ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 7, pp. 685–697. © Pleiades Publishing, Ltd., 2007.
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Barium and Strontium in the Upper Mantle of the Pamirs and Tien Shan

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Received December 28, 2005

Abstract—The distribution of Ba and Sr in deep-seated xenoliths, mantle alkaline melts, and their minerals from the Pamirs and Tien Shan and some other regions was considered. In contrast to ordinary magmatic series, the mantle rocks show a correlation of Sr with both Ca and alkalis. The most extensive accumulation of Ba and Sr in the upper mantle occurs during the processes of mantle metasomatism and melting of metasomatized materials. The influx of these elements is probably related to ultradeep plume-type sources. Ba and Sr were transported from the mantle into the crust by both high-temperature alkaline melts and low-temperature hydrothermal solutions. It is supposed that the late Alpine celestite deposits of the huge Sr province of the Mediterranean belt are of mantle origin. Geochemical provinces show distinctive concentrations and proportions of Ba and Sr in mantle-derived alkaline basic rocks, metasomatic rocks, and their minerals. The type of Ba–Sr relations is inherited by crustal rocks.

DOI: 10.1134/S0016702907070051

INTRODUCTION

The distribution of Ba and Sr has been systematically studied in mantle-derived melts (alkaline basic rocks and potassic and sodic alkaline ultramafic series, including kimberlites, lamproites, carbonatites, and their derivatives) and ultrabasic nodules [1–11 ect.]. Nonetheless, additional evidence is needed to understand the geochemistry of these elements in the processes of ultrabasic mantle transformation under the influence of modal and cryptic metasomatism (fluid-rich magmatism), which will allow us to estimate the possible composition of the sources of alkaline mafic–ultramafic magmatism, reveal the main mineral hosts of Ba and Sr, and consider the problems of mobilization, transportation, and concentration of these elements in the mantle [12–20].

The region of the Pamirs and Tien Shan is well suited for the investigation of these problems, because it comprises about 100 diatremes and even more xenolith-bearing dikes of various ages (Triassic–Neogene) belonging to various associations of alkaline mafic series. They contain abundant mantle nodules, among which metasomatic products are widespread. The geology and chemical composition of alkaline basic rocks and their xenoliths from this region, as well as the tectonic pattern of the Pamirs–Tien Shan and the character of localization and composition of diatremes were described in a number of publications [7, 8, 21–26, etc.]. Therefore, this paper presents only a short summary of these topics. We also give a reduced list of publications on the alkaline basic rocks and xenoliths of the Baikal–Mongolia region (BMR), because a more comprehensive bibliography was presented elsewhere [23].

METHODS

Ba and Sr contents were determined in rocks and minerals by X-ray fluorescence (XRF) and X-ray spectrometry (XRS) at the laboratories of the VIRG (St. Petersburg) and the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences (Moscow). The analytical sensitivity was 2 ppm Sr and 100 ppm Ba, which is insufficient for ultrabasic rocks but is quite acceptable for all other rock types considered. The quality of analyses was checked using standard samples (State Standard Samples) from the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, and the Vinogradov Institute of Geochemistry, Siberian Division, Russian Academy of Sciences. The relative standard errors were estimated as no higher than 10–20% on the basis of internal and external controls. Variations in Ba and Sr contents in rocks were higher than the analytical errors. The results of the external control (Student and Fisher tests) showed that the deviations are lower than the critical values for significance levels of 1–5%. This indicates that there are no significant differences between the concentrations determined by different methods and in different laboratories. Some methodical and analytical problems were considered in more detail elsewhere [26].

The data on the distribution of Ba and Sr and their proportions in various types of igneous rocks, xeno-

Table 1. Average contents of barium and strontium in alkaline mafic–ultramafic rocks (ppm) [1–9, 11, 21–23, etc.]

No.	Rock, zone (region)	*n*	Ba	Sr	Ba/Sr
1	Southern Gissar zone, alkaline mafic rocks A	49	2200	868	2.5
2	Central Gissar zone, alkaline mafic rocks A	23	745	782	1.0
3	Yagnob zone, alkaline mafic rocks A	49	665	1135	0.6
4	Average for series A of the southern Tien Shan	121	1203	928	1.3
5	Middle Tien Shan, alkaline mafic rocks B	18	233	600	0.4
6	Southern Gissar zone, alkaline mafic rocks B	80	906	642	1.4
7	Kugitang–Baisun zone, alkaline mafic rocks B	7	691	616	1.1
8	Average for series B	87	800	629	1.3
9	Trachytes B	18	1072	512	2.1
10	Fergusites from diatremes	7	1.15%	4300	2.7
11	Fergusites from a subvolcanic massif	9	1.31%	4000	3.3
12	Carbonatite	1	8300	2900	2.9
13	Syenite porphyries and tinguaites	70	6000	3100	1.9
14	Melt inclusions in minerals of fergusites	7	9600	8000	1.2
15	Alkaline mafic rocks, Na series of BMR	226	532	649	0.8
16	Alkaline mafic rocks, K series of BMR	86	595	1150	0.5
17	Shoshonites of island arcs and ACM	–	1120	933	1.2
18	Kimberlites	–	1070	900	1.2
19	Olivine lamproites	–	5004	2120	2.4
20	Melt inclusions in minerals of lamproites	–	1.9–3.3%	–	–
21	K alkaline ultramafic–mafic complexes	–	3440	2460	1.4
22	Carbonatites of K alkaline complexes	–	2.1%	1.1%	1.9
23	Carbonatites (Na) of melanephelinite series	–	7150	1.14%	0.6

Note: Here and in Tables 2 and 3, *n* is the number of analyses, and dashes indicate not analyzed. Rocks (regions): 1–9, Early Mesozoic alkaline mafic rocks of the Tien Shan (intraplate Ti basic rocks of series A and picrobasalt–shoshonite of series B); 10–14, Neogene fergusite–carbonatite–syenite series of the southern Pamirs; and 15–23, alkaline mafic–ultramafic series from other regions.

liths, and minerals are shown in Tables 1, 2, and 5. The statistical analysis of the linear correlations of Ba and Sr with major and trace elements was performed by I.M. Derzhavets (Tables 3, 4). The results on the rocks of the Pamirs and Tien Shan were compared with published data on the geochemistry of Ba and Sr in alkaline mafic–ultramafic igneous rocks and their xenoliths and minerals from other regions. Special emphasis was placed on the behavior of Ba and Sr in the products of metasomatic (fluid–magmatic) transformations of the upper mantle and in high-pressure mineral inclusions (megacrysts), which are fragments of disintegrated "mantle pegmatites" [12, 20].

