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OXIDE MINERAL INCLUSIONS IN PYROPES FROM THE INTERNATIONALNAYA KIMBERLITE PIPE, YAKUTIA

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INTRODUCTION

Archean cratons are underlain by highly depleted subcontinental lithospheric mantle (SCLM). Studying the deep structure, compositional features and evolution of the SCLM is one of the major problems of mantle petrology. Kimberlite pipes bring to the surface a wide variety of mantle xenoliths and xenocrysts which provide the direct information about composition of the deepest parts of the lithospheric mantle. Xenolith and xenocryst data suggest that Archean SCLM has been extensively refertilized by metasomatic processes, with the addition of Fe, Ca, and Al to depleted protoliths. There is increasing evidence of the metasomatic origin of garnets in the cratonic subcontinental lithospheric mantle. The distribution of sub-calcic garnets in the SCLM beneath the Siberian craton suggests: (1) sub-calcic garnets and diamonds are metasomatic phases in the cratonic SCLM; (2) the distribution of both phases is laterally heterogeneous on relatively small scales and related to ancient structural controls (Malkovets et al., 2007). Since the end of the 1960s mineral inclusions in diamonds have been studied in great detail (e.g. Stachel and Harris, 2008). On the basis of these data substantial progress has been reached in our understanding of diamond- genesis processes. However, studies devoted to inclusions in pyrope are extremely rare; thus inclusions in pyrope have not been studied well, but they can

provide valuable information about the genesis of this mineral in the upper mantle, which is still unclear.

SAMPLE DESCRIPTION

The pyrope crystals investigated in this work are from heavy mineral concentrate of the kimberlite pipe Internatsionalnaya, Malobotuobia field. The size of the grains ranges from two to eight mm. Those containing either single or multiple inclusions were polished to reveal them on flat surfaces. The sectioned inclusions were then analyzed mostly using electron probe microanalyzers JEOL 8200 Super Probe (MaxPlanck Institute, Mainz, Germany) and JEOL JXA-8100 (Institute of Geology and Mineralogy, Novosibirsk, Russia).

MINERALOGY

PYROPES

The pyrope garnets belong to different parageneses within the ultramafic association, dominated by lherzolite paragenesis (Fig.1). Inclusions of rutile and picroilmenite also have been found in orange low-Cr garnets of the eclogite association. The presence of large inclusions of picroilmenite in eclogitic garnet is of particular importance, as picroilmenite is a characteristic mineral of the megacryst association, which also includes red Ti-garnet, clinopyroxene, phlogopite, olivine, etc.

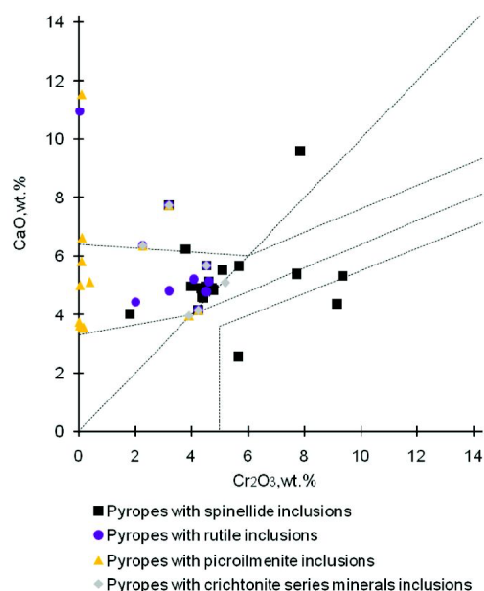


Figure 1. CaO vs Cr₂O₃ for pyropes with oxide inclusions.

OXIDES

Oxide minerals are fairly common as inclusions in pyrope. Phases identified and analyzed include chrome spinelides, microilmelite, rutile and its variations (Cr-bearing, chromium-niobium) and minerals of the crichtonite series. Pyropes can contain either only one type of inclusions or various combinations thereof. A few samples are characterized by the presence of all four differentoxide phases in a single pyrope. Sometimes combined occurrence of oxides with silicates and/or sulfides is observed in a single pyrope host.

