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THERMOLUMINESCENCE AND LEAD ISOTOPES AT THE PONIKY LEAD-ZINC DEPOSIT IN THE TRIASSIC OF THE WEST CARPATHIANS

(Textfigs. 1—7)

Abstract. By thermoluminescence investigations of carbonates at the Poniky Lead-zinc deposit it was possible to split the carbonate sequence into smaller units for subsurface correlation as well as to characterise the mineralized zone by an unusual low thermoluminescence. Lead isotopes indicate a pre-Tertiary age of the mineralization.

Besides siderite and magnesite most important in the East Alps are lead-zinc ore-deposits. They occur predominantly in triassic carbonate rocks similar to Silesian Pb-Zn deposits in Poland with which they share in the genetically most discussed group.

The Triassic of the West Carpathians is also mineralized by lead-zinc ores. Some deposits were in the past exploited on a limited scale (for example Ardoval, Pila, Pohorelská Maša, Poniky) whereas other localities can be characterized only as small economically unimportant occurrences.

Several of these deposits—most intensely those in the vicinity of the village Poniky — have been explored during the last years.

The newest results about the geology and metallogenesis of this region are given mainly in the papers by J. Kotásek, A. Grenár and V. Kudělásek (1953) and J. Losert (1962, 1963, 1963a).

In 1963 we have studied the thermoluminescence of carbonates and the isotopic composition of lead from the Poniky deposit. A brief summary of the results obtained as well as of the possibilities offered by the use of thermoluminescence and isotope investigations in the study of similar ore-deposits is given.

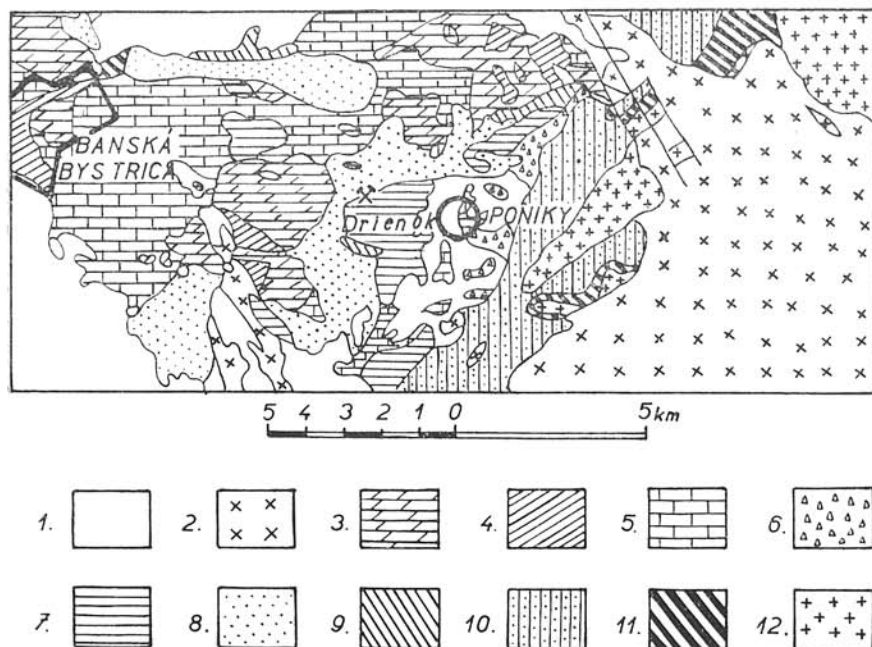
The village Poniky (Textfig. 1) is situated in Central Slovakia some 11 kilometers SE from the Town Banská Bystrica and its immediate surroundings are built prevalingly by mesozoic complexes with young-tertiary sediments in the depressions. The neogene eruptive complex of the Poľana Mt. forms the eastern and the crystalline of the Lubietová-Zone the NE boundary of this area.

From the basement (Lubietová-Zone) J. Losert described (1962, 1963) two-mica and muscovite paragneisses, amphibolites, various types of migmatites and orthogneisses as well as cataclastic granodiorites to quartzdiorites. M. Máška and V. Zoubek (1960) suppose a precambrian age of this complex and its metamorphoses. J. Kantor (1961) could by absolute dating prove that a hercynian and in the innermost zones of the Veporide crystalline a cretaceous reworking took place.

The crystalline is discordantly overlain by permian sandstones, arkoses, quartzites, graywakes and conglomerates. Acidic igneous rocks quartzporphyries, locally dynamometamorphosed into porphyroids are an important constituent too.

