The role of fluor-rich fluids in the formation of the thorianite and sapphire deposits from SE Madagascar

B. Moine
A. Ramambazafy

Lab Minéralogie, 39 allées J. Guesde, 31000 Toulouse, France

M. Rakotondrazafy
B. Ravolomiandrinarivo

Dépt de Géologie, Université d'Antananarivo, BP 906, Antananarivo, Madagascar

M. Cuney

CREGU, BP23, 54501 Vandoeuvre, France

P. de Parseval

Lab Minéralogie, Toulouse, France

Th, Zr, Ti, Al and *REE* generally behave as immobile elements in water-rock interactions involving common H_2O-NaCl solutions. Because the corresponding cations complexe favourably with F^-, these elements could be transported by F-rich aqueous fluids. However the concentrations of fluoride complexes are probably very low in most geological processes because the fluorite- and topaz-bearing assemblages buffer HF to low values. As the values of a_{HF}/a_{H_2O} for such buffers increase with increasing temperature and decreasing a_{H_2O}, deep and gas-rich fluids could carry significant concentrations of these elements. The examples of two metasomatic deposits from S.E. Madagascar document this situation.

Thorianite-bearing skarns

In the Panafrican granulites from South Madagascar, fluid circulations have produced a lot of phlogopite deposits which are hosted by synmetamorphic diopside-rich skarns. Phlogopite is the only noticeable mineralization within those skarns occurring in the western part of the granulite province (region of Ampanihy hereafter referred by "AM"). By contrast, the skarns from the eastern part (Tranomaro = "TR") also contain thorianite $((Th,U)O_2)$, hibonite $(CaAl_{12}O_{19}$ whith high concentrations of Ti, *REE* and Th), and Zr-bearing minerals (baddeleyite, zircon, zirconolite) which indicates a high mobility of Th, Zr, Ti, *REE* and Al in addition to Si and Mg (Rakotondrazafy et al., 1996). Granitic (charnockites) plutons are specially abundant at TR. Primary fluid inclusions in skarns (within corundum, spinel, anorthite, hibonite, wollastonite) as well as in regional gneisses (within garnet, quartz) are carbonic $(X_{CO_2} \geqslant 0.8)$. The corresponding isochores are consistent with the thermobarometric estimates (T = 800°C for P varying from 3−5 kbar at TR to 8−9

kbar at AM). Under the above conditions, the observed CO_2-rich fluid phase probably coexisted with a H_2O-NaCl brine which is a more suitable solvent for many elements, especially for Si.

The F-content of biotite and phlogopite from the differents rocks in the AM and TR areas are contrasted: < 2.7 wt.% F (0−1.4% Cl) for AM compared with 2.7−7.1 wt.% F (0−1.2% Cl) for TR. These data are consistent with a low activity of water in the TR area as shown in Fig. 1: stability of wollastonite or calcite and the scarcity of fluorite imply $a_{H_2O} \leqslant 0.2$ (see the shift of the quartz-fluorite-wollastonite buffer (QFW) with decreasing a_{H_2O}). The calculated a_{HF}/a_{H_2O}, and a_{HF}/a_{HCl} ratios (see Zhu and Sverjensky, 1992) in the fluids in equilibrium with the micas from the two areas are very contrasted: for T = 800°C and P = 5 kbar, $log(a_{HF}/a_{H_2O})$ ranges from −0.5 to −1.0 and from −1.4 to −2.0 for AM and TR, respectively (Fig. 1; the corresponding mean values of $log(a_{HF}/a_{HCl})$ are 0.7 and 1.7). Preliminary *in situ* Nuclear Microprobe analyses of fluid inclusions from TR have confirmed the high fluorine content (C. Ramboz and M. Volfinger, work in progress).

