Ca–BEARING STRONTIANITE, BARITE, DOLOMITE, and CALCITE FROM METAKIMBERLITE, ZARNITSA PIPE, YAKUTIA

Elena L. Sokolova
Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, mineral@fmm.ru
Ernst M. Spiridonov
Lomonosov Moscow State University, Moscow, Russia

Strontianite from metakimberlite of the Zarnitsa pipe has been studied. According to mineral assemblages and carbon and oxygen isotopic composition, strontianite and associated minerals are hydrothermal metamorphic and have been formed at the post-trap zeolite facies low-grade metamorphism of submergence.
3 tables, 6 figures, 23 references

Kimberlite pipes in the central part of the Eastern Siberian Platform cut through Paleozoic sequences of the plate cover and are of pre-trap age. Compositionally, kimberlite corresponds to ultrabasic alkaline lamprophyre with a significant amount (up to 30 – 50% by vol.) of magmatic lamellar calcite containing up to 3% by weight of Sr and 0.5% by weight of Ba (Nikishov, 1984; Mitchell, 1986). Early and Middle Paleozoic sequences comprise numerous evaporates, which are frequently saturated by brines; evaporates and brines are enriched with Sr; anhydrite and dolomite contain disseminated celestite (Geology..., 1966).

Significant part of the Eastern Siberian Platform is covered with thick sequences of plateau basalt and/or basaltic tuff, which are saturated by dykes, sills, and intrusions of gabbro-dolerite of the trap assemblage with an isotopic age of 251 Ma (Kamo *et al.*, 2003) corresponding to the Permian-Triassic boundary. The trap assemblage and underlying sequences with the pre-trap kimberlite bodies were submerged (similar to the submergence of Antarctica, Greenland, and the Baltic Shield under an ice load). All these rocks are affected zeolite and prehnite-pumpellyite facies regional metamorphism of submergence; the Rb/Sr age of low-grade metamorphism of the plate cover at the Eastern Siberian Platform ranges from 232 to 122 Ma, with the latter dating the formation of Iceland spar deposits (Spiridonov *et al.*, 2000, 2006).

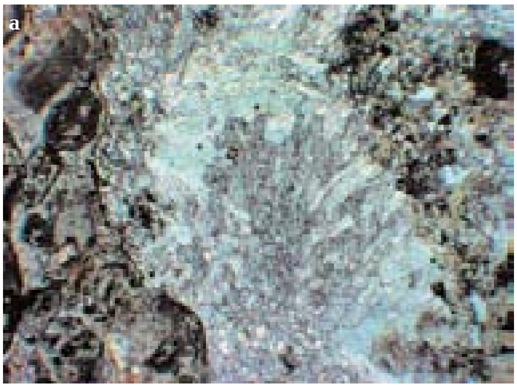
The low-grade metamorphism is characterized by the following features. 1) Extreme heterogeneity in appearance; the number of the newly formed metamorphic assemblages ranges from traces to 100% for short distance with the maximum being close to the feeders (fracture zones). 2) Fluid-dominated nature; therefore, metarocks in general are massive and not foliated and contain cracks of hydrofracturing filled with the metamorphic hydrothermal Alpine veins. 3) The potential for elevated oxidation of metamorphic fluids (Thompson, 1971; Fyfe *et al.*, 1981; Low Grade..., 1999). The Alpine veins are composed of zeolites, serpentine, silica minerals, Ca-Mg-Fe-Mn-Sr carbonates, Fe hydroxides, and Ca-Sr-Ba sulfates.

