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Y/Ho ratio as genetic indicator of sparry magnesites in south Urals, Russia

用 Y/Ho 比值指示俄罗斯乌拉尔南部晶质菱镁矿矿床的成因*

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Abstract There are two types of sparry magnesite deposits in the Southern Urals province: 1) layer-like bodies in the stratigraphic dolostone horizons; 2) lens-like bodies in the dolomitized limestones. The sparry magnesite deposits are located in the dolostones of the Lower and Middle Riphean series and are absent in dolostones units of the Upper Riphean. These two types of magnesite are distinguishing by the shape of ore bodies and size of crystals, quantity of quartz and dolomite admixtures. The resources of the first type are huge; magnesite has a coarse-grained structure with crystal size of more than 10 mm (up to 150 mm), as a rule, sharp boundaries of ore bodies with host dolomites. This type of deposits is typical for the Lower Riphean sequence. The second type of deposits has a very irregular shape of ore bodies with impregnation of magnesite crystalls into host dolomites, with relatively small size of magnesite crystals (1-5 mm). The second type predominates in the Middle Riphean sections. All the deposits possess the features of metasomatic origin. The two types of magnesite ores show distinct features of some major elements and REE distributions. Magnesites of the first type have lower contents of FeO, CaO and SiO_2 in comparison with magnesites of the second type. The first type magnesites are LREE depleted with La/Lu < 1 in comparison with country rocks of dolomites (La/Lu > 1). Magnesites of the second type have a low degree of fractionation and differences in REE distributions between magnesites and country rocks of dolomites. In this paper the importance of Y/Ho ratio is discussed, because the resemblance of this ratio in magnesites and host rocks makes it possible to separate hydrothermal and early diagenetic metasomatic processes of magnesite formation. We suggest the first type magnesites, such as the Satka and Bakal deposits with high Y/Ho ratios belong to early diagenetic stage of development of the rock-forming basin. The second type magnesites, such as the Ismakaevo and Katav-Ivanovsk deposits with low Y/Ho ratios, are related to hydrothermal processes of fluid migration.

Key words Riphean, Precambrian, Sparry magnesite, Metasomatic fluids, REE, South Urals

摘 要 乌拉尔省南部赋存有两种类型的晶质菱镁矿:1)白云岩地层中的层状矿体;2)白云质灰岩中的透镜状矿体。晶质菱镁矿矿体位于 Riphean 系列中下层的白云岩中,而在上层的白云岩单元中缺失。这两种类型的菱镁矿可通过矿体形态、晶体大小、石英和白云石含量不同来进行区分。第一种类型的菱镁矿储量巨大,菱镁矿呈粗粒结构,晶体粒径 > 10mm(最大达 150mm);一般来说,矿体与白云岩围岩界限清楚,这种类型矿床以产在 Riphean 序列下部为特征。第二种类型的菱镁矿由于菱镁矿矿体穿插进入到白云岩围岩中,矿体很不规则,菱镁矿晶体也相对较小(1-5mm),这种类型的矿体主要产在 Riphean 中部层位中。这两种矿体都显示了交代成因的特征。但这两种菱镁矿矿石在一些主量元素和稀土元素的分布上具有不同的特征:与第二种类型相比,第一种菱镁矿具有较低的 FeO,CaO 和 SiO_2 含量,与白云岩围岩(La/Lu > 1)相比,具 La/Lu < 1 的轻稀土亏损特征。第二种菱镁矿稀土分馏度较低,在稀土分配方面与白云岩围岩有差别。本文还特别讨论了 Y/Ho 值的重要性,因为该比值在菱镁矿和围岩中的类似性使得划分菱镁矿形成中的热液和成岩交代过程成为可能。因此我们认为,第一种类型菱镁矿,如具有高 Y/Ho 比值的 Satka 和 Bakal 矿床的形成属于沉积盆地发育过程中的早期成岩阶段;第二种类型菱镁矿,如具有低 Y/Ho 值的 Ismakaevo 和 Katav-Ivanovsk 矿床的形成与流体运移的热液活动有关。

关键词 Riphean 地层 前寒武纪 晶质菱镁矿 交代流体 REE 乌拉尔南部

中图法分类号 P578.61; P588.247; P534.1; P595

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1 Introduction

Sparry magnesite deposits (the so called Veitsch type, after Redlich, 1909) are the main type of magnesite for refractory production in the world. This type of magnesite deposit is spread in the Precambrian carbonate complexes and occurs in China, Northern Korea, India, Russia (Southern Urals, Yenisey ridge, Eastern Sayan, Karelia), and in the Paleozoic carbonate-terrigenous sequence of the Western Europe (Austria, Slovakia, Spain) (Anfimov *et al.*, 1980; M ller, 1989; Ellmies *et al.*, 1999; Jiang & Jiang, 2000; Prochaska *et al.*, 2000; Chen *et al.*, 2003; Jiang *et al.*, 2001, 2004; Ebner *et al.*, 2004). The origin of this strata-bound type is a subject of discussion during a long time of investigation. On one hand a strata-like shape of ore bodies and location in the shallow marine and lagoon conditions point to a connection with sedimentation (Pohl & Siegl, 1986; Urasina *et al.*, 1993), but on the other hand sedimentary precipitation of magnesite and country dolomite is not confirmed by experiments. Besides, some features of magnesite ore bodies indicate to metasomatic origin cutting of sedimentary bedding, a very irregular shape of magnesite bodies' lateral contacts (Anfimov *et al.*, 1983), a coarse-grained structure of magnesites and zebra banding as the result of dolomite replacement (Lugli *et al.*, 2000). There are envelopes of metasomatic dolomites around magnesite bodies in limestone strata of the Western Europe Paleozoic deposits (Radvanec & Prochaska, 2001).

The ore genesis of magnesite deposit can be constrained using geochemical features of the magnesite ores and their host rocks. Some geochemical features of magnesite can be regarded as metasomatic, for example, sometimes the increase of FeO in magnesite in comparison with host carbonates, some minor and trace elements can be considered as a genetic indicator of magnesite formation, because they compose specific minor mineral phases, for example Cr, Co, Ni for ultramafic rocks (M ller, 1989). The increase of REE contents sometimes reveals hydrothermal metasomatic magnesites in comparison with sedimentary carbonates; fractionation with HREE enrichment in the magnesites is quite characteristic of this metasomatic process (Morteani, 1982; M ller, 1989). Carbon and oxygen isotope composition of sparry magnesite corresponds to the model of sedimentary origin (Schroll, 2002), but there is oxygen isotope fractionation in sparry magnesites in comparison with host carbonates. Value of Y/Ho ratio, as it was shown by Bau (1996) is one of the indicators of hydrothermal alteration of carbonate and a distance of fluid migration. This ratio for the Urals sparry magnesites and country rocks is discussed in this paper.

