Luminescent geochemical anomalies in the lithosphere and haloes of ore bodies

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ABSTRACT. — Haloes of luminescent minerals around kimberlite pipes, emerald-bearing bodies in metasomatites, gold-bearing bodies, mica pegmatite veins and mountain crystal veins were first revealed and studied. They are special cases of luminescent geochemical anomalies which occur in those parts of the Earth's crust where considerable interaction of rocks and abyssal fluids took place. The fluids leached trace elements, including the luminogenous transition metals of $3d^-$, $4f$ and some other groups from the country rocks, and then accumulated and deposited them. Accumulations of Mn, REE, U and other luminogenous elements form glow centers in secondary minerals. Outcrops of photoluminescent calcite, apatite, zircon, fluorite, cerussite, chlorargyrite and uranyl minerals in altered rocks may serve as indicators of mineral deposits. Photoluminescent grains of apatite having a violet-blue glow (Ce^{3+}, Eu^{2+}) detected by sand analysis, allow mapping of secondary mechanical haloes (scattering), helpful in searching for kimberlite pipes.

Luminescence spectra of pathfinder minerals from the haloes are also presented, with the luminescent tracer elements identified in them.

RIASSUNTO. — Sono stati registrati e studiati gli aloni di minerali luminescenti presenti nei *pipe* kimberlitici, nei corpi contenenti smeraldi nelle metasomatiti, in quelle delle masse aurifere e nelle vene pegmatitiche micacee. Questi rappresentano casi particoli di anomalie geochimiche luminescenti presenti nelle porzioni della Crosta terreste nelel quali si attuano interazioni tra rocce e fluidi di origine profonda. Tali fuidi lisciviano, accumulano e depositano, prelevandoli dalle rocce ospiti, alcuni elementi in tracci inclusi i metalli a transizione luminescente $3d^-$, $4f$ e alcuni di altri gruppi.

L'accumulo di Mn, Terre rare, U e di altri elementi luminescenti forma centri di emissione nei minerali secondari. Gli affioramenti di calcite, apatite, zircone, fluorite, cerussite, clorargirite e minerali uraniferi nelle rocce alterare funziona da indicatore di depositi minerari.

I grani fotoluminescenti di apatite, che emettono bande blu-violetto (Ce^{3+}, Eu^{2+}) rilevate sulle analisi di sabbie, consentono la mappatura di aloni secondari meccanici (dispersione) utili nella ricerca dei *pipe* kimberlitici.

Sono anche illustrati spettri di luminescenza di alcuni minerali guida precisando il tipo di elemento che funge da tracciante.

KEY WORDS: *luminescence, mineral, geochemical anomaly.*

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INTRODUCTION

The emission of light excited in minerals by incidental ultra-violet (UV) radiation, known as photoluminescence (PL), is a resonance optic process different from non-resonance recombination processes such as cathodo-, X-ray- or thermo-luminescence. In the history of science, the luminescence effect was first described in 1602 by the Italian alchemist, Vincencio Casciarolla, from Bologna. He noticed an enigmatic red glow when barite was annealed with carbon after having been exposed to sunlight. Such mineral substances were called phosphors (i.e., carrying light, although phosphorus as a chemical element was unknown at that time).

Only 250 years later, in 1852, Stokes proved that the blue emission of fluorite excited by UV light had a longer wavelength and was not diffused light; he called it fluorescence, after fluorite (quoted in Pringsheim and Vogel, 1946, Pringsheim, 1949, and other works). In 1889, Wiedemann introduced the term *luminescence*, from the Latin «lumen = light + escence» (cf. ibidem). The first luminescent spectra of minerals were registered and correctly interpreted as early as in the second half of the 19th century. In 1859, Becquerel realized that the orange-red glow of calcite was related to a Mn activator (Becquerel, 1867, also quoted in Nichols *et al.*, 1928). The cathodoluminescent spectral lines of REE impurities in fluorite (Sm, Eu, Dy, Gd) were described by Urbain (1909). In 1918-1919, the PL spectra of uranium minerals (schröekingerite, autunite, and some others) were deciphered by Nichols and Howes, and the equidistant spectral lines were attributed to the uranyl ion (quoted in Nichols *et al.*, 1928).

In the 1920s, Lenard and colleagues synthesized solid luminescent materials doped with various impurities, and introduced the terms «center of luminescence» or «glow center» and «crystallophosphor» or «phosphor» (Lenard *et al.*, 1928). The most important group of phosphors was ZnS activated by Cu, Ag, Al, and other impurities.

Comparisons with synthetic pure and doped phosphors showed that WO_4^{2-} complexes were responsible for blue luminescence in scheelite and MoO_4^{2-} complexes for yellow luminescence in powellite (Tiede and Schleede, 1923; Schleede and Tsao, 1929, quoted in Pringsheim and Vogel, 1946).

R-lines of Cr^{3+} were identified in luminescent spectra of ruby, spinel, alexandrite and topaz (Deutschbein, 1932; Tiede and Lueder, 1933, quoted in Pringsheim and Vogel, 1946).

Mn^{2+} was found to show green luminescence in willemite by Leverenz and Seitz, 1939 (quoted in Leverenz, 1950).

Several REE^{2+} were first found to be responsible for broad bands in the PL spectra of some minerals. The blue glow of Eu^{2+}, red glow of Sm^{2+} and green glow of Yb^{2+} were observed in fluorite, and the blue glow of Eu^{2+} in plagioclase by Haberland *et al.* (1934, 1939). We quote these pioneering studies because they have often been ignored in recent literature. Detailed references and exhaustive historical information may be found in Pringsheim and Vogel (1946) and in the more modern work «Cathodoluminescence in Geosciences» (eds. Pagel *et al.*, 2000).

Starting from the 1960s, systematic spectroscopic studies of luminescence resulted in the identification of glow centers in as many as 280 minerals (Tarashchan, 1978; Gorobets, 1981; Götze, 2000; Gorobets and Rogozhin, 2001). In particular, centers of violet and blue (Ce^{3+}, Eu^{2+}), yellow (Mn^{2+}, Dy^{3+}) and pink (Sm^{3+}, Sm^{2+}) luminescence were identified in apatite (Gorobets, 1968; Portnov and Gorobets, 1969; Tarashchan, 1978; Marfunin, 1979). The violet glow of Eu^{2+} in microcline was described (Moroshkin *et al.*, 1987), the red glow of Fe^{3+} was described in microcline, orthoclase (adular) and plagioclases (albite, oligoclase) (Geake *et al.*, 1973; Tarashchan, 1978), and R-lines of Cr^{3+} were established in the PL spectra of some plagioclases (Bakhtin and Moroshkin, 1986).