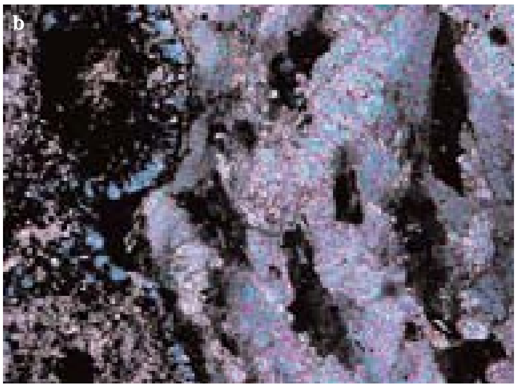
The altered kimberlite with abundant impregnation, pods, and veins of serpentine, calcite, dolomite, magnetite, pyrite, celestite, brucite-amakinite, hydrotalcite-pyroaurite, silica minerals (including pods of agate), and other low-temperature minerals, which are not modified by depth (down to 1200 – 1500 m), is considered to be the ancient weathering profile or as post-magmatic (Bobrievich *et al.*, 1959; Lebedev; 1963; Milashev, 1963; Francesson, 1968; Marshintsev *et al.*, 1980; Kornilova *et al.*, 1981; Podvysotsky, 1985). This conflicts with the formation temperature of carbonates, serpentine, magnetite, and celestite, which range from 80-130 to 210 – 250°C (Kuznetsov *et al.*, 1995; Sokolova & Spiridonov, 2006) and oxygen isotopic data (Ukhanov *et al.*, 1982, 1986). I.P. Ilupin (1961) seriously doubted the post-magmatic origin of hydrothermal Sr mineralization in serpentinized kimberlite.

The mineral assemblages of metakimberlite at the Eastern Siberian Platform correspond to the zeolite facies metamorphism (Spiridonov *et al.*, 2000): serpentine mineral is lizardite; typical

Fig. 1. Pods and veinlets of strontianite in metakimberlite: (a) sample 60063 is 10 cm in size. (b) sample M-28392 is 9.5 cm in size.

Fig. 2. (a) Photomicrograph of veinlet of Ca-bearing strontianite in metakimberlite with green lizardite. Normal light. Width of image is 4 mm. (b) Detail of (a). Metakimberlite is as fine-grained aggregates of dolomite, ankerite, calcite, and lizardite (left) and intergrowths of slightly split prismatic crystals of Ca-bearing strontianite (right). Crossed nicols. Width of image is 0.8 mm. Sample 60063.



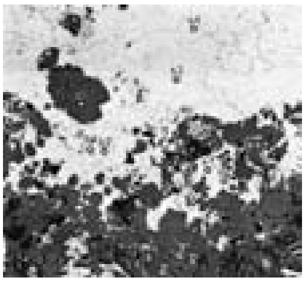


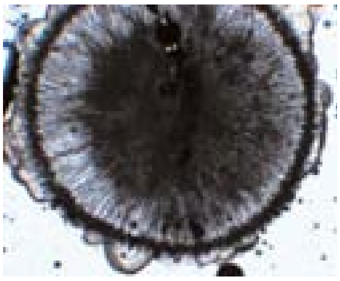
paragenetic assemblages are as follows; lizardite + calcite, lizardite + dolomite, and lizardite + goethite (Kornilova *et al.*, 1981; Nikishov, 1984; Sokolova & Spiridonov, 2006).

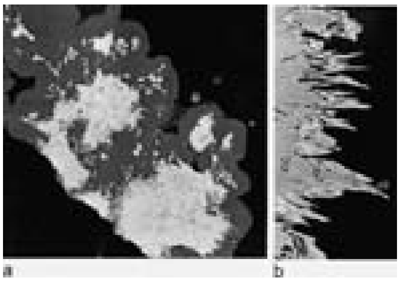
Strontium minerals, celestite and strontianite, are widespread in metakimberlite of the Mir, Udachnaya-East, Yakutskaya, Zapolyrnaya pipes, and especially in the Zarnitsa pipe (Bobrievich *et al.*, 1959; Ilupin, 1961). In metakimberlite of the Zarnitsa pipe, pods of celestite of 25 cm across and celestite veinlets are hosted in the lizardite clusters. Celestite replaces lizardite and is colorless, white, blue, reddish pink (with inclusions of tiny lamellae of lepidocrocite), and brown (with inclusions of bitumen and oil up to 0.5 mm in size). In the fracture zones, celestite is partially or completely replaced with strontianite due to the increased presence of fCO_2 in the metamorphic fluid that usually takes place as the temperature decreases (Thompson, 1971).

