Behavior of TiO₂ in Dolerits as a Possible Search Sign for Kimberlites

Mikhail Tomshin, Sargylana Gogoleva
Diamond and Precious Metal Geology Institute, Siberian Branch of Russian Academy of Science, 39, prosp. Lenina, Yakutsk, 677000, Russia
tmd@diamond.ysn.ru

Abstract. A generalization of studies of the chemical composition of dolerites of the Vilyui-Markha dike swarm (VMDS) in the Eastern part of the Siberian Platform is carried out. This belt stretches along the North-Western side of the Vilyui paleorift system (Eastern part of the Siberian platform) for almost 700 km. The formation of VMDS intrusives took place in the interval of 372 million years. The Devonian kimberlites, which formed three kimberlite fields: Malo-Botuobin, Nakyn, Suldyukar, are confined spatially to the VMDS. One is in the Southern part of the belt, and the last two are in its Central part. The formation of kimberlite pipes according to K-Ar, 40Ar / 39Ar, Rb-Sr dating is close to 362 Ma. When studying dolerites, it was found that near the kimberlites, the proportion of TiO₂ increases in the first (almost 2 times - up to 4-5% versus 2.2-2.5%) and a number of heavy rare-earth elements, such as Th, Hf, Y, Nd. An increase in the content of these elements proceeds gradually from the edge of the kimberlite field to kimberlites and reaches a maximum of 7% (a single case) directly near kimberlites. The authors suggest that the latter is indirectly associated with kimberlites. The solubility of titanium in a basite melt sharply increases with increasing pressure. The kimberlite-forming system is long-lived, associated with diapir-like kimberlite protrusion, which subsequently produces kimberlite pipes. Long before the formation of kimberlites around the diapir, possibly located in the lower horizons of the earth's crust, excessive stress pressures are created. A basite melt, penetrating through these abnormal (relative to pressure) regions, reacts with an increase in the content of titanium and HREE. Outside the kimberlite field contours, the content of the elements in question in dolerite dikes remains normal, i.e. 2-2.5%. Based on the above stated fact and the study of the geochemistry of dolerites of VMDS, the authors suggest the discovery of two more kimberlite fields within the swarm: Tenkelyakh, located 20-30 km North of the famous Nakyn field, and Orto-Kyulunke, whose location is possible in the North of the VMDS. The authors gave the names of the fields by the names of the rivers flowing through this territory.

1. Introduction
Vilyui Middle Paleozoic paleorift is a large structural element of the east of the Siberian Platform. For the first time, its rift nature was justified by K.K. Levashov [1]. Its structure was considered in more detail in [2], and the history of the structure formation is described in [3, 4]. Data on the tectonic structure, crustal structure revealed by deep seismic sounding, the wide occurrence of alkaline basalts magmatism and the presence of multiple dikes, according to A.F. Grachev [5], unequivocally point to the riftting origin of this structure. New rift-bounding faults were generated and acted as the main magma conduits, including the Vilyui–Markha fault in the northwest, the Chara–Sinsk fault in the southeast, and Kontai–Dzherba fault in the inward-dipping termination of the rift structure (Figure 1). Basites
Magmas were intruded along these rift-bounding faults forming extensive dike swarms of the same name, which point to the rift origin of the Vilyui structure. Dikes are far more prevalent across the Vilyui–Markha and Chara–Sinsk zones, while sills predominate in the Kontai–Dzherba zone, and most of them were injected into Lower Paleozoic carbonate strata. The identified fault zones have a northeast strike. Three kimberlite fields were spatially combined with the Vilyui–Markha dike swarm: Malo-Botuobin, Nakyn and Syuldyukar (Figure 1). The relationship between kimberlites and basites of the dike swarm is devoted to these works.

Figure 1. Schematic structure of the Vilyui paleorift.

1 — depressions willed with terrigenous sediments, up to 6 km thick; 2 — major uplifts; 3 — dike swarms; 4 — fronts; 5 — kimberlite fields: а – open, b – alleged (I Nakyn, II Malo-Botuobin, III Syuldyukar; IV Kyulankin, V Tenkelyakh).