MORPHOLOGY

Oxide inclusions are usually present as elongated, needle or blade-like structures with rounded or polygonal cross-section, laths, tablets, and prisms with different facets are also common. The amount of oxide inclusions in a garnet varies greatly from single needles/laths to an extremely

large number of them in some samples. The minimum thickness of elongated inclusions is a fraction of a micron, the maximum thickness (among those analyzed in the current work) is a grain of chromite (~ 0.2 mm). The formation of these large inclusions of Cr-spinel is probably due to the active processes of coalescence, during which the confluence of smaller inclusions and progressive thickening of the individual minerals occurs, accompanied by change of inclusion shape (Afanasiev et al., 2001). Chrome spinelides with isometric shapes are abundant. Spherical to elliptical forms are more common; inclusions with well-defined octahedral facets are less common. According to existing ideas such isometrization occurs in the further evolution of needle-like inclusions (Geguzin, 1974, 1975).

Most inclusions are black; large grains also have resinous lustre. Needles of rutile can be brown, gray to colorless, often transparent.

Needles often define a regular spatial arrangement in pyrope matrix. The angle between crossing needles is ~ 71 degrees (the angle between triad axes in garnet). Such a strict orientation of the inclusions in the garnet structure has been a starting point for the assumption that at least part of needle-like inclusions formed as a result of exsolution (McGetchin and Silver, 1970; Hunter and Smith, 1981; Smith, 1987).

In some cases inclusions may consist of several phases that change along a single direction (usually along the elongation). Coexistence of oxide and silicate minerals, forming one inclusion is common. Sometimes the result of the collapse of needles on individual links can be seen - former parts of the whole elongated arrangement are now separated by the substance of enclosing garnet. Around these inclusions small isometric phases are observed with compositions similar to those of needles and laths. All this points to a complex evolution of needle-like inclusions, with several of steps, such as a gradual decrease in inclusion thickness, breakup and subsequent isometrization.



COMPOSITIONAL FEATURES

Different oxide mineral compositions can be clearly seen on binary diagrams with TiO₂ content on one axis. Spinelids form a distinct field with a high content of Cr₂O₃ and low TiO₂. On another axis, any other component can be chosen, or their sum (e.g. FeO+MgO).

Chemical compositions of oxide inclusions in pyropes of the Internatsionalnaya pipe are shown in Fig. 2 (a-c). For comparison, the compositions of the following minerals are presented: 1) rutile inclusions in crustal almandine garnets of the Maiskaya pipe 2) rutiles from heavy mineral concentrate of the Internatsionalnaya pipe, and 3) oxides (mainly

armalkolites (Mg, Fe) Ti₂O₃) in lherzolite interstices, Vitim volcanic field (Litasov et al, 2006).

- Oxide inclusions in pyropes from the Internatsionalnaya pipe
- Rutiles from concentrate of the Internatsionalnaya pipe
- Rutiles in crustal garnets from the Maiskaya pipe
- Oxides (mainly armalkolites) in lherzolite interstices, Vitim volcanic field (Litasov et al, 2006).

CHROME SPINELIDS

Spinelids are the most common oxide inclusions in pyropes from the Internatsionalnaya pipe and are characterized by the general formula (Fe, Mg) (Cr, Al, Fe)₂O₄. MgO contents range from 8.7 to 18 wt. %, FeO - from 15.7 to 28.7 wt%. Contents of elements in the octahedral positions vary even more significantly: Cr₂O₃ from 19.3 - 60.8 wt.%, Al₂O₃ - from 5.4 - 42.9 wt.%. TiO₂ content is less than 3.0 wt. %, and rarely exceeds 1.5%.

PICROILMENTITE

Picroilmenite, a member of the isomorphous series ilmenite - geikielite (FeTiO₃-MgTiO₃) characterized by a high content of Mg, has been recovered in garnets of ultrabasic and eclogitic parageneses. The main difference between picroilmenites of these parageneses is in the content of Cr - ultrabasic picroilmenite is more chromium-rich and may contain up to 5.7 wt.% Cr₂O₃ in form of eskolaite component. There is a direct correlation between garnet and picroilmenite Cr₂O₃ content.

