

Luminescence of Plagioclases from Rocks of Some Ancient Structural Zones of the European Continent

V. V. Moroshkin

All-Russia Research Institute of Mineral Resources, Staromonetnyi per. 31, Moscow, 119017 Russia

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Abstract—The luminescence of plagioclase was studied for various types of sialic rocks from crystalline shields of the East European Craton and median masses in fold regions of central and western Europe. The variation of luminescence (contributions of various luminogens) bears information on the specific features of the tectonomagmatic and geochemical evolution of particular tectonic units and the geological history of the continental crust of Europe as a whole.

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INTRODUCTION

This publication is a further continuation of a study of luminescent properties of plagioclases in rocks from large, long-lived tectonic units. At the first stage of the investigation, the Fennoscandian (Baltic) Shield—the largest block of the Archean and Paleoproterozoic rocks of Europe—was studied in this respect (Moroshkin and Rassulov, 2004; Moroshkin et al., 2005). Besides the Baltic Shield, the Precambrian crystalline basement outcrops in the Ukrainian Shield, in the Voronezh Antecline, and in a number of median masses in fold regions. The Archean–Paleoproterozoic structural stage is common throughout the continent (*Tectonics...*, 1978a; Sinitsyn, 1990; Rezanov, 2002). After the breakup of Pangea 1600–1000 Ma ago (Sinitsyn, 1990; Kröner, 1982) and origination of the Neoproterozoic–Phanerozoic mobile belts, the shields and median masses of Europe underwent multifold reactivation with the formation of deep faults and rifts, metamorphism and rheomorphism of rocks, volcanism and plutonic magmatism, etc. The involvement of median masses in the sphere of investigation allowed me to expand the chronological range of the studied rocks from the Paleoproterozoic to the Miocene and to diversify the geological settings.

RESEARCH METHODS

More than 220 samples of rocks have been studied with X-ray luminescence spectroscopy (XL) and photoluminescence (PL). As well, several plagioclase grains were selected for measurements of each XL spectrum. The XL spectra were recorded on a device with an IRIS-3M generator, MDR-23 monochromator, PC control, and computer drawing of curves. PL of Eu^{2+} centers was excited by an OI-18M UF illuminator

with visual estimation of intensity (I) of luminescence using a technique applied previously (Moroshkin et al., 2005) and selective recording of spectra.¹ In Tables 1 and 2 the predominant centers of luminescence are underlined, while the centers with low-intensity bands in spectra or sporadic centers are shown in parentheses.

The samples taken from the tectonic units listed below and characterized in Tables 1 and 2 were the objects of this study.²

(1) The Voronezh Massif, or Antecline is, in fact, a marginal part of the Ukrainian Shield (Sinitsyn et al., 1984). The Paleoproterozoic and Mesoproterozoic high-grade metamorphic rocks of the basement of the East European Platform are widespread here (*Litogenesis...*, 1977). Some Archean inliers, e.g., the Kursk Block, were subsequently reactivated and reworked only insignificantly (*Tectonics...*, 1978a).

(2) The Fennoscandian (Baltic) Shield is distinguished by an extremely complex geological structure, development of rock associations of different ages, and intense tectonomagmatic reactivation over vast areas. The reactivation bore a cyclic character and was largely related to Precambrian rifting (Volodichev, 1990; Shcheglov et al., 1993; Rybakov et al., 1999).³

¹ The XL spectra are not presented in this publication, because they are broadly similar to those obtained previously with recording of the same centers ($\text{O}^{2+} + \text{Eu}^{2+}$), Ce^{3+} , Mn^{2+} , and Fe^{3+} and wide variation of I bands in spectra.

² Most samples were taken from the author's collections. Some samples were kindly placed at my disposal by the Geological Museum of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences; the samples from the Voronezh and Rhodope massifs are from the sample depository of the All-Russia Research Institute of Mineral Resources.

³ The previous results on the Baltic Shield used in this paper are supplemented by new data on plagioclases from the basement of greenstone belts, anorthosite and some other plutons.

Table 1. Luminescent properties of plagioclases from rocks in the inliers of the Precambrian basement of the East European Platform

