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ANALYSIS OF THE CHEMICAL COMPOSITION OF CHAROITE ROCKS

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The unique charoite mineralization, established on the Murun alkaline massif in the northwestern part of the Aldan shield on the border of the Irkutsk region and Yakutia, is still of great interest to some of researchers (geologists, crystallographers, geochemists, etc.). The outcrops of charoite-bearing rocks at the “Sirennyi Kamen” deposit are noted both in the indigenous outcrops and in eluvial clatters [Bondarenko, 2009]. The discovery of charoite also allowed to detect other unique minerals – canasite, tinaksite, frankamenite, mizerite, etc. The paragenesis of charoite rocks explains the fact that “pure” charoite does not occur in nature [Konev *et al.*, 1996; Biryukov, Berdnikov, 1993; Reguir, 2002; Vorobjev, 2008]. Close accretion and intergrowth of phenocrysts minerals (quartz, microcline, aegirine, tinaksite, frankamenite, arfvedsonite,

apophyllite, etc.) is observed in charoite, therefore the mineral has a complex chemical composition corresponding to the general formula $(K,Sr,Ba, Mn)_{15-16}(Ca, Na)_{32}[(Si_{70}(O,OH)_{180})](OH,F)_4 \cdot nH_2O$ [Rozhdestvenskaya *et al.*, 2010]. Charoite rocks (charoite, canasite, tinaksite, frankamenite, mizerite, etc.) are a group of alkaline calcium silicates with tubular Si-O-radicals, and therefore possess crystallochemical originality and are difficult to determine structures. The main chemical components of charoite-bearing rocks are K, Na, Ca, Si and H₂O. The secondary components are Ba, Sr, Mn, and Ti. The presence of Fe, Mg, Al and REE (Rb, Th, Ta, Ce, Sr, Zr, etc.) is noted in trace amounts. The addition of rare elements in the composition of different fluids in primary melt of Murun alkaline massif can be explained by metasomatic theory of charoite mineraliza-

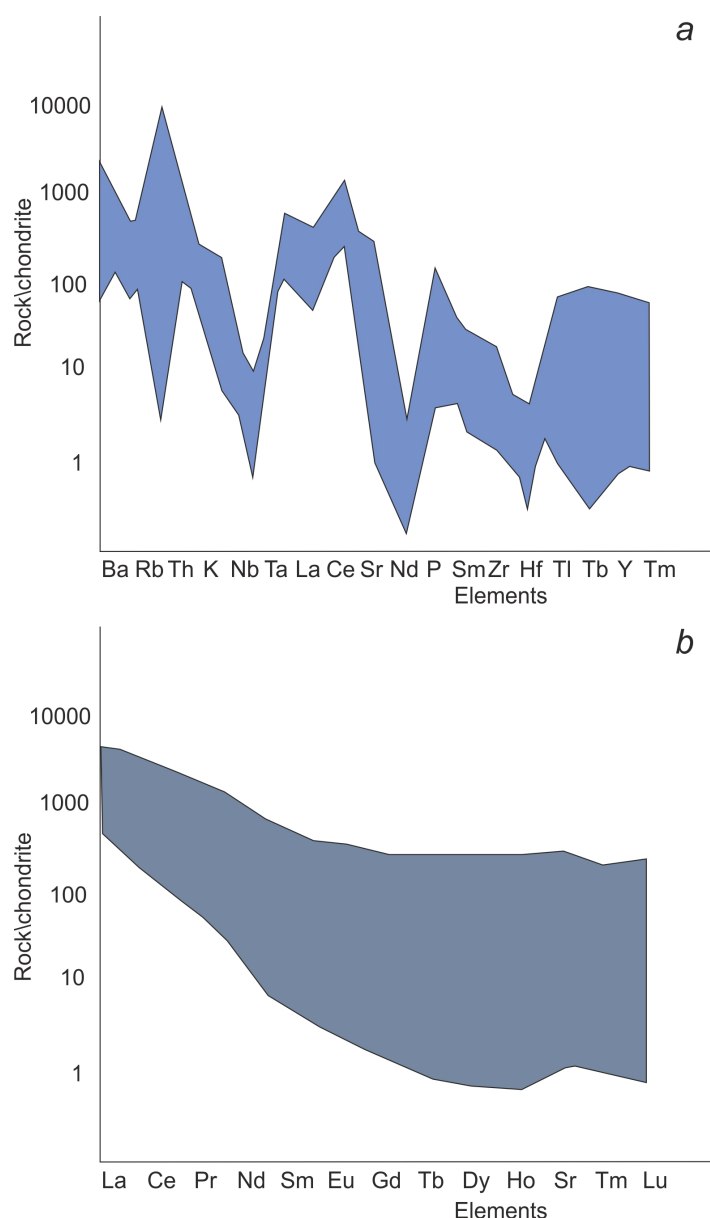


Fig. 1. Spider diagram of the heavy (a) and rare (b) elements content in the samples.