2 Geological setting

There is a huge province of sparry magnesite deposits in the Southern Urals with resources of about 1 billion tons. These deposits belong to Veitsch type (Satka type in Russia) and occur in a stratotypical place of Riphean sequence

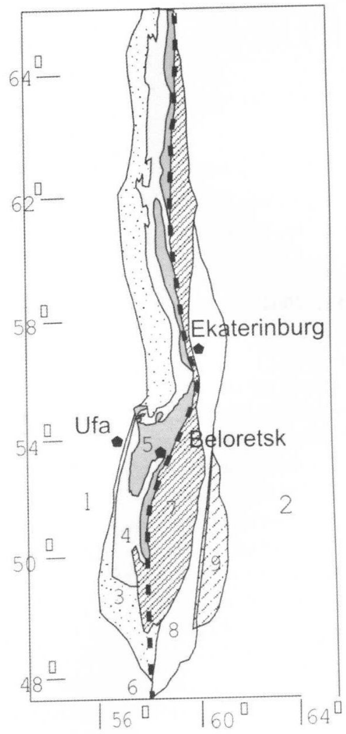


Fig. 1 Schematic geological map of Urals folded belt (Middle and South part).
1 – East-European platform (platform mantle); 2 – West-Siberian plate (platform mantle); 3 – Pre-Uralian Foredeep; 4 – West-Uralian folded zone; 5 – Central-Uralian zone (Bashkirian mega-anticlinorium); 6 – Main Uralian fault; 7 – Magnitogorsk mega-sinclinorium; 8 – East-Uralian zone; 9 – Trans-Uralian zone.

The Riphean sequence is located in the Bashkirian mega-anticline (the BMA) folded and thrusted megastructure in the western slope of the Southern Urals within the frames of the Central Urals uplift (Fig. 1). This tectonic structure has an intricate history as a result of Cadomian orogeny in the eastern margin of Baltica (in the modern geographic coordinates) and Variskan collision of the East-European platform with Asian microplates and intervening oceanic terrains. The major suture between these plates is the Main Uralian fault (Zonenshain *et al.*, 1984). The BMA borders on Paleozoic megastuctures of the Urals in the west with West-Uralian folded zone and Pre-Uralian foredeep, in the east via the Main Uralian fault with structures of the ocean crust and terrains: Magnitogorsk megasynclinorium, the East-Uralian and Trans-Uralian zones. The size of the BMA is about 300 × 100 km (Fig. 2). There are three stratigraphic series: Lower (interval of ages is 1650 ~ 1350 Ma), Middle (1350 ~ 1050 Ma) and Upper Riphean (1050 ~ 650 Ma) with a general thickness of sequence 15 km (Semikhatov, 1991). These series consist of terrigenous rocks (conglomerates, arkose and quartz sandstones, shales) in the lower part and clay-carbonate rocks (shales, limestones, dolostones) in the upper part. Lower and Middle Riphean series contain volcanic rocks in the base (basalts). There is a N/S- trending rift valley in the eastern part of the BMA in the beginning of the Middle Riphean Mashak formation, but it absent in the central and western parts of the BMA. It contains basalts, liparites and coarse-terrigenous rocks and reaches the thickness of up to 3000 m. The zircon U-Pb age of Mashak volcanic rock is 1348 ± 30 Ma (Semikhatov, 1991).

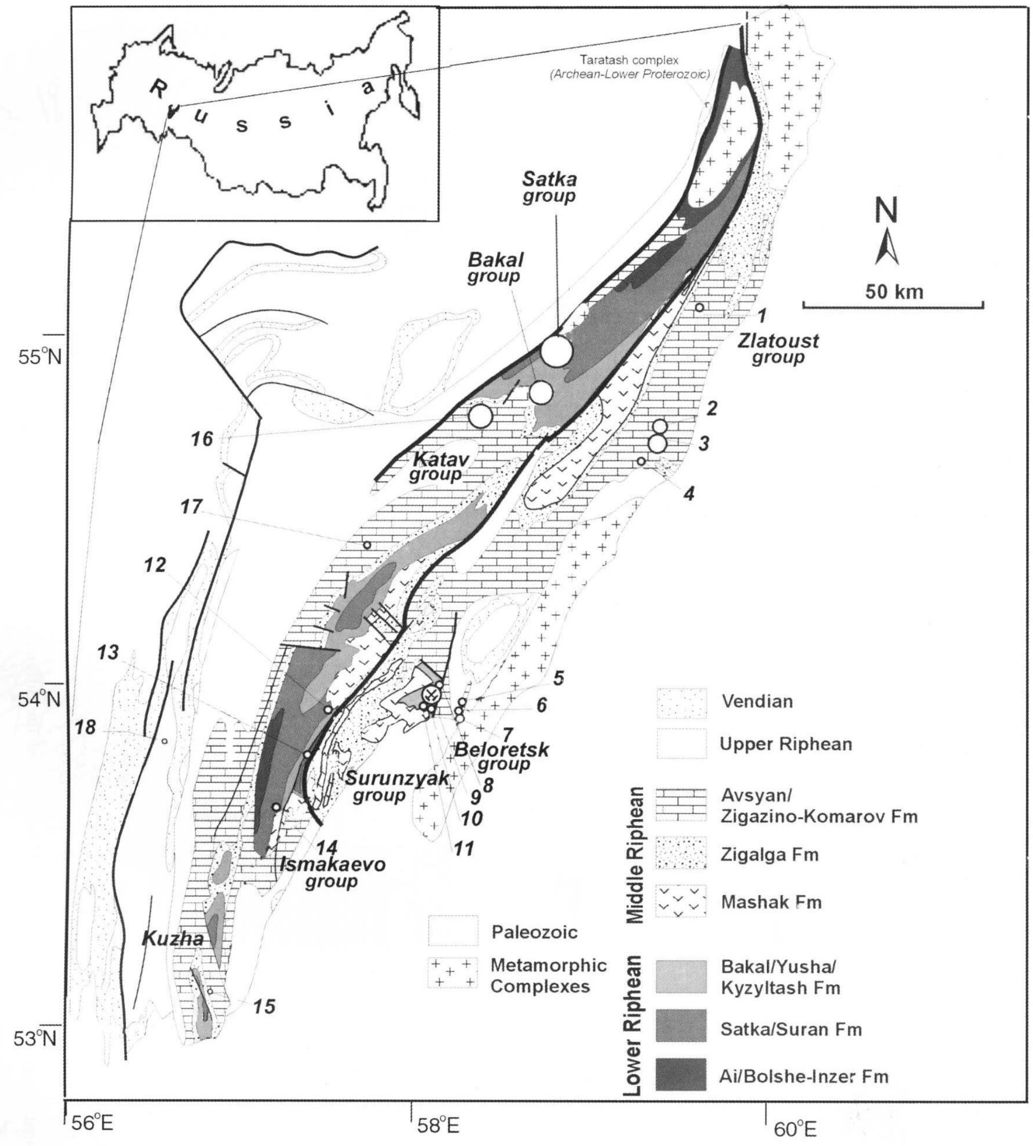


Fig. 2 Schematic geological map of Bashkirian mega-anticline. Magnesite occurrences:
1-Zlatoust; 2-Veselovskoe; 3-Semibratskoe; 4-Khutor; 5-Kataika; 6-Otnurok; 7-Egorova Polyana; 8- Aznalin; 9-Kyzyltash; 10-Yandyk; 11-Belyatur; 12 -Yusha; 13-Kardon; 14-Ismakaevo; 15-Yaru; 16-Katav-Ivanovsk; 17-Baygaza; 18-Saryshka (borehole).