The Mesozoic of the Krížna-Unit separated by a discordance from the underlying Permian consist at the basal parts mainly of conglomerates, with light-

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Textfig. 1. 1 — Sedimentary Neogene; 2 — Pyroclastics and lavas of andesites and subordinate rhyolites. Neogene; 3 — Jurassic-Cretaceous sediments; 4 — Variegated slates. Intercalations of dolomites, sandstones (Noric—Keuper stage); 5 — Dolomites of Middle-Upper Triassic; 6 — Tectonites of Middle-Upper Triassic limestones and dolomites; 7 — Dark limestones. Anisien; 8 — Quartzites, sandstones, schists. Werfenian (so called Melaphyr-series); 9 — Efusives. Lower (?) Triassic; 10 — Quartzites, schists. Locally epimetamorphosed. Werfenian; 11 — Permian; 12 — Crystalline. Schematically after geological map of ČSSR 1 : 200 000.

coloured quartzites, further sandy slates with intercalations of quartzites (Werfenian) of cellular tectonites of limestones and dolomites.

For the Keuper are characteristic variegated slates locally with thin lenses or beds of dolomites; for the Rhaetian dark organogenic, whereas for the Liassic predominantly pink (crinoidic) limestones of the „Hierlatz“ type are characteristic. Higher limestones with hornfelses, platy and sometimes calpionellid limestones (Dogger-Malm) and grey marly limestones (Neocomian) occur.

The Choč-nappe was by J. Losert (l. c.) divided into two tectonic units: the main part of the Choč-nappe and the so called partial nappe of the Flos.

The main part of the Choč-nappe has according to J. Losert on its base tectonically reduced anisian limestones of the „Guttenstein“-type not exceeding 15 m in thickness with feeble intercalations of dolomitic limestones to dolomites. Higher dolomites and dark dolomitic limestones appear. The Ladinian is represented by grey hornstonebearing limestones (Reifling-type) and probably by light, pinky limestones outcropping near the village Dúbravica. The higher laying slates and greywakes belong to the Karnic stage (Lunz-schists).

For the partial nappe of the Flos are reported: a mighty developed Werfenian

in the form of quartzites, arkoses, sandy to clayey micaceous slates (Zeiss) and marls to marly limestones (Campill). An important feature of this Werfenian is the presence of variable types of quartzporphyries (Kotásek, Losert, l. c.) and subordinate porphyrites. The eruptive bodies are localized in quartzites and slates (Zeiss), sometimes between these and marls to marly limestones, or between campilian rocks and overlaying anisian limestones. A tectonic contact is reported in this cases. It is supposed that the eruptive body had been originally uniform and was later dismembered into several segments during the alpine orogenic movements (Losert l. c.).

The Middle Triassic is represented by a cca 200 m thick complex of gray, with local transitions into dark gray limestones.

From Drienok, the most mineralized locality, intercalations of dark hornstone-bearing limestones (cca 10 m thick) and dolomitic rhythmites (1–2 m) were described.

The lead-zinc and copper mineralization is known from Drienok (3 km W of Poniky) and the eastern slopes of Stráža (3 km N of Poniky). It is restricted to the complex attributed by J. Losert to the partial nappe of the Flos, overthrust here over the Křižna-unit.

The following ore-types were distinguished:

a) bodies of metasomatic ankerite impregnated by galena, sphalerite, tennantite, chalcopyrite and pyrite. They are steeply inclined and reach as far as 3 m from fissures regarded as channels of the ore-bearing solutions.

b) subhorizontal lense-shaped veins with ankerite and minor amounts of galena, sphalerite, tennantite and pyrite.

c) rhythmically mineralized dolomites similar to sedimentary textures.

The last type originated according to J. Losert (1963) by metasomatic replacement of dolomite rhythmites as far as 10 meters from the supposed channels of the ascending solutions.

Thermoluminescence

The quality of certain minerals and rocks to emit on heating visible light is since long well known. But only during the last years D. F. Saunders (1953), F. Daniels, Ch. Boyd et D. F. Saunders (1953), J. M. Parks jr. (1953), R. E. Bergström (1956), C. W. Pitrat (1956) and others were able to transform thermoluminescence investigations into a useful research tool. The wide-range application of the thermoluminescence was possible only when new devices for the quantitative measurements of the thermoluminescence were available.

Among minerals most often limestones were subjected to thermoluminescence investigations as they are almost always thermoluminescent. The possibility to use this property for surface correlation was studied mainly by D. F. Saunders (l. c.) and R. E. Bergström (l. c.) whilst J. M. Parks (l. c.) attempted to correlate subsurface samples.

For our work a thermoluminescence equipment constructed at the Geological Institute D. Štúr by Mr. J. Lux was used. It consists of the following constituents:

A small furnace with a silver hot plate on which the samples in form of fine powder (cca 0,1 mm) are heated.

The linear heating rate (120°C per minute) is controlled by means of a hand-operated autotransformer and an iron-konstantan thermocouple.

