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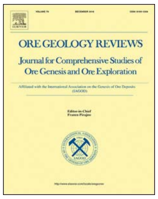

Isotopic signatures of REY mineralization associated with lignite basins in South Primorye, Russian Far East

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ABSTRACT

The paper is based on stable isotopic analyses (C, O, H) first obtained for the rare earth elements + yttrium mineralization of South Primorye and Southwest Japan in addition to recent exploration data and some K-Ar and U-Pb datings. The analyzed minerals include hydrous carbonates and clay minerals that are hosted by argillized (weathered) shale, granite, mafic rocks, and semi-lithified sediments of various (from Cambrian to Late Cenozoic) age. The data distinctly evidence that a major agent of rare metal leaching from the host rocks and their redistribution inside the lignite-bearing sediments and weathered crust was meteoric water. Its moderately acidic character was due to carbon dioxide flowing up from the mantle through faults associated with the lignite basins, in addition to organic matter and sulfides disseminated in the host rocks. Concentrated precipitation and sorption of rare earths and yttrium from the evolved meteoric water were probably caused by their neutralization or even alkalization that had resulted from CO_2 release near the surface. The previous Sr-Nd isotopic data for lanthanite-(Nd) from South Primorye indicate the upper Earth's crust origin of the ore metals. Thus, both endo- and exogenous factors significantly influenced the studied mineralization in Primorye. Juvenile CO_2 made a key contribution to meteoric waters allowing them to mobilize and redistribute ore components in the near-surface conditions. The deep-seated faults cross-cutting and bordering the lignite basins and providing the necessary conduits for the upflows of carbon dioxide are suggested to control localization of the studied mineralization.

1. Introduction

Mineralization of rare earth elements and yttrium (REY) has been known in South Primorye since the 1960s, when higher concentrations of these elements were discovered in lignite during exploration of the Pavlovka basin (Kosterin et al., 1963a). In addition, churchite-(Y), a hydrous phosphate, was found near the basin, in the weathered Lower Paleozoic shale and limestone intruded by lamprophyre dikes (Kosterin et al., 1963b). The following study defined many other REY occurrences in the Cenozoic lignites and their host volcano-terrigenous deposits, as well as in the argillized (weathered or hydrothermally altered) granite, volcanic rocks, and shales of the Paleozoic age and small cross-cutting intrusions of mafic and intermediate composition (Seredin, 1998, 2005; Seredin and Dai, 2012). The latter include dolerite and lamprophyre of the pre-Cenozoic age that are suggested to be related to large fluorine and rare-metal (Sn, W, Li, Ta, Nb, etc.) deposits (Govorov et al., 1997; Ryazantseva et al., 2003). All these crystalline rocks form the Khanka-Bureya-Jiamusi tectonic block of the easternmost Central-Asian Orogenic Belt (Fig. 1; Zhou and Wilde, 2013 and references therein).

During the last 25 years, the mineralization has been studied in South Primorye by V.V. Seredin from the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of Russian Academy of Sciences; V.I. Vyalov and E.V. Kuzavanova from the A.P. Karpinsky Russian Geological Research Institute (VSEGEI); and this paper's authors from Far East Geological Institute, Far Eastern Branch, Russian Academy of Sciences and Far Eastern Federal University (Seredin, 1998, 2005; Seredin et al., 2007, 2009, 2011; Seredin and Chekryzhov, 2012a,b; Vyalov et al., 2010, 2012; Chekryzhov et al., 2016). Some mineralogical work was made in cooperation with Chinese and Japanese researchers (Seredin and Dai, 2012; Dai et al., 2016; Miyawaki et al., 2016). The exploration works were performed by PrimorGeologiya Ltd and Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements (IMIGRE) led by E.F. Semenov in 2006–2008 and by G.N. Trach in 2012–2014. As a result, the REY ores

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have been found in the area as hydrous REY phosphate and carbonate or, more commonly, in the finely dispersed, probably nano- and ion-adsorbed forms on clay minerals, Fe-Mn hydroxides, and organic matter (lignite). These mineralization types are accompanied by various micro-inclusions of primary REY and their rare mineral phases, other native metals, and their compounds that have already been described in detail (Seredin, 1998; Seredin et al., 2007, 2009; Seredin and Dai, 2012) and will not be discussed here.

1.1. Geological outline

According to the information obtained by the previous and present research, argillic alteration, commonly described as a major constituent of the kaolin-hydromica weathering crust, is widespread in the western South Primorye. This alteration almost totally affects the Cenozoic lignite-bearing deposits and forms the crust that is as thick as 10–20 m and up to 50 m in the fault zones over the Paleozoic and Mesozoic host rocks, in particular underlying the deposits. The widely distributed Paleozoic-Mesozoic mafic dikes are commonly altered to a higher extent than the host quartz-bearing rocks such as granite, felsic volcanics, shales, and sandstones. The Late Cenozoic basalts and Eocene adakites are generally not altered, although some clay replacements were observed along fractures, as well as along the boundaries between igneous bodies and host rocks. At the same time, the felsic tuff horizons in the Cenozoic basins are often altered like their host rocks (Seredin et al., 2011). All these altered rocks are commonly poor in REY and most likely represent zones of acidic leaching of these elements. The REY-rich argillized rocks are locally distributed among the depleted ones and are distinguished from the latter only by geochemical data.

The Fe-Mn concretions and crusts with the finely disseminated REY mineralization are often associated with ore-bearing and barren argillized rocks. The characteristic feature of this mineralization is a positive cerium anomaly in the REY spectrum and enrichment in Co, Ni, and other rare metals resembling that of Fe-Mn hydroxides that are precipitated in oceanic settings (Seredin and Dai, 2012; Kato et al., 2011; Hein et al., 2013). As in the ocean, they are associated with hydrous phosphates, most often rabdophane rich in heavy lanthanides and yttrium. Sometimes, hydroxides and phosphates form microscopic conformable alternation in black sinter material.

The richest REY concentrations have been found in the carbonate ores segregated among other more common types of mineralization. The Abramovka deposit occurring in the quarry near the eastern boundary of Pavlovka-2 lignite basin is the most representative of such ores (Fig. 1). Seredin (1998, 2004) and Seredin et al. (2007, 2009) described there an explosive pipe (the Trubka orebody) surrounded by basaltic dikes that intrude the Cambrian black and gray shales and marbles of the Luzanovskaya Suite. The shales are locally pyritized and contain abundant quartz veinlets. All the rocks with REY mineralization are strongly or even totally argillized, except some small parts of the slightly-altered black shales with a dense network of carbonate veinlets situated directly below the weathering crust. According to Seredin and coauthors, these veinlets of hydrous REY carbonates (kimuraite-(Y), lanthanite-(Nd), and some others) and calcite cut not only the host shales, but all other mineralization types, in particular nontronite (brightly-green Fe-smectite) veinlets in kaoilin-hydromica argillized rocks including Fe-Mn and phosphatic films, crusts, and concretions. All these mineralization forms, which are rich in REY inside the orebodies, are poor in REY outside them.

