

The Chemical Mechanism of the Formation of Fluorite-Barite-Siderite Carbonatite in Karasug Fe-F-Ba-Sr-REE Deposit

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Abstract

Intrusive fluorite-barite-siderite carbonatite of Karasug deposit (Tuva) crystallized from ionic salt melt is dominated by iron chloride with the participation of alkali metal salts. Melt composition and main reaction of mineral formation: $\text{NaFeCl}_3 + 4\text{KF} + 2\text{Na}_2\text{Ca}(\text{CO}_3)_2 + \text{Na}_2\text{Ba}(\text{CO}_3)_2 + \text{Na}_2\text{SO}_4 = 6\text{FeCO}_3 + 2\text{CaF}_2 + \text{BaSO}_4 + 14\text{NaCl} + 4\text{KCl}$. The highest temperature (550°C - 650°C) brine-melt inclusions in minerals are pseudo-primary. Their predominant Na-K-chloride composition does not correspond to the primary melt, but is close to the residual brine-melt.

Keywords

Ferrocarnatite Ionic Melt, Chemical Reactions

1. Introduction

Karasug Fe-F-Ba-Sr-REE deposit is located in the Republic of Tuva (Russia). Carbonatite type of the deposit and intrusive genesis of carbonatites on the basis of geological and mineralogical data are proved in literature [1] [2]. Recently obtained thermobarogeochemical data on the composition of primary mineral-forming inclusions in minerals [3] do not fully agree with the idea of the intrusive genesis of carbonatites. In this work, an attempt is made to link the existing geological, mineralogical and thermobarogeochemical data with each other in order to decode the primary composition of the ferrocarnatite melt, the form of finding petrogenic components and probable chemical reactions of mineral formation.

Rare-earth fluorite-barite-siderite carbonatites form the basis of multicomponent ores of the deposit. They compose bodies of pipe- and dike-shaped form,

with a size of tens or hundreds of meters. The primary composition of carbonatites includes (average wt.%): siderite—61, barite and barytocelestite—20, fluorite—12, pyrite—3, bastnaesite—1.5, quartz—1, apatite—0.5; permanent accessory minerals—monazite, uraninite, molybdenite, rutile; sporadic minerals—magnetite, ankerite, ferrous muscovite, microcline. Siderite contains relatively few impurity components (wt.%): MnO—1.1, MgO—1.0, CaO—0.7, SrO—0.1. Carbonatites are characterized by porphyritic structure: idiomorphic crystals of 0.5 - 10 mm size of siderite, fluorite, barite, pyrite, quartz and bastnaesite are surrounded by fine-grained (<0.2 mm) fluorite-siderite groundmass. Carbonatites have a massive or directional texture, and contain angular fragments of host sandstones and granitoids, almost without having a metasomatic effect on them.

Comprehensive thermobarogeochemical study of melt and fluid inclusions in phenocrysts of cubic fluorite and hexagonal-dipyramidal quartz was made in recent years [3]. Brine-melt inclusions of 15 - 80 μm in size are referred to the primary category. They consist of solid salt phases (87 - 92 wt.%), liquid water-salt solution (10% - 6%) and liquid CO_2 (2% - 3%). The solid phases are represented by halite (45% - 48%) and silvin (32% - 30%). In addition to them in different vacuoles were observed up to five different phases, among which diagnosed: carbonates—siderite (up to 10% - 15%), ankyrite bastnaesite; sulfates—anhydrite, barytocelestite, ferricopiapite; ore minerals—galena, hematite. The temperature of homogenization of inclusions is 550°C - 650°C, and the pressure is estimated at 290 - 360 MPa.

2. Discussion

Attention is drawn to the fact that in the composition of brine-melt inclusions, there are few components that make up the material basis of carbonatites— CO_3^{2-} , Fe, Ba, Sr, F, S. In total, they do not exceed 12 - 16 wt.%. Mineral formation from such matter cannot flow magma way, that is by close simultaneous crystallization in a stable volume of introduced melt. It is necessary to flow a multiple volume of matter through the crystallization zone by the mechanism of the hydrothermal system. It can be assumed that the studied inclusions are pseudo-primary. Their composition does not correspond to the primary melt, but, as will be shown below, corresponds to the residual brine-melt. We will try to reconstruct hypothetically the probable chemical composition of the primary melt, from which fluorite-barite-siderite carbonatites were formed, as well as identify the problems that arise. Two variants of the composition are discussed below. In both cases, following [4] [5] carbonatite melt is considered to be an ionic liquid, fundamentally different from structured and polymerized silicate melts.

The first option: The primary magma is a congruent melt of the components that make carbonatite: $\text{FeCO}_3 + \text{CaF}_2 + (\text{Ba},\text{Sr})\text{SO}_4$. This melt fills and mineralizes the entire body volume of carbonatites as a result of a single act of introduction and two-stage crystallization (phenocrysts—the groundmass). This

mechanism of formation matches the observed features of the structure subvolcanic carbonatites—porphyritic structure, fluid type directional and banded textures, autolith breccias, cataclastic phenocrysts.

