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Fluorine and chlorine in apatites, micas, and amphiboles of layered trap intrusions of the Siberian Platform

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Abstract

Geochemistry of chlorine and fluorine in apatites, micas, and amphiboles in rocks from eight intrusive complexes of the Siberian Platform has been first studied on the basis of new factual and analytical data (more than 1000 analyses). The main attention is focused on minerals from layered intrusions. Most apatites show F > Cl; the maximum contents of halogens are specific to chlorapatite (6.97 wt.% Cl) and fluorapatite (6.04 wt.% F). The total f value (f = Fe/(Fe + Mg), at.%) of femic minerals varies from 2 to 98 at.% in micas and from 22 to 95 at.% in amphiboles. The Cl–f and F–f trends show an increase in the Cl content and a decrease in the F content in the minerals with increasing f. Chlorine clearly exhibits ferrophilic properties, and fluorine has magnesiophilic properties. The halogen-richest minerals are fluorophlogopite (F = 7.06 wt.%, f = 7 at.%), chlorannite (Cl = 6.30 wt.%, f = 89 at.%), and chloroferrihastingsite (Cl = 5.22 wt.%, f = 90 at.%). Coexisting micas and amphiboles in the rocks are close in f value, but the micas are richer in Cl than the amphiboles. We assume that the halogen-containing minerals crystallized at the high pressure of halogen–hydrocarbon fluids at the levels of the MW, IW, and QIF buffers. The reducing conditions of the magmatism process are also evidenced by the presence of graphite and native metals in the rocks. The similarity of the Cl–f and F–f trends of micas and amphiboles from different intrusive complexes indicates the same mechanisms of the melt differentiation and mineral crystallization.

Keywords: traps; layered intrusions; geochemistry of halogens; apatite; mica; amphibole; Siberian Platform

Introduction

Halogens are chemical elements highly reactive over a wide range of physicochemical conditions. During magmatogene processes, fluorine is intimately associated with aluminosilicate melts, and chlorine is a crucial component forming complexes with most of ore metals. The behavior of chlorine determines the migration of metals from melts (Marakushev et al., 1997). This is, most likely, due to the high solubility of chlorine in aqueous solutions and to its weak bonds with aluminosilicate melts as compared with fluorine and phosphorus.

Hydroxyl-containing minerals bear evidence of the participation of halogens in magmatic and ore-forming processes: Their crystalline structure includes fluorine and chlorine in variable amounts.

The hydrophilic properties of chlorine are responsible for its transition into a hydrous fluid separated from melt during the formation of intrusions. The decrease in chlorine content in magmatic melts does not provide insight into the initial content of this element in magmas and its loss during the evolution of a magmatic system (Kravchuk et al., 1998). This makes unclear what role halogens play in the ore-magmatic process, because the contents of chlorine and fluorine in rocks and minerals reflect not the initial contents of halogens in magmas but those at the time of their crystallization. Only water-unsaturated melts can reliably preserve initial contents of chlorine. The geochemical behavior of chlorine in reducing conditions during natural processes has been poorly studied because of its high hydrophilic properties. This gap can be filled by the new geochemical data on halogens in minerals of layered trap intrusions of different complexes in the Kureika ore district of the northwestern Siberian Platform. These minerals formed in reducing conditions (Ryabov, 2016), which is confirmed by the presence of various structural forms of

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carbon, such as micro- and nanotubes of graphite, cliftonite, flaked graphite, carbonaceous substance, and bitumens, as well as carbides, intermetallic compounds, and native metals in rocks and ores of layered intrusions (Buslaeva and Novgorodova, 1989; Nikol'skii, 1987; Ryabov and Lapkovsky, 2010; Ryabov et al., 2014).

The state of the art

The fluid regime of ore-magmatic systems in the Siberian Platform traps is a topical problem, because it significantly controls differentiation of basaltic melts and formation of layered intrusions and ore deposits, including giant PGE–Cu–Ni sulfide deposits like the Norilsk one. The above issues have been discussed in geological literature for decades; nevertheless, there is still no single concept of the basic genetic problems, although the Norilsk-type deposits have been well studied. The successful solution of the fluid regime problem in traps is hampered by the insufficient knowledge of the geochemical properties of volatiles, including chlorine and fluorine.