ALKALINE BASIC ROCKS AND THE LITHOSPHERE OF THE PAMIRS AND TIEN SHAN

The branches of the Central Asian (Hercynides of the Tien Shan) and Alpine–Himalayan (Hercynides of the northern Pamirs and Cimmerides–Alpides of the southern Pamirs) mobile belts meet in Tajikistan. The tectonic portrait of the region is defined by epicratonic ensialic structures (Andean-type active continent margins, continental rift belts, and Precambrian blocks activated in the Phanerozoic). Island arc zones and ophiolite belts are less common. The thickness of the Earth's crust is 40–60 km in the Tien Shan and up to 70–75 km in the eastern block of the Pamirs [27]. The region is characterized by the high ratio of the thicknesses of the granitic and basaltic layers, shallow occurrence and great thickness of the asthenosphere (up to 150–200 km), occasional absence of distinct Conrad and Moho boundaries (especially in rift zones), and the presence of a crust–mantle layer (V_p = 7.4–7.7 km/s) with a thickness from 4–7 to 25 km.

The basement of most zones is built up of Late Archean–Early Proterozoic blocks. The model of the lower crust was constructed on the basis of granulite xenoliths from alkaline basic rocks (7–12 kbar and 870–1000°C) and is, on average, similar to a potassic mela-andesite enriched in lithophile trace elements [28]. The composition of the upper crust corresponds to a high-K dacite [29]. The Precambrian crust contains

relatively little metabasic rocks and, especially, plagiogneisses (enderbites, <5–10%) and considerable amounts of metapelites and, to some extent, charnockites.

The alkaline basic rocks of the Tien Shan were formed in the Early Mesozoic in response to an epi-Hercynian activation (dispersed rifting). The most common rocks are intraplate titanium-rich potassic alkaline (subalkaline) basites of series A (primitive varieties contain 11–16% MgO and 340–598 ppm Ni). Pipes and dikes of subalkaline low-titanium rocks of picrobasalt–shoshonite series B, ranging from picritic basites (12.4–17.8% MgO and 280–700 ppm Ni) to trachybasalt (shoshonite), latite, and trachyte occur mainly in the southern block (southern Gissar zone). The rocks of both series (especially series B) contain chromite xenocrysts and small diamonds (0.02–0.5 mm), i.e., the zones of melt generation could reach the level of the graphite–diamond phase transition. In the western part of the southern Tien Shan belt, alkaline basic rocks associate with diamondiferous carbonatite bodies [30]. The isotopic compositions of the basic rocks ($^{87}Sr/^{86}Sr$ = 0.7043–0.7056) suggest their connection to enriched mantle sources. Both of these series contain megacrysts: K-kaersutite, anorthoclase, phlogopite, apatite, titanomagnetite, etc. are predominant in series A; whereas diopside, augite, micas, amphibole, etc. are more common in series B. Megacrysts often form intergrowths of 2–4 minerals and are similar in terms of mineral assemblages and compositions to some nodules of pyroxenite, hornblendite, glimmerite, and anorthoclasite. There is a petrogeochemical difference between the alkaline mafic rocks from the northern and southern blocks: the former are enriched in Ti, Sr, Fe, Na, and Cl but depleted in K, F, Rb, and H_2O. There is a correlation between the compositions of alkaline basic rocks and metasomatized mantle rocks.

The upper mantle of the Tien Shan (14–20 kbar and 1000–1080°C) is strongly differentiated and contains a high fraction of depleted peridotites (up to 20% on average) and diverse igneous and metasomatic pyroxenites, hornblendites, gabbros, etc. (some of them represent the crust–mantle mixture). The nodule suite is dominated by spinel (garnet–spinel) facies rocks, whereas high-pressure xenocrysts of chromite and diamond were found only in gravity and thermochemical concentrates. In general, extensive mantle alteration is characteristic with the development of hydrous potassic minerals, phlogopite and K-kaersutite, and the input of a number of lithophile trace elements (modal and cryptic metasomatism [12–20]). Several types of metasomatic rocks were distinguished: phlogopite pyroxenites and glimmerites (including unique Ba glimmerite), kaersutite–phlogopite veins, anorthoclasites, etc. Alkali feldspars always formed later than micas and other minerals. With increasing pressure, mica shows an increase in the K/Na ratio [17] and an enrichment in H_2O and F [16]. The intraregional heterogeneity of the mantle beneath the Tien Shan is manifested in that the role of harzburgites, various pyroxenites, and low-Ti glimmerites increases in the southern block (southern Gissar and Kugitam–Baisun zones), whereas amphibole Ti pyroxenites, hornblendites, gabbros, etc. are more abundant in the northern block (Yagnob and central Gissar zones). Also noteworthy are the high F/Cl ratios of micas, apatite, and amphibole and a high fraction of apatite in some hornblendites (up to 6.4% P_2O_5).

Despite the high degree of melting and metasomatic transformations, the mantle rocks of the Tien Shan contain mainly weakly oxidized spinel; moreover, moissanite and native iron were detected, and graphite occurs in significant amounts. The probable reason for these features is the migration of reduced fluid from the lower mantle and a change in the stability boundary of graphite in the low fO_2 region [31, 32]. It is supposed that at the time of established *P-T* conditions, the ancient crust grew at the expense of the crust–mantle mixture (plagioclase pyroxenites, hornblendites, and gabbros with the parameters 12–17 kbar and 900–1000°C) via the mechanism of magmatic underplating [33].

Listwaenites are ubiquitous in ophiolite complexes. However, listwaenite xenoliths in alkaline basic rocks have almost never been described in the available literature. About 50–60% of the ultramafic nodules from the Tien Shan underwent carbonation (listwaenitization). Ultramafic xenoliths from some series A and B diatremes are completely listwaenitized. It should be noted that the epi-Hercynian activation, which was responsible for the formation of listwaenites and host alkaline basic rocks, was accompanied by diverse mineralization (Hg, Sb, Pb, Zn, Cu, F, Ba, and Sr). The listwaenite xenoliths are a complex mixture of heterogeneous and polychronous minerals (elements): (a) relics of mantle material, (b) products of serpentinization, and (c) minerals (elements) of late shallow-level carbonation (200–300°C). The wide occurrence of listwaenitization in xenoliths and the existence of regional carbonation zones may indicate extensive and repeated carbon dioxide degassing from the mantle, which is additionally supported by the carbon isotopic systematic of mantle carbonates [34].

The alkaline basic rocks of the Pamirs belong to the late Miocene ultrapotassic fergusite–carbonatite–syenite series confined to a collisional orogen. Its formation reflects sharp changes in the geodynamic environment, indicating the conditions of relative tectonic quiescence (postcollisional subplatform regime). The diatremes and, especially, extended dike belts [22] cross the boundaries of tectonic zones, as well as the recent zones of cataclasis and mylonitization. On the other hand, the bodies of alkaline rocks were never affected by late deformations. They reflect the development of a postcollisional regime accompanied by extension (albeit local) and formation of permeable zones at mantle depth levels, no less than 120–130 km (judging from xenolith barometry).