The emitted light is converted into current on the photocathode and further amplified in a photomultiplier.

Both — the photomultiplier as well as the furnace are placed in a light-tight box and can be separated from each other by a light-tight slit. Over this a quartz glass or (and) interchangeable filters can be inserted. The sample is viewed by the photomultiplier through a mirror at 45° to prevent from heating. No cooling of the photomultiplier is therefore necessary.

The photomultiplier is fed by a stabilised high voltage variable direct-current power unit.

A direct-current amplifier amplifies the output of the photomultiplier. Wide-range amplification is obtained by varying the voltage per stage on the multiplier phototube and by means of the direct current amplifier itself.

The relation between the emitted light and the temperature of heating of the sample (glow-curve) is registered by a direct recording microammeter.

The furnace can be exchanged for a holder with a neon bulb, which allows standardization of operating conditions of the thermoluminescence equipment. Repeated runs on the same samples show a good reproducibility of glow-curves.

X-rays induced glow-curves are usually characterised by three peaks at about 100 , 200 and 300°C , whereas the low-temperature one is lacking in samples investigated for their natural thermoluminescence. Throughout this paper they are beginning with the low temperature one designed as peaks No 1 to 3.

The amount of samples used for the thermoluminescence investigations was not weighed in our work. A more convenient method of volume standardization was adopted.

The area around Poniky had been systematically drilled in connection with prospecting for lead-zinc ores. We had at our disposal 3 systematically sampled drilling cores: 2 from the mineralized zone and 1 which penetrated a thick sequence of barren carbonate rocks. No samples of surface outcroppings were available.

The aim of our study was to clarify if in this ore-district thermoluminescence could be successfully applied to the investigation of the lead-zinc mineralization and in subsurface correlation. Mrs. M. Strešňáková assisted in the running of the samples on the thermoluminescence equipment.

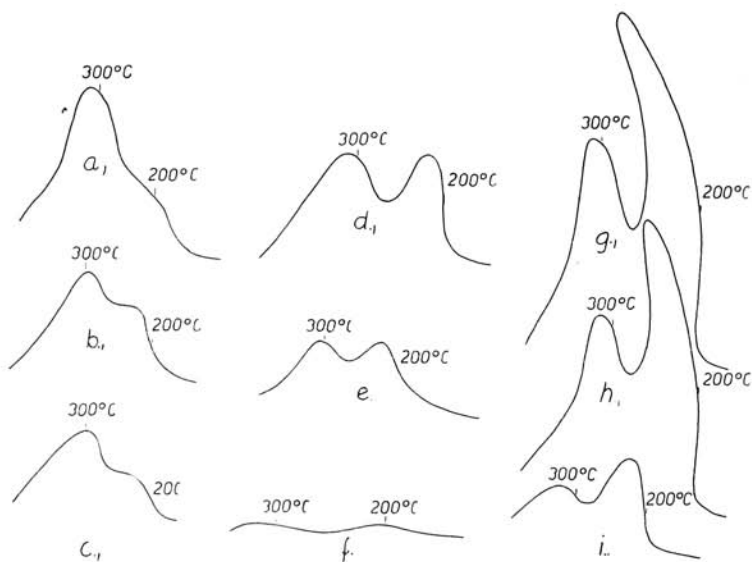
The drilling Poniky-Drienok P-9, situated in the carbonates of the so called partial nappe of the Flos cca 3 kilometers SE from Drienok was chosen as it was relatively deep and practically barren. It could therefore yield a picture about the thermoluminescence of the unmineralized carbonate sequence i. e. about the possibility of a correlation by thermoluminescence in this ore-field.

In Textfig. 2 are reproduced several glow-curves of carbonates from this boring. A wide variation in both the shape of the glow-curves as well as in intensity of the natural thermoluminescence is observed. The peak heights vary considerably. Cases with very high middle-temperature peaks (2) relative to peaks 3 to such where peak 3 is many times as high as the very small peak 2 are encountered in the boring P-9. Many glow-curves exhibit middle and high temperature peaks of almost identical heights.