The PL spectra of uranyl, UO_2^{2+}, which forms many secondary uranium minerals, were

studied in detail (Gorobets and Sidorenko, 1974). It was found that some classes of uranyl minerals (hydroxides, molybdates, silicates, vanadates) showed bright green to orange luminescence only after cooling. The PL spectra of chalcedony, opal, allophane, calcite, barite and zircon, which adsorb uranyl impurities, were obtained and interpreted (Sidorenko *et al.*, 1986).

The bluish-green PL of chlorargyrite and bromargyrite was discovered, their main centers presumably being donor-acceptor pairs of silver and halide vacancies (Gaft, 1993).

Luminescent elements are not yet reliably identified in zircon and cerussite. The broad band in the PL spectrum of zircon is not elementary (Gaft, 1993). Some lines belong to Dy^{3+} (Trofimov, 1962; Götze, 2000) and the diffused component is presumably due to radiation defects (Votiakov *et al.*, 1993). There are no adequate data concerning the origin of the broad yellow band in the PL spectra of cerussite.

The general picture of the luminescent mineral set is as follows.

The PL of a few minerals is defined by their intrinsic elements: Mn^{2+} ions, oxy-complexes of uranium, tungsten, molybdenum and titanium form luminescence centers in many «title» minerals of their corresponding metals. In such complexes, the optic electron transitions between oxygen and metal orbitals are not quenched by electron-phonon interaction with the crystal lattice. Much more often, the PL of minerals is caused by the presence of transition metal cations, in minor or trace amounts, substituting for lattice cations of similar ionic size. The main luminescent elements are: $3d$ ions of the iron group: Mn^{2+}, Fe^{3+}, Cr^{3+}, Ti^{4+}, and Ag^+ of the noble metal group; $4f$ rare-earth elements (REE): Ce^{3+}, Sm^{2+}, Sm^{3+}, Eu^{2+}, Eu^{3+}, Dy^{3+}, Yb^{2+}, Yb^{3+}, etc. They form luminescence centers which can absorb and emit light owing to electron transitions: $3d$-$3d$ in Mn^{2+}, Cr^{3+}, Fe^{3+}, etc.; $4f$-$4f$ in REE^{3+}; $4f$-$5d$ in Ce^{3+}, Eu^{2+}, Sm^{2+}, Yb^{2+} (Tarashchan, 1978; Marfunin, 1979; Walker, 1985; Waychunas, 1988; Gorobets and Walker,

1994). Mn^{2+} substitutes for Mg^{2+} and Ca^{2+} in many magnesian and calcian minerals, and REE^{3+} and REE^{2+} substitute for Ca^{2+} in many calcian minerals. Cr^{3+} substitutes for Al^{3+} in oxygen octahedra (e.g. in ruby and spinel), Fe^{3+} substitutes for Al^{3+} and Si^{4+} in tetrahedra in aluminosilicates, and so on. The systematization of luminescent minerals based on their crystal chemistry has been carried out (Gorobets *et al.*, 1995). The «Luminescence spectra of minerals» Reference Book (Gorobets and Rogozhin, 2001) includes the PL, X-ray- and cathodoluminescence spectra of more than 280 minerals, and the majority of spectral lines are ascribed to certain luminescent elements.

A number of practical applications have been developed on the basis of luminescence center identification in minerals. Exploration targets were uranium (de Neufville *et al.*, 1981; Sidorenko *et al.*, 1986), molybdenum, tungsten, lead, zinc (Seigal and Robbins, 1985), tin (Gaft *et al.*, 1988), lithium, beryllium, etc. (Bakhtin and Gorobets, 1992). Some of these methods involve remote-sensing techniques based on lidars with powerful UV lasers. In mineral processing, techniques using PL and X-ray luminescence are being developed (Gorobets *et al.*, 1997).

In the present work, haloes of photoluminescent minerals around various types of ore deposits were first revealed and studied. The aims of this paper were: (1) to represent the PL spectra of key minerals forming luminescent geochemical anomalies (LGA), especially luminescent haloes (LH) around ore bodies; (2) to summarize the main types of LGA; (3) to distinguish specific LH types in the deposits of diamond, gold, ruby, emerald, mountain crystal, etc. and to provide a first approximation of their monomeric models.

EXPERIMENTAL TECHNIQUES

First, reference specimens of all key luminescent minerals were selected from other geologic objects in order to register their PL spectra and identify the main spectral lines

corresponding to certain luminescent elements. The minerals in question are apatite, zircon, calcite, fluorite, microcline, plagioclase, scheelite, ruby, opal, chalcedony, allophane, chlorbromargyrite, autunite and cerussite. Monomineral grains ranged from 0.1 to a few millimeters in size. PL was excited by UV light (220 – 400 nm) from a mercury lamp or a UV laser (337 nm), usually, at 300K. Emission spectra (Figs. 1-2) were registered over a spectral range of 400-750 nm with the help of grating monochromators (types MDR-2 and MDR-23, Leningrad Optical Mechanical Factory, LOMO), combined with a FEU-106 photomultiplier.

Luminescent haloes were sought by means of examination of luminescent minerals in pieces of cores from exploratory holes, rock samples, and direct observation of tunnel walls. The sampling interval was usually 10 meters. Occasionally, a more detailed check was carried out, reducing the interval to 3-5 meters. Cores from nearly 200 holes of depths of about 300 meters were examined during mapping of haloes around kimberlite pipes. The boring network was 100×100 meters and the total length of cores was nearly 60 kilometers. Thus, about 6 thousand points were sampled within the kimberlite field.

The number of sampling points in the haloes of other mineral deposits described in this paper totalled nearly 4000: about 2000 points in cores, 1000 points as rock pieces, and 1000 points in tunnel walls of deposits.

Thus, the halo models mapped below are based on nearly 10 thousand points. About 30% of them showed very low PL intensity, approaching the background level. About 50% of all samples surpassed the background level by a factor of 2-3, and about 20%, by 10 or even more. The latter samples represented the peak zones of the LH of ore deposits.

The PL level was evaluated from the area concentration calculated as an average of the number of luminescent grains per 1 cm² of rock samples examined by UV. The great diversity and heterogeneity of substances and the morphology of geologic objects depending on

type and individual features of ore deposits, and of rock and mineral samples from these deposits, severely complicated data processing. Unlike chemical fluorescence analysis, the *mineralogical luminescence analysis* used in this work deals with material not chemically prepared for experiments. Moreover, the rock specimens observed under UV light were rough, broken and irregular. Their characteristic size varied from 2-3 to 8-12 centimeters. The luminescent grains on the surface of rock pieces, which served as identity elements and units of measurement (of PL level), were of different sizes and often had various hues of glow (for a single mineral). Luminescent grains in cores from the contact zone of kimberlite pipes were tiny, ~ 0.1 mm in size. Mineral grains in samples from pegmatite and hydrothermal veins were larger than 1 mm. Thus, results were based on observations carried out at the level of approximate mass analysis.