Table 2. Ba and Sr contents (ppm) in the minerals of mantle rocks [1–12, 21–23, 36, etc.]

No.	Mineral, rock	*n*	Ba	Sr	Ba/Sr
1	Phlogopites of green series nodules (B)	3	4300	207	21
2	Phlogopite megacrysts (B)	3	1800	220	8
3	Phlogopites of glimmerites (B)	2	3200	240	13
4	Ba-phlogopite from glimmerite (B)	2	15.5%	29	5345
5	Phlogopite megacrysts (A)	10	2900	291	10
6	Phlogopites of glimmerites (A)	2	1000	–	–
7	Phlogopites of black pyroxenites (A, B)	2	4500	153	29
8	Phlogopites of hornblendites (A, B)	3	3300	–	–
9	Average composition of mantle micas (A, B)	27	3200	215	15
10	Biotite phenocrysts of alkaline mafic rocks (B)	3	2700	215	13
11	Clinopyroxenes of pyroxenites (B)	2	<100	105	–
12	Megacrysts of K-kaersutite (B)	2	590	402	1.5
13	Megacrysts of K-kaersutite (A)	7	300	348	0.9
14	K-kaersutites from pyroxenite and hornblendite xenoliths (B)	3	470	520	0.9
15	K-kaersutite from a hornblendite xenolith (A)	1	–	680	–
16	Average composition of mantle amphiboles	13	453	516	0.9
17	Cr–V–Ba titanate from glimmerite (B)	10	21.8%	–	–
18	Sanidine megacryst (A)	1	700	100	7
19	Anorthoclase from an anorthoclasite nodule (A)	2	280	1460	0.2
20	Sanidines of sanidine eclogites	5	4400	5200	0.8
21	Sanidines of garnet pyroxenites	2	1.4%	4840	2.9
22	Phlogopites of garnet–phlogopite pyroxenites	2	9630	–	–
23	Biotites of sanidine eclogites	4	1.2%	–	–
24	Phlogopites of garnet pyroxenites	7	3700	–	–
25	Amphibole from hornblendite	1	–	5020	–
26	Phlogopites of glimmerites	4	1670	–	–
27	Amphiboles of garnet pyroxenites	3	–	4900	–
28	Biotite phenocryst of fergusite	1	3.7%	–	–
29	Sanidine phenocrysts of fergusites	2	3.4%	–	–
30	Apatites of fergusites	2	–	2900	–
31	Sr–F apatite (2.9–6.6% F) of fergusites	1	300	2.3%	0.01
32	Sanidine from fergusite groundmass	1	5.1%	–	–
33	Fluorapatite of syenite porphyry	1	–	2.4%	–
34	Ba-celestite	1	9.3%	–	–
35	Perovskite	1	–	1.3%	–
36	Fluorite of carbonatites	3	1020	5490	0.18
37	Sanidine of syenite porphyry	1	–	1.3%	–
38	Melt inclusions in minerals of fergusites	14	1.8%	0.71%	2.5
39	Sr calcite of carbonatites	5	0.4%	4.8%	0.08
40	Mica megacrysts	–	4500	230	20
41	Phlogopites of black pyroxenites	–	5200	289	18
42	Phlogopites of green series nodules	–	5800	440	13
43	Sanidine megacrysts from K alkaline mafic rocks	–	2450	3000	0.8
44	Amphiboles of megacrysts and xenoliths	–	330	600	0.6
45	Plagioclase of xenoliths	–	75	350	0.2

Table 2. (Contd.)

No.	Mineral, rock	*n*	Ba	Sr	Ba/Sr
46	Anorthoclase megacrysts	–	1850	2850	0.6
47	Diopside of spinel lherzolite	–	20	98	0.2
48	Clinopyroxene megacryst	–	26	91	0.3
49	Clinopyroxene of garnet peridotite	–	37	324	0.1
50	Diopside megacryst	–	–	226	–
51	Omphacite of eclogite	–	95	230	0.4
52	Phlogopite of garnet peridotite	–	1490	46	32
53	Phlogopite of MARID	–	380	120	3.2
54	Phlogopite megacryst	–	342	–	–
55	Phlogopite from kimberlite groundmass	–	2670	–	–
56	Primary phlogopite in peridotite	–	1725	21	82
57	Magmatic calcite of kimberlites	–	1600	4500	0.35
58	Hydrothermal calcite of kimberlites	–	1	370	0.002
59	Celestite	–	2300	46.9%	0.004
60	K sanidine	–	6000	3300	1.8
61	Phlogopite phenocryst	–	0.79%	–	–
62	V–Ba titanate	–	19%	–	–
63	Sr-barite	–	–	2.5%	–
64	Apatite	–	–	3.5%	–
65	Calcite of carbonatite	–	1850	4.5%	0.04
66	High-temperature calcite of carbonatite	–	760	7400	0.1
67	Hydrothermal calcite of carbonatite	–	<100	500	–
68	Apatite of carbonatite	–	80	3.5%	0.01
69	Calcite of K alkaline ultramafic rocks	–	4900	6100	0.8
70	Apatite of alkaline ultramafic rocks	–	–	0.5%	–
71	Phlogopite of K alkaline ultramafic rocks	–	5150	132	39

Note: Minerals of xenoliths, megacrysts, and phenocrysts are from (1–19) alkaline mafic rocks of the Tien Shan, (20–39) alkaline mafic rocks of the Pamirs, (40–48) alkaline mafic rocks of the BMR, (49–59) kimberlites of Yakutia and southern Africa, (60–64) lamproites, and (65–71) alkaline ultramafic rocks and carbonatites. A and B denote the series of host alkaline mafic rocks of the Tien Shan.

The series is represented by pipes, dikes, and multiphase subvolcanic bodies ranging in composition from fergusite to various syenitoids (often with leucite) and fluorite carbonatites. Postmagmatic processes resulted in fluoritization, carbonation, baritization, and development of celestite veins, REE–radioactive mineralization, and fluorite deposits [35].

The fergusites and syenites show common (serial) characteristics: first of all, rather high alkalinity and potassium content (K/Na from 3 to 6). The fergusites show negative Ti–Nb anomalies, rather low Mg/(Mg+Fe) values, and elevated Ca contents (up to 15%). The rocks are rich in volatiles, especially CO_2 and F, which are incorporated in micas, apatite, fluorite, etc. Fluorite is mainly related to carbonatite melts and contains Sr, REE, U, and Th admixtures [35]. The series cannot be unambiguously assigned to a particular association, although it is very similar to the intracontinental postcollisional associations of ultrapotassic alkaline basic rocks (tephrites–leucitites) with syenites and carbonatites [24, 36].