Differential-thermal curves of the same samples are shown in Textfig. 3. It is

PONIKY P-9

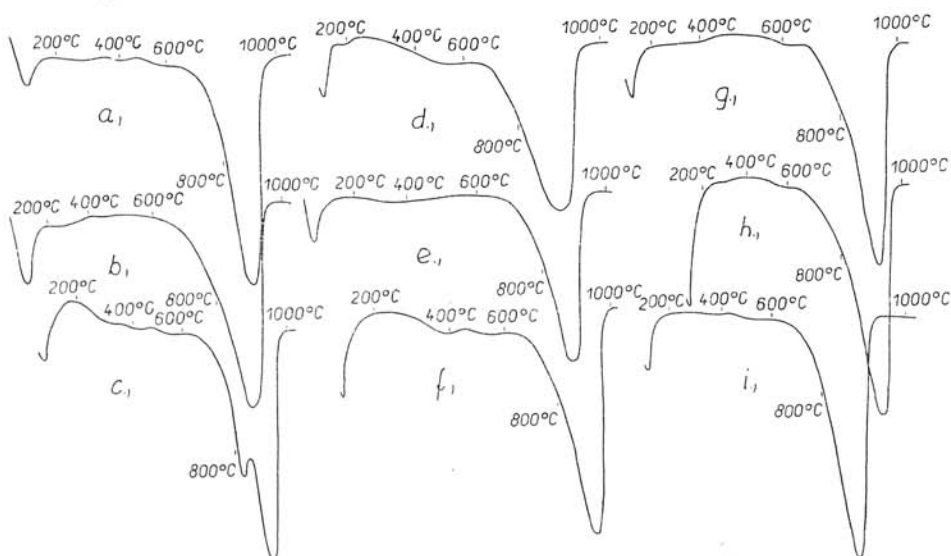
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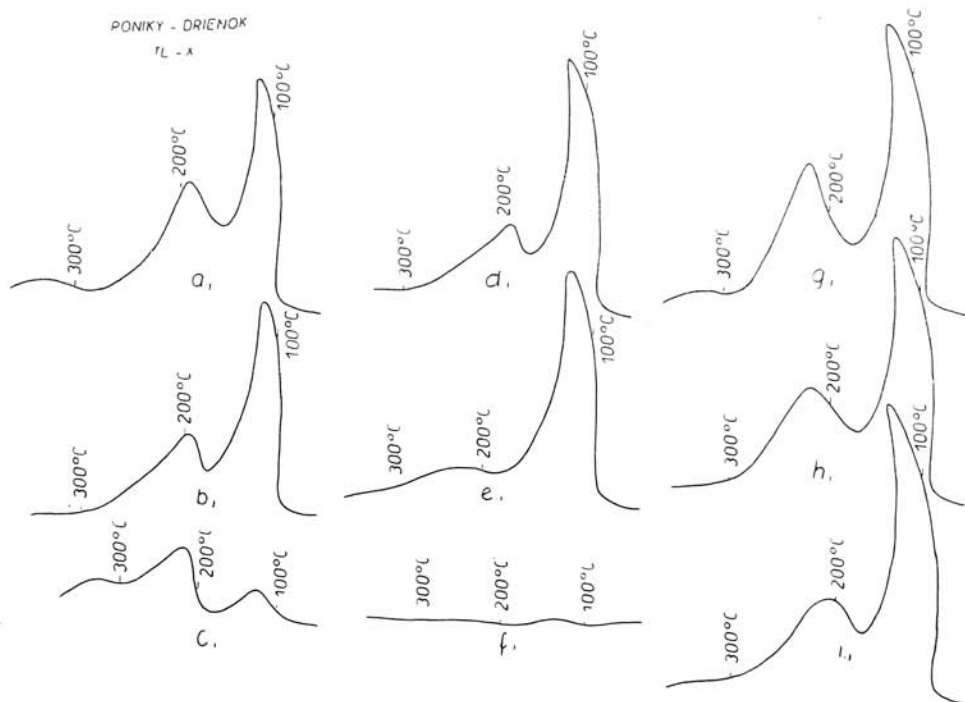
Textfig. 2. Poniky P-9.

PONIKY P-9

DTA



Textfig. 3. Poniky P-9.



Textfig. 4.

evident that with the exception of one (c — dolomite) all carbonates are characterised by very similar pattern of the DTA-curves.

Textfig. 4 reproduces the X-ray induced thermoluminescence of the same samples as shown on Figs. 2 and 3. The natural thermoluminescence of these carbonates has been annealed by heating to a temperature of 450 °C. Afterwards they were irradiated by equal doses of X-rays.

