This fringe zone represents a druse of small Sb-arsenopyrite crystals (Fig. 1). Similar crystals of this variety develop also around gudmundite. In loellingite the maximum Sb content amounts to 3.4 % in Seinäjoki and 2.7 % in Karelia. An increased nickel content in arsenides (loellingite and arsenopyrite) and the formation of own minerals of this element, namely seinäjokite and breithauptite in Seinäjoki and Sb-bearing pararammelsbergite in Karelia (Fig. 2) are also very typical. In loellingite from Seinäjoki the nickel content reaches 9 %, in Karelia — 4 %. In Karelian arsenopyrite its content does not exceed 1.3 %, marginal Sb-arsenopyrite being completely free from an admixture of this element. Arsenopyrite and loellingite are present in the form of idiomorphic crystals inside the grains of native antimony and appear to have been formed earlier, the presence inside them of cross-cutting antimony veinlets testifying to this. Loellingite had crystallized earlier than arsenopyrite, as shown by the formation of the rims of the latter around loellingite. The latest ore mineral in the quartz-antimony association is antimonite which forms fringes around antimony grains and crosses them in the form of veinlets.

Table 2

Distribution of minerals according by association

Associations	Main minerals	Minor minerals	Rare minerals
Quartz-antimony	Native antimony Quartz Arsenopyrite Loellingite	Stibnite Pyrrhotite Pääkkönenite Sb-arsenopyrite Berthierite Gudmundite	Seinäjokite Sb-westerveldite Stibarsen Aurostibite Y-and Z-minerals Pararammelsbergite
Antimony-sulphide	Pyrrhotite Gudmundite Berthierite Stibnite Arsenopyrite Marcasite	Loellingite Sphalerite Chalcopyrite Tetrahedrite Native antimony Quartz	Pyrite Chalcostibite Breithauptite

An important feature of ores from the Seinäjoki is the development in them of unique minerals incompletely saturated with sulphur (no such minerals

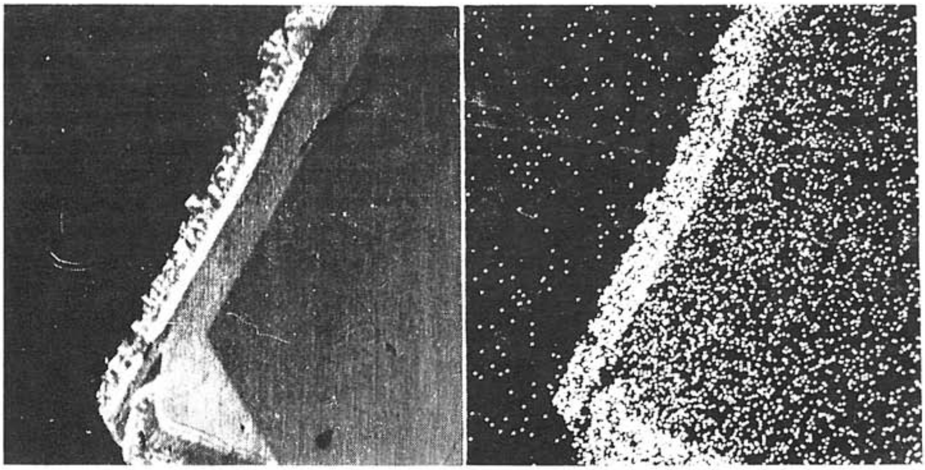

Fig. 1. Zonal crystal of Sb-bearing arsenopyrite. Seinäjoki.
Explanations: a) backscattered electron image; b) $SbL_{\alpha 1}$ X-rays image. 220 x.

have yet been recorded in Karelia). This is pääkkönenite (Sb_2AsS_2) and the minerals Y($Pb_2Sb_{20}As_8S_{19}$) and Z($PbSb_6As_2S_6$), two latters have not yet been sufficiently studied (Borodaev et al., 1982; 1983). All of them develop in