The mantle xenolith suite contains abundant garnet–phlogopite clinopyroxenites (glimmerites) and less common websterites, which were formed at pressures of up to 35–40 kbar. These values constrain the minimum pressures of generation of fergusite magmas. It can be suggested that, similar to other regions [13], the mantle source of the alkaline basic rocks of the Pamirs were composed of garnet–phlogopite clinopyroxenites (±glimmerites) with carbonates and apatite. Their composition is complementary to that of the fergusites.

The homogenization temperatures of melt inclusions in various minerals were 1000–1200°C [36], but the glasses are mainly syenitic in composition, and they therefore characterize the temperature of intermediate and near-solidus stages of crystallization. The forma-

Table 3. Matrix of the correlation coefficients of Ba and Sr with major and trace elements

		Ti	Ca	Na	K	K + Na	P	F	Mg	Ba	Sr
1	Ba	**0.66**	0.1	0.17	**0.72**	0.45	**0.70**	0.37	*–0.56*	–	*0.57*
	Sr	0.24	–0.1	**0.84**	**0.72**	**0.89**	**0.69**	0.19	*–0.74*	*0.57*	–
2	Ba	0.03	–0.39	–0.52	**0.77**	0.51	0.13	**0.85**	0.26	–	0.16
	Sr	–0.34	–0.28	0.17	0.23	0.31	0.32	–0.25	*–0.59*	0.16	–
3	Ba	*0.82*	0.60	0.49	*0.81*	*0.80*	0.30	0.21	–0.60	–	*0.84*
	Sr	**0.97**	0.71	0.58	**0.96**	**0.95**	0.29	0.24	–0.69	*0.84*	–
4	Ba	–0.18	0.58	–0.39	0.38	–0.03	–0.10	0.26	–0.19	–	0.27
	Sr	0.32	–0.48	0.60	0.19	0.65	*0.77*	0.22	–0.38	0.27	–

Note: (1) Mantle xenoliths of the southern Tien Shan, (2) mantle xenoliths of the southern Pamirs, (3) mantle xenoliths of the BMR, and (4) host alkaline mafic rocks of the southern Tien Shan. Numbers in italics indicate that the correlation coefficient is significant with a probability of 95%, and numbers in bold are correlation coefficients significant with a probability of 99%.

tion of carbonatites through liquid immiscibility, as well as the crystallization differentiation of fergusite magmas took place mainly in crustal (transitional) chambers [22, 36].

The upper mantle of the southern Pamirs. The diatremes of the region bear garnet and phlogopite pyroxenites, glimmerites, eclogites (mainly potassic, with sanidine), eclogite-like rocks, and granulites [22, 24]. The chemical compositions of the ultramafic–mafic rocks suggest their primary mantle nature. The eclogites are different from typical eclogite complexes in elevated alkalinity and potassium content. The garnets of the eclogites contain relict inclusions of potassium feldspar, biotite, hypersthene, hastingsite, etc. [25]. This indicates, first, the intrinsically high alkalinity of melts and, second, the crystallization of mantle magmas under crustal conditions. The ultramafic–mafic protoliths can be assigned to two series: (a) subalkaline potassic and low-titanium picrobasalt–shoshonite–latite series and (b) alkaline (subalkaline) potassic and titanium-rich picrite–basalt series of the intraplate type. As was noted above, the mantle melts of the two series intruded into the upper crust.

It is suggested that these rocks were subsequently submerged (probably during subduction) beneath the southern Pamirs to depths of at least 100–120 km (top of the asthenosphere). This caused their eclogite-facies metamorphism (25–35 kbar and 950–1050°C, occasionally up to 1200°C) with an additional influx of K and related elements from the mantle and partial melting. Compared with ordinary high-pressure complexes, the high- and ultrahigh-pressure rocks of the xenoliths are hotter (by 150–300°C) [37], which probably reflects the influence of mantle sources (plumes?). The gravitational differentiation and ascent of partially molten metabasic rocks in the Miocene (15–17 Ma [25]) to the Moho boundary, i.e., to the base of the ancient continental crust, resulted in its growth to a thickness of up to 75 km [24].

The formation of very thick crust and lithosphere in the collisional orogen of the southern Pamirs occurred under conditions of complex coupling of collisional–subduction and plume processes [24].

Table 4. Coefficients of linear correlation of elements in the listwaenite nodules from the southern Tien Shan

Zone	Ca–Sr	CO_2–Sr	CO_2–Ca
1	**0.81**	0.44	0.13
2	0.49	**0.80**	**0.94**
3	0.39	*0.74*	**0.86**
4	0.14	*0.76*	**0.81**
5	0.10	*0.50*	0.21

Note: Zones: (1) Yagnob, (2) Kugitang–Baisun, (3) southern Gissar, (4) central Gissar, and (5) southern Tien Shan. Numbers in italics indicate that the correlation coefficient is significant with a probability of 95%, and numbers in bold are correlation coefficients significant with a probability of 99%.

Ba AND Sr IN ALKALINE MAFIC–ULTRAMAFIC ROCKS

Alkaline mafic rocks of the Tien Shan. The highest Ba and Sr contents and elevated Ba/Sr ratios were observed in the potassic titanium-rich alkaline mafic rocks of series B (southern Gissar zone), and the minimum values were found in the intraplate sodic (K–Na) alkali basalts of the Yagnob paleorift zone of the southern Tien Shan and the Kurama zone of the central

Tien Shan (Table 1). In general, both series show high Ba/Sr ratios (about 1.3), which is in agreement with their high potassium contents. The late differentiated rocks (trachytes and syenite porphyries) show an increase in Ba and a decrease in Sr content, which results in a corresponding increase in the Ba/Sr ratio.

The main repository for Ba in the alkaline mafic rocks is Ti-phlogopite (biotite), which simultaneously shows very low Sr content (Table 2). The ratio of Ba concentration in mantle micas to that in alkaline mafic rocks is 3–10, but there is no correlation between Ba contents in the micas and mafic rocks ($R = 0.22$ and $R_{5\%} = 0.46$), probably owing to the presence of competing minerals in magma source regions. The statistical relationships of Ba and Sr with other elements are rather weak (Table 3), they are always negligible for Ba, and Sr is correlated with P only. This is probably related to the diversity of factors (often operating in opposite directions) controlling the behavior of Ba and Sr: local variations in the bulk composition and mineralogy of the source material, degree of melting, differentiation processes, etc. On the other hand, there are negative correlations of K–Mg and Ca–Na and positive correlations of F–K, F–Ti, and alkalinity–P, which reflect a decrease in the content of femic components and an increase in alkalinity and P, Ti, and F contents during melt differentiation.