The signal-to-noise ratio of the area concentration of luminescent grains in LH and in background country rocks was evaluated for each mineral observed in the halo. The numerator of the ratio is the value of area concentration of PL mineral grains taken at a certain distance from the border of the ore body, this value being calculated as an average for a narrow interval (up to 10 meters). The denominator of the ratio is related to the background value, measured sufficiently far from the ore body and characteristic of unaltered country rocks. Isolines were drawn on the basis of these mass measurements and show the PL level for each luminescent element in each mineral. Smoothed curves representing the profile models of the haloes were also plotted (see below; Figs. 3, 4).

RESULTS AND DISCUSSION

PL spectra of minerals

The typical PL spectra of minerals forming luminescent haloes of various types are shown in Figures 1-2. Identification of luminescent
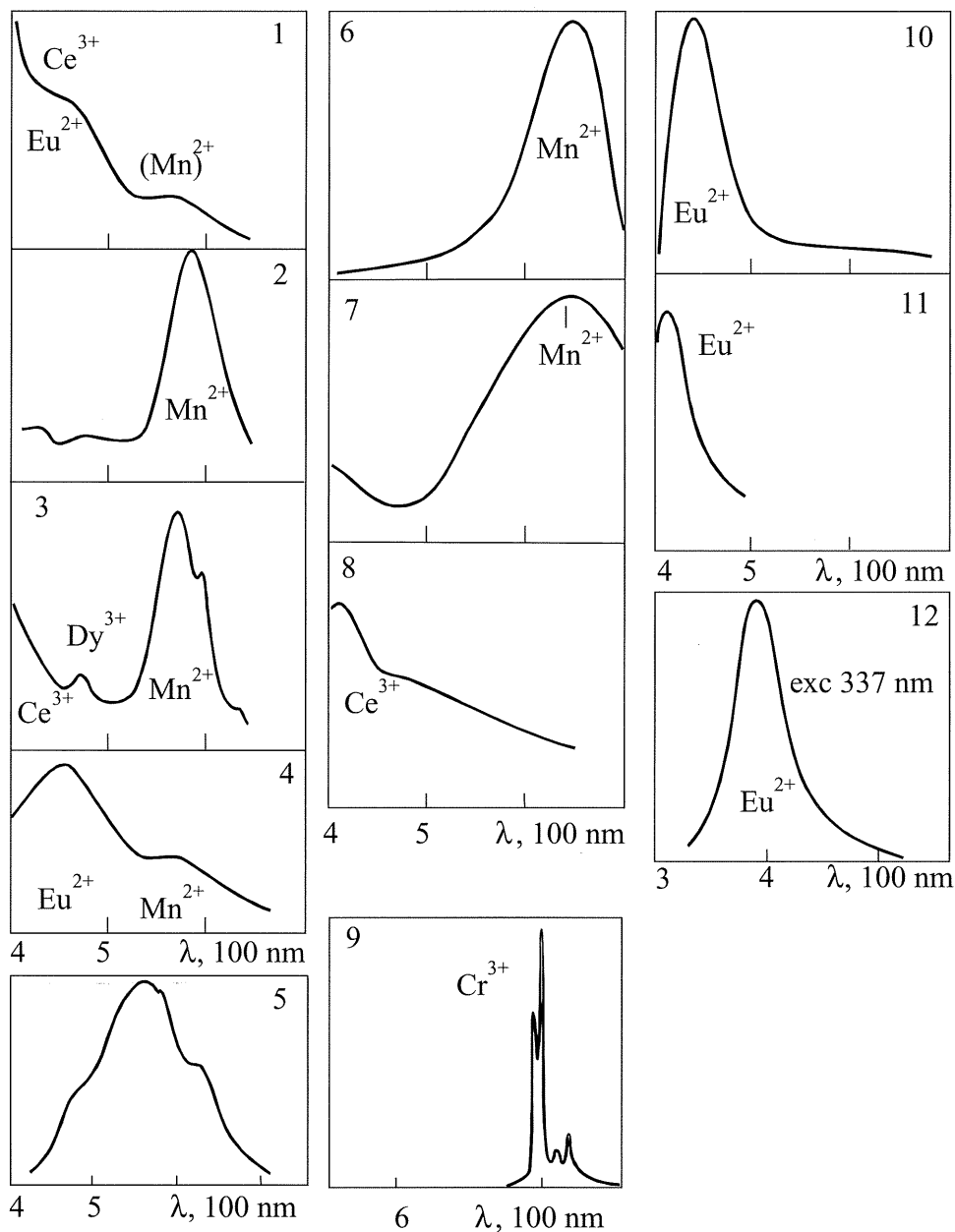
Fig. 1 – PL spectra of main luminescent minerals in the haloes: apatite with (1) bluish-violet PL kimberlite, (2) yellow and (3) pinkish glow, Emerald Mines, the Urals and (4) blue glow, mountain crystal vein Dodo, the Polar Urals; zircon (5) with yellow glow (from kimberlite pipe and from its luminescent halo) Yakutia, Russia; calcite with (6) orange, (7) pinkish and (8) bluish-violet glow, Snejnoye, skarn, the East Pamirs, Tadjikistan; ruby (9) with red glow from the Snejnoye the East Pamirs, Tadjikistan; fluorite (10) with violet-blue glow from a gold-quartz vein, Darasun, Transbaikal region (Asian part of Russia); plagioclase (11) with violet-blue glow and microcline (12) with violet glow, both from a mica pegmatite vein, Mama, Eastern Siberia, Russia.
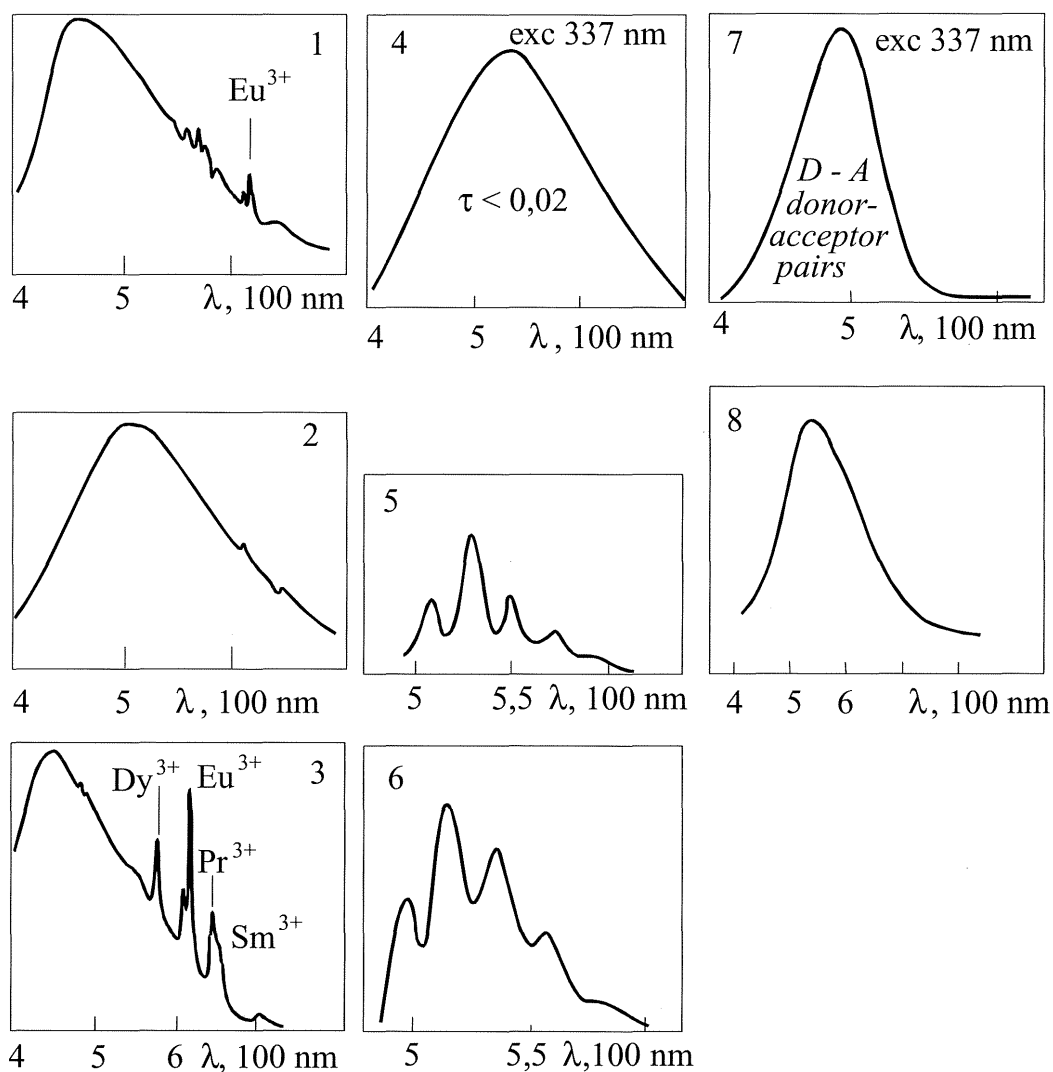
Fig. 2 – Scheelite: (1) with blue glow from greisen, Boyovka, Urals, Russia (0,01% MoO_3); (2) molybdoscheelite with yellow-white glow from skarn-greisen type deposits, Vostok-II, Far Eastern Russia (0,2% MoO_3); (3) scheelite with reddish hue of glow from a gold-bearing quartz vein, Berezovskoyie, Urals, Russia (up to 0,01% Eu_2O_3); quartz (4) with whitish-blue glow of organic impurities from a montain crystal vein, Dodo, Northern Urals, Russia; autunite (5) with green PL from an oxidation zone, Streltsovka, Eastern Siberia, Russia; chalcedony, opal, allophane (6) with green glow: PL spectra of UO_2^{2+} are essentially identical in all specimens of these minerals; chlorbromargyrite (7) with green glow under UV-laser light, Kasmanachi, Kizil-Kum, Uzbekistan (all specimens from oxidation zones of silver and silver-and-gold deposits showed similar PL); cerussite (8) with whitish-yellow PL from oxidation zone of a gold-bearing quartz vein, Kok-Bulak, Uzbekistan.