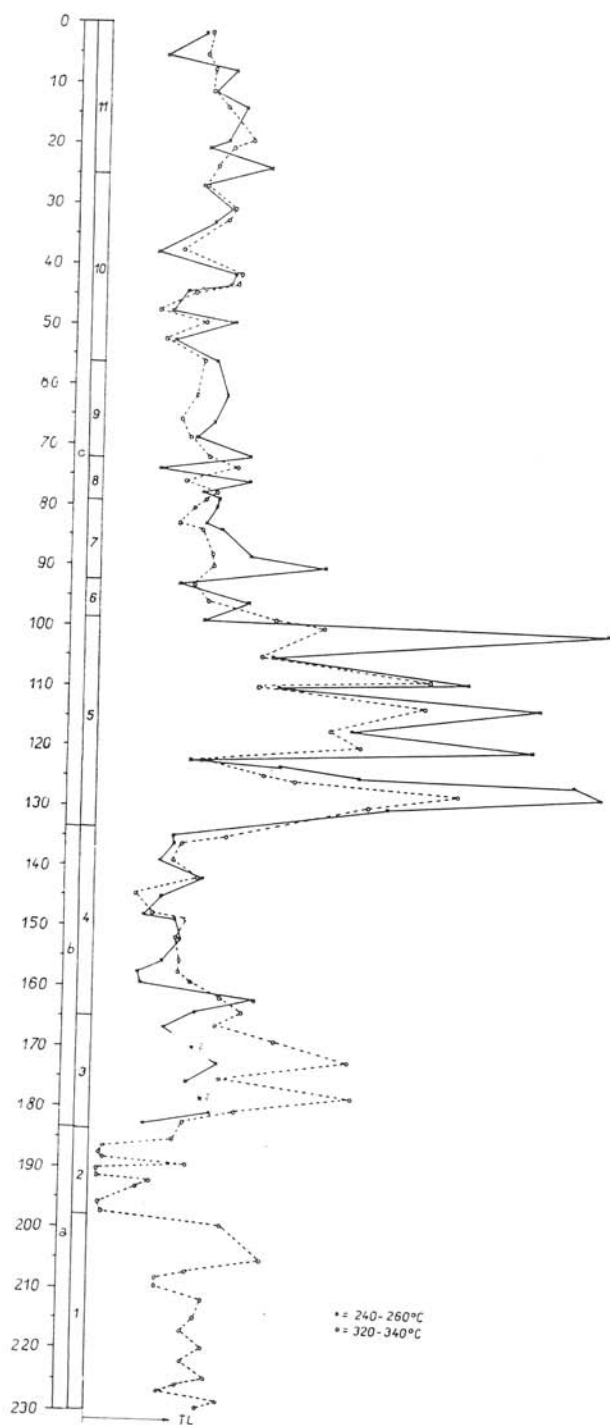
The natural glow-curves are mainly the result of structural factors, the radioactivity of the sample (dosis received) and its thermal history. In equally irradiated samples the last two are for comparison negligible (because identical) and the character of the lattice (impurities, substitution a. s. o.) plays the dominant role determining the shape of glow-curves.

By the investigation of both, the natural and artificial thermoluminescence an idea about the cumulative action of all above mentioned — on the one side and of the structural factors on the other can be obtained.

An inspection of Textfig. 2 and 4 is very instructive bearing out the difference of both methods.

The variability of the natural thermoluminescence for the boring P-9 is evident from Textfig. 5, where the depths in meters under the surface are given on the ordinate and the heights of both peaks (middle temperature-crosses; high temperature-circles) on the abscissa.

The variations in glow-curve shapes and intensity of thermoluminescence have permitted to split the carbonate sequence into 11 more or less pronounced small units (column 2, Textfig. 5).



Textfig. 5. Poniky—Drienok P—9.

1. Moderate thermoluminescence. Peak 3 is high. In our experimental arrangement is the middle temperature peak sometimes hardly discernible and masked by the ascending part of peak 3.

2. Similar relations of both peaks. Lower intensity alternating with layers almost devoid of natural thermoluminescence.

3. Section with relative high thermoluminescence. Compared with 1 the position of peak 2 is well marked on the glow-curves. Certain similarities to the higher parts of 1 can be observed.

4. Thermoluminescence less intense. Both peaks almost equally high or alternatively changing.

5. Horizon markedly differentiated from others by an unusually high thermoluminescence. Thin intercalations of limestones characterised by a somewhat lower but still high thermoluminescence occur. Peak 2 higher than peak 3 — a distinction of these parts against those of unit 3.

6. Thin transition zone with lower thermoluminescence and alternate change of peak heights.

7. Moderate thermoluminescence. Peak 2 distinctly higher than peak 3.

8. Both peaks alternate in domination.

9. Similarities to 7 can be seen. The amplitude of the middle temperature peak in places somewhat lower.

10. The glow-curves exhibit a distinct trend to maintain both peaks in nearly identical height notwithstanding that the overall intensity of the thermoluminescence is changing.

11. Moderate thermoluminescence. Once peak 2 the other time peak 3 dominates.

Unfortunately results of a detailed petrographic and stratigraphic study prepared by the workers of the Geologický prieskum (Geologic exploration) aren't yet for this boring available. So it was impossible to compare the thermoluminescence with such dates.

We had had at our disposal only small splits of samples. They did neither allow to carry out such studies, nor it has been our intention.