Fergusite–carbonatite–syenite series of the Pamirs. Alkaline mafic rocks, immiscible carbonatites, late syenite porphyries, and tinguaites of this series are enriched in Sr and, especially, Ba (Table 1). The Ba/Sr ratio is very high and the rocks resemble lamproites in this parameter. The role of Ba and Sr decreases somewhat during differentiation, probably owing to mica and sanidine fractionation. Extremely high Ba and Sr contents (up to 3.4–6.8%) were measured in some minerals of the fergusites: sanidine, fluorapatite, Ba-celestite, and Sr-calcite (Table 2). The fluorite and perovskite contain up to 5490 ppm and 1.3% Sr, respectively. Melt inclusions are also enriched in these elements. In general, almost all major and accessory minerals of this series are enriched in Ba and, to a smaller extent, Sr.

The alkaline mafic rocks of the BMR are depleted in Ba in comparison with the similar rocks of the Tien Shan and, especially, Pamirs and show moderate Sr contents. As a result, their Ba/Sr ratios are usually lower than one, even in potassic alkaline mafic rocks.

Potassic alkaline ultramafic rocks, first of all, olivine lamproites, are enriched in Ba and show high Sr contents (Table 1). Very high Ba contents of 1.9–3.3% were detected in melt inclusions from lamproites. The Ba/Sr ratio is always higher than one. Ba is incorporated in phlogopite, sanidine, and some Ba titanates; and Sr occurs in sanidine, Sr-barite, celestite, Sr-apatite, etc. (Table 2). Despite their potassic alkalinity and extremely high depths of melt generation (up to the upper levels of the lower mantle [37]), kimberlite show, in general, moderate Ba and Sr contents similar to those observed in alkaline mafic rocks. A significant portion of Sr occurs in magmatic calcite from kimberlite groundmass (to a smaller extent, in celestite and clinopyroxene), and Ba resides in micas and carbonates (Table 2).

Potassic and sodic alkaline ultramafic rocks and related carbonatites show the highest contents of Ba and Sr, and carbonatites related to Na series have Ba/Sr <1. Most of the Sr and some of the Ba are incorporated in Sr-calcite and apatite, and phlogopite is the main host of Ba (Table 2).

Ba AND Sr IN MANTLE XENOLITHS

Tien Shan

The lowest concentrations of Ba and Sr are typical of ultrabasic xenoliths. Especially low Sr contents were observed in the ultrabasic rocks of ophiolitic complexes, which characterize the upper mantle of island-arc zones and ophiolite belts. The processes of mantle metasomatism (fluidized magmatism) are accompanied by extensive Ba and Sr accumulation in various pyroxenites, glimmerites, hornblendites, anorthoclasites, and biotite–kaersutite gabbros, which are assigned in part to the crust–mantle mixture. The main mineral concentrators of Ba in metasomatized mantle rocks are micas and sanidine, sometimes Ba-titanates, Sr-anorthoclase (Na-sanidine), and, to a lesser extent, kaersutite and clinopyroxene. Almost all xenoliths and their minerals show Ba/Sr > 1 (except for the gabbros and anorthoclasites).

The contents of Ba and Sr are correlated with a considerable number of other elements (Table 3, Figs. 1–3). Ba is correlated with K, Ti, P, and Sr; and Sr, with K, Na, (K + Na), P, and Ba. Both elements are negatively correlated with Mg. The character of the correlations suggests their incorporation into common minerals (K–Na feldspars and K-kaersutite) or coupled behavior in the processes of fluid transportation and accumulation. The main metasomatic assemblage concentrating Ba and Sr includes K–Na feldspar, phlogopite, K-kaersutite, clinopyroxene, apatite, and plagioclase, i.e., the pyroxenite–hornblendite–gabbro series. The main Ba-bearing mineral is Ti-phlogopite, and a smaller fraction of Ba occurs in K–Na feldspars, K-kaersutite, and Ba-titanates.

As was noted above, the behavior of Ba is different from that of Sr, which is correlated not only with K but also with Na and total alkalinity. The correlation of Sr with Ca was never observed (although Sr occurs in some Ca minerals: clinopyroxene, kaersutite, apatite, etc.).

The maximum content of Ba was observed in a unique titanium-rich Ba-phlogopite from a glimmerite (Table 2). It contains 1.8–1.9% F, 0.5% H_2O, and a negligible amount of Sr. In addition to phlogopite, the glimmerite contains a priderite-structured Ba titanate, graphite, moissanite, native iron, and diopside.

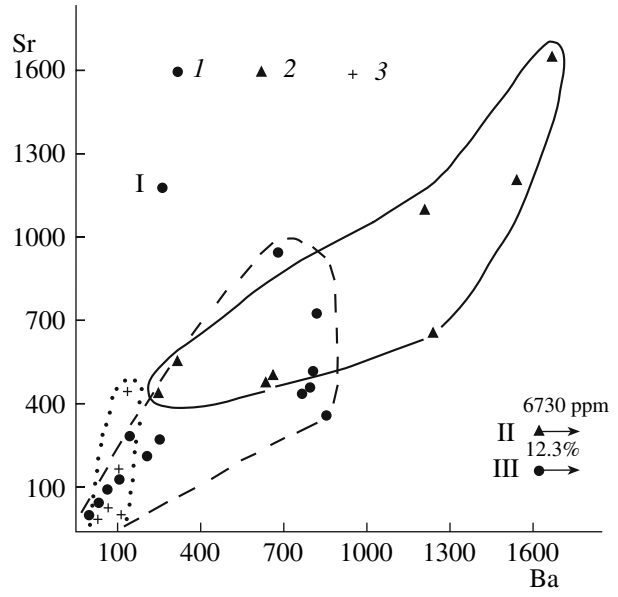

Fig. 1. Barium and strontium in mantle xenoliths from the (*1*) Tien Shan, (*2*) Pamirs, and (*3*) BMR. I–III, rocks with anomalous Ba and Sr contents plotting off the general trends: I, anorthoclasite; II, glimmerite; and III, Ba glimmerite.

