

GENETICAL PECULIARITIES OF THE MERCURY INDICATIONS NEAR SÁROSPATAK (TOKAJ MTS., NE-HUNGARY) ON THE BASIS OF FLUID INCLUSION STUDIES

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ABSTRACT

The mercury indications are NNW from Sárospatak, in area bounded by Királyhegy, Cinegés and Botkő. The cinnabar occurrences are situated in the metasomatically altered Badenian rhyolite tuff. The primary and pseudosecondary fluid inclusions of barites from Királyhegy and secondary gas-liquid inclusions of magmatic quartz grains from Botkő are studied. On the basis of fluid inclusion studies the barite crystals grew in a boiled paleohydrothermal system on temperatures 187 ± 13.1 °C and on pressures 6—20 bar. The solution composition was NaCl-CaCl₂-H₂O (-CO₂)-type with 2.31 ± 0.55 NaCl equiv. wt % concentration values. The secondary gas-liquid inclusions of the magmatic quartz grains preserved the boiled hydrothermal fluids also and the diluted, post-boiling fluids, which had lower temperatures and concentration values. The crystallisation of cinnabar probably was in connection with the boiling and the temperature depression produced by mixing of the subsurface cold waters and the hot hydrothermal fluids. On the basis of the geological and the fluid inclusion data the mercury indications as a shallow zone of a polymetallic (\pm Au, Ag) ore deposit are explained.

INTRODUCTION

Along the SE margin of Tokaj Mountains near Sárospatak and Sátoraljaújhely the traces of paleohydrothermal activity are well known. The cinnabar bearing mercury ore occurrences are situated NNW of Sárospatak in the area of Királyhegy, and Cinegés as well as Botkő.

Geological investigations were carried out at the end of the 1960's regarding the lithology and geochemistry of the ore indication (KULCSÁR and BARTA, 1969; MÁTYÁS, *et al.*, 1971).

The present work's aim to accurate our knowledge about the genetical relations of the mercury-bearing zone on the basis of the results of the fluid inclusion studies.

GEOLOGICAL SETTING

The Badenian—Sarmatian (Middle—Upper Miocene) products of the andesitic-rhyolitic volcanic activity are underlain by Middle Triassic carbonate rocks. The cinnabar occurrences are situated in the Badenian rhyolite tuff. Products of the Sarmatian igneous activity are less acidic (mixed tuff, amphibole-andesite, pyroxene-andesite), but rhyolite tuff also occurs among them (see *Fig. 1*. JASKÓ and MÉHES, 1946; KULCSÁR and BARTA, 1969; MÁTYÁS *et al.*, 1971). The Királyhegy, Cinegés and Botkő are made of rhyolite tuff altered by silicification.

On Királyhegy the double, intensively silicified alteration zones also display baritic alteration and they are aligned in S-N direction. The silicification was developed by crystallisation of the following minerals: tridymite, quartz, chalcedony I, opal I, chalcedony II, quartzin, opal II (TOKODY, 1965). The siliceous alteration is characterized by NW—SE strike on Botkó.

KULCSÁR and BARTA, (1969) described the following alteration processes: (1) siliceous metasomatism, (2) potassic metasomatism below the silicified zones, (3) baritic alteration in two phases (the younger one is developed mainly on Királyhegy), (4) alunitisation.

MÁTYÁS, *et al.* (1971) distinguished seven hydrothermal alteration facies: (1) siliceous; (2) siliceous-kaolinitic; (3) siliceous with kaoline knots; (4) hydrohematitic; (5) montmorillonitic; (6) illitic; (7) devitrificeous, respectively. The cinnabar occurs in the siliceous and hydrohematitic facies, singenetically with siliceous alteration, as well as in the cavities and brecciated zones of the silicified rocks.