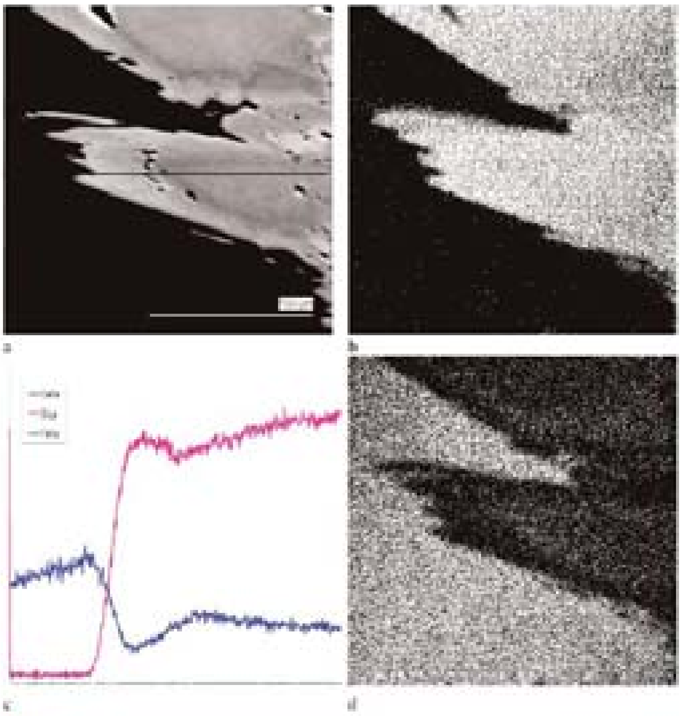
We have examined aggregates of porcelaneous (sample 60063) and spherulitic (sample M-28392) strontianite. The chemical composition has been studied with a JXA-50A electron microprobe, L.A. Pautov, analyst, Fersman Mineralogical Museum, Russian Academy of Sciences. The following standards have been used: $SrSO_4$ for Sr, $BaSO_4$ for Ba and S, diopside USNM 117733 for Ca, Mg, Mn, and Fe. BSE images have been made at the same museum. Strontium, oxygen, and carbon isotopic compositions in strontianite have been measured in the Laboratory of Isotopic Research, Geological Institute, Russian Academy of Sciences, B.G. Pokrovsky, analyst.

Sample 60063 is brecciated metakimberlite with crusts, pods and veinlets of strontianite (Figs. 1a, 2). The thickness of the veinlets is up to 4 cm. The dense cluster of strontianite is seen microscopically as a segregation of split long prismatic crystals (Fig. 2). Chemical composition corresponds to Ca-bearing strontianite with the for-









↑Fig. 3. BSE image of segregations of Ca-bearing strontianite (light) (anal. s1-s4) with numerous crystals of calcite (grey) (analysis c1), less frequent barite (anal. b1, b2), and relic lizardite (black) onto metakimberlite. Sample 60063. Width of image is 1.9 mm.

↗ Fig. 4. Photomicrograph of spherulite of strontianite of 2 mm in size with minute crystals of dolomite. Sample M-28392. Normal light.

↗↗ Fig. 5. BSE images of intergrowths of strontianite and dolomite, sample M-28392. (a) Crusts of spherulites of dolomite (grey) (anal. d1-d3) with minute inclusions of crystals of barite (anal. b3-b5) onto aggregate of prismatic crystals of Ca-bearing strontianite (white); width of image is 2.9 mm. (b) Detail of (a), druse of zoned crystals of Ca-bearing strontianite (anal. s5-s8), width of image is 0.3 mm.

