

INFLUENCE OF CHROMIUM ON REE PARTITION BEHAVIOR BETWEEN GARNET AND BASALTIC MELT

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Introduction Shimizu and Richardson (1987) reported that the sub-calcic Cr-rich garnet xenocryst and diamond inclusions are LREE enriched, contrast to its very depleted major element composition. Late stage metasomatism was inferred and thus geochemical property of this metasomatic melt is important for illustrating evolution of lithospheric mantle beneath Archean cratons. REE concentrations in the metasomatic melts have been calculated, using REE contents in garnet and the REE partition coefficients between garnet and silicate melt (Shimizu & Richardson, 1987). Evidently, the calculation results are heavily dependent on the REE partition coefficients, which is a function of P, T and major element composition.

In mantle peridotitic garnet, Al^{3+} is partly substituted by Cr^{3+} . Cr_2O_3 content in some garnet, for example inclusions in diamonds, may up to 16.0wt%. It could be expected that this substitution will evidently influence the REE partition behavior. Model calculation of REE abundance in melts that employ constant values of partition coefficient, determined from none-chromium systems, should be imprecise. Anyway, influence of Cr^{3+} on REE partition behavior is very difficult to be determined from natural samples, owing to unclear relationship with host rocks. High temperature and pressure synthetic experiments, coupled with SIMS analysis, was performed in this research, with the purpose of investigating any possible influence of Cr^{3+} on REE partition behavior. REE concentrations in metasomatic melts, which may have caused metasomatism of mantle garnets from Sino-Korea craton, are also calculated, based on newly established partition coefficients.

Experiment and analysis All experiments were carried out by using a 1000-ton uniaxial multi-anvil apparatus (SPI-1000), located in the Tokyo Institute of Technology. Both P and T of this apparatus are computer programmable. Rhenium foil was applied as sample container, and temperature was measured with W5%Re - W26%Re thermocouple, which was inserted axially in

Table 1 Experimental conditions and results

Run	Starting material	Temperature (°C)	Pressure (GPa)	Duration (Min.)	Run products
S301	JB1 + 0.0wt% CrO3	1900	7.5	30	gt + liq.
S299	JB1 + 3.0wt% CrO3	1900	7.5	30	gt + cpx + liq.
S300	JB1 + 6.0wt% CrO3	2000	7.5	30	gt + cpx + liq.
S315	JB1 + 9.0wt% CrO3	2090	7.5	30	gt + liq.
S320	JB1 + 12.0wt% CrO3	2000	7.5	25	gt + cpx + liq.

the LaCrO3 furnace assembly.

Powered standard rock sample JB-1 (alkali basalt), distributed by the Geological Survey of Japan, was used in all the experiments, because of its high REE concentration and relatively lower liquidus temperature. Various contents of Cr oxide were added into the JB-1 powder, in order to synthesize garnets with different Cr_2O_3 contents. Five sets of experiment were carried out and the experimental conditions are summarized in Table 1.

Polished sections of run products were analyzed by electron microprobe for major element composition and distribution. Concentrations of the 14 rare earth elements were measured for both garnet and quenched melts, by using of a Cameca IMS-3f SIMS instrument. Offset voltage was set to -40V for garnet measurement, and -100V for quenched melts, in order to increase analysis

precision.

Experimental results Run products consisted of garnet, pyroxene and quenched melt. Grain sizes of garnet crystals ranged from 50-80 μ m. Line scan and element distribution analyses by

Table 2 Compositions of synthesized garnets

RUN	S301	S299	S300	S315	S320
Added CrO ₃	0.0wt%	3.0wt%	6.0wt%	9.0wt%	12.0wt%
SiO ₂	42.83	41.96	40.48	40.89	40.33
Al ₂ O ₃	22.55	19.84	17.75	17.59	15.57
TiO ₂	0.44	0.76	1.04	0.55	0.65
Cr ₂ O ₃	0.14	3.82	7.31	9.94	13.24
FeO	8.21	8.53	9.75	6.80	7.84
NiO	0.01	0.07	0.04	0.01	0.03
MnO	0.27	0.21	0.29	0.28	0.26
MgO	16.61	15.13	12.20	14.40	12.37
CaO	8.73	9.40	10.16	9.05	9.56
Na ₂ O	0.40	0.31	0.41	0.41	0.49
K ₂ O	0.01	0.01	0.01	0.01	0.01
Total	100.19	100.03	99.43	99.93	100.35

electron microprobe show that all the major elements (Mg, Al, Si, Ca, Cr, Fe) in garnets distributed homogeneously over the whole crystal.

With increasing Cr oxide added in the starting materials, Al³⁺ is gradually substituted by Cr³⁺ and Cr₂O₃ contents in garnets of the five run products are 0.14wt%, 3.82wt%, 7.31wt%, 9.94wt% and 13.24wt% respectively. These values almost cover the Cr₂O₃ content range of mantle peridotitic garnet. Variations of CaO, MgO and FeO contents are

comparatively small. Furthermore, all the experiments are carried out in almost same P, T conditions, thus allow assessment of the influence of chromium content upon REE partition behavior. Major element compositions of synthesized garnets and REE partition coefficients are listed in Table 2 and Table 3.