Deeply argillized dikes at the REY occurrences in South Primorye were previously linked to the Neogene-Quaternary basaltic rocks and then to the Eocene adakites, although it was not confirmed by reliable dating (Seredin, 1998; Seredin and Dai, 2012). Nevertheless, the REY-rich alkaline tuffs were found at the presently active Changbaishan (Paektusan) Volcano belonging to the mentioned basaltic formation (Popov et al., 2008) and positioned 300–400-km to the west of the studied area (Fig. 1). These basalts occur in a within-plate setting, and they are common throughout East Asia and, in particular, including the alkaline basalts of Kyushu Island, Japan (Sakuyama et al., 2014), which contain some hydrous REY carbonates (Higashi Matsuura-gun, Saga Prefecture, Fig. 1). This site is one of a few where REY carbonates have found. Kimuraite, ($CaY_2(CO_3)_4\ 6H_2O$; stochiometric formula), a hydrous Y-carbonate was first described there (Nagashima et al., 1986).

Four potentially commercial types of REY mineralization are recognized in South Primorye (Chekryzhov et al., 2016). They are represented by deposits and occurrences in: (1) metasedimentary rocks including mafic dikes (Abramovka-type); (2) weathering crust developed on granite (Longnan-type); (3) felsic tuff; and (4) lignite. This work is focused on the Abramovka-type mineralization characterized by the following features:

1. Unusually high REY grades;
2. Diverse chemical composition with significant share of Y and heavy lanthanides;
3. Diverse mineral composition with significant proportions of carbonate and clayey ores;
4. Diverse mode of occurrence with steeply-dipping and stratiform orebodies.

The Abramovka ores provide us with key information to decipher the mineralization origin. Additional data on REY occurrences in the associated lignite basins and REY carbonates from the mentioned Japanese basalt are used for comparison to evaluate the extent of the considered ore-forming processes.

2. Data sources and analytical methods

This study is based on the data resulted from the mentioned exploration works of 2012–2014, our own field work in Russia and Japan, and the recently-conducted isotopic analyses.

Zircon grains for dating were separated from a composite sample (about 30 kg in weight) of white and greenish-gray argillized rocks of the Trubka (Pipe) orebody, an Abramovka REY deposit. The local U-Pb analyses of these grains were performed at the Center of Isotopic Studies, A.P. Karpinsky Russian Geological Research Institute (VSEGEI), Sankt-Petersburg, Russia using the standard SHRIMP II methodology.

K-Ar dating of unaltered dolerite from the core of Drill hole No. 1, an Abramovka REY deposit, was made using the standard methods at the Laboratory of Isotopy and Geochronology, Institute of the Earth's Crust, Irkutsk, Russia. For the age calculation, the following constants were applied: $\lambda\alpha = 0.581 * 10^{-10}\ \text{year}^{-1}$; $\lambda\beta = 4.962 * 10^{-10}\ \text{year}^{-1}$; 40 K = 0.01167 at.% K. The K concentration was defined as average of three flame photometric determinations, while the radiogenic Ar concentration was defined as average of two determinations by two aliquots (Rasskazov et al., 2000).

All the stable isotopic analyses were performed at the Laboratory of Stable Isotopes, Far East Geological Institute, Vladivostok, Russia using the Finnigan MAT-253 and Finnigan MAT-252 mass-spectrometers with the help of the laboratory standards calibrated using the international standards NBS-18, NBS-19, NBS-28, and IAEA-CO-8 at the SMOW and V-PDB scales. The outer truncation error (1σ) of the methods was less than ± 0.2‰. The sample treatment used some non-standard procedures (Ignat'ev and Velivetskaya, 2004a,b, 2009) that are briefly described below.

Before the C isotopic analysis, the powdered carbonate sample of 3–5 g in weight was dissolved in 100% phosphoric acid in vacuum under temperature 95 °C. The extracted CO_2 was then purified using the cryogenic separation. Oxygen was extracted from the powdered carbonate and clay samples with weight from 1 to 5 mg by heating under the infrared CO_2-laser (10.6 µm) with presence of BrF_5. After fluorination, the separated oxygen was refined in the two cryogenic traps with liquid nitrogen and a KBr absorber. Hydrogen was extracted from the hydrous carbonate and clay samples of the same weight also using the infrared CO_2-laser.