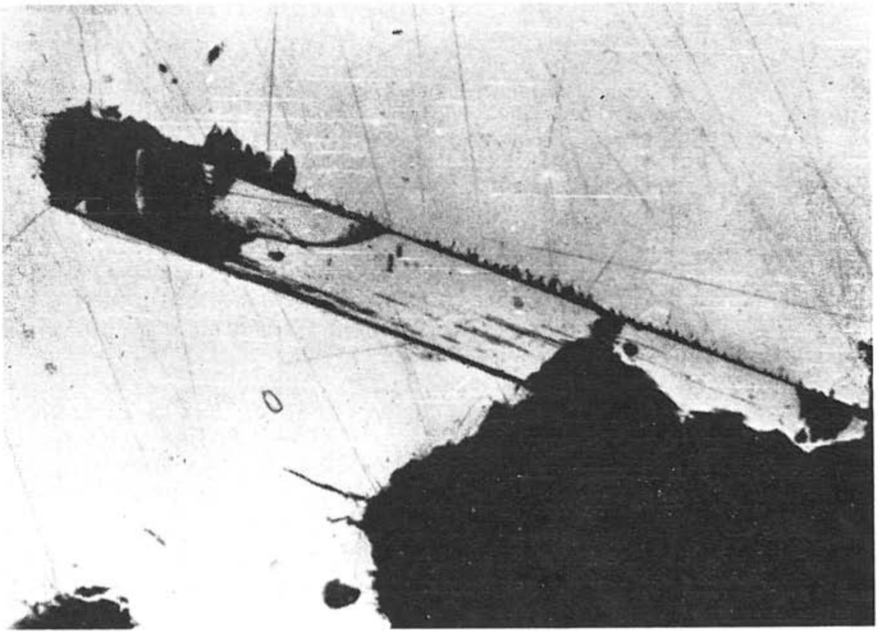

Fig. 2. Crystal of pararammelsbergite in native antimony. Karelia. 200 x.

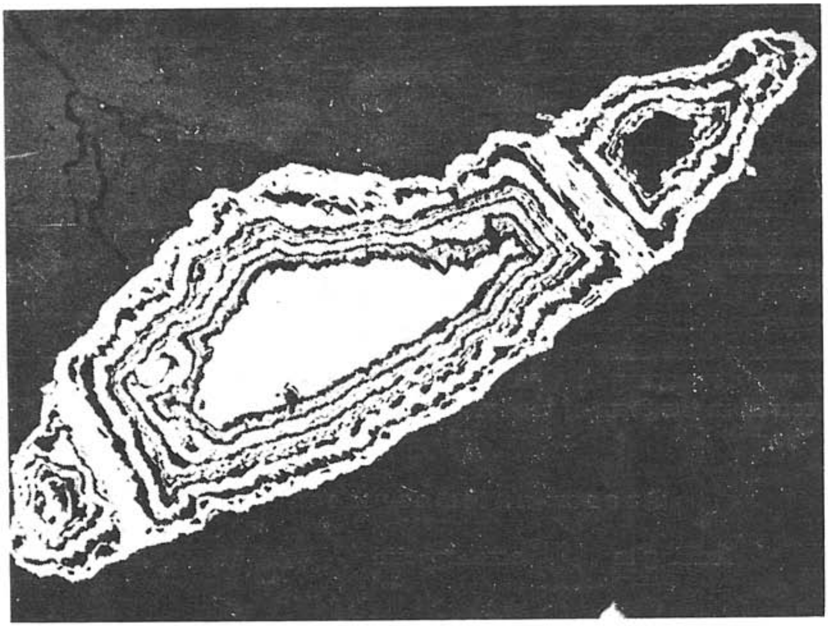

Fig. 3. Replacement texture of pyrrhotite by marcasite. Seinäjoki. 110 x.

association with native antimony and belong to the quartz-antimony association.