→ Fig. 6. Zoned crystals of Ca-bearing strontianite overgrown by dolomite: (a) BSE image, (b) X-ray map, SrLa, (c) concentration patterns of Sr, Ca, and Fe along line shown in a, (d) X-ray map, CaKa. Sample M-28392.

mula $Sr_{0.792-0.814}Ca_{0.181-0.203}Fe_{0.002-0.005}Ba_{0-0.001}[CO_3]$ (Table 1, anal. s1 – s4). Calcite with its' composition corresponding to the formula $Ca_{0.990}Sr_{0.007}Fe_{0.002}Ba_{0.001}[CO_3]$ (Table 1. anal. c1) is abundant in aggregates of Ca-bearing strontianite near metakimberlite. Rare grains of barite up to 20 μm in size with composition corresponding to the formula $Ba_{0.970-0.973}Sr_{0.009-0.023}Ca_{0-0.009}Fe_{0.004-0.012}[SO_4]$ (Table 2, analyses b1 and b2) also occur in the cluster of strontianite.

Sample M-28392 is metakimberlite with a large pod consisting of strontianite spherulites up to 4 mm in size (Figs. 1b, 4). These spherulites are composed of Ca-bearing strontianite of relatively homogeneous composition. Minute zoned crystals of dolomite (Fig. 4) and their aggregates or compositionally zoned prismatic crystals of Ca-bearing strontianite up to 1 mm long (Figs. 5, 6) have overgrown the spherulites. Prismatic crystals of Ca-bearing strontianite, which are diamond-shaped in cross-section, are partially hollow. The inner zones of these crystals are enriched in Ca and correspond compositionally to the formula $Sr_{0.720-0.726}Ca_{0.271-0.276}Fe_{0.003}[CO_3]$ (Table 1, anal. s7, s8), whereas the outer zones are enriched with Sr and correspond to the formula $Sr_{0.831-0.851}Ca_{0.148-0.162}Fe_{0-0.003}Ba_{0.001-0.002}[CO_3]$ (Table 1, anal. s5, s6). The spherulites of Ca-bearing strontianite are overgrown with solid spherulitic crusts of dolomite up to 0.5 mm thick (Figs. 5, 6), which cause brown coloration of the dolomite. The composition of dolomite corresponds to the formula $Ca_{1.007-1.030}Mg_{0.950-0.967}Sr_{0.016-0.026}[CO_3]_2$ (Table3, anal. d1 – d3). Ca-bearing strontianite is associated with minor barite. Crystals of barite are included in the

Table 1. **Chemical composition of Ca-bearing strontianite (s1-s8) and calcite (c1) from pods in metakimberlite, the Zarnitsa pipe, Yakutia**

Component, wt%	s1	s2	s3	s4	s5	s6	s7	s8	c1
SrO	60.36	59.51	61.29	59.94	61.42	63.89	55.96	56.23	0.67
CaO	7.28	8.24	7.94	7.88	6.45	6.02	11.67	11.35	55.09
FeO	0.19	0.28	0.13	0.20	0.28	0.03	0.17	0.18	0.17
BaO	0.06	–	–	0.08	0.21	0.07	–	–	0.10
CO_2^*	31.51	31.84	32.32	31.80	31.40	31.92	33.05	32.33	43.68
Total	99.40	99.87	101.71	99.90	99.77	101.93	100.85	100.09	99.71
Atoms per formula unit									
Sr	0.814	0.792	0.805	0.801	0.831	0.851	0.720	0.726	0.007
Ca	0.181	0.203	0.193	0.195	0.162	0.148	0.277	0.271	0.990
Fe	0.004	0.005	0.002	0.004	0.005	0.000	0.003	0.003	0.002
Ba	0.001	–	–	0.001	0.002	0.001	–	–	0.001
Total	1	1	1	1	1	1	1	1	1

Note: Bdl is below detection limit by electron microprobe. Mn is not detected. CO_2 is calculated by stoichiometry.