Regional structural units corresponding to the cycles of evolution of the continental crust	Tectonic units, rock complexes, and their location	Rocks, their age, and facies of regional metamorphism	Composition of plagioclase, number of samples	Intensity (<i>I</i>) of Eu ²⁺ bands in PL spectra of plagioclase	Main centers in XL spectra of plagioclase
I. Voronezh Massif (Anteclise)					
Archean Kursk Craton (Block)	Lower structural stage in the region of the Kursk Magnetic Anomaly (Mikhailovka, Belgorod, Vorontsovka areas)	Paleo- and Mesoproterozoic gneisses, migmatites, and granites of the Oboyan Group; amphibolite facies	Oligoclase, 12	Low or absent	$\underline{O}^* + (\underline{Eu}^{2+}), \underline{Fe}^{3+}, (\underline{Mn}^{2+})$
II. Fennoscandian (Baltic) Shield					
Archean cratons and blocks affected by slight and moderate rheomorphism	Relict blocks of the Archean basement (Sweden, NW and NE Ladoga region)	Lopian (Meso- and Neoproterozoic) granitoids and granite gneisses; high amphibolite facies	Oligoclase, andesine, 16	Low or absent	$\underline{O}^* + (\underline{Eu}^{2+}), \underline{Fe}^{3+}, (\underline{Mn}^{2+})$
	Greenstone belts in Kola and Karelian cratons (basement rocks)	Meso- and Neoproterozoic gneisses, granulites of Kola Group in the Central Kola iron-ore zone	Andesine, oligoclase, 22	Very low (predominant) and medium	$\underline{O}^* + (\underline{Eu}^{2+}), \underline{Ce}^{3+}, \underline{Mn}^{2+}, (\underline{Fe}^{3+})$
		Gneisses, including gray gneisses, granites, and granulites of Kola Group and Transimandra iron ore district, Kola Peninsula	Oligoclase, andesine, 14	The same	$\underline{O}^* + (\underline{Eu}^{2+}), \underline{Mn}^{2+}, (\underline{Ce}^{3+}, \underline{Fe}^{3+})$
		Archean–Paleoproterozoic gneisses and migmatites of Gimol and Nyukozero groups in Kostamuksha district	Oligoclase, 6	Low or absent	$\underline{O}^* + (\underline{Eu}^{2+}), \underline{Mn}^{2+}, (\underline{Ce}^{3+}, \underline{Fe}^{3+})$
Kareliides (Neoproterozoic–Paleoproterozoic)	Metamorphic complex of the NE Ladoga region	Paleoproterozoic gneisses and granite gneisses of the Pitkäranta Formation; andalusite–sillimanite subfacies of amphibolite facies	Oligoclase, 9	Medium to high	$\underline{Eu}^{2+} + \underline{O}^*, \underline{Mn}^{2+}$

Table 1. (Contd.)

Regional structural units corresponding to the cycles of evolution of the continental crust	Tectonic units, rock complexes, and their location	Rocks, their age, and facies of regional metamorphism	Composition of plagioclase, number of samples	Intensity (<i>I</i>) of Eu ²⁺ bands in PL spectra of plagioclase	Main centers in XL spectra of plagioclase
	Belomorian–Lapland Mobile Belt (North Karelia)	Archean–Paleoproterozoic gneisses, granite gneisses, and migmatites of Belomorian Group; kyanite–sillimanite subfacies of amphibolite facies	Oligoclase, 32	Medium (predominant) to high	$\frac{\text{Eu}^{2+}}{\text{Fe}^{3+}} + \underline{\text{O}^*}, \text{Mn}^{2+}, \text{Ce}^{3+},$
	Lapland–Kolviitsa Belt, Kola Peninsula	Paleoproterozoic plagioclase–garnet granulites of Lapland Group	Andesine, 3	High	$\frac{\text{Ce}^{3+}}{\text{Fe}^{3+}}, \text{Eu}^{2+} + \underline{\text{O}^*}, \text{Mn}^{2+},$
	Intrusive complex of NW Ladoga region	Neorachean–Paleoproterozoic biotite granites and plagiogranites of the Karlahti and Kamennogorsky deposits	Oligoclase, 16	Medium to high	$\frac{\text{Eu}^{2+}}{\text{Fe}^{3+}} + \underline{\text{O}^*}, \text{Mn}^{2+}, \text{Ce}^{3+},$
Svecofennides (Paleo- and Mesoproterozoic)	South Svecofennian Belt (SE Sweden and SW Finland, margin of Central Finland batholith)	Granites, tonalites, granodiorites, and migmatized gneisses; amphibolite facies	Oligoclase and andesine, 24	From low to high; medium is predominant	$\frac{\text{Eu}^{2+}}{\text{Fe}^{3+}} + \underline{\text{O}^*}, \text{Mn}^{2+}, \text{Ce}^{3+},$
Ripheides (Early Riphean)	Gabbro–anorthosite–rapakivi–granite association (complex)	Rapakivi granite of Salmi and Vyborg plutons, labradorites of SE Finland	Oligoclase, 10 and labradorite, 6	Low (predominant) to medium	$\frac{\text{Mn}^{2+}}{\text{Fe}^{3+}}, \text{Eu}^{2+} + \underline{\text{O}^*}, \text{Ce}^{3+},$
Dalslandides (Meso- and Neoproterozoic)	Metamorphic complex of SE Norway, Oslo district	Migmatite–gneisses affected by retrograde metamorphism of greenschist facies	Oligoclase, 4	Low	$\frac{\text{Mn}^{2+}}{\text{Fe}^{3+}}, \underline{\text{O}^*} + (\text{Eu}^{2+}),$

Table 2. Luminescent properties of plagioclases from rocks of median masses in fold regions of Europe