centers was carried out with the help of previous data obtained by our group and works by the authors mentioned in the Introduction.

Luminescent geochemical anomalies (LGA)

For a mineral to become luminescent (in this context, PL), the following three conditions must be met simultaneously: (1) the appropriate type of crystal lattice must favour the formation of intrinsic or impurity emission centers (this condition is commonly satisfied in dielectrics and more rarely in semiconductors); (2) a sufficient percentage of PL centers (usually > 0.01%) must be available; (3) small numbers of quenching centers, primarily of iron (less than 0.5 – 1.0%) must be available.

The bulk of the lithosphere is non-luminescent, because the petrogenic cations of Si, Al, Ca, Mg, K and Na are not transition elements. Their ions have no levels for intrinsic optical electron transitions in the crystal lattice of minerals. Fe is the only transition petrogenic element. Fe^{2+} is the most important quenching element because of the peculiar structure of its electron levels. Fe^{3+} can luminesce in silicates and aluminosilicates only if its content is lower than ~1%; concentration quenching starts if it is higher. The average abundance of other luminescent elements in the Earth's crust is about $10^{-3} - 10^{-6}$%, which is much lower than their limiting sensitivities (~ $10^{-3} - 10^{-1}$%). So the key rock-forming minerals, feldspars, quartz, calcite and dolomite, show no PL in background rocks such as basalt, granite and sedimentary «layers» (they may show recombination luminescence, which is not dealt with here).

The situation changes dramatically in some localized areas in the lithosphere where strong interaction of abyssal fluids and hydrothermal solutions with background rocks took place. The fluids leached rare elements, including luminogenous metals, from country rocks, accumulated and deposited them.

The two main physico-chemical factors of this process are the acid-base properties and redox potential of fluids percolating through country rocks. Unlike rocks, fluids can easily change their physico-chemical parameters while ascending to the surface. The temperature and pressure of fluids decreases, together with their basicity-acidity and redox potential. On the way from the Earth's mantle to the surface, polyvalent luminescent elements reach the peaks of their activity in fluids roughly in the following sequence: N, Cr^{3+}, Ce^{3+}, Eu^{2+}, Yb^{2+}, Mn^{2+}, Fe^{3+}, Dy^{3+}, W^{6+}, Mo^{6+}, U^{6+} and Ag^+. At the same time, hydrothermal and metasomatic processes cause iron separation and formation of its own mineral phases: sulfides, oxides, and hydroxides. These two factors result in crystallization and recrystallization of many secondary and vein luminescent minerals: calcite, apatite, fluorite, plagioclase, zircon, etc.. Ascending through fractures and faults in the Earth's crust, fluids deposit rare elements in zones of lower temperature and pressure, forming ore deposits of well-known types: kimberlite, carbonatite, nepheline syenite, pegmatite, skarn, greisen, hydrothermal veins and their derivatives. In such a way, LGA accompanying ore deposits are formed. For instance, N (in diamond), Cr^{3+} (in plagioclase, ruby, spinel), Eu^{2+} and Ce^{3+} (in plagioclase, apatite, barite, etc.) are luminescent elements accompanying deep-derived rocks related to mantle sources, whereas Dy^{3+}, Eu^{3+}, Fe^{3+}, and W^{6+} trace granite magma sources. Near the Earth's surface, the environment is strongly acidic and oxidizing owing to the nitrogen and oxygen in the atmosphere. Hence, luminescent minerals composed of ions of the highest valencies, U^{6+}, Ag^+, Mo^{6+}, V^{5+} and Cr^{6+}, occur in hypergene and sedimentary minerals: uranyl minerals, opal and chalcedony, chlor- and bromargyrite, powellite, vanadinite, crockoite, etc.. Carbonyl, carboxyl and cyclic organic molecules take an active part in the formation of luminescent centers in calcite, dolomite and rare carbonate minerals, cerussite and hydrozincite.