tion genesis [Bondarenko, 2009; Konev et al., 1996; Biryukov, Berdnikov, 1993]. There are other hypotheses of formation of charoite rocks (see review in [Marchuk et al., 2016]). Charoite rocks often contain a large amount of xenoliths, represented by potassium alkali minettes. The studying of the replacement processes of these rocks by charoite enabled us to trace the changes trend in the rare and scattered elements content. 15 charoite rocks samples were analyzed from the “Staryi” site of the “Sirenevyy Kamen” deposit. The rock composition changing is analyzed during the transition from unaltered potassium alkaline minette to almost monomineral charoite. The modeling of the decomposition of alkaline minerals in the Murun massif was carried out.

Analysis of rare earth elements distribution shows an increase of the original rock changing degree and the increase of charoite amount. These factors result in addition of light and heavy REE, but heavy and medium REE are introduced largely (Fig. 1, a, b). The elements distribution diagram becomes flatter with increasing of contamination degree. Addition and loss of the elements in the process of charoite formation and original rock changing can be clearly seen in the spider diagram (Fig. 1, a). The amount of Th, La, Ce, Nd, Sm, Zr, Hf, Tb, Yb, and Ba increases, and Ti and K reduces, and the same amount of Sr, Y, La, Rb, Nb is observed.

In addition, the thermodynamic modeling was carried out using a “Selector” PC. Modeling helped to determine the field of stability and possible paragenesis during the decomposition reaction of studied charoite rocks composition. The decomposition of charoite rocks was simulated at standard pressure ($P=1$ bar) and temperatures from 700 to 900 °C based on the multicomponent model system (K, Na, Ca, Fe, Al, Si, Ti, Mn, Sr, Ba, P, F, Cl, C, O, H), consisting of more than 120 potentially possible phases, including solid minerals, gas and aqueous solution. The average chemical composition of 15 studied samples is taken as the initial components in the model. The thermodynamics of probable products of the decomposition reaction is modeled on the databases of the “Selector” PC. Calculations show (Fig. 2) the following paragenesis from the average composition of the charoite rock at 700–900 °C: quartz (>65 mol %), wollastonite (>20 mol %), pyroxenes (mainly aegirine from 0 to 4.5 mol %), which constitute up to 97–98 mol % of the total rock volume; and about 2–3 mol % are accounted for other mineral phases (rhodonite, microcline, sphene and very small amounts of rare compounds, such as manganese oxide, barium carbonate and hydroxide, etc.). Thus charoite rocks are unstable at high temperatures and decompose already into various

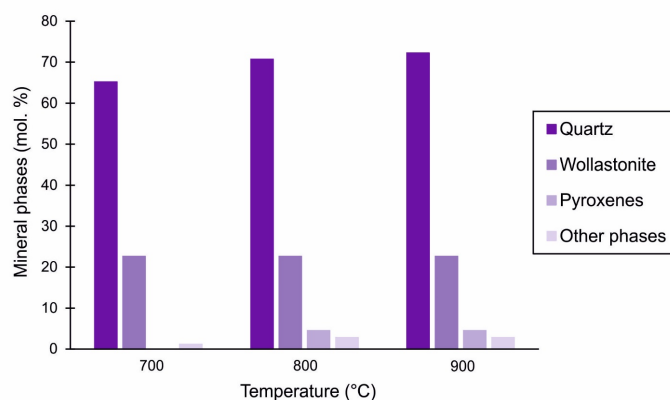


Fig. 2. Charoite rock decomposition products (mol %) using thermodynamic modeling by “Selector” PC.

mineral phases at 700 °C. Quartz and wollastonite will be the main stable products of the decomposition reaction from composition of charoite rocks over the entire temperature range. This trend is observed both in modeling the composition of “pure” charoite and in modeling the composition, for example, tinaksite (see review in [Marchuk *et al.*, 2016; Sokolova *et al.*, 2016]). The minor components of composition of charoite rocks (Mn, Ti, Ba and Sr) form own phases (rhodonite, bixbit, sphene, etc.) at thermodynamic modeling. The number of these phases may be even less, if the model takes into account the more complicated schemes of isomorphism in minerals.

The analysis of the chemical composition of charoite rocks shows that the primary alkaline-carbonate-silicate melt of charoite mineralization was particularly rich in rare, trace elements and alkaline components. Firstly, this melt was characterized by an unstable composition, which is explained by loss of the most

mobile components. Secondly, it was relatively low-temperature melt (up to 700 °C), because other mineral phases can be formed already at 700 °C from composition of charoite rocks.

The process of metasomatic charoitization of host rocks takes place with formation of charoitites, pectolites, calcite-quartz carbonatitoids and wollastonite rocks, depending on the specific conditions of the primary melt defluidization. The obtained results will be used in future studies of problem of charoite mineralization genesis.

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