

**GEOCHEMICAL EFFECTS OF RECRYSTALLIZATION AND EXOLUTION OF PLAGIOCLASE OF FERROAN ANORTHOSITE;** BRADLEY L. JOLLIFF, AND WEIBIAO HSU, DEPARTMENT OF EARTH AND PLANETARY SCIENCES AND THE MCDONNELL CENTER FOR THE SPACE SCIENCES, WASHINGTON UNIVERSITY, ST. LOUIS, MO 63130.

**Summary.** The minor- and trace-element composition of plagioclase of ferroan anorthosite is of special significance because it is used to infer the composition and the geochemical and petrologic evolution of the magma from which it crystallized. It is therefore important to understand not only the distribution of trace elements between plagioclase and melts of relevant temperature, pressure, and composition, but also whether any post-crystallization mechanisms have modified the primary plagioclase compositions. Two potential modification mechanisms are recrystallization and exsolution, driven by either late-magmatic, subsolidus, or impact processes. To test the geochemical effects of these mechanisms, we have analyzed, with electron (EMP) and ion (IMP) microprobes, plagioclase of ferroan anorthosite from within the same thin section that shows both coarse, relict igneous texture and recrystallized texture to determine the compositional trends that accompany recrystallization. We have also analyzed regions clouded with inclusions and adjacent regions that are clear of inclusions for comparison. Although the compositional variations are slight, we find that recrystallized and clear regions have lower concentrations of ferromagnesian elements, particularly Mg, consistent with exsolution of pyroxene, or exclusion of mafic components on recrystallization that were taken up by interstitial pyroxene. In most cases, but not all, recrystallized regions also have slightly higher concentrations (e.g., 5-10% higher) of the plagiophile elements Na, Sr, Ba, and Eu.

**Introduction.** Plagioclases of lunar ferroan anorthosites have very low concentrations of minor and trace elements, including Fe and Mg [1], and some have high Fe/Mg ratios [2]. When Fe and Mg concentrations of plagioclase are combined with relevant distribution coefficients [e.g., 3, 4] to determine equilibrium melt compositions, the calculated Fe and Mg concentrations in the melt are unreasonably low [5]. Phinney [6, 7] concluded that lunar ferroan anorthosites, similar to terrestrial anorthosites of granulitic metamorphic grade, have experienced a redistribution of components at high temperature for an extended period of time. Others [1] have argued that some of the compositional trends of minor and trace elements in lunar ferroan anorthosites are igneous trends. If redistribution of mafic components has occurred, what other elements may also have been affected?

Two important pieces of evidence regarding the mobility of minor elements in plagioclase of ferroan anorthosites are polygonal recrystallization textures and the presence of mafic inclusions. While some plagioclases of ferroan anorthosite do not have abundant inclusions, others are clouded with very fine-grained mafic inclusions, similar to plagioclase in eucrites [8], suggesting exsolution of mafic components. We have observed such clouding in both regular and irregular distributions, concentrated along fractures or subgrain boundaries, and along twin composition planes. Where clouding of plagioclase is observed, inclusions tend to be absent near grain boundaries and in recrystallized zones. We observe no instances of plagioclase with clouded rims and clear cores. We attribute the clouding to exsolution and clear regions of plagioclase to loss of exsolved components; clear recrystallized areas indicate that recrystallization took place under conditions in which the mafic components were less soluble in plagioclase than they were during primary crystallization. In clouded plagioclase, the mafic components are therefore part of the primary plagioclase and should be considered (as in bulk analyses) in estimates of equilibrium melt compositions.

**Experimental.** We have studied plagioclase in thin sections that show (a) recrystallization and (b) variable amounts of exsolution of mafic components. In the first experiment, we analyzed coarse, clouded, presumably primary plagioclase and adjacent polygonal, recrystallized plagioclase (in the same thin section). In the second experiment, we analyzed regions of plagioclase containing abundant inclusions and adjacent regions of few or no inclusions. In the IMP analyses, we used a spot size of ~30  $\mu\text{m}$  and we reduced the data according to the methods of [9]. Most trace-element concentrations are exceptionally low, so counting times were long (typically 4-5 hours) and the ion beam penetrated some 15-20  $\mu\text{m}$  into the sections. With this scale of sampling, we sought to obtain representative "bulk" samples of plagioclase. With the EMP, we made analyses with a range of spot sizes, but it was difficult to obtain representative analyses in clouded areas because of the scale of separation of inclusions.

**Results.** We have many EMP analyses of inclusion-bearing plagioclases from a suite of samples from North Ray Crater, Apollo 16, that was interpreted by [10] to have derived from a system that crystallized plagioclase initially deep, but which was then emplaced prior to final solidification in a relatively shallow environment. These plagioclases have a range of Fe and Mg concentrations, and in some cases, they are substantially higher than in plagioclase of other ferroan anorthosites (e.g., up to 0.4 wt.% FeO and 0.3 wt.% MgO). In one sample that contains coarse, relict igneous plagioclase and polygonal, recrystallized plagioclase, EMP results show that the Fe concentration decreased by ~20% and Mg, by >50%, and that the Na concentration increased by ~10% in the recrystallized plagioclase. Ion microprobe results show essentially the same variations, but they also suggest an increase in concentration of other plagiophile elements, Sr, Ba, and

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Eu, and a slight increase of the REE slope (Fig. 1). Comparison of regions in this and other samples that were inclusion-rich vs. clear or inclusion-poor regions also showed lowered mafic-element concentrations, but concentrations of the plagiophile elements did not in all cases vary consistently. The HREE tend to be depleted in regions cleared of inclusions, consistent with our inference that most of the mafic inclusions in these samples are augite.