The characteristic feature of the mercury indications is the existence of the cinnabar and the lack of other sulphides. The anomalous abundance of Sb, As, Tl, Ag, Ba and Sr indicates an epithermal environments and it would refer to a deeper polymetallic ore deposit. However, the drillings did not cut significant vein systems; the borehole No. Sp-14 cut some baritic-pyritic veinlets, only. The mercury-impregnated bodies on the surface are limited in the silicified zones.

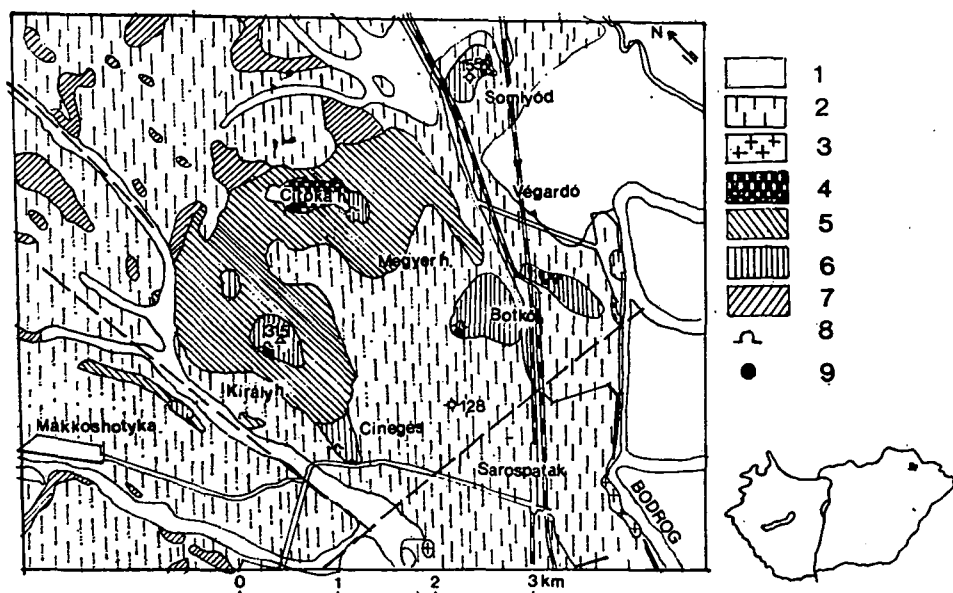


Fig. 1. Geological map of the cinnabar occurrences (JASKÓ and MÉHES, 1946).

- 1 — Holocene, 2 — Pleistocene, 3 — Sarmatian andesite, 4 — rhyolite, 5 — limonitic rhyolite tuff, 6 — Badenian silicified rhyolite tuff, 7 — pumiceous rhyolite tuff, 8 — quarry, 9 — samples

FLUID INCLUSION STUDIES

On the basis of fluid inclusion studies it is possible to determine the temperature, pressure, solution composition and concentration of the mineralizing fluids (ROEDDER, 1984). Therefore some double polished, 0.5—1 mm thin sections from barites (Ki-

rályhegy) and hydrothermal and magmatic quartz grains (Botkő) were prepared for the fluid inclusion studies. Several phase-transition phenomena were observed during the change of the temperature with application a Chaixmeca-type microthermo-chamber and Amplival Pol microscope. The measurement reproductibility was $\pm 0.1^\circ\text{C}$ in negative and $\pm 0.2^\circ\text{C}$ in positive temperature interval.

1. Inclusion types. The 1–2 mm thick irregular, tabular barite crystals grew in the cavity of the baritised-silicified rhyolite tuff. They contain large amounts of fluid inclusions. Their diameters are max. 100–120 microns. The majority of the inclusions are pseudosecondary type and they are ordered along the crystal cleavage (*Fig. 2.*). The two-phase inclusions contain liquids and 10–15 volume % gas. The large two-phase microobjects are primary type ones beside the inclusion rows (*Fig. 3.*). The secondary inclusions have irregular, planar or flag-like shape, and they usually contain only liquid (*Fig. 4.*). In certain growth zones of barite crystals the population of the large, liquid+gas and gas inclusions refer to the boiling of the mineralizing fluids (ROEDDER, 1984; *Fig. 5.*).