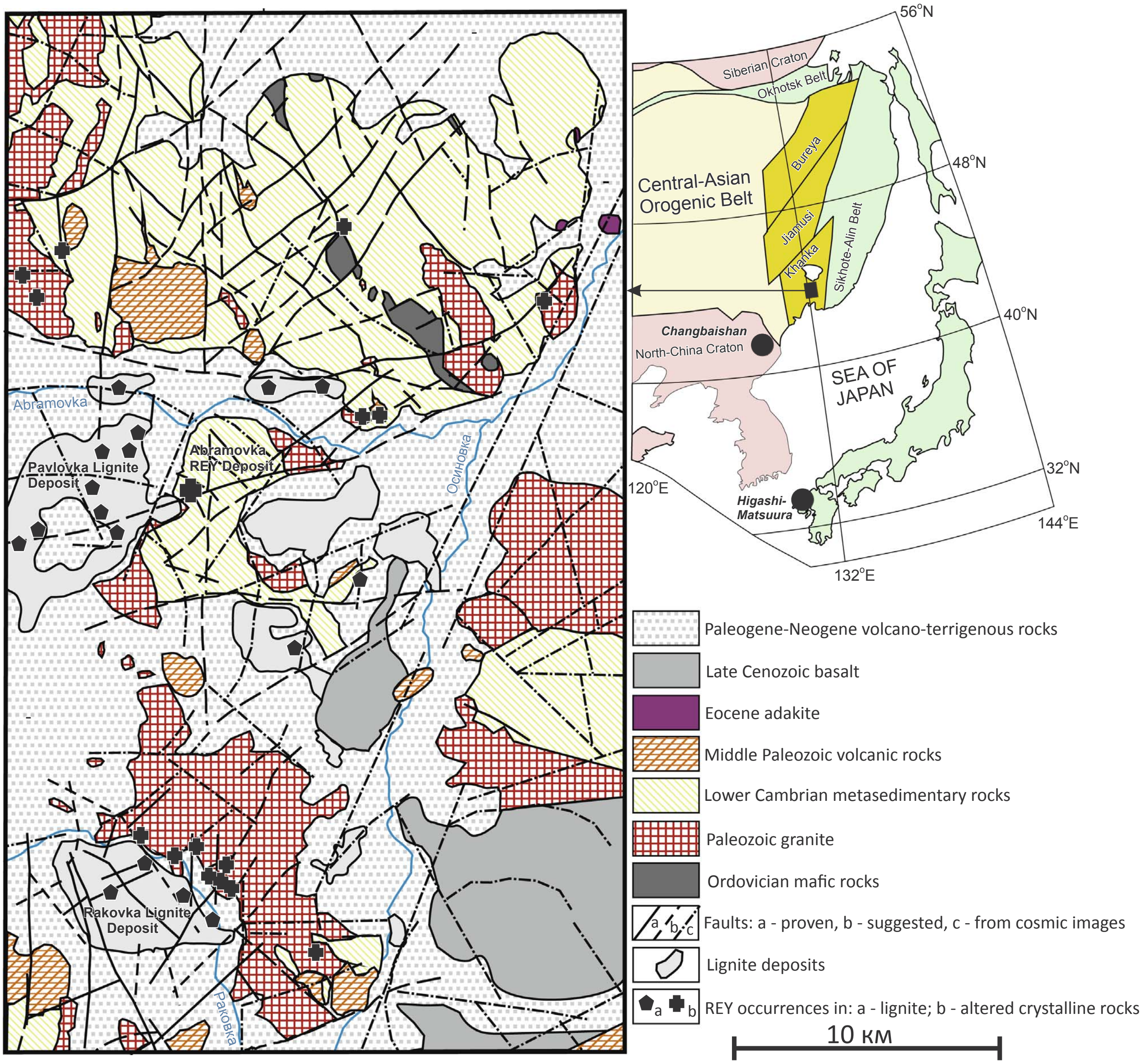

Fig. 1. South Primorye simplified geology showing occurrences of REY mineralization.

Table 1
Stable isotopic composition (‰) of REY ores and associated rocks.

Location	Sample	Mineralogy	δ Dvsmow	δ^{18}Ovsmow	δ^{13}Cvpdb
Abramovka deposit	AN 15/25	Nontronite	−112.9	15.1	n.d.
‘’	AK-15/8	Kimuraite	−98.1	25.5	−16.2
‘’	AL-15/9	Lanthanite	−94.6	24.1	−15.8
‘’	AKL-15/10	Calcite	n.d.	23.2	−19.8
‘’	AKA 15/26	Argillizite	−103.3	14.7	n.d.
‘’	AKL 15/24	Kaolinite-lanthanite	−75.5	18.5	n.d.
‘’	15–29/1	Calcite (marble)	n.d.	22.0	3.1
Pavlovka-2 basin	P-16/3	Kaolinite-illite (granite)*	−113.4	11.8	n.d.
Pavlovka-East basin	1011/2	Kaolinite-illite (mudstone)**	−133.2	11.5	n.d.
Rakovka basin basement	1059	Kaolinite-illite (mafic dyke)*	−134.3	9.6	n.d.
Higashi-Matsuura basalt	JK-15/5	Kimuraite from fissure	−87.6	28	−13.7
‘’	JL-15/6	Lanthanite from fissure	−39.5	26.5	−14.1
‘’	JKL-15/7	Calcite from fissure	n.d.	25.2	−22

n.d. – not determined.
* REY – rich rock.
** REY-depleted rock.

Table 2
SHRIMP-II U-Pb dating of zircon grains from argillizite of the Trubka orevody, Abramovka deposit.

Spot	% $^{206}Pb_c$	ppm U	ppm Th	232Th/238U	Ppm 206Pb*	(1) 206Pb/238U Age	(2) 206Pb/238U Age	(1) 207Pb/206Pb Age
PB-14-2_3.2	0.61	383	172	0.47	21.1	398 ± 6.2	398.2 ± 6.2	384 ± 100
PB-14-2_3.1	0.53	261	86	0.34	15.2	420 ± 6.8	421 ± 6.8	345 ± 120
PB-14-2_6.1	0.88	348	153	0.45	20.6	425.6 ± 7	427 ± 6.8	326 ± 190
PB-14-2_5.2	0.98	104	97	0.97	7.03	484.9 ± 9.9	484.5 ± 9.8	525 ± 170
PB-14-2_5.1	0.65	169	165	1.01	11.5	488.3 ± 8.3	487.8 ± 8.3	533 ± 120
PB-14-2_2.1	0.98	127	70	0.57	9.28	520 ± 9.4	522 ± 9.1	406 ± 210
PB-14-2_4.1	0.20	195	175	0.93	14.4	529.7 ± 8.5	529.7 ± 8.7	531 ± 63
PB-14-2_1.1	3.77	32	24	0.76	2.46	533 ± 16	535 ± 14	442 ± 620

Spot	% Discordant	Total 238U/ 206Pb ± %	Total 207Pb/ 206Pb ± %	238U/ 206Pb* ± %	207Pb*/ 206Pb* ± %	207Pb*/ 235U ± %	206Pb*/ 238U ± %	Err corr
PB-14-2_3.2	−3	15.6 ± 1.6	0.0593 ± 1.9	15.7 ± 1.6	0.0543 ± 4.6	0.477 ± 4.9	0.0637 ± 1.6	0.329
PB-14-2_3.1	−18	14.77 ± 1.6	0.0577 ± 2.4	14.85 ± 1.7	0.0534 ± 5.4	0.495 ± 5.6	0.0673 ± 1.7	0.294
PB-14-2_6.1	−23	14.52 ± 1.6	0.06 ± 2.7	14.65 ± 1.7	0.0529 ± 8.4	0.498 ± 8.6	0.0683 ± 1.7	0.197
PB-14-2_5.2	8	12.67 ± 2.1	0.0658 ± 3.2	12.79 ± 2.1	0.0579 ± 7.8	0.623 ± 8.1	0.0781 ± 2.1	0.261
PB-14-2_5.1	9	12.62 ± 1.7	0.0633 ± 2.5	12.7 ± 1.8	0.0581 ± 5.3	0.63 ± 5.6	0.0787 ± 1.8	0.313
PB-14-2_2.1	−22	11.78 ± 1.8	0.0629 ± 2.7	11.9 ± 1.9	0.0549 ± 9.2	0.635 ± 9.4	0.084 ± 1.9	0.199
PB-14-2_4.1	0	11.65 ± 1.7	0.0596 ± 2.3	11.68 ± 1.7	0.058 ± 2.9	0.685 ± 3.3	0.0856 ± 1.7	0.506
PB-14-2_1.1	−17	11.15 ± 2.5	0.0865 ± 9.2	11.59 ± 3	0.056 ± 28	0.66 ± 28	0.0861 ± 3	0.109

Table 3
K-Ar dating of unaltered dolerite from the Abramovka deposit (Drill Hole 1, Depth 95 m).