2. Basites of the Vilyui-Markha dike swarm
The Vilyui–Markha dike swarm extends along the North-Western side of the Vilyuisk paleorift for almost 700 km. The formation of belt intrusions took place in the Upper Devonian and, according to the isotope data obtained by K-Ar, $^{40}$Ar/$^{39}$Ar, Rb-Sr, Sm / Nd, fits within the intervals of 368.5-376.3 Ma. Ages of 373.7–376.3 Ma predominate. Magmatic activity in this dike swarm was associated with the intrusion of sills, chonoliths, dikes and eruptive vents of basic composition. All of them are intruded into sedimentary carbonate rocks of Cambrian and Ordovician age. The dikes are a few tens of kilometers long and range in thickness varies from 6–8 to 80 m. The thickness of the sills may reach only a few tens of meters, as indicated by drilling data. Late-stage basaltic lavas of the Appainskaya D$_{3}$ap and Emyaksinskaya D$_{3}$-C$_{1}$em Formations at the southwestern edge of the dike swarm are associated with the formation of the Vilyui paleorift valley [2,4]. The most detailed description of VMDS rocks is given in [9].
The dominant type of intrusive rocks of the Vilyui–Markha dike swarm belt is prismatic-ophitic gabbro-dolerite. A distinctive feature of these rocks is the presence of quartz, a ubiquitous late-magmatic phase, which may account for 5–6 vol.%. Most gabbro-dolerites contain 3–5% of early crystallizing phases such as bytownite (An88-80), chrysolite–hyalosiderite (Fa21-35) and less common magnesian clinopyroxene (Wo35-37 En54-52 Fs11-12). The anorthositic gabbrodolerite usually contain the largest volume proportion of early plagioclase (18–25 vol.%) – the result of a long-term evolution of the basalt melt in a pre-chamber depth environment [10]. The intrachamber mineral paragenesis of gabbro-dolerites consists of plagioclase of a more felsic composition (An78-44), augite (Wo43-37 En40-41 Fs12-21), hortonolite (Fa39-56), oxide ore minerals, and apatite. Other minerals common to Middle Paleozoic basites are hornblende, biotite, and K-feldspar. The fraction of the last two minerals together with quartz may reach 12 vol.%. The basites of the VMDS, as well as Vilyui paleorift, are ascribed to the tholeitic series (table 1, figure 2a) with SiO2 = 47.39–49.2 wt. %, Na2O + K2O = 3.07–4.92 wt. % and Na2O/K2O > 1. The work presents only data on the chemical composition of the prevailing types of rocks (table 1). It is seen that dolerites of the dike swarm are characterized by a relatively high TiO2 = 2.48-2.6 wt.% content. (about the behavior of titanium will be discussed below) and P2O5 = 0.29–0.41 wt. %. In a SiO2 vs. Na2O + K2O diagram (Figure 2b), the figurative points of the average composition of the VMDS dolerites are almost equally divided into tholeiitic and subalkaline differences of rocks.

![Figure 2. Classification and discrimination diagrams for dolerites of the VMDS.](image_url)

\( a \) — (Na2O + K2O)—FeO*—MgO [11]; b — (Na2O + K2O) — SiO2 [13]; c — Zr—Ti—Y [12] (A — island-arc tholeites, B — MORBs, C — calc-alkaline basalts, D — within-plate basalts); d — Zr/Y—Zr [14] (A, island-arc basalts; B, MORBs; C, within-plate basalts; D, island-arc basalts and MORBs; E, within-plate basalts and MORBs).
Table 1. The content of petrogenic (wt.%) and rare (ppm) elements in representative basite samples from the VMDS

| №  | MIR1 2/24 | 130/60 | T-68-233-802-38/43 | OB-802-791 | OB-566-1 | OB-534-4 |
|----|----------|--------|-------------------|----------|----------|----------|
| SiO₂ | 47.56 | 48.59 | 49.2 | 48.13 | 47.39 | 48.23 | 47.96 | 48.84 |
| TiO₂ | 3.26 | 3.57 | 2.48 | 2.53 | 4.01 | 2.6 | 3.51 | 3.11 |
| Al₂O₃ | 12.87 | 13.08 | 15.38 | 14.24 | 12.88 | 14.46 | 14.08 | 13.05 |
| Fe₂O₃ | 6.64 | 4.92 | 3.43 | 2.79 | 6.92 | 2.94 | 5.97 | 3.38 |
| FeO | 6.75 | 10.08 | 9.42 | 10.25 | 9.63 | 9.82 | 8.46 | 12.44 |
| MnO | 0.2 | 0.2 | 0.17 | 0.19 | 0.23 | 0.2 | 0.12 | 0.25 |
| MgO | 5.5 | 5.18 | 5.04 | 5.57 | 5.36 | 5.12 | 3.87 | 4.97 |
| CaO | 10.14 | 8.33 | 9.53 | 10.05 | 9.7 | 9.04 | 10.18 | 9.05 |
| Na₂O | 3.04 | 1.96 | 2.94 | 1.85 | 2.21 | 2.79 | 2.21 | 2.13 |
| K₂O | 1.86 | 1.37 | 1.32 | 2.69 | 0.91 | 0.99 | 1.15 | 1.15 |
| P₂O₅ | 0.34 | 0.41 | 0.29 | 0.31 | 0.4 | 0.41 | 0.4 | 0.32 |
| H₂O⁺ | 1.19 | 1.8 | 0.76 | 0.79 | 0.78 | 2.61 | 1.29 | 1.66 |
| Σ | 99.95 | 99.58 | 99.96 | 99.56 | 100.5 | 99.21 | 99.37 | 100.3 |