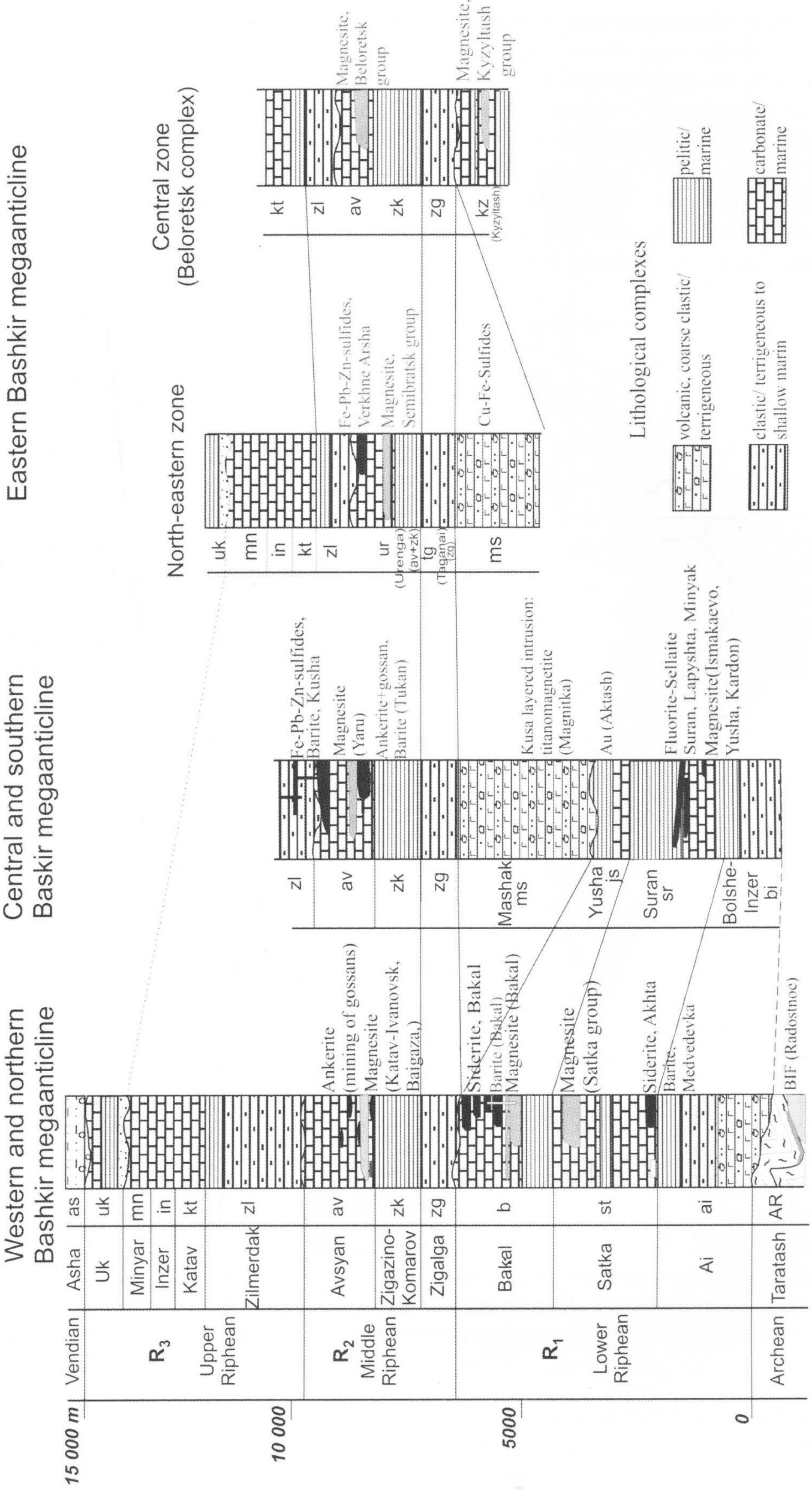


Fig. 3 Schematic stratigraphic columns and metallogeny of the different parts of the Bashkirian meganticlinorium