Sample	K, % ± σ	$^{40}Ar_{rad.}$(ng/g) ± σ	$^{40}Ar_{air}$(%) in sample	Age, Ma ± 2σ
C-1/14-95	0.98 ± 0.015	17.54 ± 0.06	8.1	241 ± 7

3. Results

Table 1 presents isotopic composition of hydrocarbonate components from veinlets that form the core of the Trubka orebody in the Abramovka deposit. For comparison, this table shows isotopic composition of marble composing the host rock assemblage of Luzanovskaya Suite. In addition, isotopic data are available on argillized rocks of this deposit and adjacent lignite basins, as well as carbonates and clay-altered basalts of SW Japan (Fig. 1). These data certainly do not confirm the previous suggestion of the hydrothermal origin of the ores (Seredin, 1998) and will be used as a key to decipher their nature in the Discussion section below.

Our dating also has not confirmed Seredin's suggestion of the Cenozoic age of dolerite from the Abramovka deposit (Seredin, 1998). The K-Ar age of the fresh rock appeared to be Early Triassic (241 ± 7 Ma), whereas the U-Pb dates of zircons from the composite argillized-rock sample showed a wide range of ages from 533 to 398 Ma (Tables 2 and 3, Figs. 2 and 3). Four of six zircon grains yielded age of 508.2 ± 15 Ma that corresponds to the major metamorphic event of the Khanka-Bureya-Jiamusi block, while the mid-Paleozoic dates of the last two grains probably reflect some later magmatic episodes (Zhou and Wilde, 2013).

In addition, exploration drilling did not find any REY ores below the zone of weathering (argillization) at the Abramovka deposit (Fig. 3). This disproves the previous suggestion that the Abramovka deposit includes a rather small (several meters across), steeply-dipping stockwork of the rich ore, coinciding with the hypothesized explosive pipe (the Trubka orebody), in addition to a more extensive (tens of meters in length) near-surface bodies of less-rich REY mineralization (Seredin, 1998; Seredin et al., 2007, 2009).

4. Discussion on origin of the studied REY mineralization

The Abramovka deposit, with its numerous dikes of alkaline mafic rocks and "explosive pipe" including a "stockwork" of REY carbonates, was until recently considered to be a direct proof of an endogenous, hydrothermal nature of the REY ores in South Primorye (Seredin, 1998; Seredin et al., 2007, 2009; Seredin and Dai, 2012). The quartz veinlets with high Ce concentrations that occur in the orebodies provide an additional evidence for that. The homogenization temperature of water-carbon dioxide inclusions in this quartz is 140–350 °C (Seredin, 1998). However, as discussed above the recently obtained data distinctly oppose this opinion.

4.1. Isotopic dating

The present isotopic dating indicates that the argillic alteration of the Trubka orebody replaced not the suggested explosive pipe, but a tectonic breccia consisting of fragments of the Paleozoic sedimentary rocks and the Paleozoic-Mesozoic mafic dikes intruding them. The age of this breccia is not defined. Perhaps it was formed in several stages, the last of which is correlated with crystallization of REY carbonates and calcite. Their formation conditions may be revealed by the homogenization temperature of gas-liquid inclusions (138–153 °C) in calcite from the "central stockwork" of the Trubka orebody (Seredin. 1998). The associated quartz veinlets might have formed in a hotter environment of the previous, probably metamorphic stage of the breccia development. If this is the case, the mentioned high Ce contents may be

