

DECOUPLING OF REE IN PLAGIOCLASE AND ORTHOPYROXENE IN THE LUNAR FERROAN ANORTHOSITE.

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Introduction: According to the canonical lunar magma ocean (LMO) model, ferroan anorthosites (FANs) were part of the lunar anorthosite crust formed via plagioclase flotation and subsequent solidification in a globally distributed LMO [1-4]. The solidification time for a globally distributed LMO is model dependent and ranges from 10^4 - 10^8 yrs [3,5,6]. At a given time during lunar crust formation, a highly simplified lunar crust would consist of a protocrust with perhaps higher mafic mineral abundance than typical FANs at the top, a growing plagioclase-rich crust largely free of intercumulus melt in the middle, and a mush layer composed of plagioclase, smaller quantities of pyroxene \pm olivine and a relatively dense, FeO-enriched melt of the LMO at the bottom. Due to their negative buoyancy relative to the plagioclase the intercumulus melts tend to “lift” the plagioclase matrix, forming “rockbergs” and perhaps even forcing the matrix to deform (compact) against the completely solidified crust [7,8]. The ability to segregate and expel significant amount of intercumulus melts from the plagioclase mush is a necessary condition for the formation of an anorthosite crust that is characterized by small mafic mineral fraction and low incompatible trace element abundance.

Segregation of intercumulus melts from their crystalline matrix due to compaction and solidification will inevitably result in chemical fractionations in the minerals and melt [9,10]. Consider two rare earth elements Sm and Nd. Nd is more compatible than Sm in anorthite ($k_{Nd}^{An} = 0.12$ and $k_{Sm}^{An} = 0.67$, [11]), whereas Sm is slightly more compatible than Nd in orthopyroxene ($k_{Nd}^{opx} = 0.023$ and $k_{Sm}^{An} = 0.038$, [12]), clinopyroxene and olivine. Furthermore, the diffusion rate of Nd (and Sm) in anorthite is very slow, ($D_{Nd}^{An} \sim 10^{-20}$ m²/s at 1200°C, An₉₃₋₉₅, [13,14]), \sim 2-3 orders of magnitude slower than that in orthopyroxene (extrapolated from [15]) but \sim 1 order of magnitude faster than that in diopside [16]. Hence it takes much longer time to diffusively re-equilibrate Nd in anorthite than in orthopyroxene, if the grain sizes are comparable. As will be shown below such large disparities in the diffusive time scale can result in significant kinetic fractionations between the plagioclase and mafic minerals when intercumulus melts percolate through an anorthositic matrix. One of the main conclusions of this study is that the REE concentrations in orthopyroxene in the FANs are likely modified by later magmatic processes.

Model: The chemical fractionations resulting from percolation of intercumulus melt through a porous anorthosite matrix are illustrated using a simple diffusion-advection-reaction model, similar to those used to study metasomatism within the Earth’s mantle [9,10]. For purpose of illustration we consider a one-dimensional anorthosite column consisting of 85% anorthite, 5% low-Ca pyroxene, and 10% melt. Initially the interstitial melt and the matrix minerals were in chemical equilibrium. The Nd and Sm abundance in the melt were 26xCI and 24xCI (CI = chondritic abundance), respectively. These correspond to the liquid left after \sim 80% crystallization of the LMO, according to the model of [17]. The infiltrating melt, expelled from the overlying and solidified anorthosite crust, is more evolved and has Nd and Sm concentrations of 85xCI and 80xCI, respectively. The crystal-melt exchange rates are estimated from the Nd diffusion date in anorthite and orthopyroxene [9,13-15]. Variations of Sm and Nd in the melt, anorthite and orthopyroxene as a function of time and position within the anorthosite mush were calculated using a finite difference method. For simplicity we assume a constant melt velocity and neglect the effects of solidification and matrix deformation in our numerical calculations. Compaction and solidification result in variations in mineral and melt proportions in the 1D column. (These more realistic cases are subjects of future studies.)

Results and Discussions: A series of numerical calculations were conducted to explore the effects of crystal-melt exchange rates on the distributions of Sm and Nd in the anorthosite. Figures 1a and 1b show an example of calculated concentrations of Nd (solid lines) and Sm (dashed lines) in the anorthite (Fig. 1a) and low-Ca pyroxene (Fig. 1b) as a function of normalized distance at 4 selected times. The parameters used in this calculation correspond to a total depth of 18 km, a duration of 10 Ma, and a melt velocity of 1 mm/yr. As shown in Figs. 1a and 1b, concentrations of Nd and Sm in the low-Ca pyroxene were more significantly modified by the infiltrating melt than those in the anorthite. This can be seen more clearly in Figs. 2a and 2b. The calculated Nd and Sm concentrations in the melt that would be in equilibrium with the orthopyroxene (solid lines) are practically identical to the interstitial melt compositions (dotted lines), whereas Nd and Sm concentrations in the melt that would be in equilibrium with the anorthite (dashed lines) are lagged behind, due to their slow diffusion rates in the plagioclase.

clase. Figures 3a and 3b show that Nd and Sm in the anorthite are significantly out of chemical equilibrium with the coexisting melt if the reaction time is reduced by a factor of 10 ($t_4 = 1$ Ma, melt velocity ~ 10 mm/yr). Hence if the FANs are formed in a relatively short period of time, < 10 Ma, say, significant decoupling of Nd and Sm in the coexisting anorthite and orthopyroxene are expected.