RUTILE

Needle-like inclusions of rutile (TiO₂) in pyrope are not uncommon, but their presence is

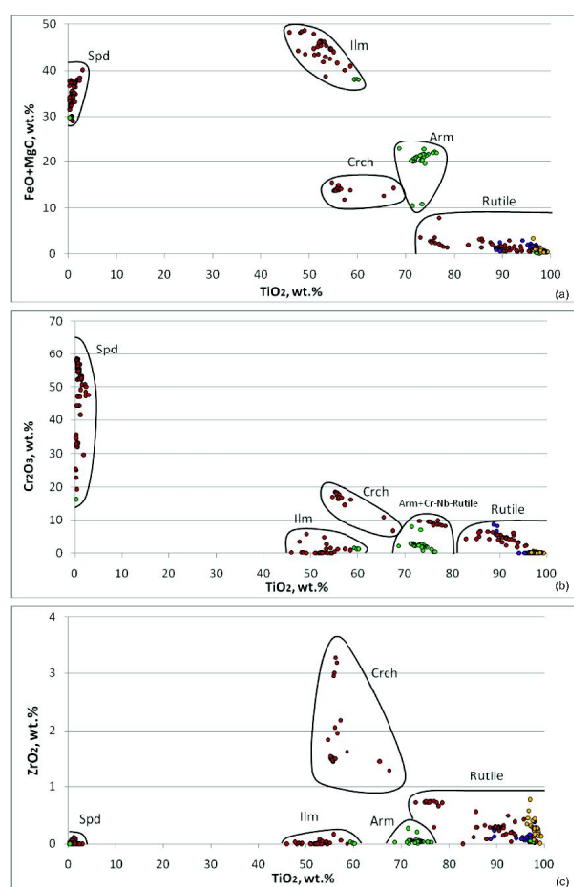


Figure 2 (a-c) Composition of oxide mineral inclusions in coordinates TiO₂-FeO+MgO (a), TiO₂-Cr₂O₃ (b), TiO₂-ZrO₂ (c)



of particular interest. According to modern ideas, rutile does not occur in rocks of peridotite paragenesis, so its presence in the form of intergrowths with pyrope can serve as additional confirmation of the metasomatic origin of the pyrope.

The chemical compositions of rutiles from pyropes of the Internatsionalnaya kimberlite pipe (ultrabasic paragenesis) has been compared with those of rutiles in crustal garnets from the Maiskaya pipe (Fig. 3). Rutile inclusions of various parageneses are characterized by notable differences in the types and contents of impurities. Rutiles in crustal garnets have much lower contents of minor elements and have a TiO_2 content about 96-99 wt.%,; among minor elements the most abundant are Fe and Zr. In contrast, rutiles in garnets from ultramafic (lherzolite) paragenesis are highly enriched in impurities. As a rule, these are mainly Cr, HFSE (Nb, Ta, Zr), and Fe. TiO_2 contents are thus much lower, and often far from 100 wt.%. Nb_2O_5 contents in rutile of mantle pyrope vary from 0.1 to 9.5 wt.%, Cr_2O_3 from 2 to 10 wt. %, Al_2O_3 up to 3.8 wt.%, FeO up to 6.5 wt. %. Comparative contents in rutile from crustal garnets are: Nb_2O_5 up to 0.3 wt. %, Cr_2O_3 up to 0.4 wt.%, Al_2O_3 up to 1.5 wt.%, FeO up to 3.2 wt.%.
Particularly noteworthy are chromium-niobium rutiles from sample INT-5, which have