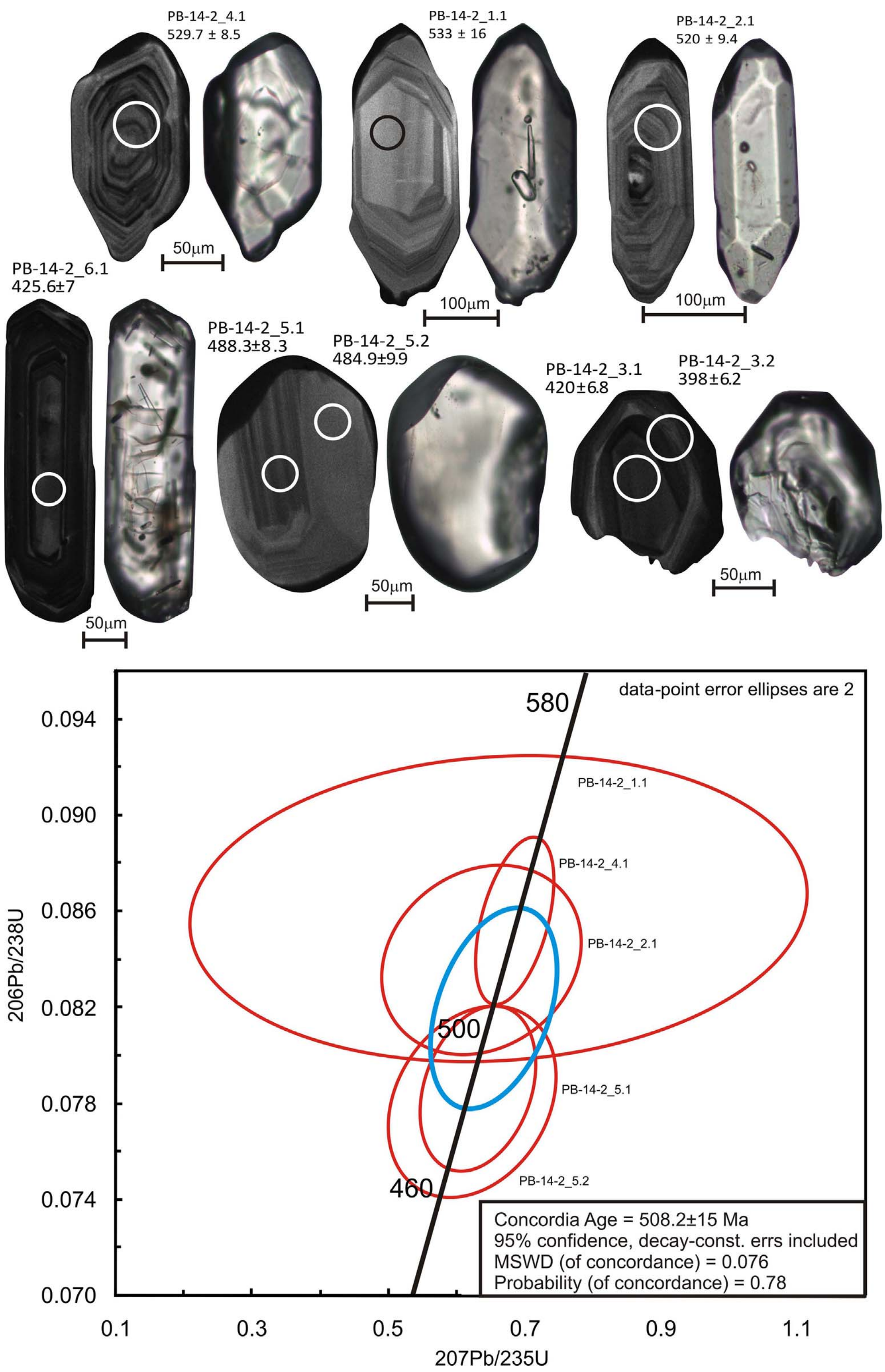

Fig. 2. Cathodoluminescent images of zircon grains from the Abramovka argillized rocks showing the SHRIMP II spots and U-Pb Concordia plots for four of six grains analyzed (see Table 2 for the analyses).

assigned to the overprinted hydroxide mineralization that is correlated with the low-temperature carbonates. This suggestion is confirmed by quartz fragments in the thicker (up to 10 cm) crusts of the Fe-Mn hydroxides (Seredin, 1998). The authors have also seen numerous Mn-Fe hydroxide films in the quartz fissures.

4.2. Radiogenic-isotope evidences

Origin of the rare metals in the studied ores may be reflected by the ratio between radiogenic isotopes of Nd and Sr in lanthanite-(Nd) of the Abramovka deposit (Seredin et al., 2009). As Fig. 4 shows, this ratio distinctly indicates an upper crustal source of these elements. This

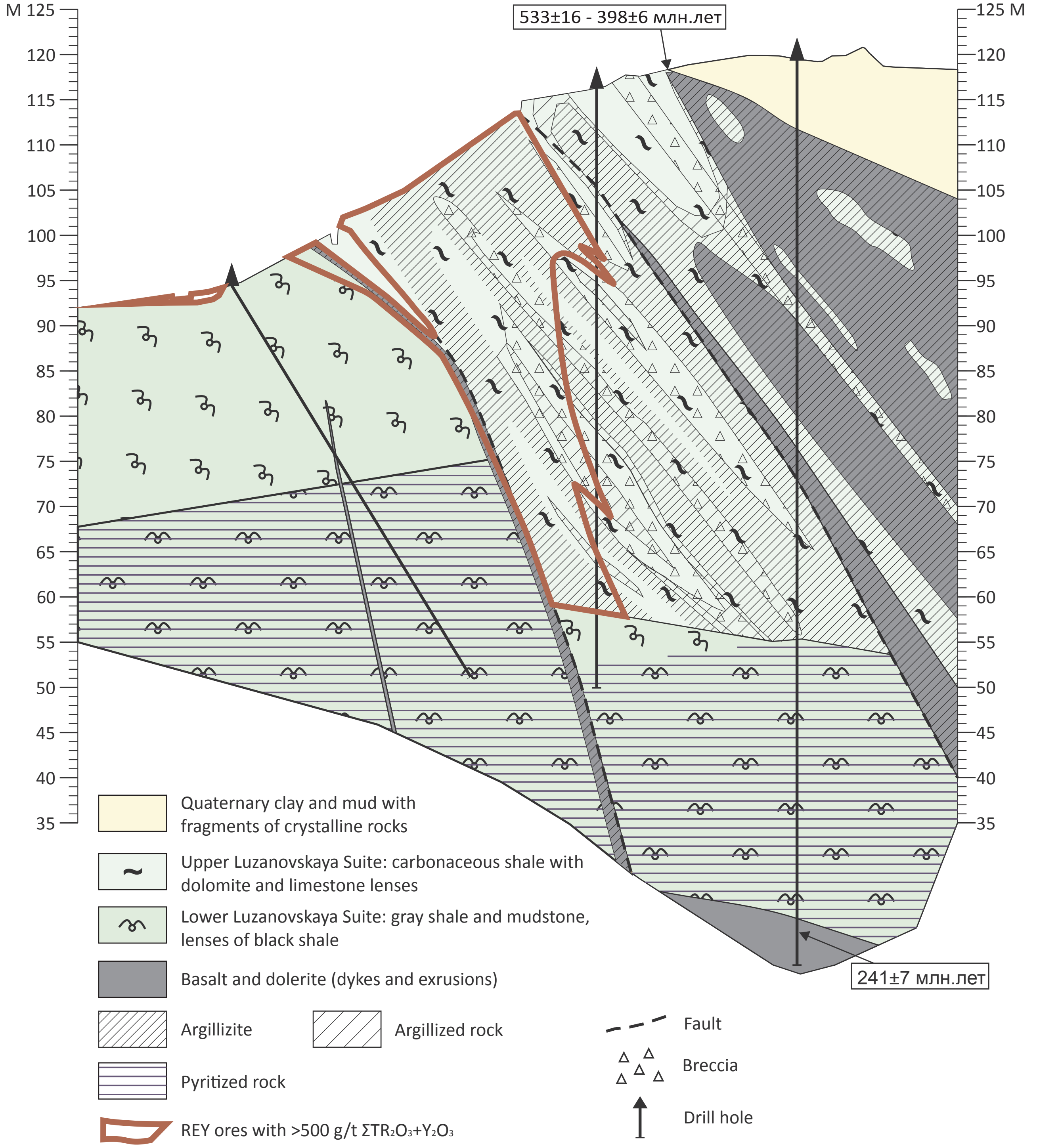

Fig. 3. Geological cross-section of the Trubka orebody, Abramovka deposit (simplified after unpublished Exploration Report by G.N. Trach et al., 2012–2014) showing the K-Ar and U-Pb dates.

makes a visible contrast to the “mafic” isotopic composition of Nd from kimuraite of the altered basalts in SW Japan (Akagi et al., 1996; Kita et al., 2012; Sakuyama et al., 2014).

