



Solubility of monazite in granitic melts and the role of liquid-liquid immiscibility in concentrating REE

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Summary

Dissolution experiments were conducted at 800°C and 200 MPa using water-saturated and flux-bearing (P+F+Li) peralkaline to peraluminous granitic melts, and several types of starting crystal products, mainly monazite, xenotime and cheralite. The experimental results on monazite and xenotime solubility show that REE concentrations at saturation of these minerals do not exceed a few 10s of ppm in peraluminous phosphorus-bearing granitic melts. The monazite solubilities are much lower than the values previously reported in the literature, and are certainly depressed by the presence of fluorine and phosphorus in our melts. The new solubility data provide explanation for the very low REE concentrations generally encountered in high-phosphorus peraluminous granites and pegmatites. In addition, reverse (i.e., recrystallisation after dissolution) experiments of cheralite display liquid-liquid immiscibility processes in our most peralkaline ($ASI_{Li}=0.85$) glass. The immiscible liquid is extremely enriched in P_2O_5 and F (35 wt. % and 28 wt.% respectively, in average) and contains several wt.% REE_2O_3 . This result shows that liquid-liquid immiscibility is a possible mechanism of REE concentration in highly-fluxed melts and should be considered in natural systems where REE are extremely concentrated (up to thousands of ppm) in magmatic rocks. This is the case of grenvillian pegmatitic granites that host abundant monazite mineralization (up to 5% of the rock volume), although the granites display a peraluminous composition.

Theory / Method / Workflow

Dissolution and reverse (i.e., recrystallisation after dissolution) experiments were conducted at 800°C and 200 MPa in cold-seal pressure vessels in Toulouse, using water-saturated and flux-bearing (P+F+Li) peralkaline to peraluminous granitic melts, and several types of starting crystal products: pure synthetic monazite and xenotime, natural Manangotry monazite, and synthetic crystals of the monazite-cheralite solid solution. Glass major element composition was analyzed by electron probe microanalyses and trace element concentrations by laser ablation ICP-MS. The composition of the monazite-cheralite crystals in the experimental products was checked by Field Emission Gun EPMA.

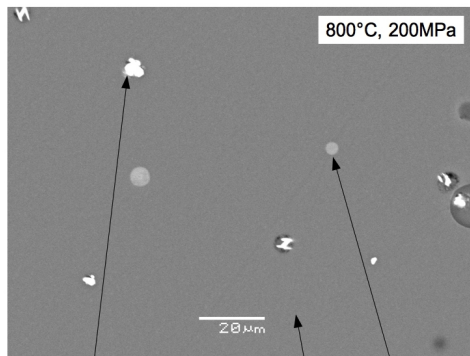
Results, Observations, Conclusions

The experimental products consist of monazite crystals disseminated in glass. Monazite solubility is estimated as $K_{monazite} = [REE]$, as shown by Duc-Tin and Keppler (2015). The sum of all REE excluding Y in the experimental glasses ranges from 9 to 19 ppm in peraluminous glass, and 36 to 96 ppm in peralkaline glass. The experimental glasses at saturation with



xenotime have Y contents of 14 ppm in peraluminous glass and 262 ppm in peralkaline glass. Plotted against the alumina-silicate index (ASI) of the glasses, our solubility data in synthetic flux-rich glasses plot on a linear correlation which is roughly parallel to the linear correlation determined from flux-poor glasses. Consequently, we suggest that P and F contents are responsible for the drastic (almost an order of magnitude) drop of solubilities. The new solubility data provide explanation for the very low REE concentrations generally encountered in high-phosphorus peraluminous granites and pegmatites, and for the compatible behaviour of REE in peraluminous systems, as the early crystallization of REE-bearing minerals (mainly monazite and zircon) leads to progressive REE depletion with liquid differentiation.

In the experiments with peralkaline glass and cheralite, perfectly rounded globules, 3-10 μm in diameter and lighter in backscattered electron images, are disseminated in the glass (Figure). The material inside the globules is vitrified and displays an average composition of 35 wt.% P_2O_5 , 28 wt.% F, 22 wt.% Al_2O_3 , 4 wt.% CaO, 5 wt.% Na_2O , and 2 wt.% REE_2O_3 . Totals close to 100 wt.% oxides indicate that water is not a significant component of this glass. The quenchable nature of that glass is in favor of an immiscible process for the formation of these globules. They show that liquid-liquid immiscibility is a potential mechanism of REE concentration in melts where REE have low solubilities.



Recrystallized monazite after dissolution of cheralite (at equilibrium with glass)		Glass		Immiscible globules	
P_2O_5	30.13	SiO_2	61	SiO_2	1.00
CaO	2.94	Al_2O_3	15.64	Al_2O_3	22.00
La_2O_3	41.92	Na_2O	3.9	Na_2O	5.13
Eu_2O_3	7.85	K_2O	6.96	K_2O	1.26
ThO_2	15.14	Li_2O	1.7	Li_2O	n.a.
		P_2O_5	3.03	P_2O_5	35.26
		CaO	0.03	CaO	2.8
		La_2O_3	0.005	La_2O_3	2.15
		Eu_2O_3	0.005	Eu_2O_3	1.64
		ThO_2	0.06	ThO_2	10.91
		F	5.2	F	24.44
		ASI(Ca,Li)	0.79	ASI(Ca,Li)	1.1

Figure. Backscattered electron image of an experiment showing the immiscible globules and their composition in wt.%.

Solgadi, F., (in prep). How thousands ppm of light rare earth elements accumulate in peraluminous granitic melts?
Van Lichtervelde, M., Goncalves, P., Eglinger, A., Montel, J.-M., Dacheux, N. (in prep) Solubility of monazite-cheralite and xenotime in high-P granitic melts, and experimental evidence of liquid-liquid immiscibility in concentrating REE.

In the Grenville Province of Québec, some peraluminous pegmatitic granite dykes display REE concentrations close to those traditionally encountered in peralkaline rocks, that is up to several thousand ppm (Turlin et al. 2017). These mineralizations are not explained by simple magmatic fractionation nor hydrothermalism, but could be the result of a liquid-liquid immiscibility process (Turlin et al. in prep) based on the preceding experimental results (Van Lichtervelde et al. in prep).

Acknowledgements

This project was funded by the French National Institute of Universe Sciences (INSU – NEEDS project).

References

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