**Discussion.** The form of Fe and Mg in plagioclase of most of our analyses is dominantly tetrahedral as in the  $\text{Ca}(\text{FM})\text{Si}_3\text{O}_8$  component [see 11]. (The reaction for the exsolution of augite is  $\text{Ca}(\text{FM})\text{Si}_3\text{O}_8 \Rightarrow \text{Ca}(\text{FM})\text{Si}_2\text{O}_6 + \text{SiO}_2$ ; however, we have not observed separate silica inclusions.) Although it has been argued by [12] that diffusion of  $\text{Na}^+$  is prohibitively slow due to the coupled  $\text{NaSiCa}_1\text{Al}_1$  exchange, perhaps the exsolution of mafic components that nucleated on fractures produced either during emplacement or by impacts, and subsequent annealing and recrystallization, aided the redistribution or re-equilibration of plagioclase under conditions different from those at first crystallization.

The compositional variations we observe among plagioclases in these samples are small compared, for example, to those seen in eucrites for clouded vs. clear plagioclase [8]. However, the trends are similar, and they indicate that exsolution is as viable a mechanism as recrystallization, or may work in conjunction with recrystallization to alter primary plagioclase compositions. It remains that compositions of plagioclase of lunar ferroan anorthosites have low Fe and Mg concentrations relative to what they likely had when first crystallized. While we can determine the trends of compositional modification due to exsolution and recrystallization, we do not know the full extent to which these mechanisms might have proceeded prior to the state in which we now find the plagioclase, i.e., they may have experienced multiple episodes of dissolution/recrystallization during their emplacement and long residence at high temperature [6].

We also find evidence in coexisting pyroxenes for the late addition of components exsolved from plagioclase. In a sample that contains inverted pigeonite with relict igneous texture, we also find smaller interstitial, unexsolved low-Ca pyroxene grains. Ion microprobe analysis of one of these grains shows elevated LREE and higher overall REE concentrations than expected for the grain to be in equilibrium with the coarse, early pyroxene (Fig. 2). Although Fe and Mg are equilibrated between the pyroxenes, the REE concentrations apparently are not, and analyses of the interstitial pyroxene would indicate a significantly different REE pattern and concentrations for the parent melt. We conclude that the interstitial grains have been modified (cf. 67075 [13]) by exchange with components exsolved from plagioclase.

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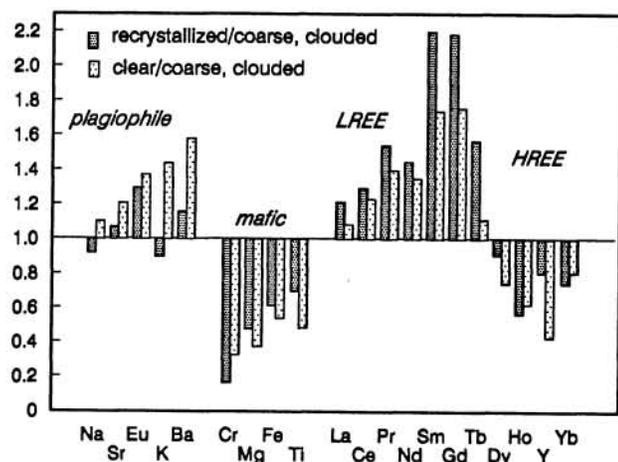


Figure 1. Concentrations of minor and trace-elements in recrystallized and inclusion-free plagioclase normalized to coarse, inclusion-bearing, relict-igneous plagioclase. Concentrations of HREE are very low and were smoothed prior to the normalization. The trends are roughly the same for recrystallized vs. inclusion-free regions.

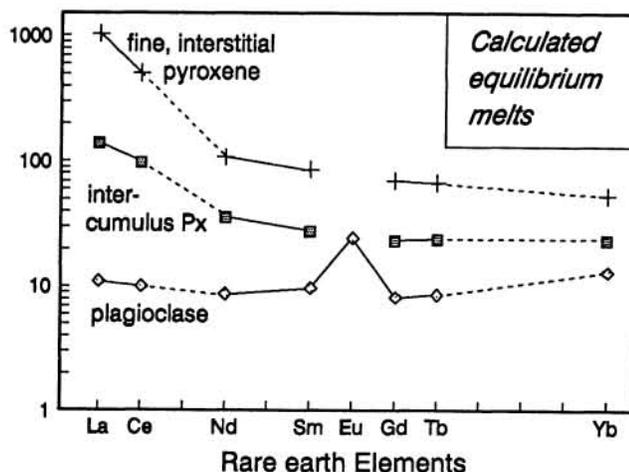


Figure 2. Chondrite-normalized concentrations of REE in melts calculated to be in equilibrium with coarse, relict igneous plagioclase, coarse, intercumulus pyroxene, and fine-grained interstitial pyroxene. Distribution coefficients for pyroxene were calculated according to [14] and those for plagioclase are from [4]. We do not propose that a melt such as the upper one actually existed.