Hydrothermal and fluids systems

Aksyuk A.M. A system of experimentally calibrated geofluorimeters

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A lot of geological endogenous processes take place at high activity of fluorine. Together with some other components fluorine accumulates during the process of magma fractionation resulting in formation of leucogranites, Li-F granites and pegmatites. Evolution of the magma and separated fluids lead to next metasomatic and ore formation processes. Major part of rare metal mineralization in granites, pegmatites, greisens and hydrothermal veins occurs at high activity of fluorine rich fluid.

The quantitative characteristics of the fluorine effect in the endogenous processes are still poorly studied, and the development of experimentally calibrated geofluorimeters is an important task of the experimental and physicochemical petrology. Such geofluorimeters can be developed, first of all, by experimentally study of the fluorine distribution between the minerals and aqueous fluid or mineral reactions between the fluorine bearing minerals within a wide range of temperatures and pressures. There are perspective for development of the geofluorimeters for widely common minerals as micas (phlogopite, biotite, muscovite, Li-micas), apatite, amphibole, tourmaline and others in which isomorphic anion replacements including fluorine can take place. These geofluorimeters allow quantitative estimations of HF concentration in fluid in equilibrium with the mineral – solid solution (its different end-members normally have a different affinity to fluorine) by the chemical composition of the mineral and its formation temperature. The mineral reactions, such as, quartz + fluorite + H_2O = wollastonite + 2HF or corundum + sellaite + H_2O = spinel + 2HF also can be used for quantitative estimation of fluorine concentration in the fluid for those mineral association taking into account their formation temperature.

The developed by the author phlogopite, biotite, muscovite, Li-mica and apatite geofluorimeters and the obtained P-T-M_{HF} parameters of the above mentioned fluorine "buffer" mono-variant reactions allowed to quantitatively estimate the effect of fluorine in the granite, skarn, and greisen fluids and demonstrate its role on the example of various granite massifs and deposits

Mica geofluorimeters.

Phlogopite geofluorimeter. The phlogopite geofluorimeter was developed using the experimental data obtained at temperatures of 500-700°C and pressures of 1-4 kbars (Aksyuk & Zhukovskaya, 1994,):

log M_{HF}(phl) = X_{Mg} [log (X_F/(1-X_F))] - 1722/T(K) - - 0.2112 +log a_{H2O} (1),

where T(K) is absolute temperature in Kelvin; M_{HF} is concentration of a neutral HF° particle in the fluid at equilibrium with mica, mol/dm³; X_{Mg} and X_F are mole fractions of Mg and F in octahedral and hydroxyl positions of phlogopite taking into account deviations of the natural phlogopite composition from pure magnesium phlogopite;

a_{H2O} is water activity in natural fluid taking into account its deviation from ideal composition through the equation $a_{H2O} = \gamma_{H2O} \cdot X_{H2O}$, where X_{H2O} is mole fraction of water in the fluid, and γ_{H2O} is activity coefficient. Such geofluorimeter gives possibility to estimate the HF concentration in fluid in equilibrium with the phlogopite. The concentration will be close to the bulk HF concentration at temperatures higher than 500°C and pressures up to 5 kbar as HF dissociation at these parameters has a little contribution to fluorine concentration. The dissociation contribution at lower temperatures and higher pressures can be calculated considering the data in HF-H_2O system, in first approximation.

Biotite geofluorimeter. Relationships between F/OH ratio in general end-members of biotite and HF/H_2O fugacity ratio in the aqueous fluid were experimentally determined by J. Munoz for different temperatures (Munoz, 1984). These "fugacity" ratios combined with our "concentration" ratios for phlogopite allowed calibration of the "concentration" affinity of the other biotite minals. If Henry coefficient for HF and H_2O in fluid is defined as h=M/f, where M is concentration and f is fugacity, the Henry coefficient ratio h_{H2O}/h_{HF} in the fluids in equilibrium with different micas must be very close to each other under the same T-P-(F content). We assume they are equal to the values obtained for phlogopite. Thus, we can obtain the relationships of affinity to fluorine by different biotite minals and yield the equation for the biotite geofluorimeter:

**log M_{HF}(bt) = log [(X_F/(1-X_F))-1722/T(K)-
-1.107X_{Mg}+ 0.216(Al-2) + 0.8958 + log a_{H2O} (2),**

where X_F=F/4, X_{Mg}=Mg/Σoct; F, Mg, Al are numbers of atoms in the biotite formula calculated for 44 negative electric charge; Σoct is sum of octahedral places in the crystal-chemical formula of mica; a_{H2O} is water activity in the natural fluid under at given T-P conditions.

Li-mica geofluorimeter. The Li-micas are typical for the most of rare-metal leucogranites and, especially, for Li-F granites. According to calculations of A.A. Marakushev (1979) Mg and Li have very close affinity to fluorine and hydrogen. It can be supposed, as the first approximation, that Li-F-OH affinity in biotite is equal to Mg-F-OH affinity. In this case, Li-mica will have the F affinity increasing proportionally to $X_{(Mg,Li)}$ = (Mg+Li)/Σoct, and the Li-mica geofluorimeter equation will be as follows:

**log M_{HF}(Li-mica) = log (X_F/(1-X_F))-
- 1722/T(K)+1.107$X_{Mg,Li}$ +0.216(Al-2)+0.8958+log a_{H2O}
        (3).**

Muscovite geofluorimeter. The muscovite geofluorimeter can be obtained by analogy with the biotite one:

**log M_{HF}(ms)=log (X_F/(1-X_F))-2270/T(K)-0.272(Li+Mg)+
0.216(6-Si) +0.185(Fe+Si-6)+1.419+log a_{H2O} (4),**

where Si, Mg, Li, Fe are numbers of the atoms per muscovite formula calculated for 44 negative electric charge.