Experiments on melting in system

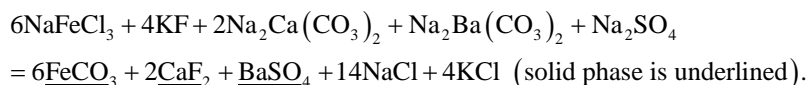
$\text{CaCO}_3(31.2\%)-\text{Ca}(\text{OH})_2(24.9\%)-\text{CaF}_2(13.5\%)-\text{BaSO}_4(10.4\%)-\text{La}(\text{OH})_3(20.0\%)$ is received glass at $T = 650^\circ\text{C}$ and $P = 100\text{ MPa}$ [6]. This proves the existence of the calcite-fluorite-barite melt under relatively low P - T conditions that are acceptable for subvolcanic carbonatites. However, siderite, in comparison with calcite, has a very low temperature of thermal dissociation 490°C at atmospheric pressure. Experiments that would show the stability of iron carbonate in magmatic conditions are unknown to the author.

The second option: The primary magma is represented by an ionic salt melt, in which in addition to rock-forming elements (Fe, Ba, Sr, Ca, O, C, S, F) there are low-melting salts of alkali metals. This is directly indicated by the dominance of chlorides Na and K in the studied inclusions.

It is possible to specify the most probable chemical form of finding the main components in the melt. Iron in high-temperature conditions forms a compound with chlorine in the form of NaFeCl_3 , KFeCl_3 [7]. Calcium in experimental and natural melts (lava of current African volcano Oldoinyo-Lengai) is in the form of double salts of the type $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, $\text{K}_2\text{Ca}(\text{CO}_3)_2$ [5]. In the same compounds may be other alkaline earth elements—barium and strontium. Sulfur and fluorine form low-melting salts— K_2S , Na_2SO_4 , NaF, KF.

A large number of sulfate in carbonatites (~20 wt.%) indicates a significant transition of primary sulphide sulfur to sulphate. Only partly the appearance of sulfate ion can be explained by the interaction of the melt with volatile components: $\text{K}_2\text{S} + 2\text{NaF} + \text{CO}_2 \uparrow + 2\text{H}_2\text{O} \uparrow = \text{Na}_2\text{SO}_4 + 2\text{KF} + \text{CH}_4 \uparrow$ (gas is indicated by an arrow, the liquid phase is without indication). Most likely, there was a sharp increase in the oxidative potential due to an external oxygen source, although its nature and method of penetration into the high-pressure magmatic system remain unclear.

To crystallize the main rock-forming minerals (siderite, fluorite and barite) from the melt, ionic exchange reactions of the type are sufficient:



In this chemical reaction, the coefficients are chosen so that the molar ratio of minerals in the reaction products corresponds to their weight ratio in carbonatites. The reaction shows that the predominance of iron chloride in the primary melt ensures the binding of alkaline elements in the chemically non-aggressive chloride form. This may explain the absence in Karasug ore field of alkali metasomatism of host rocks, which is typical for many carbonatite complexes in the world. From the same reaction it follows that the residual chloride melt is much larger in volume than the crystalline phase. The author does not find an answer to the questions: how and where a huge amount of Na-K chlorides could be

removed from the crystallizing melt and how this is reflected in the morphology and structure of carbonatites?

It is obvious that the residual chloride melt concentrated fluid components and contained the remains of rock-forming elements. To such brine investigated inclusions in minerals from fluorite-barite-siderite carbonatites are close. Pseudo-primary nature of the inclusions can be explained by the fact that crystallization occurs through ionic exchange reactions. In this case, the growing mineral in the boundary layer is constantly surrounded by a film of liquid reaction products, which are Na and K chlorides. Together with the fluid, they could be preserved in inclusions under the condition of a delayed inflow of fresh portions of the melt to the boundary layer. Such a condition may be feasible in a relatively viscous salt melt (in comparison with a hydrothermal solution).

In real conditions of carbonatite formation there may be a combination of the above two options. The main rock-forming components are present partially in the form of eutectic melting directly CaF_2 , BaSO_4 and FeCO_3 , and partly in the form of fusible salts in connection with alkaline metals. It is assumed saturation of the melt with volatile components, as evidenced by a large share of gas-liquid phase in crystal-fluid inclusions and explosive brecciation during the formation of the carbonatite bodies.

At the postmagmatic stage Karasug fluorite-barite-siderite carbonatites were subjected to pneumatolytic hematitization, hydrothermal celestinization and silicification [1]. Apparently, if hematitization in minerals of carbonatites are formed is primary-secondary crystal-liquid inclusions with temperatures of homogenization $480^\circ\text{C} - 420^\circ\text{C}$, and the hydrothermal end of the process is recorded in fluid inclusions homogenised within $380^\circ\text{C} - 250^\circ\text{C}$ [3].

3. Conclusions

When trying to decipher the physico-chemical conditions of formation of fluorite-barite-siderite carbonatite in Karasug deposit, a number of issues raise, which are of general importance for understanding the genesis of ferrocarnatite. Among them: 1) the salt carbonatite melt is an ionic liquid, and the release of minerals from it occurs as a result of ionic exchange reactions; 2) predominantly Na-K-chloride composition of crystal-fluid inclusions can be pseudo-primary, and their chemical composition does not correspond to primary carbonatite melt, but corresponds to the residual brine-melt; 3) iron in the primary melt is predominantly in the chloride form; 4) sodium and potassium salts are also present in the primary melt, but are not fixed in the products of crystallization; 5) the predominance of sulfate over sulfide in the melt raises the question about the external source of oxygen and the mechanism of its penetration in high-pressure magmatic system; 6) the mechanism for the removal of a large volume of residual Na and K chlorides from the crystallizing melt remains unclear.

High-temperature experiments in the system siderite-barite-fluorite \pm salts of alkaline metals are necessary to answer these and other issues.

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