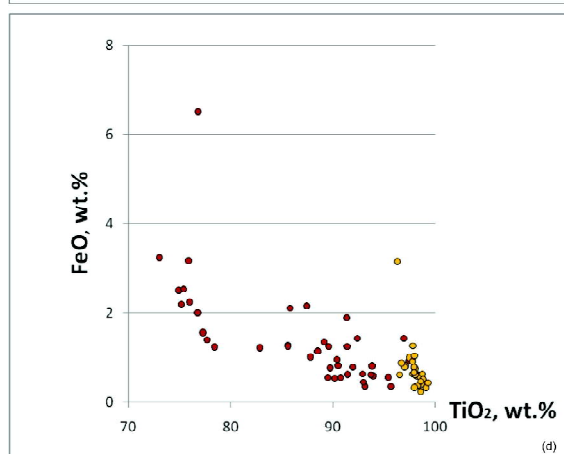
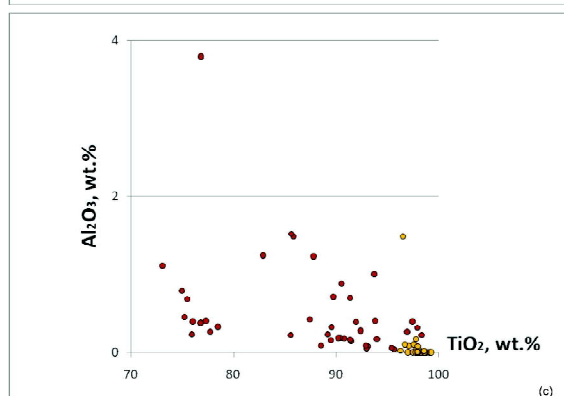
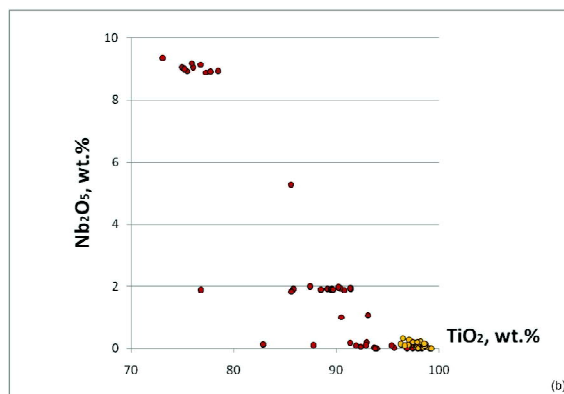
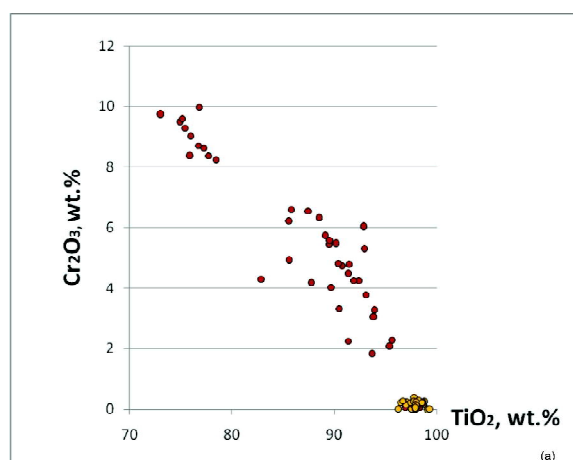


Figure 3 (a-d) Compositions of rutile inclusions in coordinates TiO_2 - Cr_2O_3 (a), TiO_2 - Nb_2O_5 (b), TiO_2 - Al_2O_3 (c), TiO_2 -FeO (d).

- Rutiles in pyropes from the Internatsionalnaya pipe
- Rutiles in crustal garnets from the Maiskaya pipe



one of the highest contents of HFSE-elements among all rutile inclusions in garnet described in the literature. Contents of Cr_2O_3 and Nb_2O_5 reach 10 and 9.5 wt.% respectively, HFSE content is over 12 wt%. TiO_2 content is near 75 wt%. Such a huge enrichment of rutile inclusions in highly incompatible elements clearly indicates simultaneous crystallization of rutile and pyrope from fluids enriched in HFSE. Typical contents of Nb in pyropes rarely reach 100 ppm, and thus the formation of Nb-rich rutiles by solid solution breakdown is very unlikely.

As for Cr_2O_3 , its high content directly indicates the type of association. HFSE-elements may not be present in rutile, but the content of Cr_2O_3 in rutile of mantle garnets is always higher than 2 wt.% (see figure 3). Also the following relationship is observed: the more chromium in the host pyrope, the higher its content in the inclusions of rutile. In crustal almandine Cr_2O_3 contents are very low (<0.3 wt.%), and rutile inclusions also have a very low content of Cr_2O_3 , which does not exceed 0.4 wt. % of particular note is sample INT-29. This orange garnet belongs to the eclogitic paragenesis. It is low in Cr_2O_3 and has a very high content of CaO (about 11 wt%). Analyzed rutile inclusions contain small amounts of impurities, and their composition is almost completely analogous to the rutiles from crustal garnets of the Maiskaya pipe.

Thus, the chemical composition of rutile as inclusions in garnet clearly reflects its paragenetic identity. Rutiles from mantle garnets are characterized by a high content of Cr_2O_3

and in some cases, a high content of HFSE. Rutiles from crustal garnets in general are characterized by low minor- element contents. For a detailed characterization of rutiles in pyrope of the eclogitic paragenesis there is not enough data at this stage.