The short and long prismatic quartz crystals occur in the cavity of the silicified rhyolite tuff on Botkő. They often contain magmatic quartz grains in their cores.

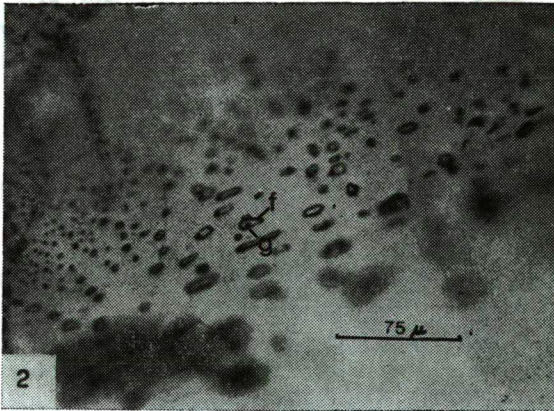


Fig. 2. Ps-S-type fluid inclusions along the cleavage of barite (Királyhegy)

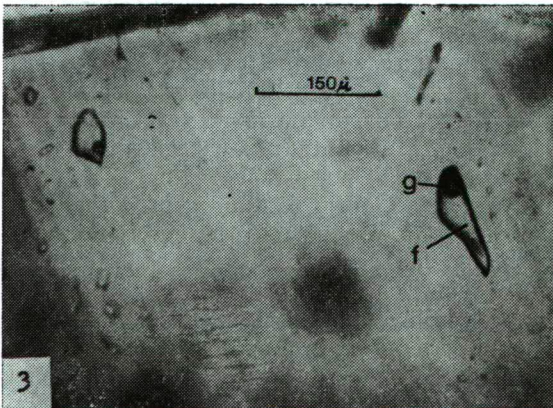


Fig. 3. P-type fluid inclusions in barite (Királyhegy)

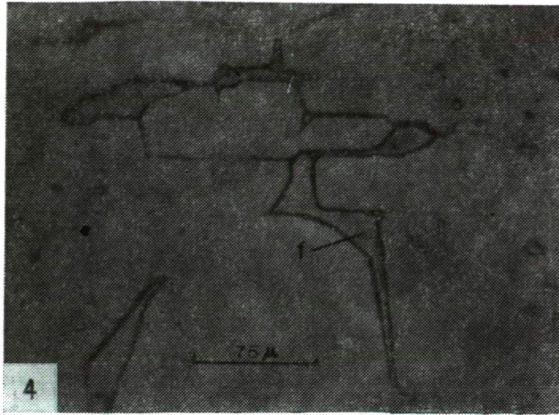


Fig. 4. S-type fluid inclusion in barite (Királyhegy)

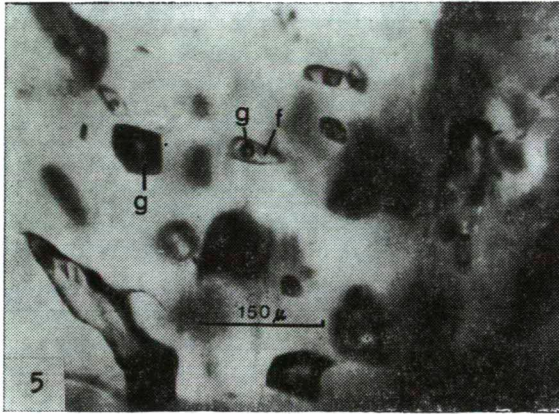


Fig. 5. Gas and gas-liquid inclusions in barite, referring to the boiling (Királyhegy)

The hydrothermal (α -) quartz crystals are unsuitable for phase-transition studies because they contain only secondary type, one-phase inclusions with small diameter.