Massif	Rock complexes and their location	Rocks and their age	Number of oligoclase samples	Intensity (<i>I</i>) of Eu ²⁺ center in PL spectra of oligoclase	Main centers in XL spectra
Armorican Massif in Variscides of NW France	Mansellian pluton (St. Malo and Mon St. Michel districts)	Vendian–Cambrian biotite and two-mica plagiogranites (Late Cadomian)	9	Low to medium or absent	Mn ²⁺ , O* + (Eu ²⁺)
French Massif Central in Variscides of S France	Rock complex of Auvergne Core (S margin of massif, vicinity of the town of Valence)	Upper Riphean–Vendian plagioclase–mica schists; epidote–amphibolite facies; slight retrograde greenschist metamorphism in Devonian and Early Carboniferous	3	Very low	Mn ²⁺ , O* + (Eu ²⁺), (Fe ³⁺)
		Late Devonian–Early Carboniferous (?) plagioclase metasedimentary rocks, Early Variscan	3	No PL	O*, (Mn ²⁺)
		Early–Middle Carboniferous biotite–plagioclase granites, Variscan	6	Very low to medium	$\overline{\text{Mn}^{2+}}, \overline{\text{O}^*} + (\text{Eu}^{2+})$
Rhodope Massif in Alpine Foldbelt, S. Bulgaria	Precambrian basement complex, Paleozoic intrusions, Late Alpine volcanic complex (N and E parts of massif)	Meso- and Neoproterozoic gneisses, granites, and migmatites of pre-Riphean basement; amphibolite facies	7	Low to medium	Mn ²⁺ , O* + (Eu ²⁺), Fe ³⁺ , (Ce ³⁺)
		Cambrian–Early Ordovician intrusive granites, Caledonian	4	Low or absent	O* + (Eu ²⁺), Mn ²⁺ , (Fe ³⁺)
		Middle Devonian–Early Carboniferous intrusive granites and granodiorites, Early Variscan	8	Very low or absent	O* + (Eu ²⁺), (Mn ²⁺ , Fe ³⁺)
		Oligocene–Miocene granodiorite and granite porphyries and andesites	8	Low or absent	Mn ²⁺ , O* + (Eu ²⁺), Fe ³⁺ , (Ce ³⁺)

(3) The Armorican Massif and the French Massif Central are situated in the Variscides and also distinguished by intense reactivation closely related to the processes in the adjacent mobile belts and emplacement of widespread Neoproterozoic and Paleozoic granitic plutons (*Tectonics...*, 1978b).

(4) The Rhodope Massif is often regarded as a part of the large Thracian Massif. The Rhodope Massif is involved in the Alpine Foldbelt of southern Europe and characterized by repeated tectonic regeneration and magmatic activity from the Early Paleozoic to the Miocene (*Tectonics...*, 1978b; Stoyanov, 1979).

The aforementioned tectonic units of Europe are listed in order of rejuvenation of metamorphic and especially igneous complexes in the course of their reactivation. Consider first the luminescent properties of plagioclases from particular tectonic units and then set forth some general evolutionary features on a scale of the entire continent.

THE VORONEZH MASSIF

As an objective of this study, plagioclases from the Oboyan Group widespread in the Archean Kursk Meganticlinorium, which is an extension of the Podol Craton in the western Ukrainian Shield (Sinitsyn, 1984), are of special interest. The group is composed of locally migmatized plagiogneisses, granites, and band iron formation (BIF). The regional metamorphism of the latter reached conditions of granulite facies, however, the amphibolite-facied metamorphism is dominant. The age of the Oboyan Group is older than 3 Ga (*Lithogenesis...*, 1977). Feldspars from the Oboyan Group are distinguished by a very low PL of Eu^{2+} and XL of other centers with predominance of the bands pertaining to the exciton O^* centers (probably in superposition with weak Eu^{2+} bands (Table 1)). Very weak Ce^{3+} bands and medium to strong Mn^{2+} bands were recorded only in the XL spectra of three plagioclase samples from diorite gneiss in the L. Tolstoi area.

THE FENNOSCANDIAN SHIELD

Since the luminescent properties of feldspars from most regional structural units of this shield were characterized in previous publications, we dwell only on rocks from the Archean blocks. The Kola and Karelian (Fennokarelian) domains of Archean consolidation are recognized in the Baltic Shield (Glebovitsky, 1993; Rybakov et al., 1999; Khil'tova et al., 2003). The age of the Lopian basement, as well as of relict Archean blocks incorporated into younger and severely rheomorphized matrix is estimated at 2.9–2.8 Ga (Tugarinov and Bibikova, 1980) or 3.15–2.6 Ga (Rybakov et al., 1999). The greenstone belts typical of the Archean cratons consist of the lower stage (basement complex), composed of gneisses (largely tonalitic gray gneisses in the Kola Craton), granitoids, granite gneisses, and granulites of marginal parts of the belts;

and the upper stage, which is made up of low-grade greenschists and phyllites with BIF members. The nature of the sialic basement remains a matter of debate. In the opinion of some researchers, the basement comprises relics of the oldest continental crust broken by deep faults that control protorifts of greenstone belts (Golivkin et al., 1988; Rybakov et al., 1999). In an alternative view, these rocks are products of anatexis of the primary mafic and ultramafic crust (Anhaesser, 1976). According to the zirconometric data (Tugarinov and Bibikova, 1980), the granite–greenstone association is coeval with high-grade metamorphic rocks (2.9–2.6 Ga). In terms of luminescence, plagioclases from the basement complex are similar to plagioclase from the rocks of the Oboyan Group (Table 1). They are characterized by a very low luminescence, especially as concerns gray gneisses. A somewhat elevated (1.5–3 times) I of ($\text{O}^* + \text{Eu}^{2+}$) bands is detected in plagioclase from granites and migmatites. The north-eastern tract of the Central Kola Zone with the Pinkenjavr, Sholtjavr, and Mount Polovinnaya deposits sharply differs from other greenstone belts with BIF (Kostomuksha ore district in the west of Central Karelia and the Transimandra ore district with Olenegorsk and Volchy Tundra deposits). In the Central Kola Zone located near the suture that separates the Murmansk Block from the Central Kola Anticlinorium, the rocks were rejuvenated in the process of Karelian tectogenesis. The rejuvenation is expressed in the extensive development of migmatized and granitized varieties of gray gneisses up to the formation of pegmatite veins. The XL of plagioclases from this zone is characterized by frequent occurrence (40% of samples) of medium-to-high I of Ce^{3+} and [$\text{O}^* + \text{Eu}^{2+}$] bands (approximately the same as of plagioclase from Proterozoic granulites) and high-intensity Mn^{2+} bands (30% of samples) most likely caused by intense reworking of these gneisses. The high-intensity Mn^{2+} and especially Eu^{2+} bands are largely characteristic of plagioclase from migmatite and pegmatoid veinlets and pockets in gneisses. At the same time, the Fe^{3+} bands of plagioclase from most samples are very weak despite a high Fe mole fraction of rocks with abundant black biotite in gneisses, dark red garnet in granulites, and occurrences of iron ore. The low luminescence of unaltered gneisses most likely is explained by their depletion in REE (Shkodzinsky, 2003).