Calculation of concentrations in the fluid phase from the estimated activities is presently quite impossible because of the poor knowledge of thermodynamic properties of CO_2- or NaCl-rich solutions. However, the effect of the contrasted activities of HF on the mobility of some elements of interest can be demonstrated in the simple case of a one molal NaCl solution. Such a preliminary calculation shows that the solubility of thorianite at 800°C and 5 kbar in a fluid in equilibrium with gneissic (or granitic) mineral assemblages is about 1.5 ppb (total F ≈ 130 ppm; Th distributed mainly among $Th(OH)_3^+$ and ThF_2^{2+}) at AM but about 80 ppb (total F ≈ 1300 ppm; ThF_2^{2+} largely dominant) at TR.
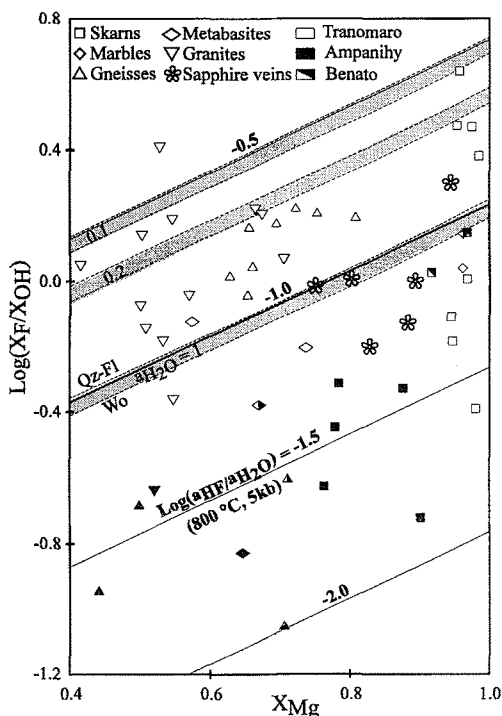
FIG. 1. $Log(X_F/X_{OH})$ vs X_{Mg} for biotite from the various rocks in the AM (Ampanihy) and TR (Tranomaro) areas .Isopleths of $log(a_{HF}/a_{H_2O})$ for fluids in equilibrium at 800°C and 5 kbar; values for the QFW buffer (with $a_{QUARTZ} = 0.8-1$) are shown for $a_{H_2O} = 1$, 0.2 and 0.1, respectively.

These results can explain the lack of thorianite in the AM area. By contrast, the fluid characterized in the TR area can carry large quantities of Th. A solution in equilibrium with the gneissic or granitic rocks and containing a few tens of ppb of Th would be able to precipitate a significant amount of thorianite as a consequence of an increase of pH due to its reaction with calcite to produce diopside and other skarn minerals. These results might apply to the transport of REE and Zr and precipitation of the corresponding minerals.

Sapphire deposits

In the Tranomaro area, extensive sapphire deposits occur as crosscutting veins within marbles and associated diopside-rich calcsilicate rocks. The veins are composed of predominant K-feldspar with minor apatite, phlogopite, corundum (sapphire) and calcite. K-feldspar clearly crystallized at the expense of calcite and diopside which implies a high mobility of Al in addition to K and Si. Carbonic ($X_{CO_2} \geqslant 0.8$) fluid inclusions (in sapphire, apatite and feldspar) are also characteristic of the sapphire deposits. The corresponding isochores indicate T 500°C for P = 2 kbar. These P-T-X conditions are in agreement with the stability of the assemblages corundum + K-feldspar and corundum + calcite (+ aqueous silica) with respect to muscovite and anorthite, respectively.

The F-content of phlogopite is also relatively high: mainly in the range 3−4.5 wt.% F for about 0.05 wt.% Cl, i.e. $X_F = 0.37-0.5$ (Fig. 1). The calculated mean value for $log(a_{HF}/a_{H_2O})$ is −2.28. G. The solubility of corundum in H_2O-HF has been measured at P = 1 kbar for T = 300 to 600°C (Zaraisky, 1994). For T = 500°C and the above HF concentration, $logm_{Al} = -3.7$, that is m_{Al} is about ten times higher than for pure water. Calculation indicates that $Al(OH)_2F$ is probably the main aqueous species. Assuming such an increase would not be highly altered through addition of CO_2, this could explain the observed high mobility of Al.

Conclusions

F-rich fluids were probably at the origin of the thorianite-bearing skarns−a unique type of mineral deposit−and sapphire bearing veins from S. E. Madagascar. Th, Al as well as Zr, Ti and REE were probably transported as fluoride complexes. These fluids were of crustal origin, probably linked to the granites, as shown by the isotopic composition of the skarns (Boulvais, 1997). Melting of biotite-bearing metasediments at a deeper level might have produced F-rich granitic magmas. Their rise and crystallization as charnockites would have released the F-rich fluids which are inferred from the exceptional composition of the micas (X_F up to 0.8).

References

Boulvais, P. (1997) PhD, Rennes Univ., France.
Rakotondrazafy M., Moine, B. and Cuney, M. (1996) Contrib. Mineral. Petro.l, 123, 190−201.
Zaraisky, G. P. (1994) In Fluids in the Crust. Equilibrium and transport properties. Shmulovich et al. ed., p. 139−62.
Zhu, C. and Sverjensky, D.A. (1992) Geochim. Cosmochim. Acta, 56, 3435−67.