The main mineral of the second, antimony-sulphide association, as mentioned above, is pyrrhotite. On evidence of Finnish geologist Pääkkönen (1966), pyrrhotite constantly occurs, though in insignificant quantities, in mica schists and thus its distribution has a regional character. As presumed by Pääkkönen, it had been formed in the process of metamorphism of melnikovite and other black unstable compounds of ferrous sulphide accumulated at the bottom of sea basins and lakes. At the deposists in question pyrrhotite is definitely inherited. Within the ore zones its separate impregnations grow larger, apparently as a result of selective recrystallization caused by incoming hydrothermal solutions. Pyrrhotite was partly redeposited, cementing fragments of metamorphic rocks in brecciation zones.

Within the ore zones pyrrhotite is replaced by marcasite forming very picturesque textures (Fig. 3).

Pyrrhotite is often surrounded by gudmundite fringes (Fig. 4) in which there are locally observed graphic (myrmekite-like) structures of intergrowth of gudmundite with pyrrhotite. Pääkkönen (1966) explains the development of such graphic structures by the replacement of pyrrhotite with gudmundite when antimony is added according to the scheme $FeS + Sb \longrightarrow FeSbS$. Pyrrhotite, as well as gudmundite fringes, are sometimes replaced by berthierite in which the relics of these minerals are occasionally preserved unreplaced. All the three minerals are, in their turn, replaced by antimonite which forms reaction margins around their grains and cross-cutting veinlets inside them.

No direct relations between pyrrhotite and antimony have been observed. In those rare cases when the two minerals occur in the same ore aggregate other sulphides — gudmundite, berthierite — are necessarily found between them.

The absence of cross-cutting allows to presume that the two associations have been formed from the same solution, but have developed under a different physico-chemical environment. The rocks were subjected to the most intense hydrothermal reworking in the sections of quartz-antimony association, which resulted in the almost complete removal of pyrrhotite.

The antimony-sulphide association has formed in the less intensively altered host rocks, in which pyrrhotite has preserved. The latter reacted with the antimony-containing, but sulphur-free solutions, as a result of which there were forming such minerals as gudmundite and berthierite, whilst native antimony was developing in a limited quantity. The order of crystallization may be conceived in the form of the following idealized scheme:

Quartz-antimony association:

loellingite → arsenopyrite → native antimony

Antimony-sulphide association:

pyrrhotite ↘ marcasite (+ pyrite)

gudmundite ↘ berthierite ↘ stibnite (+ marcasite)

Thus, typomorphic features of the peculiar antimony deposits with native antimony, which have so far been found on the Baltic shield alone, we may consider to be the following:

1. Development of two typomorphic paragenetic associations — quartz-antimony and antimony-sulphide consisting principally of a similar extremely specific set of minerals which are present in different quantitative relations.
2. Presence of Sb admixture in certain minerals of arsenic, iron, and nickel (arsenopyrite, loellingite, marcasite, pararammelsbergite, westerveldite, etc.).
3. Presence of nickel in the ores, which either enters as admixture in other minerals (arsenopyrite, loellingite) or form own minerals (seinäjokite, pararammelsbergite, breithgauptite).
4. Development of minerals with sulphur deficit (pääkkönenite, etc.).

Results of this study and published experimental and thermodynamic data enable to discuss some physico-chemical conditions of ore formation in these deposits. We shall now try to evaluate two factors of equilibrium — temperature and fugacity.

The temperature of the formation of the quartz-antimony mineral association can be evaluated by means of minerals-geothermometers (Tab. 3).