4.3. Stable-isotope evidences

The diagram of Fig. 5A was built to identify carbonates of different origin in general (Rollinson, 1993; Cerling and Quade, 1993; Bowman, 1998), but it is not very informative in the studied case. The C-O isotopic ratios of the studied REY ores do not correspond to any common types of carbonate, they are just closer to carbonates of diagenetic concretions and modern soil, indicating their authigenic nature. Meanwhile, isotopic characteristics of marble from the Abramovka host rocks plot in the corresponding field of limestone and marble, confirming the accuracy of the analyses and suitability of the diagram.

The diagram of Fig. 5B shows the fields of authigenic calcite from the sandstone aquifers and fracture zones of the Great Artesian Basin, eastern Australia (Dawson et al., 2013). This graph allows distinction between the carbonates formed as: (1) sandstone and coal cement precipitated from fresh and evolved (basinal brines) meteoric waters;

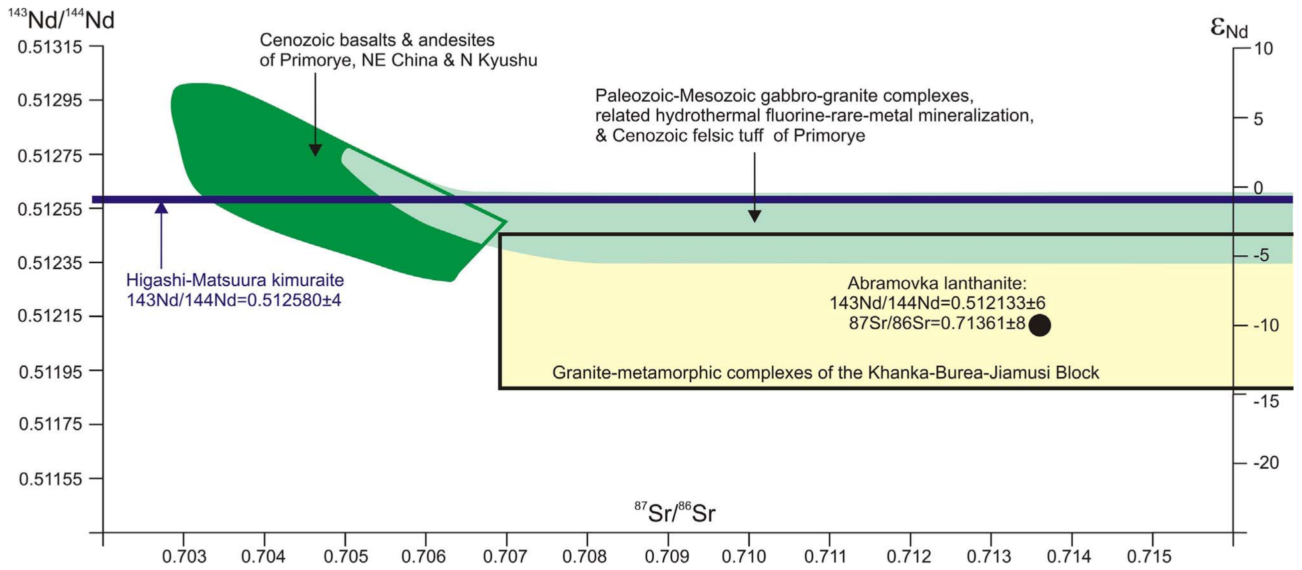

Fig. 4. The ^{143}Nd/^{144}Nd vs. ^{87}Sr/^{86}Sr ratios in carbonates from the REY mineralization of South Primorye (Seredin et al., 2009) and SW Japan (Akagi et al., 1996) compared with those in their possible source rocks (Wu et al., 2000; Popov et al., 2008; Kita et al., 2012; Jahn et al., 2015; Dai et al., 2016).

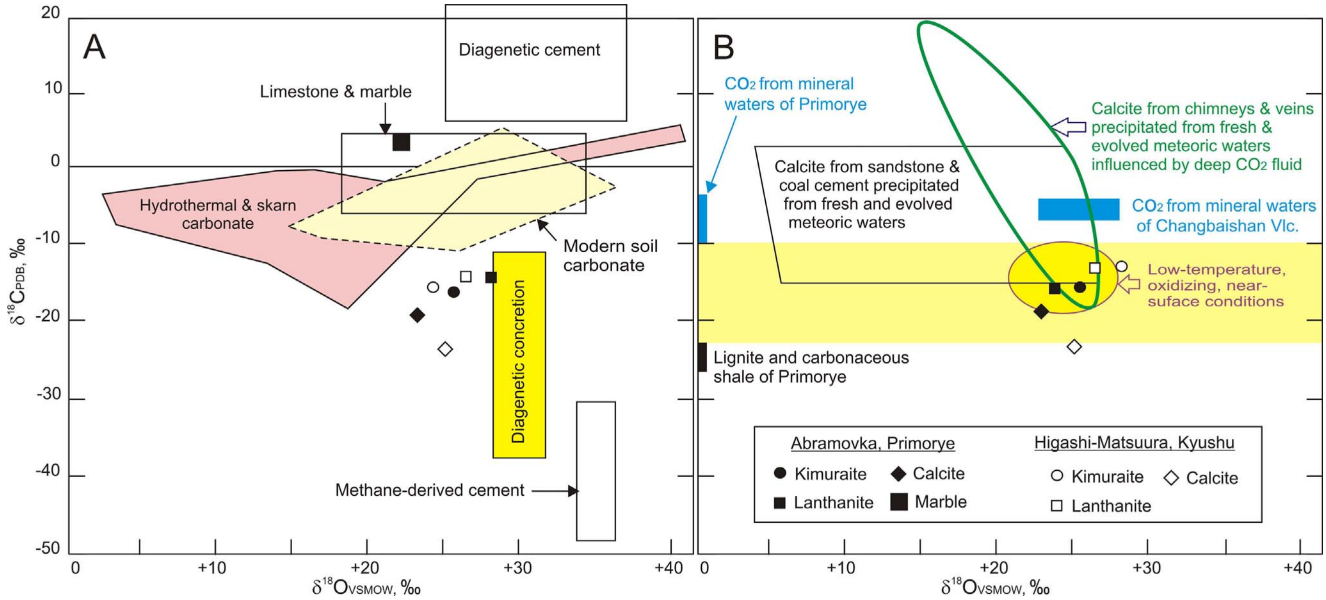

Fig. 5. The δ^{13}C/δ^{18}O discrimination diagrams showing the isotopic composition of carbonates from the REY mineralization of South Primorye and SW Japan: A – after Rollinson (1993) with additions from Cerling and Quade (1993) and Bowman (1998); B – based on the data from Dawson et al. (2013) with additions from Chelnokov et al. (2013) and the authors' unpublished data.

and (2) chimneys and veins associated with fault zones and joints providing channels for the mantle-derived CO_2 upflows. The latter carbonates are enriched in minor and trace elements, REY in particular. According to the modeling, calcites with the lowest δ^{13}C and highest δ ^{18}O were deposited in low-temperature, near-surface, highly-oxidizing conditions (Dawson et al., 2013). As shown in Fig. 5B, carbonates of the Abramovka and Higashi-Matsuura locations have comparable isotopic signatures. It is also meaningful that they plot in between the δ ^{13}C values characteristic of deep-sourced CO_2 and organic matter of lignite and carbonaceous shale. This most likely indicates a complex nature of these minerals which resulted from interaction of meteoric waters with carbon-bearing host rocks and mantle-derived fluid.