The hexagonal-dipyramidal magmatic quartz grains occur mainly in the hollow-fractured zones of the silicified rhyolite tuff. The magmatic quartz crystals contain large amounts of volcanic glass inclusions (Fig. 6.). The magmatic quartz grains became fractured in consequence of the tectonical forces, which affected the silicified brittle rock. The paleofluids penetrated into the microfractures and they dissolved the glass inclusions along the fractures and finally the fluids were captured in the cavity of the dissolved glass (Fig. 7.). KOZŁOWSKI, (1981) and KOZŁOWSKI and METZ, (1985) described similar dissolution events in magmatic quartz grains.

The walls of the microcavity have often uneven, etched surfaces because of the dissolution (Fig. 8.).

The glass inclusions reacted with the hydrothermal fluids, probably until the healing of the microfractures, so their dissolution would have been complete. The

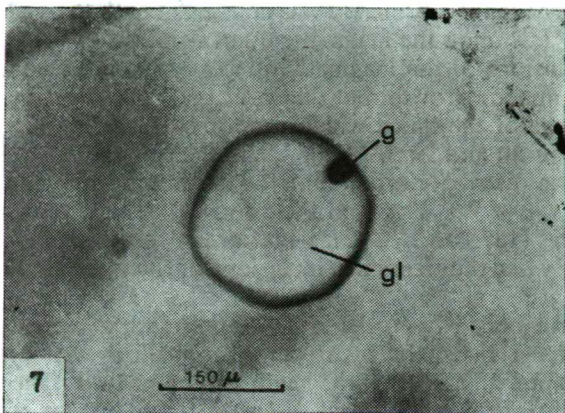


Fig. 6. Glass inclusion with gas bubble in magmatic quartz grain (Botkó)

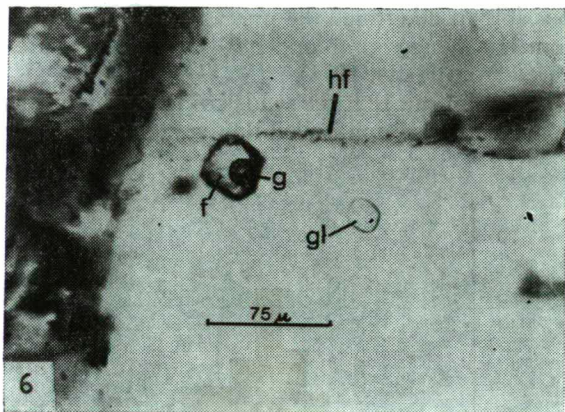


Fig. 7.: Fluid inclusion filling the place of the dissolved glass inclusion along a healed microfracture (Botkó)

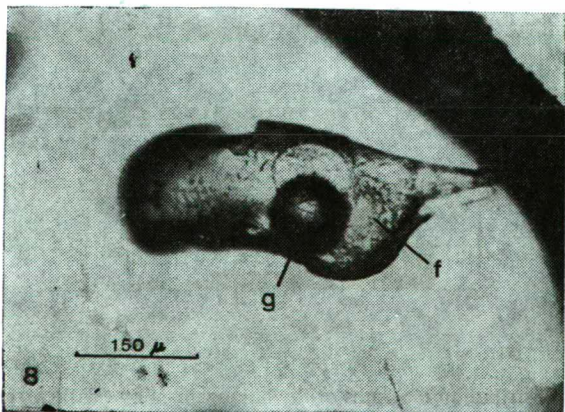


Fig. 8. Fluid inclusion with etched inner surface (Botkó)

healing of the microchannels probably was connected with the growth of the hydrothermal quartz crystals upon the magmatic quartz grains.

The fluid inclusions of the magmatic quartz grains are secondary type relating to the time of the mineral growth, but they are applicable to reconstruct the physico-chemical parameters of the fluids which were present during the hydrothermal activity (e.g. TAKENOUCI and IMAI, 1975).

2. *Results.* The distribution diagrams of the homogenization temperatures are showed on Fig. 9.a and 9.b. The fluid inclusions of the barites are homogenized at higher temperatures (187 ± 13.1 °C) than that of had been prevailed in the paleohydrothermal system when the secondary inclusions of the magmatic quartz grains have been formed.