Note. Here and further in similar tables. Trace elements were analyzed by ICP-MS with an Elan 6100 DRC (Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Element, D.Z. Zhuravlev), Major oxides were analyzed by wet chemical technique at the Laboratory of Physicochemical Analytical Methods (Geology of Diamond and Precious Metals Institute, Siberian Branch, Russian Academy of Sciences).
Nh/Nb*=0.3618×Nh/(La·Th), Eu/Eu*=Eu/(Sm×Gd)* 0.5, n – values normalized to chondrite composition [Sun, McDonough,1989]

In the Zr–Ti–Y and Zr/Y–Zr discrimination diagrams [12, 14], these rocks plot in the within-plate basalt field (Figure 2c, d). These dolerites have a low Mg-number (34–47), indicating fractionation of a mafic melt before its ascent to the present-day chamber. Siderophile element abundances in these rocks correlate well with their Mg-numbers. The chondrite-normalized REE patterns in these rocks (Table 2) show a strong REE fractionation ((La/Yb)n = 9.4–4.2) and almost absent negative Eu anomalies (Eu/Eu* = 0.80–1.06). They show close affinity to OIB.

3. Basites near kimberlites

An analysis of the chemical composition of the dolerites of dikes located within the boundaries of the Nakyn kimberlite field showed the following: near kimberlites, the content of TiO2 and a number of heavy rare-earth elements such as Th, Hf, Y, Nd sharply increase (Table 1). This increase is gradual. So, for example, outside the field in the Tsepochechniy intrusion and in the dike on the river Markha, the content of TiO2 is 2.33 and 2.23 wt. %, corresponding to its normal content for dolerites of VMDS (Figure 3a, Table 1). Inside the field along its edge, about 10 km from the Nyurba pipe kimberlites in the Lindakit intrusion, the proportion of TiO2 is 2.83 wt. % In the 38/43 dike, located 3 km from the same pipe, 3.94 wt. %, and in dikes located in the immediate vicinity of the pipe (at a distance of 500-700 m from it) already reaches 4.45-4.65 wt. % (see Table 1 and Figure 3). At the same time, the petrographic and mineralogical characteristics of dolerites remain the same. A similar analysis of the chemical composition of dolerites located in the contours of the Malo-Botuobin and Suldyukar kimberlite fields showed the same result. In the area of the Malo-Botuobin field beyond its borders, the TiO2 content in the dolerite dike performing the Eastern fault is 2.4 wt. %, in the Central fault dike at its southern end (about 1 km from the kimberlite pipe Mir) is 3.9 wt. %, and in the same dike in contact with kimberlite - 4.2 wt. % (Figure 3b). On Ygyatta area (the area of the kimberlite pipe Suldyukar) in dolerites of dikes located north of the river Ygyatta (Figure 3c, Table 3), the titanium fraction (2.51, 2.2-2.5 wt.%) is typical for dolerites of BMDS. To the South, in the Erkutey dike, the amount of TiO2 increases to 3.49 wt. %, and further South, in dolerites exposed by the 1/7 well, it increases to 4.43 (Table 3, Figure 3c). South-East of the point 1/7 in 10 km and 20 km are dikes 1/17 and Holomolokh (respectively), in which the content of TiO2 is reduced to ordinary values (in the first-2.7 and in the second – 2.31 wt. %). That is, these dikes are located outside the proposed kimberlite field, outside the zone of influence of kimberlites. At the same time, to the West, 12 km from the 1/7 dike, dolerite xenolith in which the TiO2 content reaches 6.03% was raised in the kimberlite of the Suldyukar pipe (Table 3, Figure 3c). From the foregoing, a logical geochemical change in dolerites is seen, primarily in the behavior of titanium and a number of heavy rare-earth elements, in the presence of kimberlites.
**Figure 3.** The position of the dolerite dikes relative to kimberlites: a - Nakyn; b - Malo-Botuobin, c - Suldyukar fields.
Table 2. Chemical composition (wt. %, g / t) of representative samples of dolerites of the Nakyn kimberlite field