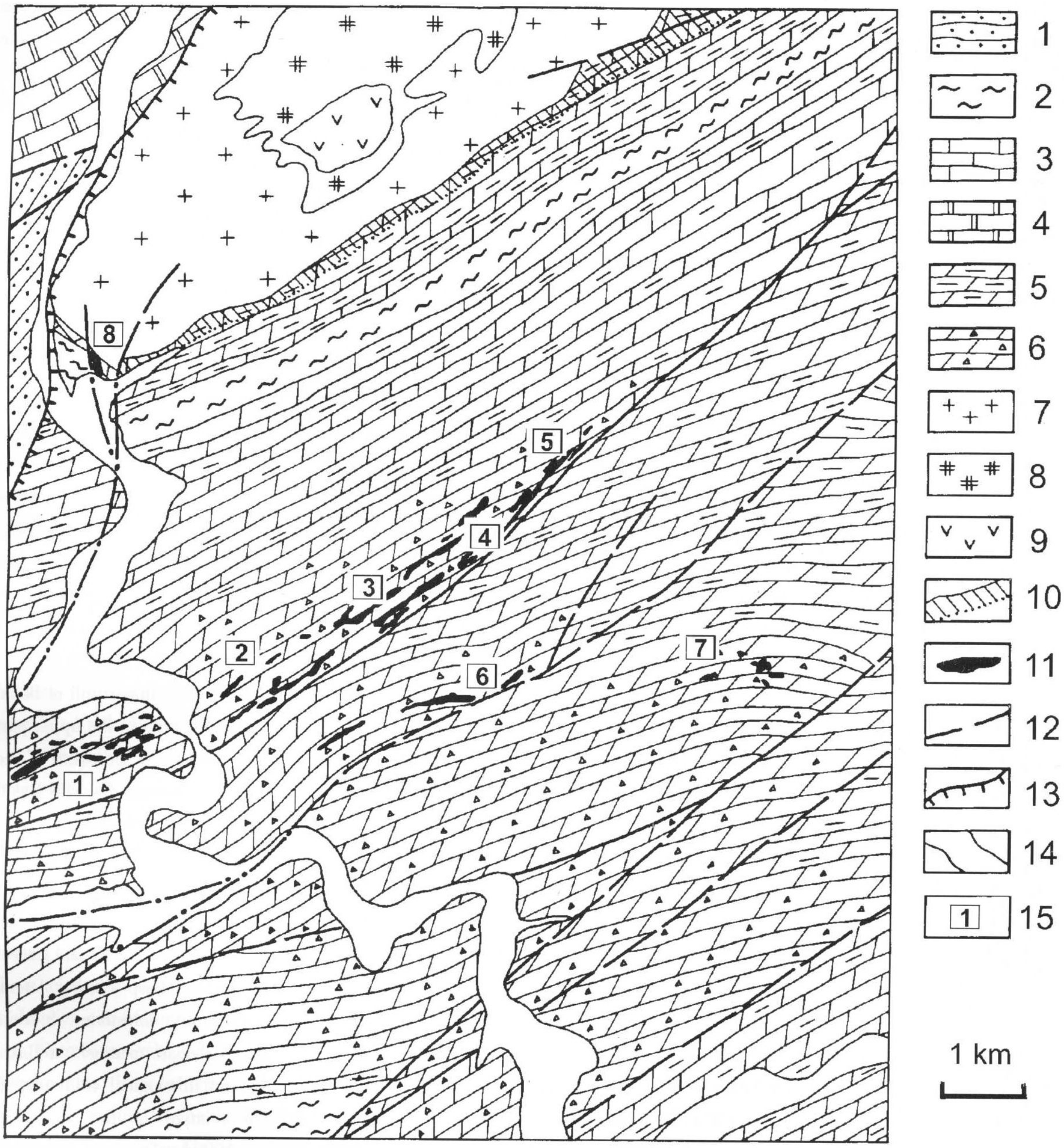


Fig. 4 Geological map of Satka ore field.
1-arcose sandstones (Upper Riphean); 2-black slates; 3-limestone's (Upper Riphean); 4-calcareous marl (Upper Riphean); 5-clayey dolomites (Lower Riphean Satka fm.); 6-massiv, brecciated and laminated dolomites (Karagay member of Lower Riphean Satka fm.); 7 ~ 9-Berdiaush rapakivi massif: 7-granite rapakivi; 8-sienite rapakivi; 9-nepheline sienite; 10- contact marble; 11-magnesite bodies; 12-faults; 13-Bakal-Satka regional thrust; 14-alluvium; 15-magnesite deposits: 1 ~ 5 Satka deposit, parts: 1- Karagay, 2- Melnichny, 3-Palenikha, 4-Volchegorsky, 5-Stepnoy; 6-Nikolskoe; 7-Berezovskoe; 8-Elnichnoe.

The Riphean sequence deposited predominantly in shallow sedimentary basin in the eastern part of the East European platform (Ufa-Gozhan aulacogen). There are unconformities and erosion of underlying stratigraphic units in the base of the series. As the majority of lithological and geochemical indicators point, during the Lower and part of the Middle Riphean time these sedimentary basins existed in humid and semiarid climate, while in the Upper Riphean time predominantly in arid conditions (Maslov *et al.*, 1999). The Upper Precambrian sedimentary sequence was folded and thrusted by some stages of tectonic activity, and the modern structure of the BMA consists of different synclinoriums and anticlinoriums (Giese *et al.*, 1999). Their main tectonic stages were Cadomian and Variscan. Generally sedimentary rocks are affected by burial epigenesis in the western and central parts of the BMA and greenschists/amphibolites in the eastern part of megastructure. There are very rare intrusive massifs in the BMA and some generations of diabase dykes, having regional spreading. Berdyaush rapakivi granit massif with the age of 1354 ± 20 Ma (zircon U-Pb, Semikhatov, 1991) occurs near the Satka ore field and exposes contact affect on magnesite. As it was shown for the Lower Riphean SMD diabase is younger than magnesite with the presence of contact metamorphic aureoles of dolomite marble and brusite. In Bakal ore field it was found a short time window (about 70 Ma) for the formation of magnesites between lithification of carbonate rocks and intrusion of the diabase dykes (Krupenin & Ellmies, 2001).

Magnesite deposits are located at two levels in the Lower Riphean sequence in dolomite horizons of Suran/Satka formations and Kyzyltash/Bakal formations and at the single level of Avzyan formation of the Middle Riphean (Fig. 3). There are some different types of stratabound deposits in the terrigenous-carbonate units of the BMA. Siderite deposits of Akhta and the largest in the world Bakal ore field have the reserves of about 1 billion tons. Other deposits have a middle level of reserves: barite deposits Medvedevka, Kuzha, Tukan etc.; Pb-Zn deposits Kuzha, Verkhne-Arshinka, Nikolaevka etc.; fluorite deposit Suran, some small gold deposits; ankerite mineralization as the precursor of gossans and limonite deposits.

The province of sparry magnesite consists of several ore districts, which contain ore groups and some single sparry magnesite deposits (SMD) and occurrences. There are the following districts for the Lower Riphean (LR) sequence: Bakal-Satka, Surunzyak, Ismakaevo and for the Middle Riphean (MR) sequence: Zlatoust, Beloretsk, Katav, Kuzha (see Fig. 2). Sparry magnesite deposits are located in the dolostones of the Lower and Middle Riphean series and are absent in dolostones units of the Upper Riphean. The Satka deposit has geological reserves about 300 Mt. Just this deposit is the place of refractory production, because other SMD have a bit worse conditions. The annual output of "Kombinat Magnesit" enterprise is 2.4 Mt of raw magnesite and 600 Kt of periclase powder and different refractory wares. There were exploited such SMD as Katav-Ivanovsk (reserves ore about 0.4 Mt), Kyzyltash (16 Mt), Aznalin (1.9 Mt). In previous time were explored in different degree the following SMD: Semibrtskoe (375 Mt), Bakal (3.7 Mt), Ismakaevo (115 Mt), Egorova Polyana (0.15 Mt).

It was established that a complex of geological and geochemical features allows the distinguishing all the deposits into two main groups: 1) layer-like bodies in the stratigraphic dolostone horizons; 2) lens-like bodies in the dolomitized limestones. The resources of the first group are huge; magnesite has a coarse-grained structure with crystal size of more than 10 mm (up to 150 mm), as a rule, sharp boundaries of ore bodies with host dolomites. This type of deposits is typical for the Lower Riphean sequence. The second group of deposits has a very irregular shape of ore bodies with impregnation of magnesite crystalls into host dolomites, with relatively small size of magnesite crystals (1 ~ 5 mm). The second type predominates in the Middle Riphean sections. All the deposits possess the features of metasomatic origin (Krupenin, 2002).

The Satka ore field occurs in the northern part of the BMA and belongs to Satka Fm. (stratigraphic equivalent of Suran Fm.) in the middle part of the Lower Riphean sequence. Some layer-like large and a lot of small magnesite ore bodies are located in the Karagay stratigraphic dolostone horizon in the upper part of Satka Fm. The thickness of ore bodies reaches 40 m. There is a magnesite band, spreading for 12 km in NE direction on the western slope of Satka syncline (Fig. 4). Some tectonic faults cut this belt in different parts, which are the boundaries of single deposits. There is a magnesite Elnichnoe deposit in a tectonic bloc at the contact with a Berdyaush pluton of rapakivi granite in the western part of the Satka ore field. This deposit is deformed by pluton and has secondary dolomitization at the contact zone of the layer-like ore body. Magnesites of Satka ore field have the best quality in the province. There are admixtures of dolomite (about 2% CaO), quartz, Mg-chlorite, rare talc (about 1% SiO_2), accessory pyrite, marcasite and sphalerite.