It has been well documented that the REE abundance in the plagioclase and orthopyroxene in FANs, (and some cumulate eucrites and Mg-suite rocks) are decoupled [18-21]. For example, REE abundance in melts derived from ion probe analysis of low-Ca pyroxene is often higher than that derived from the coexisting plagioclase [21]. Two explanations were proposed in the literature (i) inconsistent crystal/melt partition coefficients for the pyroxene and anorthite, and/or (ii) REE abundance in the pyroxenes was reset by subsolidus processes [18,20,21]. We have shown in this study that melt flow and melt-rock reaction is a viable mechanism through which REE abundance in orthopyroxene are fractionated from that in the plagioclase. The calculated melt compositions in equilibrium with the anorthite are likely a record of earlier magmatic history, perhaps the melt composition from which the plagioclase was crystallized in the LMO. Nd and Sm abundance in the low-Ca pyroxenes are likely modified by the adcumulus processes, in addition to subsolidus re-equilibration. As shown in Figs. 2c and 3c, melt flow and melt-rock reaction can also fractionate Nd from Sm in the orthopyroxene, which may have important implications for the Sm/Nd systematics in the FANs.

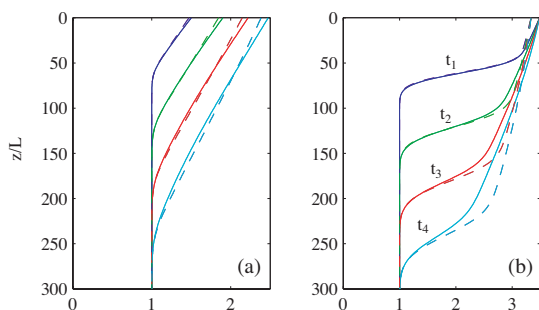


Fig. 1. Calculated concentration profiles of Nd (solid lines) and Sm (dashed lines) in the anorthite (a) and orthopyroxene (b) as a function of normalized depth in the anorthosite mush at 4 selected times. The concentrations were normalized to the initial Nd or Sm concentrations in the respective minerals. If we assume a length scale of 60 m (for each unit of z/L) these profiles correspond to a time sequence of 2.5, 5, 7.5 and

10 Ma. The Nd and Sm diffusivities in the melt are assumed to be 10^{-10} m²/s.

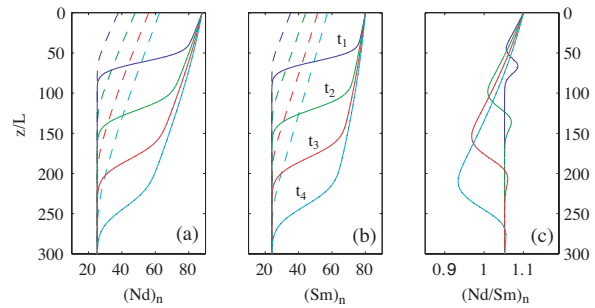


Fig. 2. Calculated Nd (a) and Sm (b) concentrations of the melt that would be in equilibrium with the anorthites (dashed lines) and orthopyroxenes (solid lines) shown in Fig. 1 ($C_f = C_s/Kd$). Melt compositions are normalized to CI. (c) CI normalized Nd/Sm ratio in the melt that would be in chemical equilibrium with the orthopyroxene. The dotted lines represent the interstitial melt compositions.

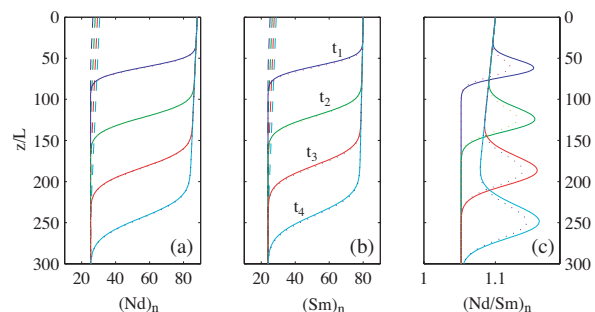


Fig. 3. Similar to Fig. 2 but at a shorter time scale ($t = 0.25, 0.5, 0.75,$ and 1 Ma). The dotted lines represent the interstitial melt compositions.

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