In the case of a boiled hydrothermal system the vapour pressure of the solution equal with (or higher than) the hydrostatic (in shallow system) or the lithostatic (in deeper system) pressure. During the heating of an inclusion the bubble dissappear when the pressure of the liquid is equal with its saturated vapor pressure. The results of this meditation are that in the case of a boiled hydrothermal system the homogenization temperatures of the inclusions approach the real temperature of a mineral growth and it is possible to determine the pressure of the hydrothermal system. The barites derived from Királyhegy grew under 6—20 bars pressure (with the application of data borrowed from HAAS, 1971).

It is important to point out that the values of the homogenization temperatures reflect the true temperature of a non-boiled fluid system, if they are corrected by the

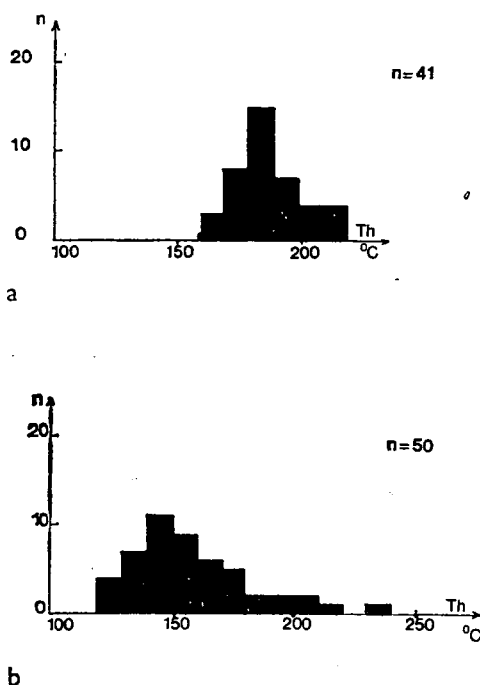


Fig. 9. Distribution diagrams of the homogenization (Th) temperatures
 a — barites from Királyhegy
 b — magmatic quartz from Botkő

so called „pressure correction“. We think that the pressure values were not significantly different in time of the origin of the secondary fluid inclusions of the magmatic quartz, than the pressure values of the barite growth. On the basis of POTTER'S (1977) pressure correction data this very low pressure values do not affect significantly the homogenization temperatures, so the mentioned homogenization data reflect the true temperature of the paleofluids for the Botkő samples, too.

The fluids froze below -40°C during the cryoscopic studies. In all case we observed knot- or brush-like NaCl-hydrate. The melting temperature of the hydrate during the slow heating of the samples by the room air was also measured. The detected cotectic temperatures refer to a NaCl-CaCl₂-H₂O solution composition (HAYNES, 1985). The solution composition did not differ on the Királyhegy and Botkő (Table 1.). CO₂-hydrate was also observed in some inclusions which disappeared before the melting of the ice. The presence of the CO₂-hydrate refer to the low density CO₂-content of the gas phase of the inclusions.

The concentration data which were calculated from the melting point depression of the ice (POTTER *et al.*, 1978) are significantly different. The barites derived from Királyhegy grew from such solutions which had higher concentration values than the fluids on Botkő had (Fig. 10.a and Fig. 10.b.). On the basis of the temperature and concentration data the density of the fluids were different from each other. The lower mean density values of the barites reflect the influence of a higher temperature (Table 1).