Bakal group of deposits is situated in the upper unit of Bakal Fm. (stratigraphic equivalent of Kyzyltash Fm. in the upper part of the Lower Riphean sequence) and occurs 20 km south of the Satka group. The SMD of Bakal Fm. partly coincides with Bakal siderite ore field, the largest in the world. The magnesite bodies lie in the widespread Shuidin dolostone horizon with a thickness of 50 ~ 60 m within the unit of slates and limestones intercalation with the thickness of about 1 km. The magnesite layer-like bodies locate in the lower part of a dolostone horizon and have a thickness from 3 to 30 m. They have sharp cutting lateral contacts with host laminated and stromatolite dolostones. Siderite metasomatic bodies occur in all five carbonate members of Bakal Fm. There are a lot of geological and lithological evidences of secondary nature of the siderite relative to the magnesite (Krupenin, 1999; Ellmies *at al.*, 1999). Our new data show that magnesite was formed before 1360 Ma (time of diabase penetrating during the Mashak event), but siderite metasomatically replaced country rocks of limestones, dolomites and partly magnesites only during the next tectonic event near 1010 ± 100 Ma (Krupenin & Ellmies, 2001; Krupenin, 2001). In magnesite main admixtures are present: dolomite (5 ~ 10%), quartz, calcite, Mg-chlorite and sulfides consist of less than 1%. The content of FeO varies from 0.44% to 5.39 % and is connected with secondary influence of sideritization and Fe-dolomite admixture in the magnesite.

Ismakaevo deposit occurs in the southern part of the BMA and locates in the lower part of Suran Fm. (stratigraphic equivalent of Satka Fm.). This deposit occurs very closely to the Mashak riftogenic zone. There is a very complicated tectonic structure of this deposit. The thickness of ore lens-like bodies reaches 400m. They lie concordantly with strongly folded country carbonate sequence, which is represented by dolostones and dolomitized limestones. Quartz admixture reaches 8 %, dolomite 5 ~ 6%, Mg-chlorite 2%, graphite, talc and calcite accessory. There is iron admixture in magnesite with FeO contents from 1.8 to 4.22%.

In the central part of the BMA there is a Surunzyak group of SMD with a large Kyzyltash deposit and some others. These deposits are located in the schist-carbonate unit of Kyzyltash Fm. (stratigraphic equivalent of Bakal Fm.) of the Lower Riphean sequence. Magnesite bodies occur in intercalation of dolomite-limestone beds and quartz-sericite-graphite, talc-chlorite schists with the thickness of about 400 m. There are 10 lens-like magnesite bodies with the thickness up to 70 m and the length of strike to 400 m in the Kyzyltash deposit. Ore lodes occur conformably with country carbonate rocks. Quartz admixture makes up – 15%, dolomite – 3 ~ 4%, talc – 2%, sericite, Mg-chlorite, calcite, sulfides - accessory. The content of FeO in magnesite ranges in 0.12 ~ 4.11%.

As a rule, limestones overlie magnesite-bearing dolomite horizons in all of the deposits. It is quite typical the presence of brecciated dolomites in the magnesite-bearing horizons.

Generally, the mineral composition of the Lower Riphean magnesite ores is simple and makes up 95 ~ 99% of magnesite. Admixtures include quartz, dolomite, Mg-chlorite (pennine), pyrite, disseminated carbonaceous (shungite), talc, very rare calcite microscopic veins, clastic biotite, apatite, rutile. Talc is found in different deposits as small lenses and nests in the contact parts of ore bodies. In the country dolomite rocks, all these mineral-admixtures are also present, additionally mica and hydromica can be found.

Katav-Ivanovsk deposit occurs in the Middle Riphean Avzyan Fm. It is a typical deposit of the Middle Riphean, because it occurs in the lower part of Avzyan Fm. (Kataskin Member). This member consists of dolomites and dolomitized limestones, sometimes with beds of black slates; a thickness of sequence varies from 200 to 700 m. There are some lens-like and layer-like ore bodies at one level with a thickness reaching 5 m. Boundaries of ore bodies are a zone of disseminated fine and middle-grained magnesite in the dolomite. The length of ore bodies is 700 ~ 1100 m. Admixtures of magnesite are quartz and black cherts, dolomite and calcite.

The largest SMD of the Middle Riphean sequence Semibratskoe deposit occurs in the eastern part of the BMA, in the Urenga fm. (the eastern equivalent of Avzyan fm.) and has reserves of about 300 Mt. It locates in dolomite marble and sericite-graphite schists and possesses similar features of distribution as the Katav-Ivanovsk deposit. Talc is a widespread admixture in this deposit.

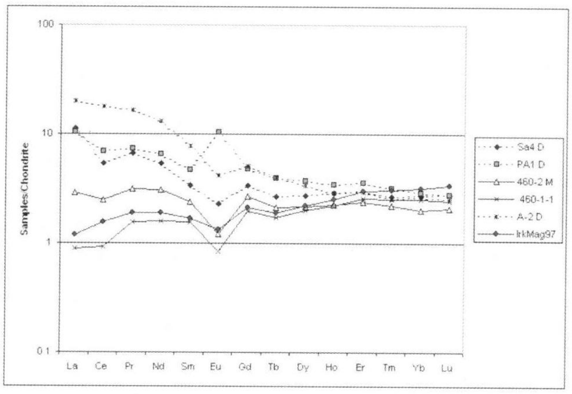
3 Some geochemical features of the Urals sparry magnesites

3.1 Major elements:

A bulk of statistic data shows that magnesites of the first group have lower contents of FeO, CaO and SiO_2 in comparison with magnesites of the second group (Table 1). As a rule, iron is an isomorphic admixture for Mg^{2+} in the crystal lattice of magnesite. Sometimes there are breinerites in the Middle Riphean deposits with total FeO reaching nearly 11 wt.% (Krupenin, 2002). CaO contents in magnesite are due to dolomite admixture. SiO_2 contents are due to quartz of sedimentary origin (quite often cherts for Avzyan Fm.) and/or Mg-chlorite and sometimes with talc in deposits affected by metamorphism (Kyzyltash, Semibratskoe). It is important to emphasize that for the Southern Urals province the content of FeO in magnesites is always several times more than that in the country rocks of dolomites.

3.2 Trace and rare earth elements:

Concentrations of trace elements in magnesites are similar to those in country rocks of dolomites and correspond to Clarke level for carbonate rocks (Ellmies *et al.*, 1999). Such element-indicators for base and ultramafic magmatic rocks such as Ni, Co, Cr, Cu do not show enrichment in magnesites. REE contents in magnesites and country rocks are of typical sedimentary rocks (Taylor & McLennan, 1985), and show enrichment with the increase of terrigenous mixture (Table 2). REE and trace elements were analyzed by ICP-MS method (Perkin-Elmer/Sciex Elan Model 500) in GeoForschungs Zentrum, Potsdam, as described by Dulski (1994). There is always a visible mineralogical control for the first group of magnesites in chondrite (C_1) normalized REE distribution patterns. The magnesites are LREE depleted with La/Lu < 1 in comparison with country rocks of dolomites (La/Lu > 1). It can be a result of fractionation and the decrease of LREE, which is related to metasomatic recrystallization (Müller, 1989). REE distributions in dolomites are typical of Ca-bearing minerals with primary fractionation (La/Lu > 1) because effective ionic radius of Ca and LREE is close. Magnesite does not contain Ca in the lattice, but Mg has an effective ionic radius close to HREE. Consequently during metasomatic replacement, LREE will be rejected and HREE will be inherited by magnesite (Fig. 5a). There is a slight Ce and Eu negative anomaly in both dolomites and magnesites, inherited from marine carbonates. The more coarse-grained magnesites show further decrease of LREE and increase of HREE (Krupenin, 2002). An unusual slight positive Eu anomaly (Fig. 5a) is observed for a single sample of secondary dolomite marble from a contact zone between magnesite and diabase dyke from the Satka ore field. This feature is typical of hydrothermal conditions with temperatures of more than 250℃. It depends on the exchange of Eu valence and the size of the effective ionic radius (Bau, 1991). The same REE feature is typical for magnesites from Ismakaevo SMD (Fig. 5b), suggesting a hydrothermal origin of this deposit.