The Riphean anorthosite–rapakivi granite association of southern Finland and the northern Ladoga region should be noted. Plagioclases from the Salmi pluton have been studied previously (Moroshkin et al., 2005). The XL spectra of plagioclase from the Vyborg pluton demonstrate more intense (in comparison with plagioclase from Proterozoic granulites) Ce^{3+} and ($\text{O}^* + \text{Eu}^{2+}$) bands in combination with a brighter PL of Eu^{2+} along with lower I of Mn^{2+} and especially Fe^{3+} centers (2.5–4 times). The Ylammaa pluton of southeastern Finland, which is associated with the Vyborg anorthosite pluton, contains light (almost white) plagioclase (labradorite) with a very high labradorescence

(spectrolite). This plagioclase is distinguished by a rather appreciable (medium on the accepted scale) brightness of PL of Eu^{2+} , high-intensity Mn^{2+} bands, and relatively weak Ce^{3+} and Fe^{3+} bands.

In general, the Fennoscandian Shield is characterized by a sharp increase in luminescence of Eu^{2+} and Ce^{3+} centers and, to a lesser extent, Mn^{2+} center in plagioclase from rocks of the Neoproterozoic–Paleoproterozoic Karelian cycle in comparison with Paleo- and Mesoproterozoic rocks; somewhat lowered I of Eu^{2+} and Ce^{3+} centers in plagioclase from the Svecofennides; and their disappearance in plagioclase from the Dalsland rocks. The progressive decrease in luminescence of plagioclase from the Paleo- to Neoproterozoic is followed by a sharp increase in I of all impurity centers in plagioclase from the rocks pertaining to the Riphean cycle, primarily in oligoclase from rapakivi granite. This increase was probably related to the emplacement of granites along the deep fault zone that surrounds the Baltic Shield in the south and provided by the supply of granitic and anorthositic materials from a great depth over a long time (Tugarinov and Bibikova, 1970). The Dalsland reactivation that post-dated the Riphean cycle was expressed much less intensely and only in the south of the Scandinavian Peninsula (Rybakov et al., 1999). In contrast to subalkali rapakivi granite, the Dalsland granites occur as relatively small plutons and are normal in composition. Hence, the effect of deep-seated sources was much stronger in the case of the large Riphean subalkali granitic and gabbroic plutons than in the case of the Dalslandites. The high-intensity Ce^{3+} and Eu^{2+} bands in the luminescent spectra of plagioclase from the Riphean serve as indicators of deep sources of these elements (Portnov and Gorobets, 1981; Malinko, 1989).

In passing to the consideration of plagioclase from rocks of median masses, a few comments are necessary. The median masses in the fold regions of Europe are much younger than the shields and massifs of the East European Platform. The Archean basement is exposed only locally, in cores of some anticlinoria, and the younger, Meso- and Neoproterozoic rocks in the Rhodope Massif, Neoproterozoic and Early Paleozoic rocks in the massifs of France are predominant. The age of metamorphism and magmatism in these massifs is younger, respectively. Thus, the median masses continue the general evolutionary trend of the continental Earth's crust in Europe, and this tendency is recorded in the luminescent properties of minerals. I clearly realize the fragmentary character of consideration of these massifs due to an insufficient number of samples from Western Europe in comparison with the samples from Russia.

THE ARMORICAN MASSIF

The Armorican Massif is the classic median mass of the European Variscides. The Mansellian Tectonic Zone of this massif is composed of the Neoproterozoic

sequences related to the epoch of Cadomian (Baikalian) folding. The Neoproterozoic (Brioverian) sequences (low-grade slates, sandstones, and flyschoid rocks) are cut through by the large Mansellian granitic pluton related to the final orogenic phase of the Cadomian cycle. The medium- and coarse-grained two-mica plagioclase and two-feldspar granitic rocks are exposed over a vast area near the St. Malo Bay. Feldspars reveal low- to medium-intensity PL of Eu^{2+} center (Table 2); moderate ($\text{O}^* + \text{Eu}^{2+}$) and Mn^{2+} bands with intensity ratios 0.5–1.5 are recorded in XL spectra. A weak Ce^{3+} band was recorded only in one sample. Judging from XL spectra and PL of Eu^{2+} in feldspars, the Mansellian granites are markedly depleted in impurities (lumino-gens). It should be noted that these granites are barren. The U, Sn, and W deposits are related to the much younger Variscan leucogranites.

THE FRENCH MASSIF CENTRAL

The studied rocks pertain to the Auvergne Core that occupies most of the massif (Tectonics..., 1978a). The main volume of the core consists of mica (with plagioclase and quartz) schists metamorphosed under conditions of epidote-amphibolite facies and biotite–plagioclase leucogranite (Velichkin et al., 2004; Peterlongo, 1971). The schists are Brioverian in age and metamorphosed in the process of the Cadomian folding (Chenevoy and Ravier, 1971) with the subsequent retrograde metamorphism, widespread feldspathization and anatexis (Velichkin et al., 2004). Plagiogranites are apparently paligenetic, at least, partly. The uranium and fluorite vein deposits and greisen and quartz-vein tin and tungsten deposits are related to these granites and less abundant rare-metal granites of the same age.