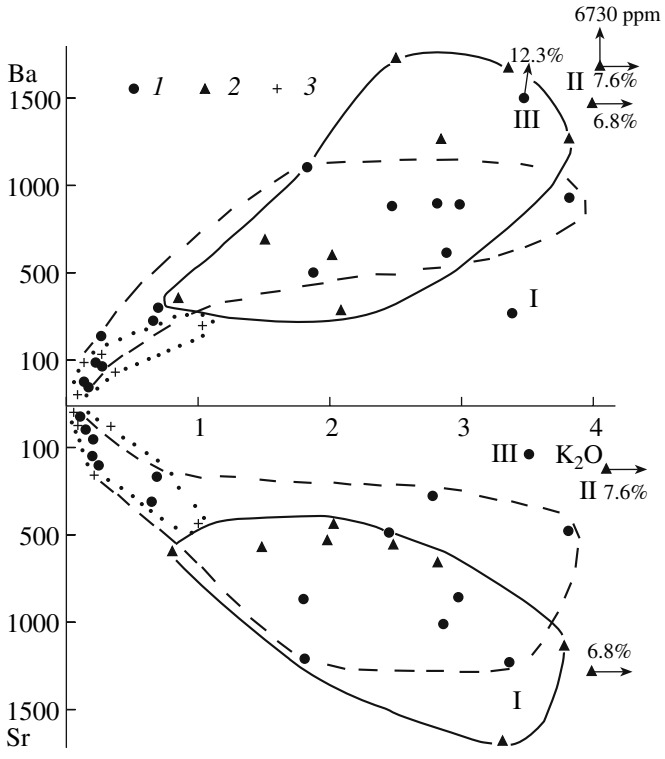

Fig. 2. Correlation of Ba and Sr contents (ppm) with K_2O (wt %) in mantle xenoliths from the (*1*) Tien Shan, (*2*) Pamirs, and (*3*) BMR. Other symbols are the same as in Fig. 1.

As was noted above, the ultrabasic xenoliths underwent extensive carbonation (listwaenitization) accompanied by Sr enrichment (300–500 ppm on average and occasionally up to 2300 ppm). Similar to carbonatites and kimberlites, the main Sr-bearing mineral is carbonate, mainly calcite. The correlation analysis of the series Ca–Sr–CO_2 revealed a much higher correlation of Sr with CO_2 than with Ca (Table 4). This emphasizes a geochemical connection between Sr and CO_2 and may indicate a mantle source for both components. This is in agreement with the mantle isotopic composition of carbon (3–7‰) of carbonates from pipes and regional carbonation zones [34].

The listwaenites contain various epithermal minerals, including antimonite, fluorite, cinnabar, sphalerite, galena, gold, barite, and celestite. There is evidence for the occurrence of at least two activation events in the Hercynian evolution of the Tien Shan. These events were probably related to the generation and ascent of mantle plumes (superplumes) and related lithospheric diapirs. They could result in the mobilization from the

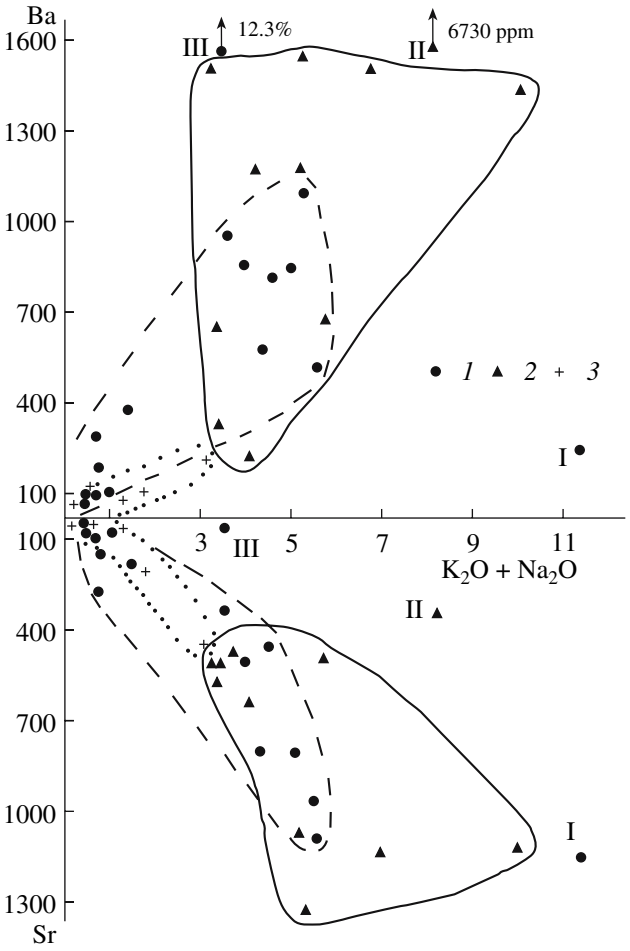

Fig. 3. Correlation of Ba and Sr contents (ppm) with total alkalis (wt %) in mantle xenoliths from the (*1*) Tien Shan, (*2*) Pamirs, and (*3*) BMR. Other symbols are the same as in Fig. 1.

Table 5. Average contents of barium and strontium (ppm) in deep-seated xenoliths from alkaline mafic rocks and kimberlites [1–7, 9–19, 21–24, 35–37, 39]

No.	Xenolith rock	*n*	Ba	Sr	Ba/Sr
1	Spinel harzburgite	7	<100	38	–
2	Spinel lherzolite	10	<100	59	–
3	Olivine websterite (±phlogopite)	6	175	166	1.1
4	Spinel clinopyroxenite (±phlogopite)	10	100	109	0.9
5	Magnetite–phlogopite wehrlite	2	382	165	2.3
6	Spinel clinopyroxenite (±garnet)	5	100	75	1.3
7	Olivine pyroxenite (±phlogopite, kaersutite, plagioclase)	6	261	272	1.6
8	Phlogopite–amphibole pyroxenite	4	863	182	1.8
9	Phlogopite pyroxenite, glimmerite	9	857	444	1.9
10	Ba glimmerite	2	12.3%	102	1206
11	Titanomagnetite–kaersutite–phlogopite rock	2	960	358	2.7
12	Hornblendite (±phlogopite, anorthoclase, plagioclase)	9	500	819	0.6
13	Apatite–phlogopite hornblendite	5	858	805	1.1
14	Biotite–augite–kaersutite gabbro	8	592	972	0.6
15	Amphibole–pyroxene anorthoclasite	2	250	1200	0.2
16	Apoperidotite listwaenite	58	–	655	–
17	Ultrabasic rocks of ophiolite complexes from the region	15	–	18	–
18	Phlogopite–garnet websterite	2	1760	–	–
19	Garnet clinopyroxenite (±phlogopite)	6	647	530	1.2
20	Hornblendite	1	240	450	0.5
21	Garnet–phlogopite pyroxenite (±sanidine)	8	1238	1076	1.2
22	Glimmerite	5	6730	316	21
23	Bimineralic eclogite (±kyanite)	6	293	537	0.5
24	Sanidine eclogite (±kyanite)	17	1653	1654	1.0
25	Biotite eclogite (±sanidine)	4	1240	626	2.0
26	Plagioclase eclogite (±sanidine)	1	580	500	1.2
27	Quartz syenite, subalkaline granite	2	1490	1200	1.2
28	Spinel harzburgite	10	47	28	1.7
29	Spinel lherzolite (±phlogopite)	15	111	40	2.8
30	Spinel websterite (±phlogopite)	5	76	53	1.4
31	Spinel clinopyroxenite	10	98	158	0.6
32	Phlogopite–amphibole pyroxenite	3	157	460	0.3
33	Garnet peridotite	12	42	36	1.2
34	Eclogite	22	101	125	0.8
35	MARID	5	500	284	1.8