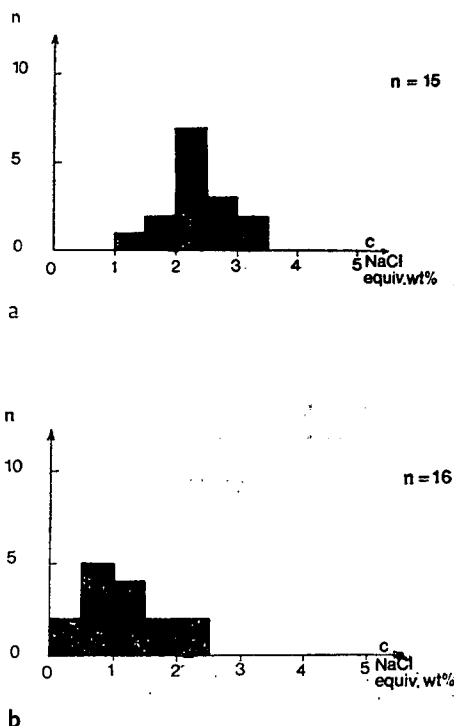


Fig. 10. Distribution diagrams of the concentration (c) values
 a — barites from Királyhegy
 b — magmatic quartz from Botkő

TABLE 1

Fluid inclusion data from Királyhegy (barite)
and Botkő (magmatogenic quartz)

	Barite		Magmatogenic quartz	
	m	s. d.	m	s. d.
Th	187.9	13.1	158.1	23.7
T1	-26.7	5.5	-27.4	3.1
T2	-1.4	0.3	-0.9	0.8
c	2.31	0.55	1.45	1.35
d	0.895	0.016	0.911	0.024

Th — homogenization temperature
 T1 — first melting point of ice (cotectic temperature)
 T2 — melting temperature of ice
 c — concentration (NaCl equiv. wt. %);
 d — density (g/cm³)
 m — mean value
 s.d. — standard deviation

DISCUSSION

The boiling of the hydrothermal system was not obvious in the samples from Botkő by the fluid inclusion petrography. Comparing the *Figures 11.a and 11.b* it is clear that the fluid inclusion data of the magmatic quartz crystals reflect on the double evolution trends of the hydrothermal solution. The Th and T2 data of the magmatic quartz from Botkő have positive correlation in the high temperature interval, which is similar to the inclusion data of the barites. This correlation is characteristic to the boiled systems (HEDENQUIST and HENLEY, 1985b).

The melting temperatures of ice become higher in the inclusions which have lower homogenization temperatures in the samples from Botkő (*Fig. 11.b*). This fact would refer to the mixing of the hydrothermal fluids and the subsurface ground water. So the secondary inclusions of the magmatic quartz grains also demonstrated the evolution of the paleofluids after the boiling. The decrease of the boiling probably was in connection with the cooling caused by influx of the cold ground water.

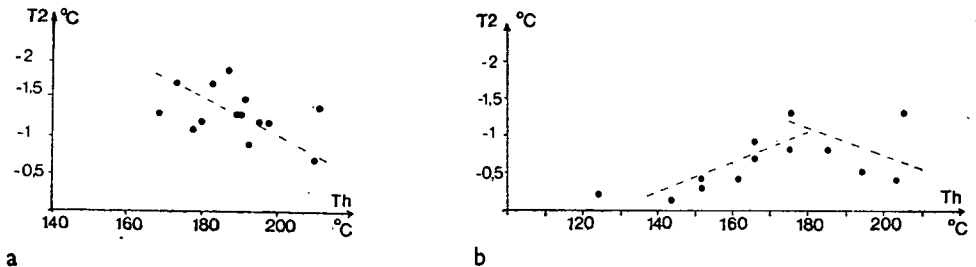


Fig. 11. Relations between the homogenization (Th) and melting temperatures (T2)

a — barites from Királyhegy
 b — magmatic quartz from Botkő

The following factors are favourable for the deposition of cinnabar (SMIRNOV *et al.* 1983): (1) chemical changes during the reactions between the fluids and rocks, (2) rising of the oxygen fugacity in the shallow zone of the hydrothermal system, (3) The dilution of the fluid by influx of the vadose water.

About 150 °C temperature the low (<9) pH values are favourable for the deposition of cinnabar (KOLONIN and PTITSY, 1972). The low pH values are characteristics in the condensation zone of a boiled volcanic-subvolcanic hydrothermal system (DRUMMOND and OHMOTO 1985). The boiling is favourable for the separation of mercury from other elements (WHITE *et al.*, 1971).