The isotopic signatures of the studied carbonates well fit the hydrogeochemical pattern of the region, where the common mineral waters are moderately acidic (hydrocarbonate) in composition and characterized by high partial pressure of mantle-derived CO_2 and REY enrichment (Chudaeva et al., 1999; Shand et al., 2005; Chelnokov and Kharitonova, 2008; Chelnokov et al., 2013). Japanese researchers have also concluded precipitation of hydrous REY carbonates from meteoric waters (Akagi et al., 1996; Jiao et al., 2013).

4.4. General discussion

The data herein presented show evidence of a heterogenous origin of carbonates from the REY occurrences in South Primorye and SW Japan. Their rare metals are sourced from the surrounding rocks which are upper crustal rocks for Primorye and within-plate basalts for Japan. The carbonate components are, on the one side, exogenous, related to local meteoric waters reacting with organic matter and, on the other side, endogenous, related to carbon dioxide from a deep source. The deep source is likely associated with fluid upflows and within-plate magmatism which occurred above the oceanic slab stagnated in the

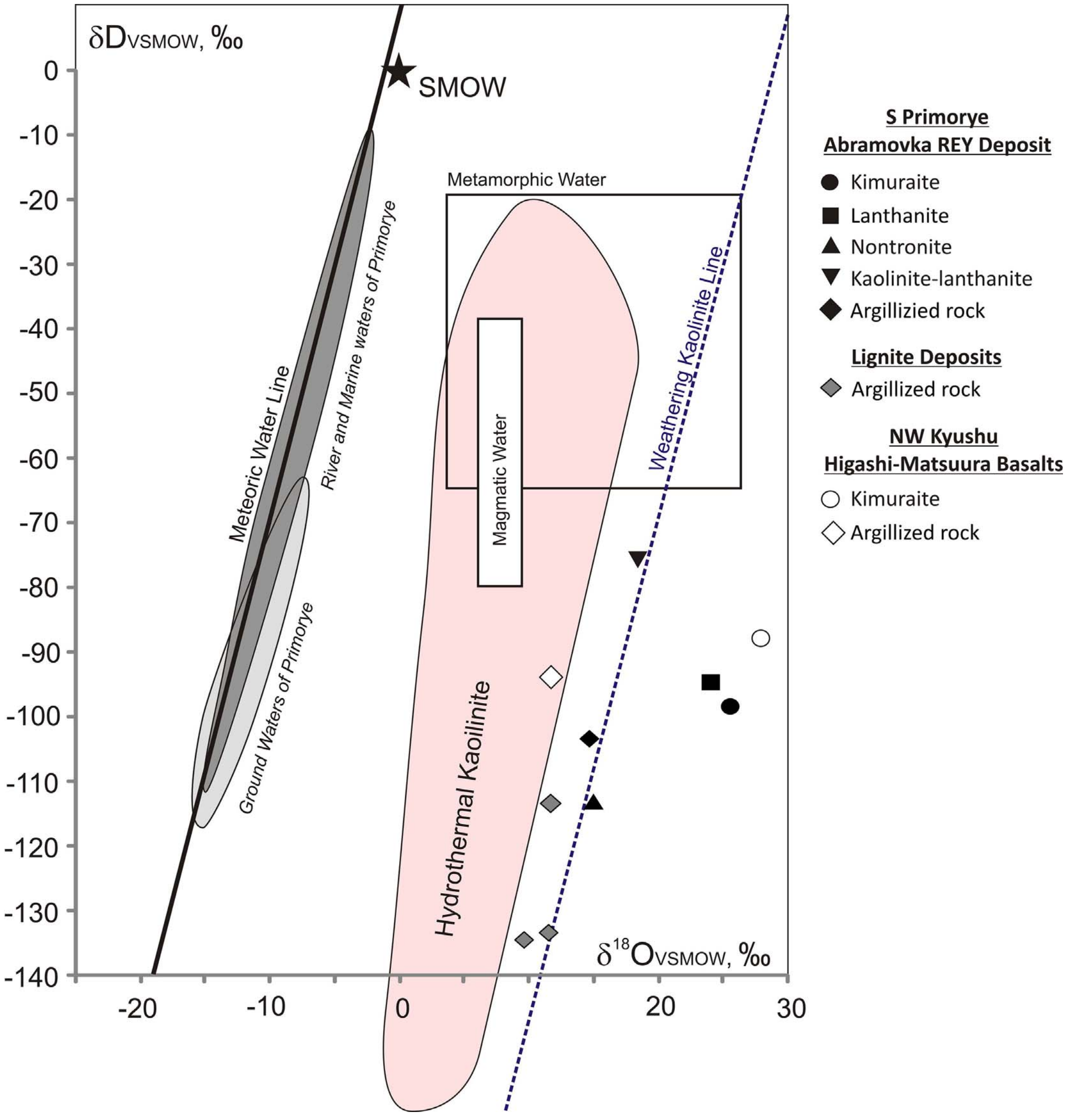

Fig. 6. O-H isotopic ratio in clay minerals, kaolin-hydromica argillized rocks and hydrous carbonates of South Primorye and SW Japan. Reference fields and lines of the minerals of different origin are from Taylor (1979), Shepard and Gilg (1996), Chelnokov and Kharitonova (2008).

transitional mantle (Wei et al., 2016). This is demonstrated by the isotopic signatures of CO_2 from thermal waters of the active Changbaishan Volcano (Shangguan et al., 1997), which are close to those of the mineral waters from Primorye (Chelnokov et al., 2013). The studied carbonates show fractionation resulted from a reaction of isotopic exchange between carbon of organic and mantle origin (Fig. 5B).