Systematization of the LGA is given in the Table. It was obtained from experimental data, which included some thousand samples of dozens of PL minerals from different types of LGA.

TABLE 1

Systematization of luminescent geochemical anomalies (LGA) in the lithosphere with the help of specific sets of the luminescent elements (in brackets) in minerals.

1	2	3		4
Type of LGA	Subtype of LGA	Geological objects		Key PL minerals and luminescent elements
SUPER-FICIAL	Biogenous Chemogenous	Bogs and other superficial bodies of bio-organic substances		Inanimate bio-organic substances (*ST*)*
Main lumi-nescent molecules and elements		Bituminous limestone, shale		Oils, bitumen (*ST*)*; carbonates, sulphates (*ST*)
singlet-triplet organic molecules		Salt marsh		Chemogenous organic substances, halides, carbonates, sulphates
carbonyl-containing organic molecules	Zones of oxidation of ore deposits: U^{6+}, Mo^{6+}, V^{5+}, Cr^{6+}, Ag^+.	Uranium deposits		Uranyl and vanadyl minerals (UO_2^{2+}, VO_4^{3-}); chalcedony, opal, allophane, kaolin, calcite, barite (UO_2^{2+}- adsorp.)
cations: U^{6+}, Mo^{6+}, V^{5+}, Cr^{6+}, Ag^+		Polymetallic deposits		Chlorargyrite (Ag^+, Cl^- - vacancies); hydrozincite, cerussite, anglesite, smithsonite, calcite, barite («CO»); willemite (Mn^{2+})
	Eluvium placer subtype: W^{6+}, Mo^{6+}, U^{6+}, Mn^{2+}, Ce^{3+}, Eu^{2+}, N.	Source material	Greisens, high-temperature hydrothermal deposits	Powellite, wulfenite (MoO_4^{2-}); crocoite (CrO_4^{2-}); opal (UO_2^{2-})
			Greisen, albite	Zircon (radiation defects RD)**, scheelite (WO_4^{2-}, MoO_4^{2-}), cassiterite (?), apatite (Mn^{2+})
			Carbonatite	Calcite (Mn^{2+}), apatite (Ce^{3+}, Eu^{2+}), zircon, baddeleyite (RD**, Ti^{4+}, REE^{3+})
			Kimberlite	Diamond (N), apatite (Ce^{3+}), zircon (RD)**

Table 1: CONTINUED

1	2	3	4
ABYSSAL Main luminescent elements: W^{6+}, Mo^{6+}, Dy^{3+}, Yb^{2+}, Sn^{2+}, Mn^{2+}, Eu^{2+}, Eu^{3+}, Sm^{3+}, Sm^{2+}, Ce^{3+}, Ti^{4+}, Cr^{3+}, S_2^-, N	Crust subtype W^{6+}, Mo^{6+}, Eu^{3+}, Eu^{2+}, Dy^{3+}, Sm^{3+}, Sm^{2+}, Yb^{2+}, Mn^{2+}.	Au-hydrothermal, poor sulphide deposits	Calcite (Mn^{2+}), scheelite (WO_4^{2-}, MoO_4^{2-}, Eu^{3+})
		Hydrothermal, polymetallic, Au-Ag, rare metal deposits	Calcite (Mn^{2+}), fluorite (Eu^{2+}, Yb^{2+}, Sm^{2+}), barite
		Skarns	Calcite (Mn^{2+}), scheelite (WO_4^{2-}, MoO_4^{2-}), scapolite (Mn^{2+}, S_2^-) datolite and danburite (Ce^{3+}, Eu^{2+}, Yb^{2+}), wollastonite (Mn^{2+}), fluorite (Eu^{2+}, Yb^{2+})
		Greisens, albitites	Fluorite (Eu^{2+}), scheelite (WO_4^{2-}, REE^{3+}), apatite (Mn^{2+}, Dy^{3+}), cassiterite (?)
		Rare metal pegmatites	Apatite (Dy^{3+}, Mn^{2+}), spodumene (Mn^{2+})
		Muscovite pegmatites	Plagioclase and microcline (Eu^{2+})
	«Mantle» subtype Cr^{3+}, Ce^{3+}, Eu^{2+}, Ti^{3+}, Ti^{4+}, S_2^-, N	Nepheline syenites	Apatite (Ce^{3+}, Eu^{2+}, Sm^{3+}, Mn^{2+}), sodalite (S_2^-), (Ti, Zr)-silicates (Ti^{4+})
		Carbonatites	Calcite (Mn^{2+}), apatite (Ce^{3+}, Eu^{2+}), baddeleyite and zircon (Ti^{4+}, RD**)
		Kimberlites	Diamond (N), apatite (Ce^{3+}), zircon (RD**)

* *ST* means singlet-triplet molecules.
** RD means radiation defects.

Although LGA represent potential ore objects, most of them have no commercial value.

Luminescent effects around ore bodies were observed in their contact zones in the form of haloes.

Haloes of luminescent minerals in and around ore bodies

Luminescent haloes were discovered and mapped in the following mineral deposits (Figs. 3, 4).

