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The Ti, Mn, and Na oxide distribution in kimberlite pyropes of Angola as criterion of diamond grade

Introduction. Pyrope is one of the leading typomorphic minerals of most mantle parageneses in kimberlites. The compositions of pyropes are the most informative and best studied as representatives of minerals of mantle peridotite and eclogite parageneses. They are widely used for solving genetic and special petrological problems, as well as for prospecting for diamondiferous kimberlites on the basis of studying the compositions of pyropes from pipes of different diamond content. To determine diamond grade Ti, Mn, and Na in pyropes from kimberlites of the Angola diamond bearing sub-province, the triangular diagrams of their ratios is proposed.

Research methods. The **JX-8230 microprobe**, allows determining the composition of minerals by **WDS** and **EDS** spectrometers simultaneously (**Fig.3**). The proposed method for the interpretation of analytical data makes it possible to reduce the accumulation time of X-ray pulses and to increase the beam current by an order of magnitude (up to 300 nA), which increases the ratio of the useful signal to the background several times.

- This increases the sensitivity and shortens the time for the determination of trace elements in minerals. The detection limit for impurity elements in the indicator minerals of kimberlites can be increased to 15 ppm with a relative error of less than 5% (**Table 1**). The use of this analysis technique makes it possible to simultaneously register the entire spectrum of the main chemical elements in the mineral with an energy-dispersive spectrometer **EDS** and four impurity elements – Mn, Ni, Ti and Na – with wave spectrometer **WDS** [5].

Table 1. Parameters of measurement of trace elements on the JXA-8230 microprobe

No	Element	Peak(mm)	Net(cps)	Bg-	Bg+	S.D.(%)	D.L. (ppm)	K-raw (%)
1	Mn	146,119	316,6	94,4	73,0	0,69	23	1,096
2	Ni	115,451	83,1	914,7	721,6	5,53	15	0,075
3	Na	129,425	60,1	386,1	273,5	4,92	14	0,215
4	Ti	87,938	959,8	988,1	624,9	0,55	19	0,691

Note: measurements of impurity elements (**Element**) were carried out at an accelerating voltage of 20 kW, a beam current of 300 nA and a pulse accumulation time of 120 seconds at the peak and 30 seconds for measurements against the background; **S.D. (%)** – relative measurement error; **D.L. (ppm)** – detection limit of elements in ppm; **Net (cps)** – network signal intensity; **K-raw (%)** – content without corrections; Peak (mm), **Bg** – the place where the peak and background signals are measured.

Main results. The diagrams **Fig.1** shows the compositions of these oxides in pyropes with their breakdown into cluster groups (CG) of Dawson J.B., Stephens W.E. classifications. It complements the generally accepted diagrams **[1,2,3]** and creates an opportunity to determine the degree of diamond content of kimberlites and their belonging to the same field or cluster of kimberlite pipes. The diagrams shows the ratio of oxides of the main trace elements in pyropes of Angola kimberlites with diamonds and dots – Mn, Ti and Na in the diamondiferous kimberlites (Luele, Chyuzu) and in empty ones (Shandongu, Lx 150).