At Sárospatak the cinnabar crystallised during two periods: syngenetically with the silification and another in the brecciated zones. We demonstrated the boiling of the hydrothermal system by fluid inclusion studies. The kaolinitic and alunitic alteration of the rocks refer to an acidic system, also. On the basis of the geological data (KULCSÁR and BARTA, 1969) the cinnabar in some case occur as a sublimated product on the walls of the cavities and fractures. The fluid inclusion data and the geological observations suggest that the cinnabar would crystallised at 170—200 °C during the boiling of the hydrothermal system.

The fluid inclusion studies also provided some proofs for the mixing phenomena between the hydrothermal (hot) fluids and the subsurface (cold) water. So the crystallisation of the cinnabar would be connected to the mixing events also because of the cooling and the (possible) increasing oxygen fugacity. The final conclusion is: the mercury indication have been formed in the near surface or marginal zone of a boiled system, where the condensation of the vapour and acidic gas and the mixing of the fluids are the characteristic phenomena. This result is in harmony with the anomalous Hg, As, Sb, Tl, Pb, Ba and Sr element population, which is very similar to the recent ore deposition in the geothermal fields (Waiotapu, New Zealand; HEDENQUIST and HENLEY, 1985b).

The investigated mercury occurrence is in the temperature interval of the mercury deposits characterized by the data of the Table 2. However, the ore indication displays transitional features to the volcanic-subvolcanic, epi-mesothermal polymetallic ore deposits by the connection between the temperature and concentration data (*Fig. 12*).

Around Sárospatak and Sátoraljaújhely the silicified rhyolite tuff occurs on the Bányi-hegy, also. This volcanic rock was altered by potassium metasomatism, and it contains a sulphidic-gold type ore occurrence which have been exploited in the Middle Ages on Bányi-hegy (GÖBEL, 1954; VARGA, 1961).

The potassium metasomatism had also passed off in the district of the mercury occurrences (KULCSÁR and BARTA, 1969). The rock alteration zonality (siliceous, kaolinitic, illitic, montmorillonitic) is well known in the mercury-bearing „siliceous caps“ of the precious metal deposits (Buckskin Mountains, Nevada; VIKRE, 1985), and similar hydrothermal alteration zones were described by MÁTYÁS, *et al.* (1971) near Sárospatak. On the basis of the possible analogy, the presumed genetical connection would accurate by further fluid inclusion studies between the mercury indication and the gold ore indication near Rudabányáska.

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TABLE 2

Fluid inclusion data from various Hg-deposits

Deposit	Mineral	Th	C	References
Djilkidal (I)	quartz	110—150	30.4 (3)	BORISENKO <i>et al.</i> (1974)
Kurumdu-Ayri (I)	quartz	120—170	27.5	
	ankerite	130—160	12—15	
Kuvay (I)	quartz	145—170	10 (3)	
Cagan-Uzun (I)	quartz	150—190	8.2 (3)	
	ankerite	140—200	8.2 (3)	
Aktash (I)	quartz	120—190	10	
	calcite	130—215	0.5—2 c	
Ak-T ul (I)	quartz	130—150	3.5—6 c	
	calcite	125—135	4—9	
Cheremshanka (I)	quartz	135—165	6—7 c	
Suhoskoe (I)	quartz	115—180	0.5—2.5 c	
Gorhon (II)	quartz	155—185	17.8 (4) c	
Gal-Haya (III)	fluorite	160—190	4.5—6 c	
	quartz	190—240	1.5—3 c	
Karasu (IV)	calcite	110—130	0.5—1.5	
	quartz	180—225	3.5 (5)	
Palianskoe (V)	quartz	130—220	1.5—4	
	quartz	75—140	0.5—1	
Terlinghay (VI)	quartz	100—165	17 (6)	BORISENKO <i>et al.</i> (1979)
	quartz	120—145	25 (6)	
	barite	90—110	22 (6)	
	quartz	90—95	20—25	
	barite	70—80	20—25	
	carbonates	70—80	12—15	
	fluorite	60	12—20	
Chazadir (VI)	quartz	120—180	40.9 (1)	
	barite	130—140	7—9 c	
	cinnabar	100—155	39.7 (3)	
	cinnabar	90—110	20	
Slaviansk	fluorite	225—240		ZATSIKHA (1973)
	siderite	220—280		
	quartz	200—220		
Rovni (VII)	quartz	230—210	2—11	ZATSIKHA and GALABURDA (1985)
Szilhegy (VII)	quartz	248—255	3	
Soymi (VII)	quartz	140	5 (2)	
Csontos (VII)	quartz	230	1.5	