The widespread Variscan granites, volcanic rocks, anatectites, and diaphorites mark several stages of Variscan Orogeny. The polymetamorphism resulted in the rather complicated present-day pattern of the basement (Chenevoy and Ravier, 1971), which hampers the genetic interpretation of luminescent properties of feldspars. Plagioclase from schists (largely veinlets and small pockets) is characterized by low-intensity PL of Eu^{2+} and a rather intense XL of Mn^{2+} (Table 2). As schists are replaced with fine-grained metasomatic rocks, the luminescence of impurity centers almost disappears. In this regard, these metasomatic rocks differ from the metasomatic rocks that locally developed in mica-bearing pegmatite fields of northern Karelia (Moroshkin et al., 2005, Fig. 1d), where plagioclase reveals XL with high-intensity Mn^{2+} and Ce^{3+} bands in the spectra and the bright PL of Eu^{2+} . This discrepancy may be a result of different depths of metasomatic alteration and different metamorphic grades of protoliths.

The Variscan intrusive granites are characterized by high-intensity Mn^{2+} bands in the XL spectra of plagioclases from all samples (I varies by 2.6 times) and elevated luminescence of Eu^{2+} centers. Enrichment in Mn

is typical of rare-metal leucogranites (Moroshkin et al., 2001), which are potentially ore-bearing (Velichkin et al., 2004). PL of Eu^{2+} in plagioclase may be related to the mesoabyssal character of Bi-plagioclase granites, whereas the rare-metal granites, especially Li-F, are hypabyssal. Therefore, the PL of Eu^{2+} center as an indicator of relatively great depth and reducing conditions of mineral formation is not found in plagioclases from rare-metal granites.

In general, the intensity of luminescence of Eu^{2+} and Mn^{2+} centers in plagioclase from Bt-plagioclase granites of the French Massif Central sharply increases. These granites are related to the main (Sudetic) phase of folding and orogenesis of the West European Variscides (Early–Middle Carboniferous) and correspondingly to the most intense tectonomagmatic reactivation of this massif.

RHODOPE MASSIF

The Rhodope Massif is a part of the large Thracian Median Mass that occupies the central position in the Balkan Peninsula between the Alpine foldbelts (*Tectonics...*, 1978b). The significant part of the massif is composed of Precambrian paragneisses, amphibolites, and other rocks metamorphosed under conditions of amphibolite facies. Metamorphism is prograde, and diaphorites are localized only in the zones of subsequent reactivation. Proterozoic biotite granites and leucogranites are abundant as well. The massif experienced multifold tectonomagmatic reactivation, affected by the adjacent mobile zones of different ages (Stoyanov, 1979). As a result, volcanic and plutonic Phanerozoic rocks are widespread. The samples of rocks from the Narechen and Beden districts in the north and northwest of the massif and the vicinity of the Zlata base-metal deposits were used in this study.

The Precambrian rocks are composed of gneisses migmatized to variable extents, granites, and granodiorites. The PL of Eu^{2+} is low (Table 2) and elevated in plagioclase from granites, leucosome of migmatites, and augen gneisses. The medium- to high-intensity Mn^{2+} bands and moderate (rather high-intensity in leucogranite) Fe^{3+} bands are recorded in XL spectra of the same samples; weak Ce^{3+} bands are noted in plagioclase from leucosome. In general, the moderate luminescence of impurity centers is typical of Proterozoic rocks despite their progressive amphibolite-facies metamorphism largely related to the Early Cadomian (Assintian) Orogeny (*Tectonics...*, 1978a).

The Caledonian stage of reactivation developed rather weakly in form of discrete plutons of plagioclase and two-feldspar biotite granites. Plagioclases from these plutons are characterized by low luminescence of Mn^{2+} and Eu^{2+} centers (Fe^{3+} center in one sample) and absence of Ce^{3+} luminescence. The luminescence of plagioclase from Variscan granites, granodiorites, monzonites, and quartz porphyries is still lower (Table 2).

Weak Mn^{2+} bands are detected in XL spectra; the medium-intensity Mn^{2+} and Fe^{3+} bands were established only in one sample; the PL of Eu^{2+} is very weak as well. Note that abundant Variscan granites in the Rhodope Massif, like their Caledonian counterparts, are virtually barren.

Plagioclases from the Alpine volcanic and hypabyssal intrusive rocks, which are abundant and bear base-metal and copper mineralization, differ in fluorescence from Paleozoic granitoids. The weak or completely absent PL of Eu^{2+} is combined with XL, which demonstrates the medium- to high-intensity of the Mn^{2+} band and relatively low- to medium-intensity Fe^{3+} bands in five samples of silicic rocks (granodiorite and granite porphyries and rhyolites). In three andesite samples, the XL of Mn^{2+} is very low and the bands of other impurity centers and PL of Eu^{2+} are not detected.

Thus, plagioclases from the Precambrian metamorphic rocks and especially granitoids of this age are the richest in impurity luminogens. Plagioclase from the ore-bearing hypabyssal silicic rocks of the Alpine cycle is less luminescent (mainly Mn^{2+} centers). Caledonian and Variscan granitoids are distinguished by low luminescence of all centers identified in plagioclases, including the through exciton centers related to the defects of the crystalline lattice.