On the basis of these data on the chemical composition of rutile and by using the diagrams TiO_2 - Cr_2O_3 and (to some extent) TiO_2 - Nb_2O_5

rutiles can clearly be assigned to mantle or to crustal paragenesis. The most distinctive feature is the high content of Cr_2O_3 in the rutiles of mantle paragenesis. The results can be used as reliable application in prospecting for kimberlite bodies.

MINERALS OF CRICHTONITE SERIES

Minerals of the crichtonite series have rather complicated compositions and structures. The general formula for the group is $\text{AM}_{21}\text{O}_{38}$, where site A takes cations with a large radius (Sr, Pb, REE, U, Ca, Na, K, Ba), and site M takes smaller cations (Ti, Fe, Cr, Al, Zr, Mg). The name of the mineral is defined by the dominant cation in A position: Sr for crichtonite, Ca - loverengite, Na - landauite, Pb - senaite, REE - davidite, Ba - lindsleyite, K - mathiasite (Rouse and Peacor 1968; Grey et al. 1976; Gatehouse et al. 1978; Haggerty et al. 1983).

Chemical compositions may vary greatly but the distinctive feature of the minerals of this group is enrichment in incompatible and rare elements. Also, it is generally accepted that the minerals of the crichtonite series in mantle rocks reflect mantle metasomatism, with the metasomatic environment being enriched in incompatible elements and volatiles (Erlank and Rickard 1977; Jones et al. 1982; Jones 1989; Haggerty 1983, 1991a). The presence of such rare minerals as inclusions in pyrope strongly supports a model of pyrope crystallization from metasomatic fluids enriched in incompatible elements.

CR CONTENTS OF GARNET HOST AND INCLUSIONS

As noted above, the composition of the inclusions may reflect the geochemical conditions of their formation.

Fig. 4 shows the relationship between Cr_2O_3 content in various types of inclusions with the Cr_2O_3 content of their garnet host. There is an obvious positive correlation, which suggests that

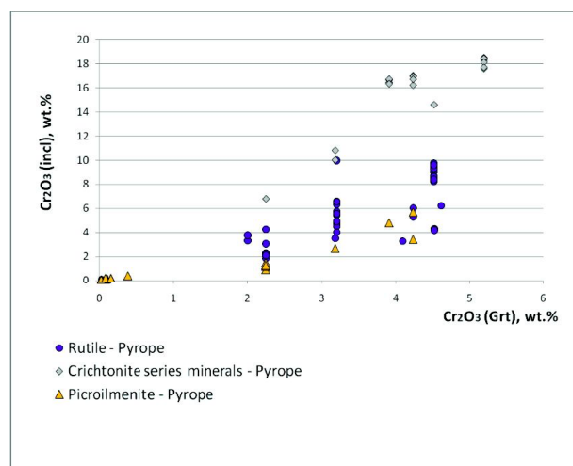


Figure 4. Cr₂O₃ content of host garnet and inclusions.

the pyrope host and its inclusions are in equilibrium in terms of Cr.

SUMMARY AND CONCLUSIONS

During studying of oxide mineral inclusions in garnets from heavy mineral concentrate of the kimberlite pipe Internatsionalnaya have been discovered and analyzed such mineral phases as chrome spinelids, picroilmenite, rutile and crichtonite-series minerals. The most common inclusions are chrome spinelids, which are one of the rock-forming minerals of lithospheric mantle peridotites.

The presence of inclusions of rutile enriched in Nb and Ta, picroilmenite and rare crichtonite-series minerals, enriched in incompatible elements such as LILE, HFSE, REE, whose genesis is conventionally associated with the processes of mantle metasomatism, suggests that at least some of the pyropes have been formed from fluids related to mantle metasomatism. At this stage of the study we can't determine the nature and type of metasomatic fluid/melt, from which such pyropes crystallized. This requires further detailed geochemical studies.

The data obtained on the chemical composition of rutiles as inclusions in garnets of

mantle and crust associations make it possible by using diagrams TiO₂-Cr₂O₃ and TiO₂-Nb₂O₅ to refer such rutiles to one of these assemblages. The most distinctive feature is the high content of Cr₂O₃ in rutiles of mantle paragenesis. These results can be used as reliable indicators in prospecting for kimberlite bodies.

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