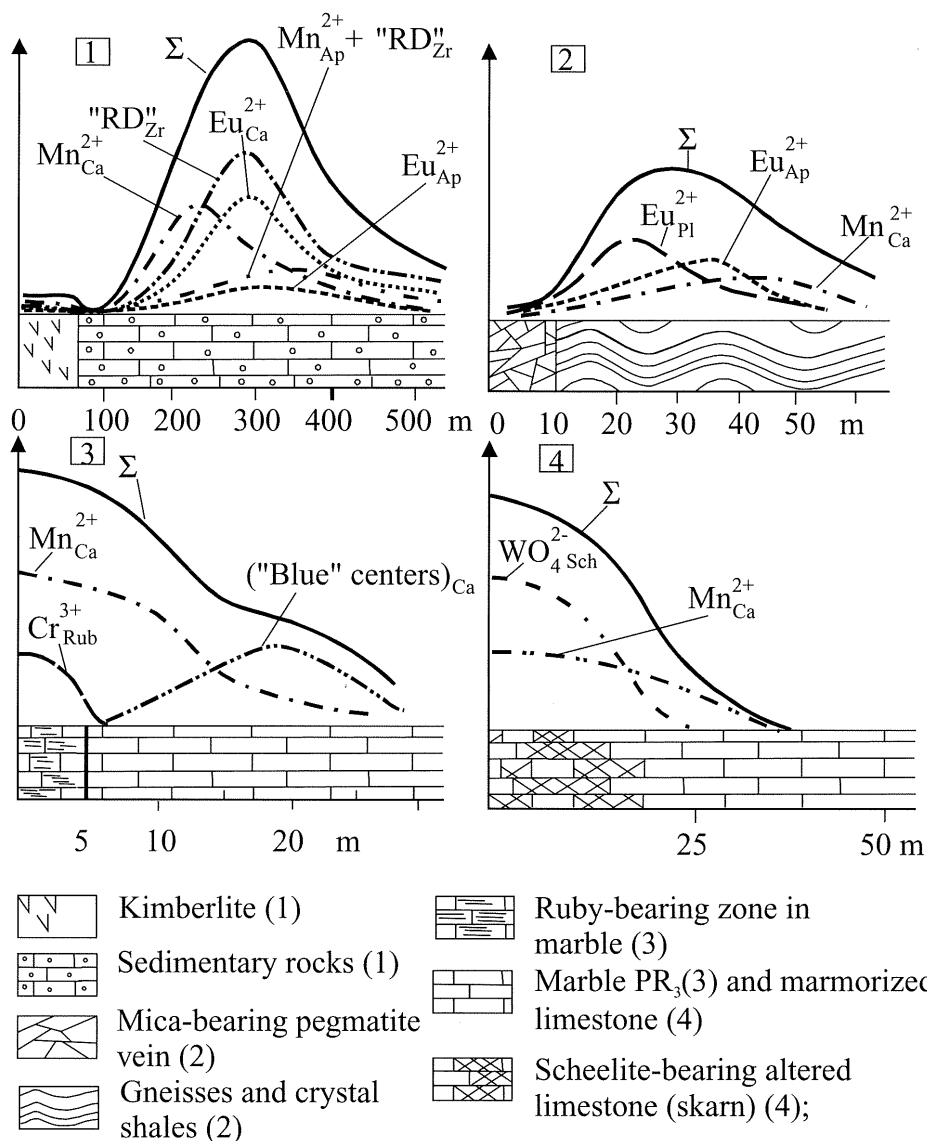*Haloes of kimberlite pipes* (Fig. 3 (1)). Sharp

Fig. 3 – Schematics of photoluminescent haloes in:
1 - contact zone of a kimberlite pipe; 2 - contact zone of mica-bearing pegmatite vein; 3 - ruby-bearing skarn; 4 - scheelite-bearing skarn. (Ca – calcite, Zr – zircon; Ap – apatite; Rub – ruby; Sch – scheelite; Pl – plagioclase; Fl –fluorite; Cer – cerussite).

discontinuous contact zones of pipes always surprised explorers. The PL characteristics of calcite, apatite, zircon and scarcer barite and fluorite show the considerable influence of kimberlite on their country rocks: LH stretch up to some hundred meters and even to 1-1.5 km outside kimberlite borders. The kimberlite pipes of the Arkhangelsk (Northern European
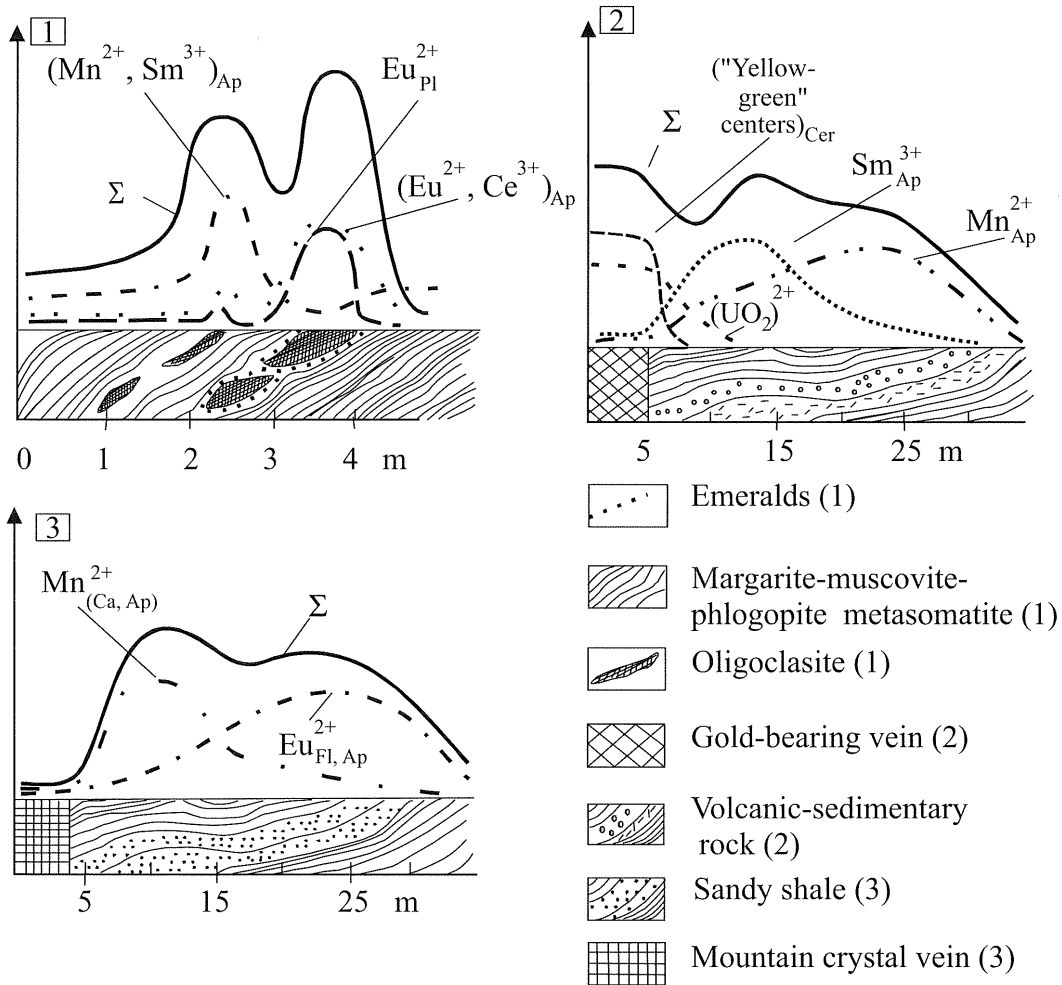
Fig. 4 – Outlines of photoluminescent haloes in: 1 - emerald-bearing metasomatic bodies; 2 - gold-bearing ore bodies; 3 - mountain crystal vein. (Ca – calcite, Zr – zircon; Ap – apatite; Rub – ruby; Sch – scheelite; Pl – plagioclase; Fl –fluorite; Cer – cerussite).