Note: (1–17) Mantle (crust–mantle) nodules in the alkaline mafic rocks of the Tien Shan, (18–27) mantle (crust–mantle) nodules in the alkaline mafic rocks of the Pamirs, (28–32) mantle (crust–mantle) nodules in the alkaline mafic rocks of the BMR, and (33–35) mantle nodules in kimberlites. Analyses (1–4), (16), (28–30), and (33) are xenoliths of the green series, and all other rocks are xenoliths of the black series.

mantle, transportation, and concentration of ore matter in the crust. These processes occurred in the Mesozoic, when alkaline mafic rocks were formed in response to dispersed rifting, and in the Late Cenozoic, when the final almost amagmatic orogeny took place in the region. Of special importance in this context are the Late Cenozoic celestite deposits, which were previously interpreted as being of hydrothermal–vadose ori-

gin (200–250°C). The tremendous scales of Sr deposits, their confinement to belt structures, and spatial relation to the Mediterranean mobile belt [38] do not exclude their possible connection to mantle sources. There are some analogies between the mechanisms of formation of these deposits and listwaenite xenoliths: both could be related to carbon dioxide degassing from the mantle.

Southern Pamirs

The xenoliths from the fergusites of the region are assigned to the high-pressure potassic pyroxenite–glimmerite–eclogite association. Compared with the Tien Shan nodules, they contain much more Ba and Sr (Table 5) and show significantly higher Ba/Sr values. Despite a strong decrease in the role of Ca, high Sr and Ba contents are inherited by late differentiates. There is a statistical relationship of Ba with K and F, which indicates Ba incorporation into micas and sanidine. Sr is distributed among several minerals, including sanidine, amphibole, apatite, Ba-celestite, fluorite, and Sr-calcite. Such a character of Sr distribution decreases the number and strength of its correlations with other elements. There is a negative correlation of Sr and Ba with Ca, and Sr is more tightly correlated with alkalis than with Ca. The lowest Ba contents were found in low-potassium rocks, hornblendites and bimineralic and plagioclase eclogites (Ba/Sr < 1). The glimmerites are most enriched in Ba. Both Ba and Sr are simultaneously incorporated into sanidine.

BMR

The mantle xenoliths of the BMR are relatively depleted in Ba and Sr, and Ba/Sr < 1 both in metasomatic rocks and in alkaline mafic rocks. Although the relationships of Ba and Sr are similar in many respects to those described for the Tien Shan xenoliths (Table 3), their trends are significantly different (Fig. 1). Similar to the Tien Shan, Sr and Ba contents are not correlated with Ca.

Kimberlites

The contents of Ba and Sr increase from garnet peridotites to eclogites and MARID xenoliths (Table 5).

DISCUSSION

The ultrabasic upper mantle of the Pamirs–Tien Shan proper is characterized by extremely low Ba and Sr contents. The development of modal metasomatism (fluidized magmatism) results in a considerable increase in Ba and Sr contents, and these elements become indicators of these processes. The enrichment of alkalis, Ba, Sr, and other elements in the upper mantle suggests their influx from deeper (sublithospheric) mantle levels. The contents of these elements increase to higher levels in mantle-derived alkaline mafic–ultramafic melts (alkaline mafic rocks, lamproites, K and Na alkaline ultramafic series, and related carbonatites), which are formed at great depths by the melting of metasomatized mantle materials, from phlogopite harzburgites to pyroxenites (±Sr-calcite and other phases). The moderate contents of Ba and Sr in the deepest kimberlite magmas [5, 37] indicate that the enrichment of Ba and Sr depends on both pressure and the type of metasomatism.

In contrast to Li, Cs, Sn, and B, which may significantly accumulate in alkaline mafic rocks and mantle metasomatic rocks but have practically no mineral concentrators (cryptic metasomatism resulting in their occurrence in gas–liquid inclusions, defects of crystal lattices, and microclusters [16, 18 etc.]), Ba and Sr almost always form their own minerals (modal metasomatism). As to the relationships with volatile components, Ba and Sr show affinities to mantle melts and metasomatic assemblages enriched in CO_2 (CO_2 > H_2O), F, and P.

The existence of statistical relationships of Ba and Sr with each other and with other major and trace elements in the mantle xenoliths and alkaline mafic rocks reflects their occurrence in common mineral concentrators or similar behavior in metasomatic and magmatic processes. Both Ba and Sr are negatively correlated with Mg, which suggests a decrease in Mg content during the metasomatism and melting of ultrabasic materials with simultaneous accumulation of Ba and Sr. There is a very strong correlation between Ba and K (±Ti, F) reflecting the occurrence of these elements in micas. In contrast to the common igneous series, mantle metasomatic rocks and alkaline mafic rocks show no crystal chemical relationship between Sr and Ca [1], although Sr is often correlated with alkalis (with both K and Na) and, occasionally, with P. In addition, high Sr contents were reported from low-Ca trachytes, agpaitic alkaline syenites, and other rocks. On the other hand, there are mantle rocks (e.g., kimberlites and carbonatites) in which Sr occurs mainly in Ca minerals (Sr-calcite, apatite, clinopyroxene, amphibole, etc.). Thus, Sr is correlated in mantle rocks with both alkalis and Ca. In general, Sr is distributed among a greater number of minerals than Ba, which results in weaker statistical relationships of Sr.

Although Ba and Sr are in general connected with each other, they are uncoupled in some cases. This is primarily related to micas, which concentrate Ba but are usually depleted in Sr. The extreme case is Ba-phlogopite with 15.5% Ba and only 29 ppm Sr at high Ti and F (Ba titanate from the same rock contains 21.8% Ba). In contrast, high Sr and low Ba contents are characteristic of Sr-calcite, apatite, celestite, and clinopyroxene. In upper mantle metasomatic rocks, the main repositories for Ba are micas, to a lesser extent sanidine, and, in part, K-kaersutite containing both Ba and Sr. Sr occurs in K–Na feldspars (anorthoclase and Na-sanidine),

Sr-calcite, and to a lesser extent, apatite, clinopyroxene (Sr increases with depth), celestite, etc.