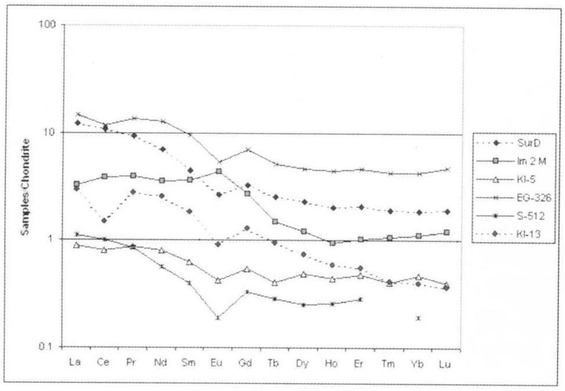


Fig. 5 Plots of REE distributions in the Urals province magnesites and country rocks of dolomites;

a: SMD of the first group: Satka ore field: Sa4 D host dolomite; PA1D recrystallized secondary dolomite in the contact of magnesite and diabase dyke; 460-2 middle crystalline magnesite; 460-1-1 giant crystalline magnesite; Bakal ore field: A-2 D host dolomite; IrkMag97 coarse-grained magnesite; b: SMD of the second group: Ismakaevo deposit: SurD - host dolomite of Suran fm.; Im-2 sparry magnesites; sparry magnesits and dolomites of the Middle Riphean: KI-5 magnesites, Katav-Ivanovsk deposit; EG 326 - sparry magnesite, Egorova Polyana deposit; S-512 - sparry magnesite, Semibratskoe deposit; KI-13 host dolomites, Katav-Ivanovsk deposit

Table 1 Average chemical composition of sparry magnesites from Urals Riphean deposits

	Deposits	N	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	LOI	P_2O_5	S
1	Satka**	110	1.0	0.01	0.3	0.2	0.6	0.03	46.0	0.8	0.04	0.02	50.8	0.01	0.1
2	Elnichnoe**	16	0.8	0.02	0.3	0.3	1.4	0.05	45.3	1.2	0.03	0.04	50.6	0.017	0.15
3	Bakal	4	0.42		0.14	0.57	3.73	0.03	40.49	5.33			49.69	0.13	
4	Kyzyltash	4	1.37	0.02	0.41	0.64	1.53	0.05	44.13	0.56	0.05	0.05	50.21	0.01	
5	Ismakaevo**	144	5.1		0.5	2.2*			43.3	0.9			46.7		
6	Semibratskoe**	23	0.9	0.03	0.3	1	5	0.14	41.6	1.6	0.05	0.06	49	0.04	0.11
7	Katav-Ivanovsk	4	5.68		0.29	1.33	1.85	0.09	38.12	4.34	0.05	0.12	46.90	0.02	

Comments: N-numbers of samples; *-Fe_2O_3 + FeO; **-after (Urasina *et al.*, 1993).

Table 2 Minor and rare earth elements in the Lower and Middle Riphean magnesites and host rocks of dolomites of the Southern Urals

Element	Sa 4	PA 1 Re-Dol	460-2	460-1-1	A-2 b3 Irk	IrkMag97	Suran1 Dolomit	Im 2	KI-5	EG-326	KI-13	S-512
Rb	< 0.1	< 0.1	< 1	< 1	1.499	0.5	1.26	0.441	0.909	0.137	0.12	
Sr	31.298	127.986	0.944	1.638	34.941	90.3	26.9	4.946	23.509	1.953	122	
Y	8.230	9.485	6.417	6.427	4.575	7.93	3.35	1.718	0.853	10.158	1.17	
Zr	0.387	0.590	0.196	< 0.1	2.316	0.15	3.24	1.204	1.052	0.598	0.5	
Cs	0.017	< 0.01	0.0245	0.0197	0.126	0.02	0.046	0.030	0.0345	0.0282	< 0.02	
Ba	3.529	12.034	4.660	5.309	37.322	9.7	7.2	2.659	11.814	3.941	17.2	
La	2.626	2.451	0.676	0.207	4.707	0.28	2.87	0.771	0.211	3.467	0.689	1.120
Ce	3.255	4.201	1.484	0.560	10.740	0.95	6.51	2.300	0.486	7.107	0.903	1.006
Pr	0.593	0.658	0.280	0.140	1.477	0.168	0.83	0.349	0.0783	1.201	0.246	0.853
Nd	2.445	2.958	1.392	0.726	5.885	0.85	3.17	1.601	0.365	5.806	1.161	0.568
Sm	0.502	0.694	0.351	0.228	1.152	0.249	0.65	0.530	0.0930	1.411	0.269	0.394
Eu	0.128	0.588	0.0673	0.0474	0.233	0.075	0.15	0.243	0.0239	0.299	0.051	0.189
Gd	0.660	0.950	0.525	0.385	0.9935	0.42	0.64	0.537	0.106	1.366	0.251	0.331
Tb	0.097	0.144	0.077	0.0629	0.1451	0.069	0.09	0.054	0.0148	0.186	0.034	0.284
Dy	0.660	0.898	0.528	0.485	0.8161	0.533	0.56	0.291	0.119	1.129	0.180	0.255
Ho	0.160	0.191	0.125	0.122	0.160	0.14	0.11	0.052	0.0244	0.247	0.033	0.260
Er	0.477	0.567	0.379	0.412	0.467	0.475	0.33	0.162	0.0761	0.741	0.088	0.288
Tm	0.065	0.077	0.053	0.0609	0.0624	0.074	0.05	0.026	0.00988	0.103	0.010	
Yb	0.442	0.467	0.325	0.414	0.428	0.521	0.31	0.181	0.0755	0.695	0.064	0.194
Lu	0.068	0.068	0.0507	0.0591	0.0621	0.082	0.05	0.030	0.0097	0.114	0.009	
Hf	< 0.05	0.05	< 0.05	< 0.05	0.0718	0.03	0.09	< 0.05	< 0.03	< 0.03	< 0.03	
Pb	0.554	1.398	2.623	2.753	6.521	1.77	1.36	0.701	4.319	1.451	3.76	
Th	0.135	0.058	0.0477	0.0186	0.979	0.1	1.43	0.266	0.145	0.264	< 0.1	
U	0.910	0.757				0.651	0.31	0.098	0.147	0.114	0.16	

Comments: Samples numbers correspond to fig. 5.

Magnesites of the second group have a low degree of fractionation and differences in REE distributions between magnesites and country rocks of dolomites (Fig. 5b). Possibly it is due to the absence of recrystallization in the Middle Riphean SMD. It is proposed that recrystallization of the Lower Riphean SMD depends on secondary heating and fluid migration. The reason for this process can be the Mashak riftogenic event at the beginning of the Middle Riphean time.