Table 2. **Chemical composition of barite associated with strontianite from pods in metakimberlite, Zarnitsa pipe, Yakutia**

Components, wt. %	b1	b2	b3	b4	b5
BaO	63.14	64.11	61.97	61.42	63.89
SrO	1.03	0.42	2.20	2.15	1.79
CaO	0.01	0.23	0.44	0.21	0.45
FeO	0.12	0.38	*na*	*na*	0.24
SO_3	33.90	34.58	34.46	34.09	35.51
Total	98.20	99.71	99.07	99.06	101.88
Atoms per formula unit					
Ba	0.973	0.970	0.936	0.941	0.938
Sr	0.023	0.009	0.049	0.049	0.039
Ca	0.000	0.009	0.018	0.009	0.018
Fe	0.004	0.012	-	-	0.007
SO_4	1.000	1.000	0.997	1.001	0.998
Total	2	2	2	2	2

Note: na is not analyzed

Table 3. **Chemical composition of dolomite associated with strontianite from pods in metakimberlite, Zarnitsa pipe, Yakutia**

Components, wt. %	d1	d2	d3
CaO	30.86	31.38	30.74
MgO	21.30	21.21	20.39
SrO	1.46	0.91	1.12
CO_2^*	48.11	48.18	46.88
Total	101.73	101.68	99.13
Atoms per formula unit			
Ca	1.007	1.022	1.030
Mg	0.967	0.962	0.950
Sr	0.026	0.016	0.020
Total	2	2	2

Note: Fe, Mn and Ba are not detected. CO_2 is calculated by stoichiometry.

spherulites of strontianite or are located adjacent to them in surrounding dolomite. Barite contains up to 2.2 wt.% SrO; its chemical composition corresponds to the formula $Ba_{0.936-0.941}Sr_{0.039-0.049}Ca_{0.009-0.018}Fe_{0-0.007}[SO_4]$ (Table 2, anal. b3-b5).

Strontium isotopic composition in the examined strontianite samples is uniform with the $^{87}Sr/^{86}Sr$ ratio of 0.7080 (sample 60063) and 0.7084 (sample M-28392). The δO^{18} (SMOW) values of the examined samples are different and are +11.7 (sample 60063) and +14.8 (sample M-28392). The δC^{13} (PDB) values of the examined samples are strongly variable and equal -0.7 (sample 60063) and -9.9 (sample M-28392). Our data on strontium isotopic composition are close to the data reported in (Kostrovitsky *et al.*, 1983; Exley & Jones, 1983). Magmatic calcite from kimberlite or host evaporite sequences are both probable sources for Sr in metamorphic hydrothermal strontianite. Oxygen and carbon isotopic compositions in strontianite correspond to hydrothermal carbonates (Ferrini *et al.*, 2003).

Thus, Ca-bearing strontianite, barite, calcite, and dolomite from metakimberlite of the Zarnitsa pipe are metamorphic hydrothermal; this assemblage have arisen under low temperature zeolite facies conditions.

Acknowledgments

This study was supported by the Russian Foundation for Basic Research, project no. 07-05-00057. We are grateful to L.A. Pautov and B.G. Pokrovsky for high-quality electron microprobe and isotopic analyses.

References

Bobrievich, A.P., Bondarenko M.N., Gnevushev, M.A., et al. (**1959**): Diamond deposits. Gosgeoltekhizdat, Moscow (in Russ.).

Geology of the Siberian Platform (**1966**): (I.I. Krasnov, M.N. Lur'e, and V.L. Masaitis, eds.) Nedra, Moscow (in Russ.).

Exley R.A & Jones A.P. (**1983**): $^{87}Sr/^{86}Sr$ in kimberlite carbonates by ion microprobe: hydrothermal alteration, crustal contamination, and relation to carbonatite. //Contrib. Mineral. Petrol 83, 288 – 292.

Ferrini, V., Martarelli, L., de Vito C., Çina, A. & Deda, T. (**2003**): The Koman dawsonite and realgar-orpiment deposit, Northern Albania: influences of processes of formation. //Can. Mineral.41, 413 – 427.

Francesson, E.V. (**1968**): The petrology of kimberlites. Nedra, Moscow (in Russ.).

Fyfe, W.S., Price, N.J. & Thomson, A.B. (**1978**): Fluids in the earth's crust: their significance in metamorphic, tectonic, and chemical transport processes. Elsevier Scientific Pub. New York.

Ilupin, I.P. (**1961**): On the origin of strontium minerals in kimberlitic pipe of West Yakutia. //Proc. Miner. Museum, Acad. Sci. USSR. 12, 212 – 217 (in Russ.).