The argillic alteration typically accompanying the REY mineralization discussed above has clearly exogenous isotopic characteristics of hydrogen and oxygen regardless of their enrichment or depletion in REY. In Fig. 6, only clay-altered basalts of Kyushu Island plot in the field of hydrothermal kaolinite; that may be related to a thermal influence of the lava flow. Other plots of clay rocks from the Abramovka deposit and adjacent lignite basins, as well as their crystalline basement are aligned close to the weathering kaolinite line (Shepard and Gilg, 1996). The O/H isotopic ratios of hydrous carbonates plot away from this line towards heavier oxygen values. This may be explained by their closer relation to mantle-derived CO_2 with δ^{18}Osmow values analyzed in thermal waters of the Changbaishan Volcano (Shangguan et al., 1997) being very close to those in the studied carbonates (Fig. 5B).

4.5. Genetic model

The following model may be suggested to outline the origin of REY mineralization in South Primorye. Meteoric waters descend through the semi-lithified, lignite-bearing deposits and fractured crystalline rocks become moderately acidic as a result of reaction with organic fossils and sulfides, as well as carbon dioxide flowing up along faults from deep sources. These processes result in leaching of some rare elements including REY to form the observed large amounts of argillic weathering crust, which is depleted in rare earths and yttrium. Meanwhile, interaction of water with aluminosilicate rocks and CO_2 degassing make it neutral or even mildly alkaline triggering REY precipitation as hydrated Fe-Mn oxide, phosphate, and carbonate. The most active precipitation in all forms, including the rare REY carbonates, should occur at the places of artesian-water discharge associated with CO_2 release under low-temperature, highly-oxidizing, near-surface conditions. The resulting REY-rich ores may be concentrated along the flanks of lignite basins bounded and cut by normal strike-slip faults (Fig. 7). The Abramovka deposit that we studied occupies such a position (Fig. 1).

It should be mentioned finally that higher amounts of REY in the hydrocarbonate mineral waters (Chudaeva et al., 1999; Shand et al.,

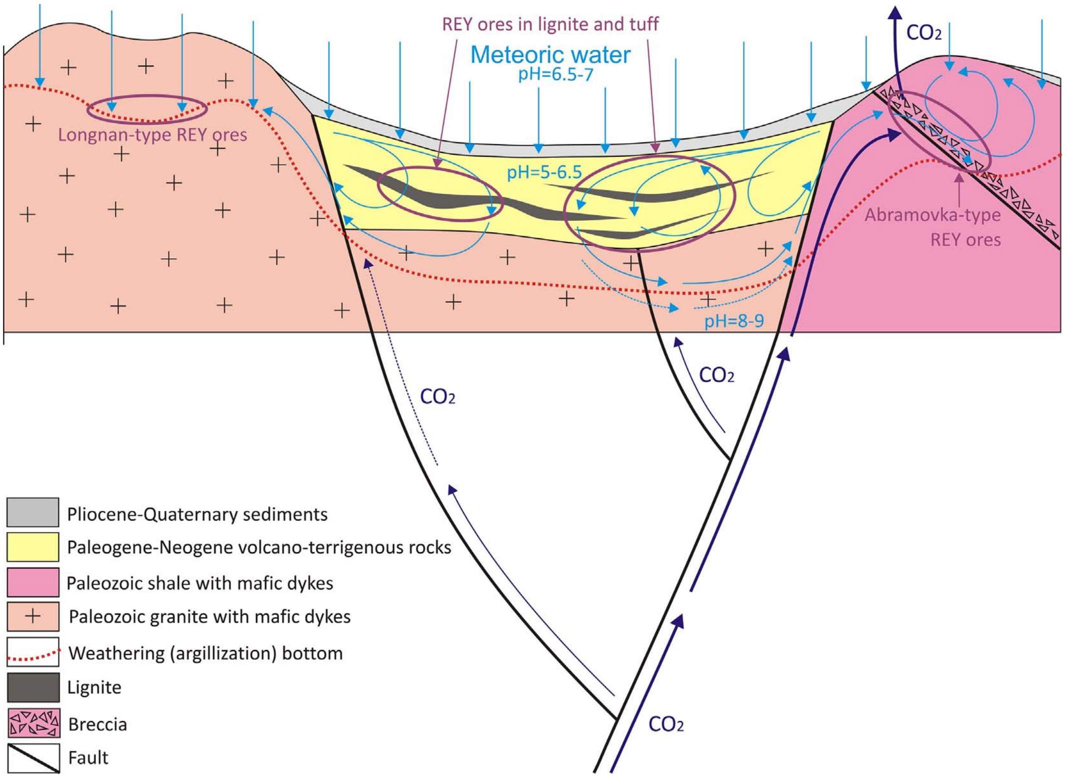

Fig. 7. Suggested model of REY mineralization associated with lignite basins of South Primorye.

2005; Chelnokov and Kharitonova, 2008), the recent Chagbaishan Volcano tuffaceous unit (Popov et al., 2008), and altered Late Cenozoic basalts of SW Japan (Akagi et al., 1996; Jiao et al., 2013) provide clear evidence that the described complex ore-forming processes are still active in the region. However, their peak activity might be associated with the widespread Oligocene-Miocene pyroclastics (Dai et al., 2016), a consequence of highly explosive volcanism that is commonly associated with extensive CO_2 degassing. According to the model presented above, the latter might significantly intensify the REY mineralization.

5. Conclusions

The following conclusions can be made as a result of the present work:

1. The upper Earth's crust rocks, which were weathered by hydrocarbonate waters of meteoric origin, are suggested to be main sources of rare earths and yttrium for the Abramovka REY deposit and probably other REY occurrences in South Primorye. However, a key feature of this weathering is CO_2 ascending from the Earth's mantle along the deep-seated faults, which makes the meteoric waters moderately acidic and mobilizing numerous rare metals, including REY. The presence of organic material and sulfides in the lignite-bearing and metasedimentary rocks might also influence this process.
2. The significant REY precipitation results from neutralization or even the alkalinity of the waters circulating in the semi-lithified Cenozoic deposits and fracture zones, that is caused by their reaction with the host aluminosilicate rocks. This process is strongly accelerated by CO_2 release from the artesian waters under oxidizing, near-surface conditions. The highest REY concentrations in the hydrous carbonate ores were probably deposited in such a way.
3. Therefore, the REY mineralization of South Primorye is complex in origin, including the roles of exogenous (meteoric waters circulating through the uppermost Earth's crust) and endogenous (CO_2-bearing fluid from mantle) factors.
4. Exploration for REY ores of the Abramovka type should be oriented on the near-surface zones of deep-seated faults bounding and crosscutting the lignite basins with widespread clay-weathered rocks commonly depleted and locally enriched in REY.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.oregeorev.2018.01.018.

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