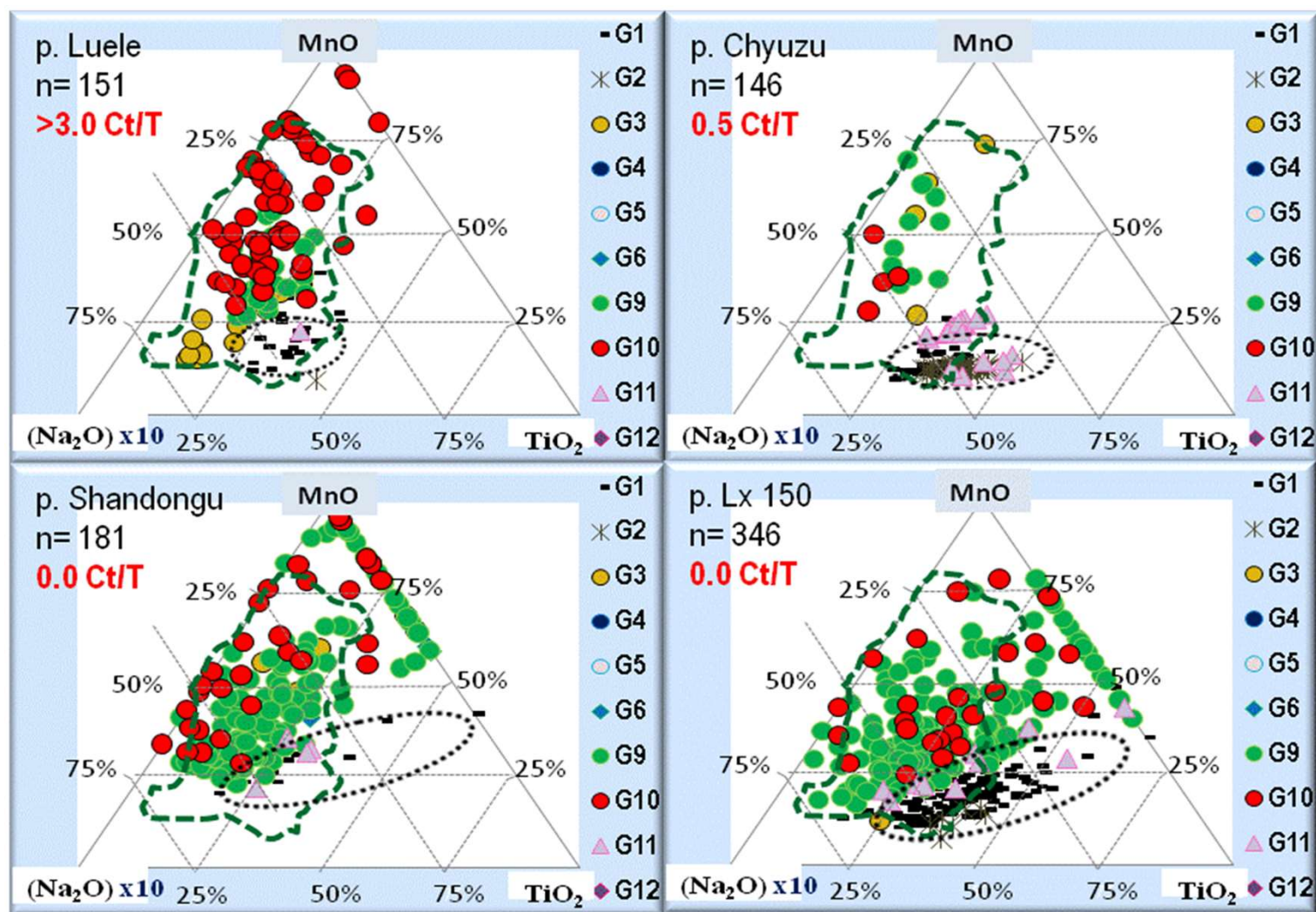


Fig. 1. Triangular diagrams of Na₂O-TiO₂-MnO of pyrope compositions of Dawson and J.B., Stephens W.E. cluster groups (CG) [3] from Angola kimberlite pipes of varying diamond content. Green dotted line – compositional area of pyropes of highly diamondiferous kimberlites of the Luele pipe; black dotted line – region of high titanium pyropes CG (G1, G11); location of analysis points corresponds to Dawson J.B., Stephens W.E. CG (G1-G12); Ct/T – diamonds content; n=151 – number of analyzed pyrope grains.