|        | Tsepochechniy | Lindakit | 38/43-30, 38/43-91 | Dolerites of dikes near the Nyurba kimberlite pipe |
|--------|---------------|----------|-------------------|--------------------------------------------------|
| SiO2   | 48.40         | 46.59    | 47.19             | 47.48                                            |
| TiO2   | 2.33          | 2.83     | 3.14              | 4.65                                             |
| Al2O3  | 14.16         | 12.45    | 13.12             | 13.91                                            |
| Fe2O3  | 2.56          | 5.52     | 3.03              | 3.47                                             |
| FeO    | 11.26         | 10.18    | 11.44             | 9.66                                             |
| MnO    | 0.20          | 0.17     | 0.20              | 0.15                                             |
| MgO    | 5.61          | 6.66     | 6.01              | 6.02                                             |
| CaO    | 9.81          | 9.34     | 8.08              | 8.83                                             |
| Na2O   | 2.31          | 2.18     | 2.46              | 2.87                                             |
| K2O    | 1.10          | 1.69     | 1.28              | 1.88                                             |
| P2O5   | 0.28          | 0.62     | 0.38              | 0.50                                             |
| H2O+   | 1.36          | 0.93     | 3.16              | 1.96                                             |
| CO2    | 0.13          | -        | 0.33              | -                                                |
| S      | -             | 0.10     | -                 | 0.12                                             |
| F      | -             | 0.22     | -                 | 0.08                                             |
| Σ      | 99.51         | 99.50    | 99.61             | 101.59                                           |
| Th     | 1.97          | 3.20     | 2.86              | 4.38                                             |
| U      | 0.57          | 0.98     | 0.83              | 1.15                                             |
| Nb     | 22.86         | 33.65    | 36.23             | 42.20                                            |
| Ta     | 1.47          | 2.34     | 3.06              | 2.92                                             |
| Zr     | 189.25        | 278.67   | 248.50            | 313.33                                           |
| Hf     | 4.70          | 6.95     | 6.35              | 7.61                                             |
| Y      | 30.78         | 40.50    | 33.50             | 28.93                                            |
| La     | 19.02         | 29.75    | 27.40             | 37.50                                            |
| Ce     | 44.63         | 68.20    | 63.38             | 87.48                                            |
| Pr     | 6.04          | 9.01     | 8.33              | 11.68                                            |
| Nd     | 26.62         | 38.77    | 36.49             | 50.82                                            |
| Sm     | 6.38          | 8.90     | 8.28              | 10.72                                            |
| Eu     | 1.94          | 2.65     | 2.57              | 3.18                                             |
| Gd     | 6.51          | 8.91     | 8.02              | 9.04                                             |
| Tb     | 1.03          | 1.39     | 1.25              | 1.26                                             |
| Dy     | 6.04          | 8.24     | 7.11              | 6.52                                             |
| Yb     | 2.95          | 3.97     | 3.09              | 2.25                                             |
| Lu     | 0.43          | 0.58     | 0.43              | 0.32                                             |
| ΣHREE  | 128.25        | 197.00   | 176.00            | 225.00                                           |
| Ga     | 21.09         | 21.55    | 23.04             | 24.38                                            |
| Be     | 0.96          | 1.39     | 1.49              | 1.45                                             |
| Cd     | 0.56          | 0.77     | 0.48              | 0.62                                             |

THREE: 128.25 + 197.00 + 176.00 + 225.00 + 296.00
Table 3. Average values of the chemical composition (wt.%) of the dolerites of Ygyatta area

|     | 1     | 2     | 3     | 4     | 5     |
|-----|-------|-------|-------|-------|-------|
| SiO₂| 48.49 | 46.57 | 48.48 | 46.84 | 48.77 |
| TiO₂| 3.49  | 4.43  | 2.7   | 2.31  | 6.03  |
| Al₂O₃| 13.29 | 14.72 | 14.42 | 15.43 | 18.18 |
| Fe₂O₃| 5.51  | 3.62  | 3.71  | 2.62  | 5.47  |
| FeO  | 9.45  | 8.84  | 10.21 | 10.89 | 5.97  |
| MnO  | 0.19  | 0.14  | 0.18  | 0.16  | 0.06  |
| MgO  | 5.07  | 6.69  | 6.04  | 7.17  | 4.48  |
| CaO  | 9.03  | 7.62  | 7.39  | 8.82  | 0.77  |
| Na₂O | 2.07  | 2.25  | 1.98  | 2.24  | 0.56  |
| K₂O  | 1.27  | 2.46  | 3.37  | 1.47  | 3.22  |
| P₂O₅| 0.65  | 0.58  | 0.47  | 0.6   | 0.59  |
| H₂O+ | 1.39  | 1.21  | 0.85  | 1.41  | 4.19  |
| CO₂  | 0.00  | 0.00  | 0.6   | 0.00  | 1.92  |
| S    | 0.06  | 0.12  | 0.08  | 0.10  | 0.11  |
| F    | 0.08  | 0.06  | 0.04  | 0.04  | 0.00  |
| ∑    | 100.14| 99.31 | 99.92 | 100.08| 100.32|