part of Russia) and Mirniy (Yakutia, Russia) ore fields have been studied. The LH in both regions consist of: (1) PL mineral zone, 20-50 m thick; (2) zone of concentration of PL minerals, over an interval of 50-400 m; (3) zone of decreasing contents of PL minerals, several hundred meters thick, passing into the background rock. The ratios of PL grain concentrations in zones (2) and (3), which express the signal-to-noise ratio, are on average 110/3 for calcite, with generally red PL of Mn^{2+} showing hues from orange-red to pinkish-purple (Fig. 1 (6, 7)), 280/4 for calcite with bluish-violet PL (Fig. 1 (8)), 0.7/0.06 for apatite with yellow PL of Mn^{2+} (Fig. 1 (2)), 1.1/0.02 for apatite with bluish-violet PL of

Ce^{3+} and Eu^{2+} (Fig. 1 (1)), and 2.5/0.02 for zircon with yellow PL (Fig. 1 (5)). Obviously, the enormous masses of country rocks were affected by mantle fluids and recrystallized. At the same time, abyssal elements Zr and P and REE were fixed in a form of zircon, apatite, etc.. Heating favoured Mn^{2+} incorporation into calcite and apatite. Taking into account these LH, it is recommended that the fine-grained sand fraction (<0.25 mm) should be analysed separately from the coarse fraction – in contrast with current practice. The peculiar PL of metasomatic minerals in the fine non-magnetic fraction, apatite (with impurities of Ce^{3+}, Eu^{2+}), barite and zircon, reveal the mechanical dispersion haloes of these minerals around kimberlite pipes.

Haloes around kimberlite-like pipes due to mechanical scattering of minerals were also detected with the aid of sand analysis. Searches were carried out in the Pechora-Timan region (Northern European part of Russia). The aim was to select the most promising local magnetic anomalies from dozens detected during an aerial survey. The key mineral indicator in the sand samples was apatite, showing a weak bluish-violet glow of Ce^{3+} and Eu^{2+}. More than 400 sand samples were examined under a mercury UV lamp. About 10% of them had one to four grains of apatite, of a kind called «mantle» type. In addition, almost all samples contained a great number of zircon grains with bright yellow PL. Some samples also contained apatite grains with yellow PL of «granitoid» type, which were useless for kimberlite exploration. The most informative was the non-magnetic fraction smaller than 0.25 mm. Occurrences of apatite of «mantle» type within haloes surrounding some magnetic anomalies (Fig. 5) significantly increase the probability that a source of mantle fluids is located under them. Since apatite is softer and more susceptible to chemical decomposition than the classic mineral indicators of kimberlites, such as pyrope, picroilmenite and chromspinelides, it may be transported no more than 1-2 kilometers from its original location. Therefore, apatite with

bluish-violet PL may be considered as a new indicator of kimberlites (and other «mantle» rocks) and even more reliable than other mineral indicators.

Boring of anomaly points identified by the aerial survey and fitted to the haloes mapped with the help of sand PL analysis showed that these anomalies were related to pipes and dykes or kimberlite-like rocks of picroporphyrite type. Apatite grains with violet PL were also found in these bodies. This fact confirmed the «mantle» origin of apatite grains in the sand samples.

The new modification of sand analysis described above was successfully applied by us in Yakutia and the Yenisei (Asian part of Russia) ridge during searches for «mantle» rocks.

Haloes of mica pegmatite veins (Fig. 3 (2)). LH up to 20 m thick were mapped in gneisses and micaschists in the deposits of the Mama-Tchuya and Biriussa regions of Eastern Siberia (Asian part of Russia). The main PL minerals in the LH are albite-oligoclase with violet-blue glow and microcline with violet glow of Eu^{2+} (Fig. 5 (2, 3)). This cation is indicative of (K, Na) metasomatism, which promotes country rock recrystallization in a reducing environment.

Haloes in skarn (Fig. 3 (3-4)). LH up to 20 m thick were discovered in the ruby-bearing skarn of the Snejnoye deposit in the East Pamirs, Tadjikistan. The skarn is situated in carbonate terrigenous rock intruded by granitoids and pegmatite. The main PL mineral is calcite. Its glow is red (Mn^{2+}) inside the ore zone and bluish-violet or purple outside it. Ruby shows red PL (Cr^{3+}) (Fig. 4), allowing the detection of tiny ruby grains in sands. The highest level of PL is observed inside ore bodies.

Likewise, scheelite-bearing skarn is characterized by the most intense PL inside ore bodies, owing to the blue glow of WO_4^{2-} in scheelite (Fig. 2 (1)) or the yellow glow of MoO_4^{2-} in molybdoscheelite (Fig. 2 (2)). The red PL of calcite (Mn^{2+}) was observed inside and outside ore bodies forming rather thin LH.
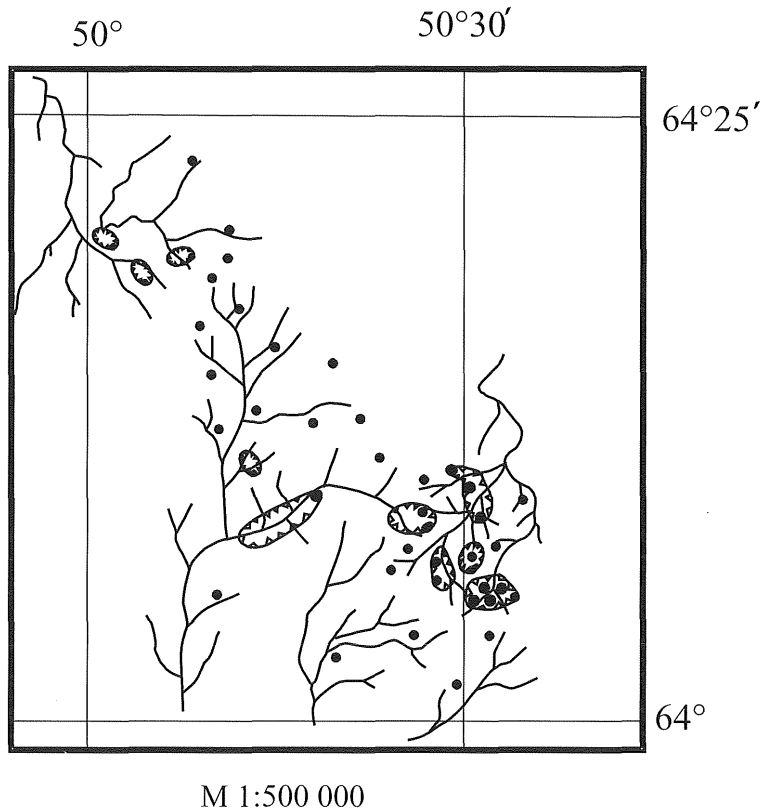
Haloes of emerald-bearing bodies in