The geochemistry of chlorine and fluorine, playing a crucial role in ore-magmatic processes, was long paid little attention by geologists and has not been studied yet. There are scarce geochemical data on halogens in minerals of the regional rocks. The Upper Talnakh intrusion is the only object where halogens were studied in detail (Ryabov et al., 2014). These data, however, do not give an idea of geochemistry of trap halogens in general and of the behavior of halogens in ore-bearing intrusions as compared with ore-free ones.

Within the Siberian Platform traps, the role of chlorine in the ore formation was studied by the example of magnesioferrite deposits of the Angara–Ilim type (Pavlov, 1961, 1975). Chlorine might also be involved in the ore formation in Norilsk-type sulfide deposits, as suggested by the presence of halogen-containing apatites and micas, Cl-containing sulfides, and palladium chloride in their ores (Distler et al., 1999; Karpenkov et al., 1981; Rudashevskii et al., 1979; Ryabov et al., 2014).

At present, the participation and role of halogens in melt differentiation and sulfide ore formation are still an open question. It cannot be solved without a preliminary research into the general geochemistry of halogens in traps; therefore, first it is necessary to study the behavior of F and Cl in halogen-containing minerals.

The goal of this work is to elucidate the geochemical behavior of F and Cl in magmatogene apatites, micas, and amphiboles of intrusive rock complexes in the northwestern Siberian Platform.

Stony material and analysis

In this paper we summarize the results of long-term mineralogical and geochemical studies of the behavior of fluorine and chlorine in the intrusive traps of the northwestern Siberian Platform, which were performed at the Institute of Geology and Mineralogy, Novosibirsk. The main focus was maid on the new factual and analytical material on the intrusive complexes of the Kureika ore district of the northwestern Siberian Platform. Geological field studies (documentation of outcrops and borehole cores, sampling and cameral treatment of materials) were carried out by the geological team of Laboratory 213 of the Institute of Geology and Mineralogy. The expedition works and analytical studies were financially supported by LLC Norilskgeologia and Public Joint Stock Company "Mining and Metallurgical Company "Norilsk Nickel". X-ray spectral analysis of minerals was performed on Camebax-Micro and JEOL JXA8100 microprobes at the Analytical Center for Multielemental and Isotope Research of the Institute of Geology and Mineralogy, Novosibirsk. The composition diagrams were constructed based on our data on the composition of apatites (200 analyses), mica (570 analyses), and amphiboles (260 analyses) from intrusive complexes of the Kureika ore district. The earlier published data (Ryabov et al., 2014) and new data on the intrusions of the Norilsk complex were used for comparison.

Halogen-containing minerals in traps

According to the composition of parental magma, the Siberian Platform traps are derivates of tholeiite-basaltic, picrite-basaltic, and trachybasaltic melts. The traps are divided into effusive and intrusive; the former traps are subdivided into several formations, and the latter ones, into several intrusive complexes and types of intrusions (Lur'e et al., 1962; Ryabov, 2016; Ryabov et al., 2014).

In this work we studied the intrusions of the Kureika (kr), Kuz'movka (kz), Katanga (kt), Agat (ag), and Norilsk (nr) complexes of normal rocks and of the Ergalakh (er), Pyasina (ps), and Tymer (tm) complexes of alkaline rocks. The halogen-containing minerals of these intrusions are apatite, mica, and amphibole; therefore, the geochemistry of F and Cl in the traps was studied by the example of these minerals. In volcanic formations, we examined apatite from trachybasalts and trachyandesite-basalts, because it is the only halogen-containing mineral in effusive rocks and occurs solely in derivates of subalkalic melts.

Apatite

Distribution of apatite in the igneous rocks of traps is controlled by the content of P_2O_5 in the parental magma. In phosphorus-rich ($P_2O_5 = 0.42–1.5$ wt.%) derivates of subalkalic melts, apatite is present in effusive and intrusive rock facies. Phosphorus-poor volcanic rocks produced from tholeiite-basaltic ($P_2O_5 = 0.18$ wt.%) and picrite-basaltic ($P_2O_5 = 0.14$ wt.%) melts lack apatite, and among the intrusive derivates of these melts, apatite is present in pegmatites and pegmatoids.

In **the volcanic strata**, the products of subalkalic melts are found in the Ivakin (P_2iv) and Yuryakh (T_1jr) Formations. The Ivakin Formation is a member of nappes of different compo-