Variations of partition coefficients are summarized as follows:

(1) Cr₂O₃ content in the synthesized garnet ranges from about 0 to 14wt%, but it does not cause evident change in the partition coefficients of HREE (Fig. 1a). This shows that HREE partition coefficients between garnet and silicate melt are not greatly influenced by Cr₂O₃ content in garnet;

(2) Partition coefficients of LREE are evidently influenced by major element composition. As to run S301, in which no Cr oxide was added, partition coefficients of LREE are much smaller than all the Cr-added runs. For example, D_{Ce} in run S301 is 0.015, to be only about 1/3 of the average value of Cr-added runs. It indicates that compatibility of LREE in garnet increases when it contains a lot of chromium;

Table 3 Variation of REE partition coefficients of garnets

RUN	S301	S299	S300	S315	S320	Average of Cr-bearing Gt
Cr ₂ O ₃	0.14%	3.8%	7.3%	9.9%	13.2%	
La	0.005	0.022	0.026	0.023	0.014	0.021
Ce	0.015	0.056	0.048	0.041	0.037	0.045
Pr	0.040	0.107	0.090	0.081	0.089	0.092
Nd	0.056	0.233	0.155	0.118	0.150	0.164
Sm	0.169	0.496	0.302	0.267	0.396	0.365
Eu	0.275	0.658	0.407	0.343	0.421	0.457
Gd	0.321	0.757	0.532	0.586	0.695	0.643
Tb	0.403	1.373	0.710	0.745	0.904	0.933
Dy	0.824	1.490	1.045	1.264	1.514	1.328
Ho	1.441	2.567	1.968	2.227	2.982	2.436
Er	1.513	2.170	1.780	2.586	2.522	2.264
Tm	1.494	1.673	1.641	2.123	2.111	1.887
Yb	1.615	1.723	1.607	2.119	2.038	1.872
Lu	1.688	1.416	1.502	2.720	3.174	2.203

(3) In all the Cr-added runs (S299, S300, S315, S320), no systematic increase in compatibility of LREE with Cr₂O₃ content has been observed. Partition coefficients of LREE in all the four Cr-added run products are almost same within experimental uncertainty.

For simplicity, data obtained in run S301 could be considered as REE partition coefficients between garnet and silicate melt, in which no or only seldom Cr exist. For the

lack of evident difference, average data of all the four Cr-added runs are believed to represent Cr-bearing system (Fig.1b). Yb/Ce value of none-Cr garnet is 110.8, much steeper than the average Cr-bearing garnet, which is only 41.2.

Discussion In the garnet crystal structure, REE elements share the 8-coordinated triangular dodecahedron site with Mg, Fe²⁺ and Ca. Substitution of Cr³⁺ (r=61.5 pm) for Al³⁺ (r=53.0 pm) in octahedron enlarges the size of dodecahedron, which make it feasible for larger REE (especially LREE) ions to locate in and thus increases its compatibility. It can be expected that this effect is not so evident for comparatively smaller HREE. In garnet formula with 12 oxygen, (Al+Cr) values in garnets of run S315 and S320 exceed 2.0, to be 2.10 and 2.15 respectively. This indicates that part of chromium in garnet are possibly in +2 charge, and enter the dodecahedron site instead of octahedron one. It may be a reason why we fail to find systematic increase in compatibility of LREE with chromium content in garnets.

Selected garnet xenocrysts from Shengli 1 and No.50 kimberlite pipe of China, which covered a very wide range of chemical composition, and garnet inclusions in diamonds, are measured by SIMS for determining its REE distribution pattern. It was found that sub-calcic Cr-rich garnets are LREE enriched, similar to that reported by Shimizu and Richardson (1987), but lherzolitic garnets are normally depleted. A positive correlation between ratios of LREE/HREE and Cr/(Cr+Al) was also verified. These observations also indicate that Cr³⁺ may affect the partition behavior of

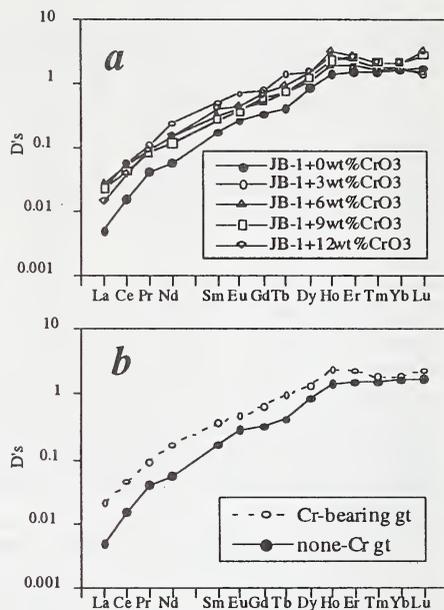


Fig 1 Changing of partition coefficients with chromium contents in garnets

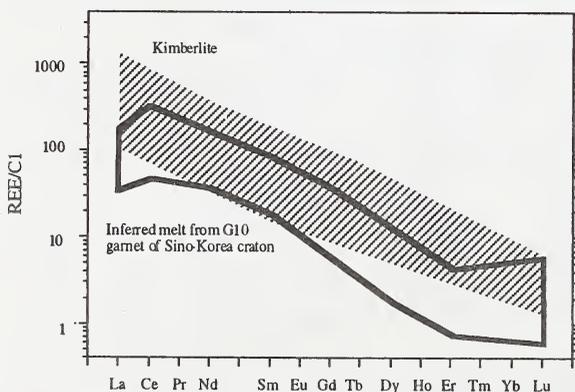


Figure 2 Composition of REE in kimberlites and the inferred metasomatic melt

REE to some extent, and to be perfectly consistent with this experimental results.

REE concentrations in melts, which may have caused metasomatism of sub-calcic Cr-rich xenocrysts and inclusion garnets of Sino-Korea craton, are calculated using the partition coefficients of this study. Results are shown in Fig. 2, comparing with REE in kimberlites. It was found both are almost same. These results support the suggestion that at least some mantle metasomatism is related to the interaction of kimberlitic magma with refractory peridotite in the lower lithospheric mantle (Odling, 1995; Kinny and Dawson, 1992).

Reference

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