Fig. 5 – Scheme of magnetic anomalies (dots) mapped during aerial survey for kimberlite-bearing deposits in Pechora-Timan region (European part of Russia). Areas of dots overlapping occurences of apatite (violet glow) in sands were recommended for subsequent boring.

metasomatites (Emerald Mines, Urals, Russia) (Fig. 4 (1)). Beryllium ore bodies may be subdivided as follows: (1) muscovite-quartz-plagioclase; (2) margarite-plagioclase veins without emerald; vein-disseminated metasomatic zones: (3) poor in emerald, (4) rich in emerald. Apatite outcrops show yellow (Mn^{2+}) (Fig. 1 (2)), pinkish (Mn^{2+}, Ce^{3+}, Eu^{2+}) (Fig. 1 (3)) and bluish-violet (Ce^{3+}, Eu^{2+}) PL; its spectrum is similar to the PL spectrum of apatite from kimberlite (Fig. 1 (1)). The average frequency ratios of the occurrence of grains with yellow-pinkish PL to that with bluish-violet PL are 5.3, 1.8, 1.8, and 1.0 in zones (1)-(4), respectively (Kuprianova and

Moroshkin, 1987). An additional indicator of emerald is plagioclase with violet-blue PL of Eu^{2+} (Fig. 1 (11)). In zones (1) – (3), its outcrops range from a few percent up to 40% of the total surface and in zone (4) it is up to 100%. Since Cr^{3+} forming green centers in beryl is related to mantle fluids, a similar nature may be presumed for Eu^{2+} and Ce^{3+} centers in apatite and plagioclase. Thus, the latter may serve as pathfinder minerals in emerald exploration.

Haloes of gold-bearing ore bodies (Fig. 4 (2)). These were observed in gold-quartz veins (Darasun) and skarn (Andriushkinskoye) in Transbaikalia (Asian part of Russia); black

shales of the Central Kizil-Kum; volcanic rocks of the Kuramin ridge (Kotch-bulak) and the Okhotsk-Chuckchee mountain belt (Karamken, Khakandjia, Dukat, Asian part of Russia); and lower Palaeozoic terrigenous rocks of Central Mongolia (Boro) (Bushev and Portnov, 2000). The LH are related to outcrops of apatite (bluish-violet PL of Ce^{3+} and Eu^{2+}, yellow PL of Mn^{2+}) (Fig. 1 (1, 2)), fluorite (blue PL of Eu^{2+}) (Fig. 1 (10)), calcite (orange-red PL of Mn^{2+}) (Fig. 1 (6)), scheelite (two intense red lines of Eu^{3+} in the background of the blue glow of WO_4^{2-}) (Fig. 2 (1)) and molybdoscheelite (yellow PL of MoO_4^{2-}) (Fig. 2 (2)).

The luminescence of Eu^{3+} in scheelite must be especially mentioned. Narrow red lines at 612 and 616 nm were first observed in the PL spectra of scheelite from quartz veins (Gorobets and Nauczyciel, 1975; Gorobets and Kudina, 1976). They were particularly intense in the PL and XL spectra of scheelite from gold-bearing quartz veins (Fig. 1 (12)) (Gorobets, 1986; Uspenski et al., 1989). Even the visually reddish hue of luminescence of europium impurity in scheelite may be observed. Geochemical studies show that Eu^{3+} in scheelite may serve as an ore guide (e.g., Uspenski et al., 1998).

Sometimes quartz, especially its later varieties, shows whitish-blue PL due to organic impurities. Hypergene minerals such as chlorbromargyrite, uranyl minerals, and opal with uranyl impurities display green PL (sometimes, only at low temperature); cerussite shows bright yellow PL related to unknown impurities. All these minerals are not easily detected without the luminescence method, and contribute much to LH detection.

Haloes of mountain crystal veins (Dodo, Puyva, Northern Urals and Kyshtym, Central Urals, Russia) (Fig. 4 (3)). These LH were traced up to 100 meters along vein directions at thicknesses of up to 40 meters. The main PL minerals are calcite (red glow of Mn^{2+}), apatite (pinkish-yellow PL of Mn^{2+}, Dy^{3+}, Sm^{3+} or bluish-violet PL of Eu^{2+}; the latter spectrum is given in Fig. 1 (4)), adularia, microcline and albite (dull-red PL of Fe^{3+}). The country rocks

are completely free of such PL minerals, whereas their average contents in the contact zone are up to 10-40 grains per 1 cm^2. Quartz, zeolite and kaolinite show bluish-white PL due to organic cyclic impurities. The association of PL minerals in the contact zone depends on the country rocks: calcite prevails in amphibolites, and apatite and fluorite occur in gneisses. The zonal structure of LH was observed: the intense glow of Mn^{2+} in calcite and apatite of the inner zone of LH indicates heating and the relatively more oxidizing and acidic character of hydrothermal solutions forming the veins. Alteration processes in the country rocks were more reducing and less acidic.

CONCLUSIONS

PL centers in minerals are formed of transition elements of $3d$ (metals of the iron group), $4f$ (REE), $5f$ (uranium), and $4d$ and $6d$ groups (molybdenum and tungsten). In geology, they are considered as ore elements. The distribution of luminescent elements in the lithosphere is frequently controlled by ore-forming fluid-hydrothermal processes, mostly by their acid-base properties and redox potential. This is why metasomatic-hydrothermal bodies are usually accompanied by luminescent geochemical anomalies (LGA) consisting of PL calcite, apatite, fluorite, plagioclase, zircon and other vein and ore minerals. Classification of such anomalies has been carried out according to the PL mineral associations occurring in various altered rocks. LGA may sometimes coincide with ore objects, although they frequently have no ore deposits of commercial value.

Haloes of luminescent mineral outcrops have been discovered around ore bodies stretching up to tens and hundreds of meters in hydrothermal and metasomatic deposits of gold, diamond, ruby, emerald, mountain crystal and mica. The haloes are caused by the accumulation of transition luminescent elements (Mn, TR, U, etc.) in calcite, apatite, zircon and other minerals crystallizing in the hydrothermal

process of host rock alteration. They may be used as indicators of diamond, emerald, ruby, mountain crystal, silver, tungsten, molybdenum, uranium, and other ores.

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