4 Y/Ho distributions in magnesite deposits

Y/Ho is a characteristic feature of carbonate genesis. Primary Y/Ho ratio for magmatic carbonates varies in the range of 24 ~ 34 and shows charge-and-radius-controlled (CHARAC) trace element behavior in geochemical system, or chondritic ratio (Bau, 1996). It is characteristic of a twin pair of coherent elements with similar charge and ionic radius, such as Y and Ho, Zr and Hf. The first pair of elements possesses a concentration, which it is possible to check up in carbonate rocks. In aqueous solution the behavior of elements is distinguished from the CHARAC behavior in silicate melts. Marine carbonates precipitate in the geochemical system with complexing ligands and have Y/Ho varying from 35 to 60. It is a little bit less than that for the seawater (Y/Ho from 40 to 70). Hydrothermal carbonates have Y/Ho ratio smaller than those of the rocks from which Y and Ho have been mobilized (Bau, 1996). For hydrothermal carbonate the decrease of Y/Ho ratio is progressive with the increase of migration distance.

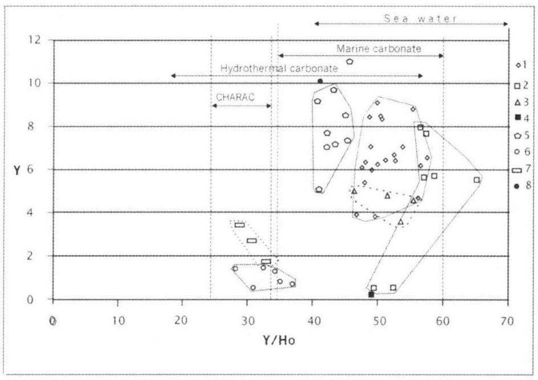


Fig. 6 Distributions of Y vs Y/Ho for magnesites from Southern Urals province.

1-Satka ore field; 2-Bakal ore field; 3-Elnichnoe deposit of Satka ore field; 4-Salda Goulu alkaline (soda) lake, Turkish (sample of Dr. Ellmies); 5-Kyzyltash; 6-Katav-Ivanovsk; 7-Ismakaevo; 8-Egorova Polyana.

Distribution of Y/Ho ratio vs. Y for different magnesite deposits of the Southern Urals province shows that dots of single ore fields or deposits occur in local areas (Fig. 6). It can be a result of specific genetic peculiarities of magnesite forming in a single ore field. Magnesites of Satka and Bakal ore fields and Kyzyltash deposit of the Lower Riphean sequence are located in the range of 40 ~ 65 Y/Ho ratio, corresponding to marine carbonate, however, magnesites of Katav-Ivanovsk (the Middle Riphean sequence) and Ismakaevo (the Lower Riphean) belong to hydrothermal carbonate area (all data applied is shown in Table 3).

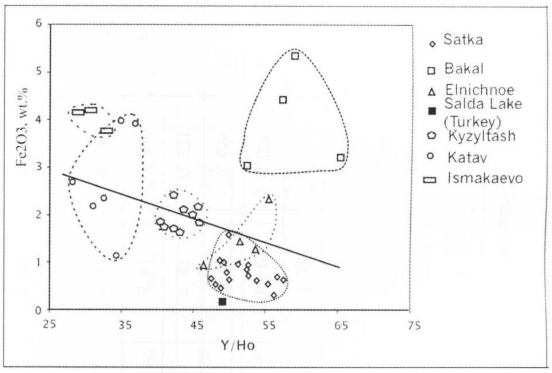


Fig. 7 Distribution of Fe_2O_3 vs Y/Ho for magnesites from Southern Urals province. The same captions as in Fig. 6.

It was obtained regularity in distribution of Y/Ho versus Fe_2O_3 total content for magnesite deposits of the Southern Urals province (Fig. 7). There are close areas of points in different ore fields, which allow the distinguishing of different objects. Magnesites of large layer-like deposits of the first group (Satka, Bakal, Kyzyltash) show a low content of Fe_2O_3 and high values of Y/Ho ratio, similar to marine carbonates. Only magnesites from Bakal Fm. have a higher content of Fe_2O_3, but it can be influenced by secondary sideritization in this ore, as in the same stratigraphic unit there is the Bakal siderite ore field. Our investigations allow getting the evidence of secondary nature of siderite according to magnesite. Previous investigation of magnesites in the frame of the whole Bakal ore field demonstrated varying Fe_2O_3 content from 0.44% to 5.39 % in dependence on proximity of siderite ore. Other magnesite ore fields, which belong to the second group, have a high content of Fe_2O_3 and a low Y/Ho ratio typical of hydrothermal carbonates. This regularity is emphasized by the location of dots for the Ismakaevo deposit. Magnesites with positive Eu anomaly were obtained just for this deposit. According to geochemical property of Eu to have transition of Eu^{3+} in Eu^{2+} with the temperature above 25℃ (Bau, 1991) this feature demonstrates a relatively high temperature of magnesite formation in the Ismakaevo deposit. A geological

Table 3 Contents of Y, Ho and Fe_2O_3 in magnesite of Southern Urals province

Sample	Y	Ho	Y/Ho	Fe_2O_3
Katav-Ivanovsk:				
KI-5	0.853	0.024	35.057	3.960
KI-10	0.710	0.019	36.890	3.920
ki-15	0.553	0.018	30.983	2.170
KI-16	1.462	0.052	28.208	2.680
KI-LAR-1	1.297	0.038	34.281	1.150
KT-324	1.471	0.045	32.523	2.340
EG-326	10.158	0.247	41.149	1.960
Salda Lake:				
G1	0.245	0.005	49.097	0.180
Kyzyltash:				
KY-28-1	9.688	0.224	43.217	1.660
KY-28-2	7.335	0.161	45.461	2.170
KY-28-3	7.124	0.163	43.608	2.130
KY-28-4	8.519	0.189	45.034	1.990
KY-28-5	10.992	0.241	45.679	1.860
KY-28-6	7.036	0.166	42.284	2.400
KY-IV-36Mg	7.687	0.182	42.224	1.700
KY-IV-36Dm	5.062	0.124	40.907	1.760
KY-123m	9.174	0.225	40.751	1.910
Satka:				
PA 4	4.660	0.083	56.265	0.290
SA 5	7.060	0.144	48.918	0.450
Kar94Mag	8.487	0.168	50.399	
458-2	6.221	0.129	48.117	0.540
458-4	3.833	0.077	49.684	0.780
458-7	8.348	0.165	50.585	
459-1	3.928	0.084	46.817	
459-2	9.084	0.182	49.897	1.570
459-3	5.969	0.122	49.098	1.000
460-1	5.372	0.112	48.037	
460-1-1	6.427	0.122	52.669	0.710
460-2	6.417	0.125	51.267	0.950
461-3	6.650	0.127	52.500	0.860
260-0-1	8.455	0.173	48.816	1.020
K1M	6.677	0.127	52.700	0.940
K4M	6.268	0.125	50.007	0.640
K5M	6.072	0.128	47.583	0.660
K8M	6.522	0.113	57.662	0.660