Only a rough subdivision of the carbonate sequence in the boring P-9 could therefore be realised on this material (from bottom to top):

a) Gray fine-grained dolomites, locally brecciated; in their upper part with crystalline dolomites.

b) Predominately dark limestones of the „Guttenstein“-type, quite subordinate dolomitic limestones.

c) Predominately grey sometimes darker or lighter limestones. In places thin intercalations of organodetritic (algal) and crinoidic crystalline limestones occur.

J. Losert (1962, 1963) reports for the Anisian of his partial nappe of the Flos en bloc: light coloured limestones with insertions of dark nodulous limestones and dolomitic rhytmities; partially grey to greyblack limestones; for the Ladinian-grey dolomites.

Taking into account the thermoluminescence as well as the scarce data about the petrographic behaviour obtained by macroscopic observation of the splits the following subdivision of the carbonate sequence could be realised:

1. Dolomites-grey, fine-grained, locally brecciated. Medium thermoluminescence.

2. As 1 but alternating with crystalline dolomites. Thermoluminescence low to very low.

3. Dolomitic limestones. Thermoluminescence relatively high.

4. Dark limestones, mainly in their upper part with thin irregular veinlets of white calcite („Guttenstein“-type). Medium to low thermoluminescence, alternative changing of peak heights.

5. Grey, locally light-coloured, elsewhere darker limestones. Insertions of richer organoclastic material. Thermoluminescence exceptionally high. Middle-temperature peak dominating.

6. Grey limestones. Alternate change of peak heights.

7. Grey limestones with local transitions into crinoidic limestones. The low-temperature peak is higher.

8. Grey limestones. Medium thermoluminescence and alternating domination of peak heights.

9. Grey limestones. Similar trends in thermoluminescence as in 7 remains of crinoids very rare.

10. Grey limestones. Both peaks tend to have equal heights.

11. Grey limestones. Alternate domination of peaks.

Our splitting of the carbonate sequence into smaller units based on the thermoluminescence investigations differs considerably from the subdivision reported by J. Losert (l. c.). But certain analogies can be traced to the subdivision of the partial nappe of Flos as carried out by J. Bystřický (personal communication) according to detailed mapping and stratigraphic investigations. He distinguishes:

- a) Grey dolomites.
- b) Dark limestones of the „Guttenstein“-type.
- c) Light-coloured limestones with Dasycladaceae.
- d) Dark grey nodulous limestones („Reifling“-type).
- e) Grey crinoidic limestones.
- f) Grey limestones of the „Wetterstein“-type.

The following comparison of his results with our thermoluminescence investigations seems most probable:

- a) Grey dolomites correspond to 1 and 2 in our subdivision.
- b) Dark limestones of the „Guttenstein“-type. Subdivided by us in a lower (3) and upper (4) part with more typical signs.
- c) The light-coloured locally organodetritic limestones are incorporated in our unit 5 with the most pronounced thermoluminescence, where also darker limestones are observed.
- d) Dark limestones of the „Reifling“-type. From our limited material it isn't unequivocally clear whether they are present in the boring in a reduced form (unit 5 to 6?) or entirely lacking.
- e) To the crinoidic limestones corresponds probably our 7, distinguished by a typical thermoluminescence and lense-shaped occurrences of crinoidic limestones.
- f) Limestones of the „Wetterstein“-type. Accordig to their thermoluminescence they were split into four distinct parts (8—11).

The thermoluminescence studies carried out on the core of the well P-9 resulted in a spitting of thick; carbonate sequence in to small units comparable to those obtained by detailed mapping and stratigraphic investigations. In many cases a more precise subdivision could be realised.

Unfortunately we couldn't study the persistency of both glow curve shape and intensity of thermoluminescence of the units laterally within a wider area as no closely spaced samples from other wells in tectonically little disturbed zones were available.

Our results agree in the main features with those obtained by J. Bystřický (personal communication) about the so called partial nappe of the Flos for

which he proposed the designation series of Drienok regarding it as belonging to the Gemeride instead of Veporide unit as done by J. Losert.

Two other wells were chosen for the study with the aim to elucidate the influence of the ore-bearing processes on the thermoluminescence of carbonates in the ore-bodies and their immediate vicinity.

The boring D-5 (see section, Textfig. 6) from the northern slopes of the Drienok penetrated from the surface to a depth of cca 100 m the complex of grey limestones of the „Wetterstein“-type. The part mineralized by galena, sphalerite, tennantite and pyrite laying between 100 and 165 m. This part is characterised by an unusually low thermoluminescence.

Similar glow-curve patterns can be recognised in the boring D-20 (Textfig. 7). Beneath grey limestones of the „Wetterstein“-type with a moderate thermoluminescence there is a zone rich in caverns. Only sparse, weathered and for the running of glow-curves unsuitable samples were from this part of the core available. The irregularly mineralized zone extends from some 95 to 165 m. As in the former case a strikingly low to almost lacking thermoluminescence is observed.