Apatite geofluorimeter. The relationship between the apatite composition (its fluorine content), temperature and

HF concentration in the equilibrium fluid can be obtained from the experimentally derived equation for the phlogopite geofluorimeter, the calculated phlogopite-apatite geothermometer by Zhu and Sverjensky (1992), and biotite-apatite parageneses (Wang and Jeng, 1990). The apatite geofluorimeter will be as follows:

$$\log M_{HF}(ap) = \log [(X_F/(1-X_F))]_{ap} - [3657 - 5.246P(kbar)]/T(K) + 0.7 + \log a_{H2O} \qquad (5).$$

This equation gives estimations of HF concentrations in fluids of the Yuantoushan granites close to calculated ones by the biotite geofluorimeter (in the limit ±0.001-0.084 in the range $\log M_{HF}$ from −2.7 up to −3.2).

Fluorine "buffer" mineral reactions.
The following mono-variant fluorine "buffer" mineral reactions can be also used as fluorine content in fluids indicators:

quartz+fluorite+H_2O=wollastonite+2HF (6),

corundum+ sellaite+H_2O=spinel+2HF (7),

that are more typical for metamorphic rocks and skarn parageneses. According to our experimental studies at temperatures of 500°C, 600°C, 700°C and pressure of 1 kbar the correlation of HF concentration (mol/dm³) and temperature will be described by following equations:

$$\log M_{HF}(Wol) = 0.162 - 2275/T(K) \quad (\pm 0.163) \qquad (8),$$

$$\log M_{HF}(Spl) = 0.417 - 2045/T(K) \quad (\pm 0.025) \qquad (9)$$

for the first and the second equations, respectively.

Fluorine in natural fluids.
The HF concentration estimates obtained by experimentally calibrated geofluorimeters for natural fluids related to formation of different granitoids, skarns and ore deposits revealed the two trends of fluorine behavior in granite and hydrothermal fluids (Fig.).
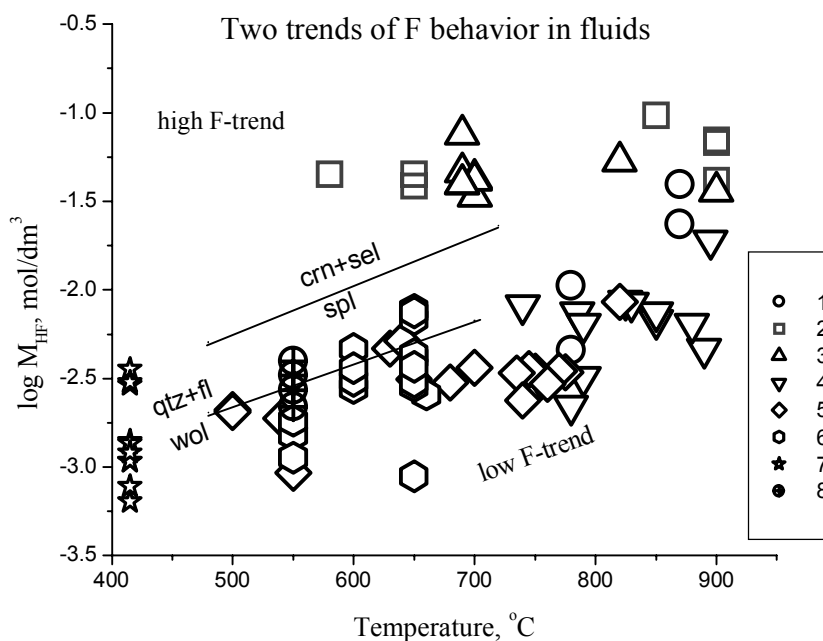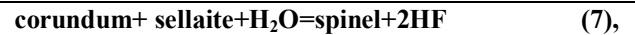

Fig. HF concentration in fluid associated with granites, marbles and skarns. (1 – Kaldyrminsky, 2 – Akchatau, 3 – Kyzylraisky of the Central Kazakhstan granite complexes. Granitoids of Cu-Mo deposits: 4 – Aksug, Eastern Tuva; 5 – Shakhtoma, Transbaikalia, 6 – marbles and skarns of phlogopite deposits, Siberia. Granitoids and skarns of Western Cordilleras: Cantung E Zone, 8 – Circular

Fluorine rich high F-trend characterizes rare metal leucogranites, Li-F granites and topaz-bearing granites or rhyolites and related deposits and near ore alterations. It describes relatively high F concentrations in fluid ($10^{-1.5}$ – 10^{-1} mol/dm³ HF and even up to 0.7-1.0 mol/ dm³ for the Ta-Nb Orlovka and Etyka deposits, Transbaikalia) that remain almost constant within the temperature interval of 500-900°C. The other fluorine poor, low F-trend, where HF concentration decreases by almost two orders of magnitude within this temperature interval, describes the different granitoid massifs of Kazakhstan, Urals, Siberia, Taiwan, as barren as Cu-Mo mineralized, and also the granulite facies metamorphic rocks and most of skarns and related deposits. These two trends reflect the two types of fluorine behavior in natural systems: perfectly mobile one for the high F-trend and inert one for the low F- trend.

References:

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