DISCUSSION

Beginning discussion of the obtained experimental data, remind that the following stages are recognized in the tectonic evolution of Europe: (1) Paleo- and Mesozoic stage represented by the Oboyan Group in the region of the Kursk Magnetic Anomaly; (2) Meso- and Neozoic (Lopian) stage extensively developed in the Baltic Shield; (3) Karelian–Svecofenian (Neozoic–Mesoproterozoic) stage of reactivation of the East European Platform; (4) Riphean–Dalsland (Neoproterozoic) stage of progressive metamorphism, which encompassed the western part of this platform; (5) Cadomian (Baikalian) stage of progressive metamorphism and granite formation; (6) Caledonian stage, poorly expressed in the Rhodope Massif; (7) Variscan stage of the intense granitoid magmatism in median masses; and (8) Alpine (Cretaceous–Miocene) stage, characterized by the formation of hypabyssal minor intrusions and volcanic rocks in the Rhodope Massif.

Consider briefly the characteristic features of luminescence of plagioclase from the rocks that formed or experienced cardinal reworking at the stages listed above.

(1) The Archean complexes are represented by slightly reactivated plagiogneisses of the Oboyan Group in the region of the Kursk Magnetic Anomaly, tonalite–granite association in the basement of greenstone belts, and relict blocks of the Archean basement in the East European Platform. Oligoclases and

andesines from rocks of this group are distinguished by the very low luminescence of impurity centers. This is especially valid for the least altered rocks of the Oboyan Group, which are virtually unaffected by superimposed metamorphism or granitization. Despite amphibolite-facies metamorphism of these rocks locally attaining conditions of granulite facies, the Eu^{2+} and Ce^{3+} centers in plagioclase typical of Proterozoic rocks have developed here insignificantly. Similarly low luminescence was established in the basement of greenstone belts. Plagioclases from the intensely reworked (involved in rheomorphism) tonalites of the central Kola iron-ore zone (system of greenstone belts of the Kola Craton) markedly differ from other plagioclases (Table 1). The Ce^{2+} , Mn^{2+} , and to a lesser extent, Eu^{2+} centers are typical of altered (granitized or impregnated by pegmatoid veinlets) tonalitic gneisses, whereas the marginal granulites of this zone and other greenstone belts have moderate to medium intensity of Ce^{3+} and Eu^{2+} bands (in contrast to granulites from the Lapland–Kolovitsa Mobile Belt). Thus, the Archean rocks demonstrate a distinct correlation between the intensity of luminescence of impurity centers, primarily LREE, and the tectonic regime of the formation of ancient continental crust.

(2) The Karelian and closely related Svecofennian stages are often regarded as a common Paleo- and Mesoproterozoic stage of the origination and further development of the Precambrian mobile belts. Diastrophism at the Archean–Proterozoic boundary, the most important in the Earth's history, resulted in the development of the extensive rift system in the territory of the present-day East European Platform, the vigorous fragmentation and reworking of the Archean basement, and the mass granitization of gneiss sequences (Kröner, 1982; Sinitsyn, 1990; Rybakov et al., 1999). These global processes are accounted for by abrupt enlargement of convective cells in the mantle and related heating and extension of the sialic crust above the ascending mantle plumes. The increased heat flow in the zones of mobile belt formation and ascension of juvenile streams of volatile (H_2O , F, Cl, CO_2 , CO) and mobile components (LREE, K, Na) were imprinted in luminescent properties of plagioclases. In rocks of the Karelides and to lesser extent of Svecofennides, plagioclases are distinguished by bright PL of Eu^{2+} , intense Ce^{3+} and Mn^{2+} bands along with Fe^{3+} bands in Svecofennides (Table 1). The especially high luminescence of REE centers is observed in plagioclases from high-grade metamorphic rocks of the Belomorian and Lapland–Kolovitsa belts distinguished by elevated pressure of metamorphism (Volodichev, 1990), intense migmatization and granitization, and development of extensive fields of mica-bearing and ceramic pegmatites in the Belomorian Zone.

In contrast to the rocks of mobile belts in the Svecofennides with their active tectonic movements and magmatism, the pre-Riphean basement of the Rhodope Massif, though composed of amphibolite-facies metamorphic rocks with the participation of ultramafic and

granitoid rocks, nevertheless is a tectonic unit that was formed during low activity of metamorphosing and ore-forming fluids, as supported by the absence of ore-bearing sequences, plutons, and fault zones of Proterozoic age and suppressed retrograde metamorphism (*Tectonics...*, 1978a). Plagioclases of the Precambrian rocks from the Rhodope Massif largely reveal moderate XL of Mn^{2+} and Fe^{3+} centers, i.e., crustal components. In contrast to similar rocks of the Svecofennides and especially Karelides, the Ce^{3+} and Eu^{2+} centers are not typical. This example clearly shows that the luminescent properties of feldspars are controlled by the development of large structural units of deep origin and active fluid regime during the formation of metamorphic and igneous complexes rather than by the grade of metamorphism.

By the end of the Svecofennian stage, the prevalent granitoid magmatism gave way to basaltic magmatism and waning tectonomagmatic processes (Shcheglov, 1993) that mark the transition to the platform regime in the tectonic evolution of the western East European Craton.