Sample	Y	Ho	Y/Ho	Fe_2O_3
K9M	7.048	0.131	53.857	0.610
K10M	6.151	0.109	56.653	0.700
K11M	8.813	0.159	55.399	0.540
Elnichnoe:				
EL 2	4.766	0.092	51.543	1.420
EL 11	3.588	0.067	53.619	1.250
EL 12a	4.998	0.108	46.450	0.940
EL 13b	4.563	0.082	55.582	2.300
Bakal:				
IR75-M	5.497	0.084	65.203	3.210
Gaev94	7.690	0.134	57.388	
IrkMag97	7.930	0.140	56.643	
Irk94MS	5.709	0.097	58.747	
386k	5.709	0.097	58.747	5.340
BMz-D	0.477	0.010	49.445	
BMz	0.546	0.010	52.443	3.040
MgCK	5.624	0.098	57.172	4.450
Ismakaevo:				
Im 1	2.689	0.088	30.727	4.180
Im 2	1.718	0.052	32.907	3.760
Im 3	3.443	0.119	28.904	4.120
Eugui, Spain, Average of 25 samples (Lugli *et al.*, 2000):				
EugDol	8.728	0.248	35.235	1.012
EugMgz	5.984	0.186	32.139	1.017
Average values for country rocks of ore deposits (quantity of samples)				
Satka deposit:				
Dolomites(19)	9.095	0.182	50.043	
Elnichnoe:				
Dolomites (3)	9.801	0.194	50.561	
Bakal:				
Limestones (5)	1.784	0.032	56.467	
Dolomites (30)	6.970	0.186	37.456	
Siderites(23)	6.753	0.208	32.405	
Ankerite vein	20.013	0.600	33.346	
Ismakaevo:				
Dolomite (2)	6.358	0.194	31.905	
Katav-Ivanovsk:				
Dolomites (15)	1.598	0.048	33.361	
Upper Riphean sequence				
Limestones (2)	2.036	0.046	44.709	

position of this deposit on the border of the Middle Riphean Mashak rift graben with a contrast basalt-rhyolite magmatic complex does not contradict to such conclusion.

In Figure 8, we demonstrated relations between average values of Y/Ho ratio in magnesites and host rocks in the same ore fields. There is regularity that magnesites have a similar Y/Ho ratio in comparison with country rocks of dolomites, but a little bit less Y contents. Chemical property of Y and a metasomatic process of magnesite formation can explain it. During the last process in accordance with the principle of mineralogical control, LREE subtraction predominates in magnesite in comparison with dolomite (Bau & Moeller, 1993). In this process Y has properties similar to lanthanides, but its effective radius has a value of 1.02 in comparison with 1.015 of Ho. Because of the effective radius of Y somewhat larger than Ho, its chemical property is close to LREE and explains its predominating extraction from the system.

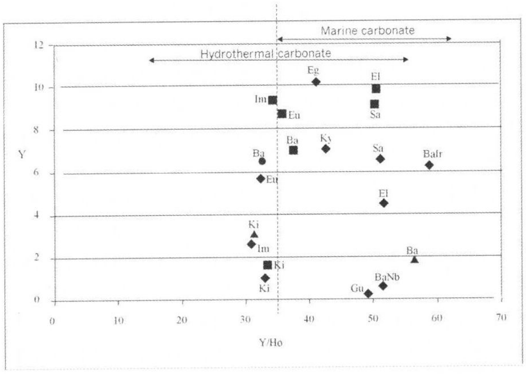


Fig. 8 Distributions Y vs Y/Ho for magnesites and country rocks.

1-magnesites; 2-dolomites; 3-limestones; 4-siderites. Ba Bakal ore field; Balr - Bakal ore field, Irkuskan quarry; BaNB - Bakal ore field, Novobakal quarry; Sa - Satka ore field; El - Elnichnoe; Ki - Katav-Ivanovsk; Im - Ismakaevo; Ky - Kyzyltash; Eg - Egorova Polyana; Gu - Salda Goulu; Eu Eugui (Spain)

It is seen in Figure 8 that host limestones or dolostones for associated magnesites and siderites of the Bakal ore field occur relatively at the right side of the plot, but in the adjacent area. It can be explained by some resemblance of diagenetic environments for country rocks and magnesite ores on the one hand (in case of high values of Y/Ho ratio), and the influence of hydrothermal process on the other hand (in case of lower values of Y/Ho ratio). So we can state that Satka and Bakal magnesite ore fields are connected with a diagenetic process, whereas the Bakal siderite ore field displays a hydrothermal feature. This conclusion is also true for Katav-Ivanovsk and Ismakaevo magnesite deposits. In this case not only magnesites, but also country rocks are also subjected by secondary alteration.

Chemostratigraphic investigation in the Riphean place region confirms this conclusion. In the Lower Riphean sequence limestones of the Bakal formation with a primary $^{87}Sr/^{86}Sr$ isotopic ratio (0.7046), typical of the Lower Riphean were found, that made it possible to estimate Pb-Pb age of Bakal limestones formation (1430 ± 30 Ma, Kuznetsov *et al.*, 2003). The same work is in progress for the Satka formation. It means that in the Bakal-Satka region country rocks preserve their primary features and are not altered by a hydrothermal process. Just within the limits of Bakal siderite ore deposits were found dolomitised limestones and metasomatic dolomites, fulfilling envelopes around siderite bodies. For these dolomites, $^{87}Sr/^{86}Sr$ isotopic ratio increases up to 0.7292. $^{87}Sr/^{86}Sr$ ratios of siderites vary from 0.7226 in lateral to 0.7391 in central parts of siderite bodies. These samples were also used to obtain a Pb-Pb age of metasomatic siderite (Kuznetsov *et al.*, 2000). We associate the origin of ferruginous siderite-forming fluids with dewatering of thick clayey units of Lower Riphean, buried in the lower part of paleohydrogeological basin (Krupenin, 1995, 1999; Kuznetsov *et al.*, 2000). A high value of radiogenic strontium can be inherited from a high content of hydromica in Lower Riphean slates. Chemostratigraphic study revealed that sedimentary rocks with primary geochemical features were absent in all investigated carbonate sections of the Middle Riphean. It reveals intensive epigenetic alterations of the Middle Riphean sequence in the researched sections. For the comparison in Figure 8 are shown average values (calculated from 25 dolomites and 25 magnesites) for hydrothermal-metasomatic magnesite deposit in Eugui, Western Pyrenees, Spain (Lugli *et al.*, 2000). It reveals the same relations between magnesites and host rocks of dolomites and the regularity of position in the area of hydrothermal carbonates.

5 Conclusions

In conclusion, we suggest that the use of Y/Ho ratio with a complex of geological and geochemical features allows us to distinguish different origin of sparry magnesite deposits from the Southern Urals province. Satka and Bakal ore fields, containing SMD with layer-like ore bodies in the dolostone horizons and high Y/Ho ratio belong to early diagenetic stage of development of the rock-forming basin. This data is in agreement with a new evidence of evaporating origin of Mg-bearing solutions for metasomatic process, including the Satka-Bakal region (Prochaska *et al.*, 2003). On the other hand, Ismakaevo, Katav-Ivanovsk, and probably other Middle Riphean SMD with lens-like ore bodies in dolomitised limestone units and increasing

FeO contents in magnesites relate to hydrothermal (kathagenetic) processes of fluid migration. Low values of Y/Ho ratio can indicate to a long distance of fluid migration in the paleohydrogeological basin. Our investigations reveal that Y/Ho ratio can help to determine a relative time and kind of metasomatic processes.

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