- Impurity elements in pyropes, as a rule, in their relationship with basic oxides, have peculiarities of their distribution in various paragenetic types of garnets from mantle associations of ultrabasic and eclogite rocks, and also characterize the degree of their transformation during metasomatism.
- The Na_2O content for the compositions of low-chromium pyropes is the main sign of their crystallization with diamonds, which is reflected in the Na_2O - TiO_2 diagram by J. Gurney [2].
- The TiO_2 is undoubtedly an important and significant impurity oxide that determines diamond content and, to a large extent, determines the CG of pyropes according to Dawson J.B., Stephens W.E. [3]: its content in **G3**, **G10**, **G9** is low, <0,3%; in **G1** – medium, 0,3-0,6% and **G2** – high, > 0,6 wt.%.
- The MnO content in kimberlite pyropes, as a rule, does not exceed 0,6 wt%. Changes in the contents of this oxide can occur in the process of metasomatic transformations of pyropes, which affects the diamond content in kimberlites [4].
- From the presented diagrams (**Fig. 1**) it can be seen that 97,5% of the compositions of pyrope grains from the highly productive kimberlites of the Luele pipe lie in the diamond-bearing contour, while high-magnesian-chromium pyropes CG **G10**, whose share is 46%, together with pyropes CG **G9** – 21%, evenly distributed over this area and prevail over the rest of the CG. Medium-high titanium CG **G1-G4** and **G-11** are compactly concentrated in the lower area of the diamond-bearing contour, next to the low-titanium **G3**.

- In low diamondiferous kimberlites of the Chyuzu pipe, about 65% of pyrope grains fall into the diamondiferous contour, while the compositions of CG **G10** and **G9** are represented by less than 10% of grains, 90% of grains are high-medium titanium CG **G1**, **G2** and **G11**, and the compositions of single pyropes CG **G3** shifted to the upper region of the diamondiferous contour.
- The non-diamond pipes Shandongu and Lx-150 are also characterized by the displacement of CG **G10** (16% and 7%, respectively) and **G9** to the upper part of the diagram, with a predominance of the proportion of pyropes **G9**, with an outflow of diamond content up to 30-50% of the grain compositions. The proportion of high-titanium **CG G1, G2, and G11** (up to 25% in the Lx-150 pipe) is quite large here, most of the compositions of which go beyond the diamond-bearing contour of kimberlites.
- Earlier it was found that certain concentrations of MnO in pyropes from ultrabasic parageneses correspond to the parameters of the «diamond window» – a region on the MgO-MnO diagram characterized by the most favorable PT conditions for their joint crystallization with diamonds, into which the compositions of pyropes exclusively from diamondiferous kimberlites are projected [4]. The composition of the pyrope grains of ultrabasic paragenesis of highly diamondiferous kimberlites (≥ 3 Ct/T) of the Luele pipe in the 455-610 m block is projected in the MgO-MnO diagram with 58% falling in the «diamond window»; in the Chyuzu weakly diamondiferous pipe (0,5 Ct/T) 40% grains of such pyropes fall in the «diamond window»; in Shandongu non-diamondiferous kimberlite – 56% of the grains of such pyropes are located in the «diamond window» (Fig. 2).

- In this case, as for triangular diagrams, it is not so much the number of pyrope grains in the contour of the «diamond window» that matters as the proximity of their compositions to its center. It is obvious that the compositions of pyropes from the kimberlites of the Luele pipe are grouped mainly in the center of the «diamond window» region, while the compositions of pyropes from the Shandongu pipe are significantly shifted from it. In addition, the kimberlites of the Shandongu pipe do not contain pyropes of diamond paragenesis according to Sobolev N. [1].
- It can be assumed that the crystallization of the Dawson-Stephens CG of pyropes corresponding to the diamondiferous area on the Na₂O-TiO₂-MnO diagrams (Fig. 1), coinciding with the MgO-MnO «diamond window» central area (**Fig.2**), took place in the most favorable environment in terms of PT parameters together with diamonds.