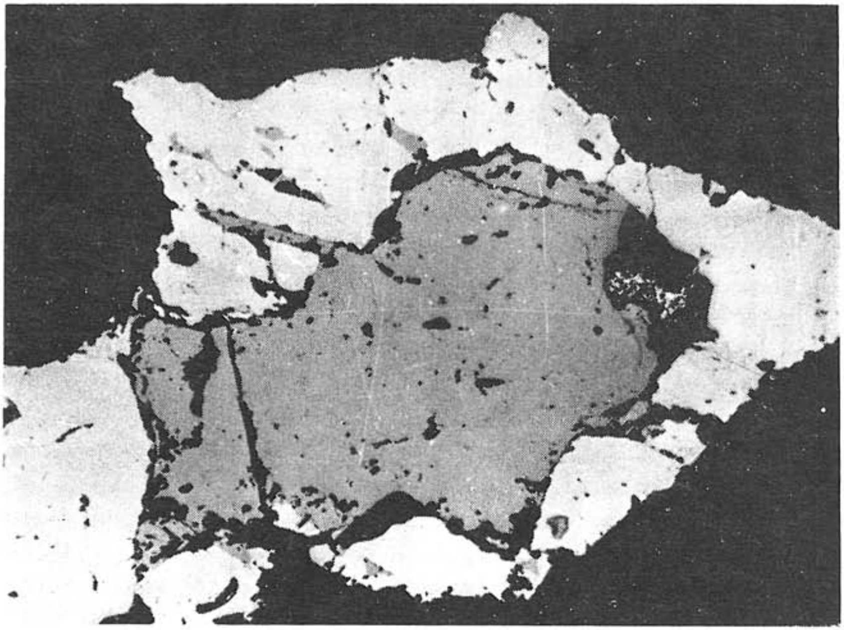

Fig. 4. Pyrrhotite (gray) surrounded by gudmundite rim (white). Karelia. 110 x.

The data listed in the Table show that temperature of the quartz-antimony association formation was rather high (~ 400—500 °C). The results of homogenization of fluid inclusions in quartz are in good agreement with this conclusion. The formation of the antimony-sulphide association was taking place under lower temperature conditions, as determined by the upper thermal stability limit of gudmundite (280°) and monoclinic pyrrhotite (250°).

The sulphur fugacity calculated for ore deposit Seinäjoki (Borodaev et al., 1982; 1983), varies from 10^{-17} to 10^{-15} atm at 400 °C and from 10^{-15} to 10^{-20} at 280 °C. This is much lower than those of sulphur fugacity, which according to Barton (1969;1971) are characteristic of the process to hydrothermal sulphide mineral formation (stibnite deposits). Since mineral associations in Karelia are similar with those in Seinäjoki the same ranges of sulphur fugacity appear to be in both deposits.

Thus the conditions of ore formation in these unique deposits were very specific. These deposits have been formed at relatively high temperatures for antimony ore deposition and under an extremely low sulphur fugacity for the hydrothemal process. These two factors have led to the formation of the unique antimony ores composed practically of monomineral native antimony and unusual associations of native metals, intermetallides and minerals undersaturated with sulphur.

Table 3

Temperature conditions of formation of antimony deposits with native antimony

Association	Geotermometer	T, °C	Author
Quartz – antimony	solubility of S in loellingite (mass %)		Clark, 1960
	3.4	702	
	3.0	650	
	~2	~500	in Seinäjoki, this study
	content of As in arsenopyrite coexisting with loellingite + pyrrhotite (at %)		Kretschmer–Scott, 1976
	34.0	330	
	37.0	550	
	35.3–36.3	440–510	in Seinäjoki, this study
	34.6–36.3	370–510	in Stepanova Guba, this study
	content As (mass %) in native Sb coexisting with Sb_2AsS_2 (synthetic analogue of pääkkönenite)		Luce et al., 1977
	14.9	500	
	12.1	425	
	11.0	~400	in Seinäjoki, this study
	content of Sb (mass %) in Sb-arsenopyrite		Gamjanin et al., 1981
	8.0	450	
	14.5	550	
	4.8–12	360–500	in Seinäjoki, this study
	7.4–17.6	440–650	in Stepanova Guba, this study
	homogenization temperatures of fluid inclusions in quartz	360–400	in Seinäjoki, this study
		340–350	in Seinäjoki, Balitsky et al., 1976
		320–410	in Stepanova Guba, this study
Antimony-sulphide	gudmundite stability	280±10	Clark, 1966
	monoclinic pyrrhotite stability	<250	Scott – Kissin, 1974
	homogenization temperatures of fluid inclusions in quartz	220–230	in Seinäjoki; Balitsky et al., 1976

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