Mg#  | 38    | 47    | 39    | 48    | 42    |
| n    | 7     | 6     | 6     | 6     | 1     |

Note: 1-Erkutey dike; 2-1/7 dike; 3-1/17 dike; 4-Holomolokh dike; 5-xenolith of dolerites from kimberlites of the Syuldyukar pipe; n - number of analyses.

4. Results and discussions

A study of the VMDS basites showed that among the magmatites of the belt with a typical content of micro- and macrocomponents, local areas appear with sharply different contents of titanium and a number of heavy rare-earth elements (HREE). It is established that kimberlites are confined to these sites. It is also significant that kimberlites are younger formations in relation to dolerite dikes: ~ 362 versus ~ 374 million years (respectively). Therefore, kimberlites could hardly directly affect the change in the geochemistry of dolerites, especially in the absence of direct contact between them. Although this connection is obvious.

The work of A.I. Zaitsev, on the study of the Rb-Sr isotope systems of kimberlites of Yakutia, showed that Kimberlite formation was long. According to the results of studies of the isotope systems of kimberlites of the Mir, Udachnaya, Taezhnaya, Botuobin, Aikhal deposits and other authors [15], it was found that the onset of kimberlite-forming processes could be close to 420 million years, while the age of the kimberlites themselves was ~ 361-363 million years. Given this, it is logical to assume that kimberlite formation could have an indirect effect on basites. Experimental work A.Ya. Medvedev [16] showed that the titanium content in the basalt melt increases with increasing pressure. Modeling with Emeishain basalts [17], Le Zhang and colleagues showed that basalt magmas with higher titanium and HREE contents can appear as a result of partial melting of a PM type mantle source in the garnet stability field at higher pressures than in the case of melting ordinary tholeiites [17]. In connection with the foregoing, the following is assumed. At the time of the formation of the asthenospheric basalt lens, located at the boundary of the co-mantle and associated with the formation of the Vilyui paleorift [4], Kimberlite protrusion already existed. A local unstable region was formed above the latter at the foot of the basalt lens. It was here, when the basalt lens of the Vilyui paleorift was formed, favorable conditions could arise for the partial melting of the mantle material with the smelting of the high-titanium and HREE-enriched basalt melt. The latter, rising upward, reached the basalts of the subcrustal lens, where it ensured the appearance of localized areas enriched in titanium. Subsequently, the magmatic melt, penetrating into the upper horizons of the Earth's crust, formed the VMDS dikes. The alignment of the geochemical composition between the high titanium basites and the rest of the melt was insignificant. It is in this way that the local appearance of dikes of high-titanium basites among dolerites of VMDS can...
be explained. Subsequently, kimberlites infiltrated into the field of dolerite dikes with a high content of titanium and HREE, already prepared by the channel, prepared primarily by high-titanium basites, using the created weakened zones. It is for this reason that high-titanium dolerites can be used as a search criterion for kimberlites.

5. Conclusions
1. The local distribution of high titanium and HREE dolerites among VMDS dolerite dikes is associated with partial melting of the mantle source in the garnet stability region under the influence of kimberlite protrusion.

2. With the subsequent joint introduction of ordinary and titanium-enriched basites magmas that formed VMDS, the relative geochemical isolation of the melts is preserved, which ensured the location of dikes with a high content of titanium and and HREE.

3. Kimberlites were introduced after the formation of VMDS magmatites. And they used magma-bearing zones prepared by magmatites and, above all, high-titanium basites. Therefore, kimberlites are located in the distribution area of dolerite dikes with high titanium and HREE. The latter is characteristic of all three kimberlite fields associated with the VMDS.

4. Based on a study of the geochemistry of VMDS dolerites, the authors suggest the discovery of two more kimberlite fields within the belt: Tenkelyakh, located 20-30 km north of the famous Nakyn field, and Kyulunke, located in the northern part of the VMDS. The authors named the fields after the rivers that flow through this territory.

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