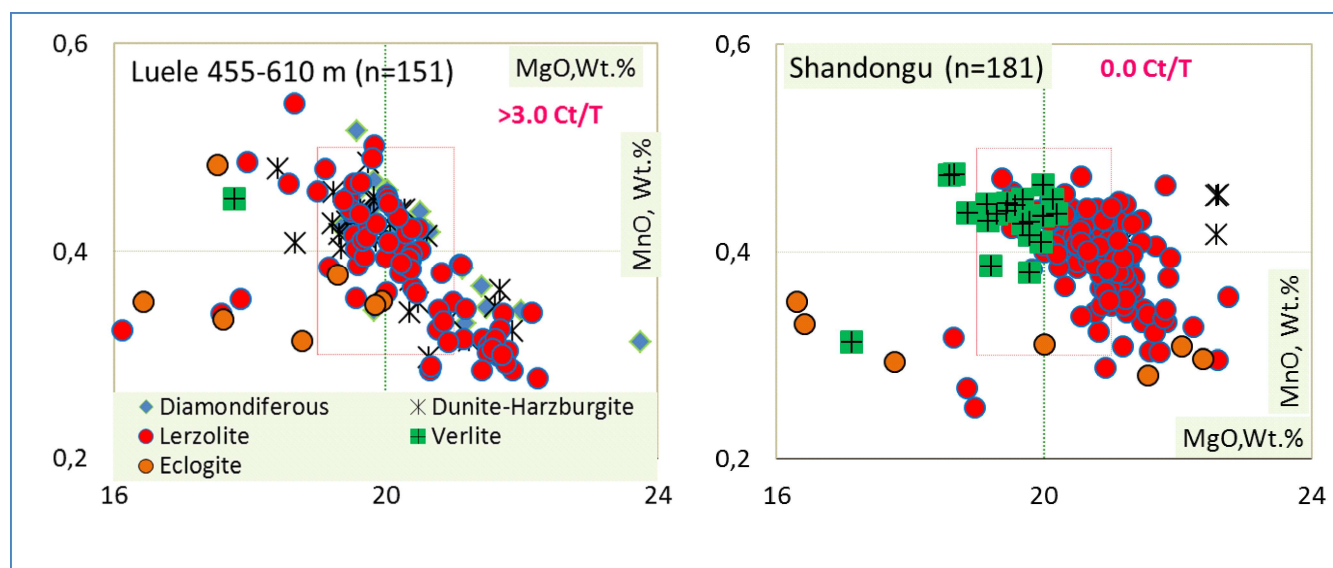


Fig. 2. MgO-MnO diagram of the CG of pyrope mantle parageneses according to Sobolev N. [1] of the Luele highly diamondiferous and Shandongu non-diamondiferous pipes; rectangle in the diagrams – MgO-MnO «diamond window»; n = 151 – the number of analyzed pyrope grains.

CONCLUSIONS

- The new JX-8230 microprobe (**Fig.3**) have an analytical ability to quantitatively determine trace elements in kimberlite pyropes. This gives grounds to put forward new evaluation criteria proposed on the diagram of **Mn, Na, Ti oxides**, well complementing the main chemical and mineralogical criteria for diamond content of kimberlites, proposed earlier by a number of authors **[1,2,3]**.
- On the triangular diagrams of pyrope compositions (Fig.1), divided into Dawson-Stephens CGs [3], high-, weak- and non-diamondiferous kimberlites clearly differ in the structure of distribution of compositions of high-Mg-Cr (**G10**), low-Cr (**G9**) and high-medium-Ti (**G1-G4, G11**) groups, which is of practical importance for the diamond potential of kimberlites assessment. Evaluation of the diamond potential of kimberlites by the MgO-MnO «diamond window» **[4]** criterion also requires taking into account the distribution structure of these pyrope compositions relative to the center of its region.
- The presented microprobe analysis technique of MIK (MSD) composition will be useful for specialists of the new **Angolan mineralogical diamond laboratory of IGEO-ENDIAMA**.

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Fig.3. X-ray spectral microanalyzer JXA-8230 in the laboratory of NIGP AK ALROSA systems EX-943100FL1Q, RESO 129eV. Ivanov A. as a microprobe operator.

THANKS FOR ATTENTION