Very instructive bearing out the marked differences is the comparison of the positive borings (D-5, D-20) with the negative one (P-9). The latter is not only devoid of any lead-zinc mineralization but also of nonthermoluminescent carbonates so abundantly developed in the vicinity of the ores.

The rapid decrease of the thermoluminescence in the mineralized carbonates seems to depend on the introduction of iron during the metasomatism on one and a recrystallisation on the other hand.

The very lack of thermoluminescence seems to be a useful tool in the prospecting for lead-zinc mineralizations in this ore-district.

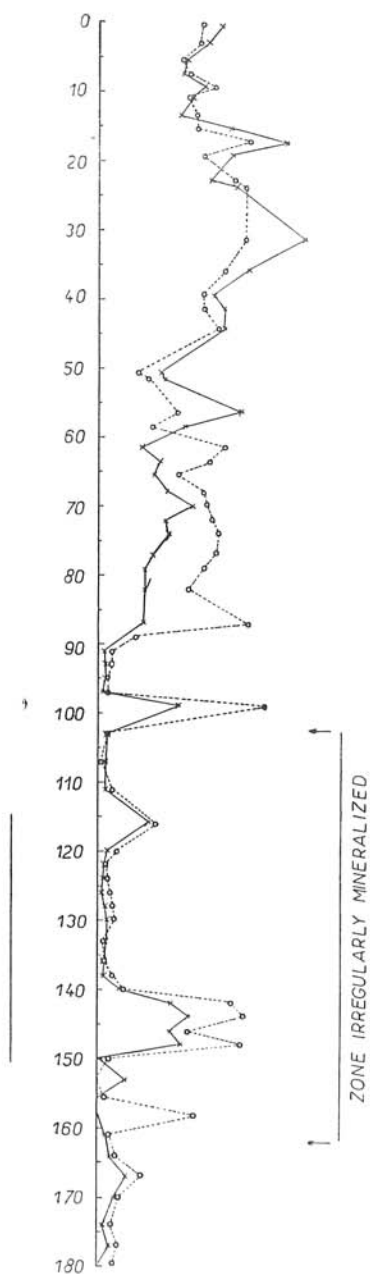
Lead isotopes

As already mentioned the most detailed informations about geology and ore-deposits of the Poniky area are those by J. Losert (l. c.). The papers by J. Kotásek — A. Grenár — J. Kudělásek (1953) and J. Kravjanský (1962) are also dealing with the same subject.

The posttectonic nature of the lead-zinc mineralization at Poniky regarding the Alpine-Carpathian orogenesis is stressed by J. Losert (1962) and a cretaceous or young-tertiary age of the deposits admitted. The last interpretation is based on the proximity of a mighty complex of neogene pyroclastics and effusives of the Poľana Mt. and on certain differences as compared to other occurrences from the Triassic.

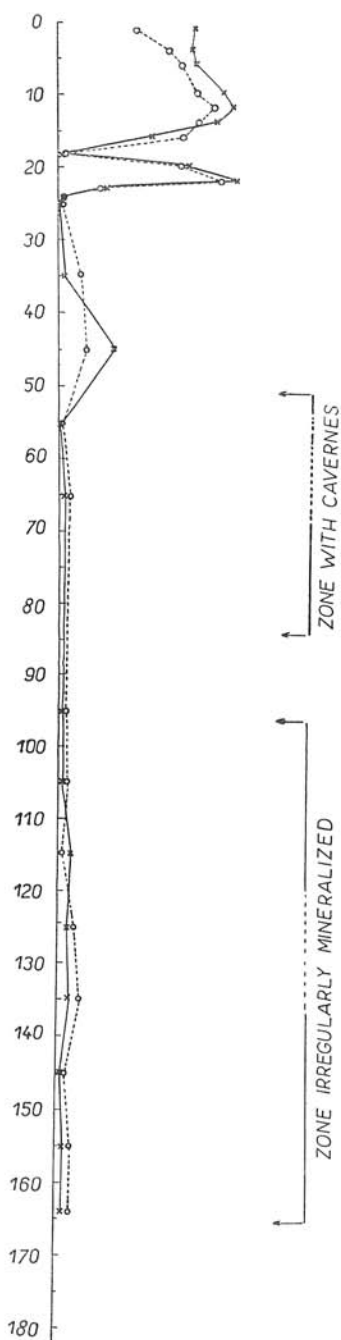
A similar view about the cretaceous age of the mineralization was expressed by J. Kravjanský (l. c.).