(3) The Riphean stage was related to precisely this inversion of the tectonic regime. The extended and deep fault zones that surround the Baltic Shield in the south and the Ukrainian Shield in the west were formed during this stage, which is characterized by the plutonic gabbro–anorthosite–rapakivi–granite association. The intense alkali-granitic and basic magmatism controlled by deep, long-lived faults (*Tectonics...*, 1978a; Tugarinov and Bibikova, 1980) led to an increase in the luminescence of oligoclase from rapakivi granite (Mn^{2+} , Ce^{3+} , Eu^{2+} , and Fe^{3+} centers) and labradorite from anorthosite (Eu^{2+} and Mn^{2+} centers). It is noteworthy that the intensity of luminescence of Eu^{2+} and especially Ce^{3+} in oligoclase of the large Vyborg pluton is markedly higher than in oligoclase from the relatively small Salmi pluton.

(4) The Dalsland stage of the epiplatform rifting is limited in the area of its occurrence and is characterized by local development of high-grade metamorphism and plutonic magmatism. Medium-intensity XL of Mn^{2+} centers in plagioclase from migmatized gneisses and extremely low luminescence of Eu^{2+} and Fe^{3+} are typical (Moroshkin and Rassulov, 2004). Thereby, the XL of Mn^{2+} most likely was inherited from the Svecofennian stage of progressive metamorphism and migmatization of gneisses.

(5) The Cadomian (Baikalian) stage also did not develop very widely in the western part of the European protocontinent and was characterized by limited occurrence of granitoid magmatism and metamorphism of greenschist and epidote–amphibolite facies. The low intensity of Cadomian tectogenesis accounts for the low PL of Eu^{2+} and moderate XL of Mn^{2+} of plagioclase in the barren Mansellian granites of the Armorican Massif and crystalline schists of the French Massif Central.

(6) Caledonian folding encompassed vast areas in northern and northwestern Europe. The formation of large alkaline plutons, kimberlite fields, and carbonatites at the northern and northeastern margins of the Baltic Shield is also related to this stage (Rybakov et al., 1999). In median masses of the Variscides and Alpides, the Caledonian activation is manifested only as sporadic granitic plutons in the Rhodope Massif. The character of luminescence of plagioclase from Caledonian granites (see above) is consistent with such poorly expressed reactivation.

(7) The Variscan stage, on the contrary, is distinguished by intense development of the Variscan fold zones in central and western Europe and the extensive occurrence of granitoid and volcanic rocks in all median masses, especially in the French Massif Central and the Bohemian Massif (*Tectonics...*, 1978b). In comparing the Variscan granites of the French Massif Central situated in the center of the Variscan province and granites of the Rhodope Massif, which occupies a marginal position in this province and is only slightly affected by Variscan reactivation, one can see a distinct difference in the luminescent properties of plagioclases from the granites of both massifs. The widespread ore-bearing granites of the French Massif Central are distinguished by appreciable (up to medium in brightness) PL of Eu^{2+} and high intensity of Mn^{2+} bands in the XL spectra of plagioclases, whereas luminescence of all kinds in plagioclase from the Rhodope granites is very low. It cannot be ruled out that such a difference in properties directly correlates with their ore potential and the abundance of granites are caused by relations of granites in the French Massif Central to the main (Sudetic) phase of folding of the West European Variscides, which was accompanied by intense synorogenic magmatism. The Paleozoic granitoids of the Rhodope Massif were formed during the early Variscan stage of subsidence and deposition of volcanic and sedimentary sequences and are localized in small troughs within the massif.

(8) The Alpine stage is the second, in importance, epoch of Phanerozoic folding and tectogenesis in Europe. The structural units of the Alpine Mediterranean Belt contain numerous fragments of older structural elements, including the Precambrian basement. The Rhodope Massif is one of the largest pre-Alpine fragments. The Late Alpine volcanic and sedimentary complexes and hypabyssal minor intrusions (mainly silicic dikes) are widespread therein. The rather large Pb, Zn, and Cu deposits are related to these igneous rocks in the areas of tectonic regeneration in the north and east of the massif (Stoyanov, 1979). The intensity of the superimposed ore-bearing magmatism is reflected in appreciably increased luminescence of plagioclase (Mn^{2+} , Fe^{3+} , and to a lesser extent, Eu^{2+} centers). The high luminescence of plagioclase is especially characteristic of rhyolites and granitoids. The

Ce^{3+} band was recorded in one sample of granodiorite porphyry.

Thus, a rather distinct tendency in the evolution of luminescent properties of plagioclase may be outlined on the basis of the aforementioned data. The increase in luminescence of impurity centers, first of all, Eu^{2+} and Ce^{3+} , is related to the stages of the most vigorous tectogenesis and rifting, deep faulting, intense magmatic activity, and metamorphism. These processes proceeded with the active participation of deep-sourced materials. The direct effect of the ascending mantle diapirs and the release of juvenile flows of reduced fluids enriched in rare metals (Sinitsyn, 1999; Kröner, 1982) or mobilization of these components and their removal from the lower sialic crust along with H_2O , CO_2 , and F in the process of high-grade metamorphism (Collerson et al., 1982) may be alternative mechanisms of mass transfer. Anyway, the appearance of reduced and mobile centers in feldspars marks the active tectonomagmatic regime, when the deep-rooted faulting and rifting make the crust permeable and accessible to the deep-seated materials. Hence, the gain of Eu^{2+} , Ce^{3+} , and Mn^{2+} in plagioclases is a process syngenetic to the accumulation of ore components in tectonically active zones and in the formation of ore deposits, especially base- and rare-metal ones. This correlation, noted previously for the Baltic Shield (Moroshkin et al., 2005), is inherent to the reactivated French Massif Central, Rhodope Massif, and Europe as a whole.