In principle, upper mantle metasomatic rocks can be considered as sources of alkaline mantle melts. However, there are some differences. For instance, K–Na feldspars enriched in Ba and Sr could hardly play any significant role in melt sources because of their high silica contents. The main concentrator and source of Ba (as well as K, F, Ti, etc.) in alkaline mafic–ultramafic melts is probably phlogopite (±Sr-barite, sanidine, Ba-titanates, etc.). Sr is connected with a series of minerals, including Sr-calcite and to a lesser extent, apatite, K–Na feldspar, clinopyroxene, celestite, etc. Mantle melts can be considered as final stages of formation (homogenization) of mantle metasomatic rocks.

Ba and Sr, as well as some other elements (e.g., F), can be supplied from the mantle into the crust with either high-temperature melts (alkaline basic rocks, lamproites, alkaline ultramafic rocks, and carbonatites) or medium- and low-temperature hydrothermal solutions (barite, celestite, fluorite, etc.). In some cases, the difference between the two types of processes is obliterated. For instance, the separation of potassic alkaline mafic magmas into silicate and sulfate–carbonate phases is supported by the occurrence of primary sulfate and calcite inclusions in pyroxenes from potassic alkaline mafic rocks (celestite, Sr calcite, and others [39]). Celestite and strontianite were reported from kimberlites [5]. The important role of sulfate S was detected from the incipient stages of alkaline mafic magma formation to metasomatic carbonatites (with up to 15–20% of Ba and Sr sulfates) [39]. The unmixing of the ultrapotassic fergusites of the Pamirs into immiscible liquids resulted in the formation of Sr-calcite, Ba-celestite, Sr-apatite, Ba-scapolite, and Ba–Sr-bearing fluorite [35, 36]. Fluorite crystallized from the magmatic (1050°C) to hydrothermal (460°C) stages [35]. Barite and celestite form at lower temperatures.

The extensive carbonation (listwaenitization) of ultrabasic xenoliths from the Tien Shan (200–300°C) was accompanied by the influx of Sr, which appeared to be closely connected with CO_2 rather than with Ca (Table 4). The carbon isotopic compositions of carbonates from alkaline mafic diatremes and zones of regional carbonation indicate a mantle source for CO_2. The late Alpine deposits of Sr that were previously regarded as vadose–hydrothermal (200–250°C) compose a large celestite province, which largely coincides with the Mediterranean mobile belt [38]. They are probably related to mantle sources. In addition to the tremendous scales of the deposits and their confinement to belt structures, indirect evidence is provided by the finding of high-temperature celestite, barytocelestite, magmatic Sr-calcite, etc. in alkaline mafic–ultramafic rocks of definitely mantle origin.

Large segments of mobile belts (geochemical provinces), for instance, Tien Shan and BMR in the Central Asian belt, show different concentrations and proportions of Ba and Sr in alkaline mafic rocks, mantle metasomatic rocks, and their minerals [23]. The most important feature of the Pamir–Tien Shan province is the high value of Ba/Sr > 1, which, in turn, reflects a generally high potassium content in the rocks of the lithosphere.

The contents of Ba and Sr increase in the Pamir–Tien Shan region from crustal metamorphic rocks and granitoid [28, 29] to mantle alkaline basic rocks and metasomatic rocks. It can be supposed that large geochemical (metallogenic) provinces form under the influence of ultradeep (sublithospheric) fluid–magma processes of the plume type [40].

CONCLUSIONS

(1) The ultrabasic mantle of the region is characterized by very low Ba and Sr contents. The accumulation of these elements in mantle metasomatic rocks and alkaline mafic–ultramafic melts is probably related to their influx from deep (sublithospheric) mantle sources of the plume type.

(2) The existence of statistical correlations of Ba and Sr with each other and with other major and trace elements in the mantle xenoliths and, to a lesser extent, host alkaline mafic rocks reflects their incorporation into common mineral concentrators or coupled behavior in metasomatic and magmatic processes. The very strong correlation of Ba with K(±F, Ti) reflects the affinity of these elements with the major Ba concentrator, mica. In addition, Ba is incorporated in sanidine, K-kaersutite, Ba-titanates, etc. [41].

In contrast to common magmatic series, Sr is not correlated with Ca in mantle metasomatic rocks and alkaline mafic rocks but is often connected with alkalis (both Na and K) and, occasionally, with P. Furthermore, high Sr contents were observed in Ca-poor trachytes, agpaitic alkaline syenites, and other late differentiated rocks. On the other hand, in some types of mantle rocks (e.g., carbonatites and kimberlites), Sr occurs mainly in calcic minerals (Sr-calcite, apatite, clinopyroxene, amphibole, etc.). Thus, mantle rocks show statistical and geochemical (crystal chemical) relationships of Sr with alkalis and Ca. In the upper mantle metasomatic rocks, Sr occurs in K–Na feldspars (anorthoclase and sanidine), Sr-calcite, and to some extent, in apatite, clinopyroxene, celestite, etc. On the other hand, K–Na feldspars enriched in Ba and Sr could hardly play any important role in the sources of alkaline mafic–ultramafic magmas because of the high silica content in these minerals.

(3) Ba and Sr can be supplied from the mantle into the crust both with high-temperature melts (alkaline mafic rocks, lamproites, K–Na alkaline ultramafic rocks, and carbonatites) and with medium- to low-temperature hydrothermal solutions (barite, celestite, fluorite, and other minerals). The carbonation (listwaenitization) of ultrabasic xenoliths from the Tien Shan is accompanied by the influx of Sr, which shows a close

affinity to CO_2 rather than to Ca. The carbon isotopic compositions of carbonates from alkaline mafic diatremes support the mantle source of CO_2 and probably Sr.

(4) The late Alpine Sr deposits that were previously thought to be of vadose–hydrothermal origin (200–250°C) compose a huge celestite province coinciding in fact with the Mediterranean mobile belt. The giant scale of the province, its confinement to belt structures, finding of high-temperature celestite, barytocelestite, and magmatic Sr-calcite in mantle-derived alkaline mafic rocks, carbonatites, and kimberlites, and some analogies between the mechanisms of formation of listwaenite xenoliths and celestite deposits do not exclude the possible mantle nature of these deposits.

(5) Large segments of mobile belts (geochemical provinces), in particular, Tien Shan and BMR in the Central Asian belt, show different contents and proportions of Ba and Sr in mantle-derived alkaline mafic rocks, mantle metasomatic rocks, and their minerals. In the Pamir–Tien Shan province, the contents of Ba and Sr increase from crustal metamorphic rocks and granites to mantle metasomatic rocks.

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