In connection with the existence of an extensive acidic volcanism of probably triassic age it is necessary to take into account the possibility of certain genetic relations of the mineralization to this magmatism. J. Losert (1962) admitted for the lead-zinc ores of the dolomitic rhytmities a syngenetic origin. Later (Losert 1963) they were interpreted as a product of selective metasomatism issuing from ascending solutions in fissures, whose country-rocks have also been impregnated by Pb-Zn-ores and replaced by steep irregular bodies of Fe-dolomites to ankerites.



x = 240-260°C
o = 320-340°C

Textfig. 6. Poniky—Drienok D—5.



x = 240-260°C
o = 320-340°C

Textfig. 7. Poniky—Drienok D—20.

As to the age of the mineralization the following possibilities exist:

a) All ore-types originated by hydrothermal metasomatic processes during the cretaceous metallogenetic epoch.

b) Similar origin but of young-tertiary age.

c) Syngenetic origin (dolomitic rhytmities) with a latter mobilisation or addition into epigenetic vein-shaped or metasomatic bodies.

At the Geologic Institute D. Štúr we have massspectrometrically analysed (M. Rybár) the lead of galena from typical epigenetic veinlets from the pit (N of Drienok).

The isotopic constitution of this sample:

204	206	207	208
1,360	24,98	21,29	52,37
1,000	18,37	15,65	38,51
5,444	100,00	85,20	209,62

For the prevailing young-tertiary ore-deposits of the Alpine-Carpathian system the isotopic composition of lead varies (J. Kantor — M. Rybár 1964):

204	206	207	208
1,326—1,350	25,15—25,42	20,98—21,19	52,04— 52,53
1,000	18,77—19,05	15,70—15,90	38,56— 39,49
5,250—5,333	100,00	82,96—83,97	204,72—209,40

The lead-zinc deposits of the East Alpine Triassic occurring in limestones („Wetterstein“-type) are according to Grögler — Grünenfelder — Schroll (1961) characterised as follows:

204	206	207	208
1,338—1,354	24,79—24,96	21,21—21,35	52,48— 52,66
1,000	18,38—18,60	15,68—15,88	38,78— 39,37
5,376—5,441	100,00	85,05—85,59	210,27—212,47

The isotopic constitution of lead in epigenetic veinlets of the Poniky deposit shows in many respects similarities to lead mineralizations occurring in analogous stratigraphic positions in the East Alpine Triassic. But it is markedly different from deposits of unequivocally proved tertiary age. The scattering is partly only apparent as it concerns galenas analysed by different methods and in different laboratories.

The lead-zinc mineralization in the middle triassic carbonates at Poniky can't have genetic relations to the young-tertiary metallogenesis even though it is situated in proximity of the important neogene volcanic center of the Poľana Mt. and bears certain features not observed in other deposits in the West Carpathian Triassic. It is Pre-Tertiary as evidenced by isotope ratios of lead.

It seems probable that deposits of this type (those of the East Alps included) could have been formed only between the Middle Triassic and Upper Cretaceous. The isotopic constitution of their leads is similar to undoubtedly variscian deposits of West Europe and would therefore not be in a strong contradiction with a primary triassic age of the mineralizations. This would also explain the limitation of the main ore-bodies prevailing to middle-triassic carbonate rocks, whilst they are almost in lacking higher laying carbonate horizons.

On the other hand the prevailing part of the epigenetic ores — so often observed in the Triassic — couldn't have been introduced before the Upper Cretaceous.

Whether hydrothermal, primarily epigenetic or remobilised mineralization — a problem much discussed by investigators of the East Alpine metallogenetic province.

If a juvenile origin and upper cretaceous to lower tertiary age of the mineralization is admitted then the isotopic constitution of the leads in these deposits is characterised by a pattern designated by Houtermans as anomaly of the Bleiberg- (B-) type. The reasons for this „anomaly“ aren't yet well understood as investigations in this respect are still too scarce.

Further detailed studies regarding geology, mineralogy, geochemistry, the mutual relations between different types of Pb-Zn mineralizations in triassic carbonates are needed.

Isotop investigations of lead are still also very restricted and unsystematic. Entirely lacking are data about the isotope ratios of trace-lead in sedimentary carbonates and eruptives as well as those from well dated pre-tertiary deposits. No less important are sulphur isotope ratios. A throughout study by all this methods would certainly result in a reliable genetic interpretation of these ore-deposits.

Investigations hitherto carried out have demonstrated the usefulness of thermoluminescence in the splitting of carbonate sequences into smaller units in subsurface correlation provided systematically close sampled material from sufficient large sections is available.

An unusually low to lacking thermoluminescence is characteristic for the studied carbonates of the ore-bodies and their immediate surroundings. This property can be used as criterion in the prospecting for lead-zinc ores in the Poniky ore-field. A pre-tertiary age of the ore-deposit follows from lead isotope studies.

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Review by B. Campbell.