This relationship likely has global implications. In Europe, the correlation of the luminescent properties of feldspars with tectonomagmatic and fluid activity during the formation of tectonic units and rock complexes is revealed at several levels.

(i) At the continental level, the correlation is expressed in a maximum intensity of luminescence of Eu^{2+} , Ce^{3+} , and Mn^{2+} centers in rocks of the Karelides as derivatives of the most vigorous diastrophism in the history of the continent, accompanied by high-grade metamorphism, formation by the extended migmatite-granite belts, large granitoid plutons, and pegmatite fields. The Karelian stage continued after the period of the subplatform regime and the deposition of flysch sequences (Rybakov et al., 1999) in the form of intense Svecofennian movements and magmatism, largely of the palingenetic-anatectic type, which resulted in the emplacement of immense batholiths and ultrametamorphic complexes in central and southwestern Finland. Plagioclases from these complexes are also characterized by high luminescence of the main impurity centers, which, however, yields to that of Karelides in intensity (I of bands is 3–4 times lower). The next wave of reactivation and increasing intensity of luminescence of REE and Mn^{2+} centers fell in the Riphean stage, when the extended belts of rapakivi granite and labradorite plutons were formed. The distinct peaks in intensity of the luminescence of plagioclase, mainly of Mn^{2+} centers, were established for the subsequent

cycles of folding and tectogenesis. These peaks fell in the stage of reactivation of median masses, related to the main phases of folding and orogeny in the adjacent mobile zones (Variscan granites in the French Massif Central and Alpine silicic volcanics and hypabyssal granitic intrusions in the Rhodope Massif). As well, the intensity of XL of Mn^{2+} centers and PL of Eu^{2+} centers decreases (especially of the latter). Thus, five main waves of increasing intensity of the luminescence of plagioclase, which are recognized at the stages of endogenic activity in Europe, progressively waned in the time interval from Neoproterozoic–Paleoproterozoic to Miocene.

(ii) At the level of large tectonic units, the same tendency in the evolution of luminescent properties of plagioclase is clearly expressed in the Baltic Shield owing to its great size, geological complexity, and multistage evolution (Moroshkin and Rassulov, 2004; Moroshkin et al., 2005). In the median masses that underwent repeated reactivation, the increasing intensity of the luminescence of Mn^{2+} , Eu^{2+} , and occasionally Fe^{3+} centers is related to the formation of the most abundant and ore-bearing rock complexes.

(iii) In separate tectonic zones, the peaks of luminescence can also be detected, for example, the luminescence of Ce^{3+} and Eu^{2+} centers in plagioclase from Proterozoic granulites, migmatite–granite–gneiss complexes, and especially muscovite pegmatites of the Belomorian and Lapland–Kolvița belts in the Baltic shield.

CONCLUSIONS

(1) The evolution of the luminescent properties of plagioclases from metamorphic and igneous rocks of stable tectonic units of Europe bears a cyclic character and is expressed in the variation of intensities of bands of the main luminogens: Eu^{2+} , Ce^{3+} , Mn^{2+} , and Fe^{3+} . The five peaks of sharp increase in XL and PL of plagioclases established in the geological history of Europe are related to the epochs of the most vigorous diastrophism and tectonomagmatic reactivation. The intensity of luminescence of plagioclase gradually decreases from the Karelian to the Alpine cycle in accordance with the general waning of endogenic activity in the continental Earth's crust of Europe.

(2) In the pre-Riphean cycles, Eu^{2+} and Ce^{3+} are the major luminogens in plagioclase. In the post-Riphean rocks, plagioclase is largely characterized by luminescence of Mn^{2+} . This shift may be explained by the increase in thickness of the continental crust with time, migration of sources of granitic magma to shallower crustal levels, and as a consequence, by the decreasing contribution of deep-seated, most likely subcrustal fluids to metamorphism and granite formation. Since they are indicators of deep-seated mineral formation (Portnov and Gorobets, 1981) and related to the activity of reduced fluid–magmatic systems, Eu^{2+} and Ce^{3+} ions

are replaced by Mn^{2+} ions in plagioclase, while the influence of mantle sources decreases and abyssal palaeogenetic–anatectic magmatism gives way to meso- and hypabyssal intrusions.

(3) The same trend as for the entire continent is traced for shields and median masses. This is expressed most strikingly in the largest Fennoscandian Shield. The correlation of luminescent properties of feldspars with the intensity of tectonomagmatic processes and depth of origination of tectonic zones is revealed at different levels of the structure and evolution of the Earth's crust.

(4) Intensity of luminescence of impurity luminogens in plagioclase (especially Eu^{2+} and Mn^{2+}) correlates with the ore potential of tectonic zones and magmatic bodies, primarily granitoid. This correlation is the most evident in median masses within the Phanerozoic fold regions, where the intensity of XL of Mn^{2+} centers and PL of Eu^{2+} centers appreciably increases in plagioclase from ore-bearing rocks related to the main phases of folding and orogenesis. Hence, the luminescent properties of plagioclases may be used for regional forecasting and estimation of the ore potential of tectonic zones and rock complexes. In this way, it is possible to assess not only intrusions of rare-metal granites and zones of greisenization and feldspathization (Moroshkin et al., 2001), but also the normal granites and plagiogranites that are more abundant in ancient tectonic zones, as well as metamorphic rocks.

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