Kamo, S.L., Czamanske, G.K., Amelin, Yu., Fedorenko V., Davis D. & Trofimov V. (**2003**): Rapid eruption of Siberian flood-volcanic rocks and evidence for coincidence with Permian-Triassic boundary and mass extinction at 251 Ma. //Earth Planet. Sci. Lett. 214, 73 – 93.

Kornilova, V.P., Nikishova, L.V. & Nikishov K.N. (**1981**): Minerals of the serpentinite group from kimberlitic rocks of Yakutia. //In: Pragenesises of minerals of kimberlitic rocks. Yakutian Division, Siberian Branch, Acad. Sci. USSR Press (65 – 81) (in Russ.).

Kostrovitskii, S.I., Dneprovskaya, L.V. & Brandt, S.B. (**1983**): Correlation of Sr, C, and O isotopic compositions in carbonates from kimberlite of Yakutia. //Dokl. Acad. Sci. USSR 272, 1223 – 1225 (in Russ.).

Kuznetsov, G.V., Matsyuk, S.S. & Zinchuk, N.N. (**1995**): Hydrothermal calcite from kimberlites of Yakutia. //Zap. VMO. No. 6, 87 – 100 (in Russ.).

Lebedev, A.A. (**1963**): On hydrothermal stage of kimberlite serpentinization in connection with finding of brucite. //In: Petrography and mineralogy of diamond primary deposits. Acad. Sci. USSR Press, Moscow 8, 71 – 86 (in Russ.).

Low-grade metamorphism (**1998**): (M. Frey & D. Robinson, eds.). Blackwell Science, Oxford.

Marshintsev, V.K., Zol'nikov, G.V. & Nikishov, K.N. (**1980**): Carbonates of kimberlite at the Siberian Platform. //In: Endogenic carbonates of Yakutia. Nauka, Novosibirsk (18 – 35) (in Russ.).

Mitchell, R.H. (**1986**): Kimberlites: mineralogy, geochemistry, and petrology. Plenum Press, New York, London.

Nikishov, K.N. (**1984**): Petrological and mineralogical model of kimberlite process. M.: Nauka. (in Russ.).

Podvysotsky, V.T. (**1985**): Serpentine-carbonate mineralization in kimberlite. //Zap. VMO. No 2, 234 – 247. (in Russ.)

Sokolova, E.L. & Spiridonov, E.M. (**2006**): Goethite and lizardite paragenesis - typical formation of metakimberlites and hosted metaperidotite xenoliths under zeolite facies conditions. // New Data on Minerals 41, //86-90.

Spiridonov, E.M., Kirov, G.N., Ivanova, P.V. & Yanakieva, D.Ya. (**2006**): Post-skarn hydrothermal rocks in diatrem of basalt of the trap assemblage, Rudnogorsk deposit, southern Siberian Platform. //In: Volcanism and geodynamics. Buryat Sci. Centre Press, Siberian Branch, Russian Academy of Sciences 3, 771 – 775 (in Russ.).

Spiridonov, E.M., Ladygin, V.M., Simonov, O.N., Kulagov, E.A. & Stepanov, V.K. (**2000**): Metavolcanic rocks of the prehnite-pumpellyite and zeolite facies of trap assemblage, Noril'sk district, Siberian Platform. Moscow State University Press, Moscow (in Russ.).

Thompson A.B. (**1971**): PCO_2 in low-grade metamorphism; zeolite, carbonate, clay mine rals, prehnite relations in the system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}CO_2\text{-}H_2O$. //Contrib. Mineral. Petrol. 33, 145 – 161.

Ukhanov, A.V. & Devirts, A.L. (**1982**): Meteoric origin of water responsible for the serpentinization of Yakutia kimberlite. //Dokl. Acad. Sci. USSR 268, 706 – 710 (in Russ.).

Ukhanov, A.V., Ustinov, V.I. & Devirts, A.L. (**1986**): Low temperatures of serpentinization of kimberlite in Yakutia: evidence from oxygen isotopic study. //Dokl. Acad. Sci. USSR 288, 466 – 469 (in Russ.).