Th — homogenization temperature (°C)
 C — concentration: NaCl wt % (without symbols) Symbols: solution composition

- (1) — NaCl + CaCl₂ + KCl
 (2) — NaCl + KCl
 (3) — NaCl + Na₂CO₃
 (4) — NaCl + MgCl₂
 (5) — Na₂CO₃
 (6) — NaCl + CaCl₂

c — CO₂ in the solution

- I — High-Altai
 II — East-Sayan
 III — Yakutia
 IV — Middle-Asia
 V — Chukotka
 VI — Tuva
 VII — Transcarpathia

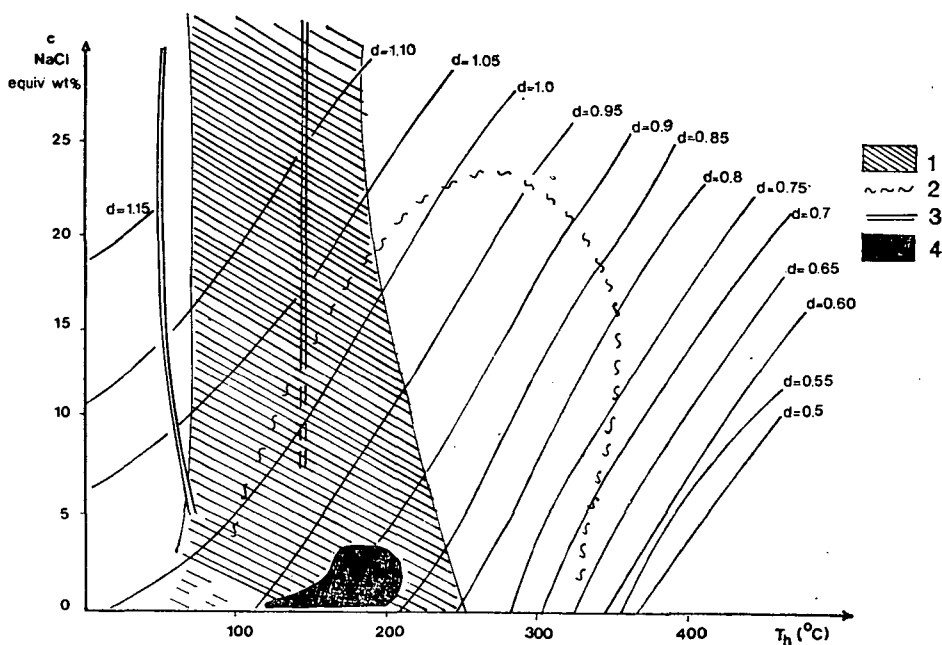


Fig. 12. Distribution of the fluid inclusion homogenization temperatures (T_h) and concentration (c) values from various mercury deposits.

- 1 — mercury deposits (references are on the table 2.)
- 2 — volcanic-subvolcanic polymetallic deposits (GATTER, 1985)
- 3 — Mississippi-Valley type deposits (GATTER, 1985)
- 4 — data from Sárospaták
- d — density of fluids

Symbols on the photomicrographs: f —liquid, g —gas, gl —volcanic glass, hf —healed microfracture

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