FE - MG DIFFUSION IN OLIVINE: A COOLING RATE INDICATOR
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Various experimental approaches have been employed in order to estimate both the relative and absolute cooling rates of lunar rocks. Controlled crystallization rate studies conducted by Lofgren et al. (1) and Walker et al. (2) have shown that variations in cooling rate can account for much of the textural and mineralogical variations in Mare basalts. However, this type of approach has several uncertainties built into it (3). The kinetics of the reequilibration of elemental partitionings, e.g. Zr between ilmenite and ulvöspinel (4), have been modelled so that absolute cooling rates can be estimated for certain lunar rocks. However, sufficient concentrations of the pertinent minor elements must be present for precise analyses to be made.

Of the major igneous rock-forming minerals (e.g. pyroxene, plagioclase, olivine), the complications of the phase equilibria and kinetics within the pyroxene and plagioclase systems are well known. The relatively simpler chemistry of olivines should therefore lend itself to geothermometry.

The present study was directed at the olivine system, in particular, the diffusion of Fe$^{2+}$ and Mg$^{2+}$ within compositionally zoned olivines. Partitioning of Fe$^{2+}$ and Mg$^{2+}$ between olivine and orthopyroxene has been shown by Medalis (5) to not be significantly temperature dependent over the temperature range 900 - 1300°C. Hence, diffusion across olivine-pyroxene grain boundaries can be assumed to be minimal, and the reequilibration of zoned olivines is largely one of response to prolonged cooling. Thus, a given primary compositional gradient will tend to decrease (i.e. "smooth out") with time at slow cooling rates.

EXPERIMENTAL PROCEDURE: Isothermal heating experiments were conducted to test the validity of interdiffusion coefficient determinations of Misner (6) for Fe$^{2+}$ and Mg$^{2+}$ diffusion using natural specimens of forsterite (Fo$_{92}$) and fayalite (Fa$_{100}$). Chips from these phases were polished (to 1µm), sawed into 3mm cubes, and joined together across the cleaned, polished surfaces by wrapping them with Ag-Pd$_{30}$ foil, in turn wrapped with Pt wire. The reactants, Fo$_{92}$ and Fa$_{100}$, therefore, defined diffusion couples for this experiment.

Two sets of experiments were designed to evaluate any possible grain boundary effects upon diffusion of cation species between phases in the couple: 1) A sample was simply sealed in an evacuated silica tube, duplicating the technique used by Misner (6); and 2) a free-floating silica rod, exerting a load...
of \approx 5 \text{ lbs/in}^2 \) on the sample ("hot pressing"), was sealed in an evacuated silica tube. The loaded capsule was designed to minimize grain boundary effects upon cation diffusion rates.

Both charges were heated at \(1000^\circ\text{C}\) for 311 hours, quenched, mounted in epoxy and a polished surface prepared such that the compositional profiles, measured with an automated, MAC 400S electron microprobe, were those across the center of the contact surface between forsterite and fayalite.

In spite of some complications, associated with noticeable breakdown of fayalite to magnetite + quartz, compositional profiles away from the grain boundary into \(\text{Fo}_{92}\) duplicated those obtained by Misner (6). Also, no difference between profiles in the unloaded and loaded samples could be detected. As a result, the interdiffusion coefficients for \(\text{Fe}^{2+}\) and \(\text{Mg}^{2+}\) determined by Misner from the Boltzmann-Matano solution (7) were validated.

**KINETIC MODEL:** The minimum cooling rate necessary for the production of compositional zoning in an olivine grain during cooling has been determined. At equilibrium, there are no concentration gradients in the forsterite-fayalite system, which exhibits complete solid solubility. The extent to which a grain approaches equilibrium during cooling depends upon the as-solidified concentration profile, as well as upon the thermal history (cooling rate).

Forsterite concentration profiles have been calculated using the diffusion data of Misner (6), who showed that the interdiffusion coefficient, \(D\), is a function of both temperature and composition. Lacking information about the as-solidified concentration profile, it has been assumed that at the solidus, there was a step-function in the forsterite concentration within the grain. That is, there were no initial compositional gradients in a diffusion couple defined by a Fo-rich core and Fa-rich rim. This assumption directs attention to the minimum cooling rates associated with the preservation of a given gradient since a system with any finite gradient and the initial concentration profile would equilibrate more rapidly than one with a step-function profile. It has also been assumed that there is no flux either across the center of the grain or across the grain boundary.

The equation solved is the one-dimensional equation in which the diffusion coefficient is a function of composition and therefore position. The diffusion coefficient is also a function of temperature which is, itself, a function of time.

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D(C(x), T(t)) \frac{\partial C}{\partial x} \right)
\]

where \(C\) is the mole fraction of magnesium, \(x\) is distance, \(T\) is temperature, and \(t\) is time, and the expression of Eqn. (2) was given by Misner (6).

The initial conditions are:

\[
0 < x < x_1 \quad C(x, 0) = C_1; \quad x_1 < x < x_1 + x_2 \quad C(x, 0) = C_2
\]

These conditions can be changed to include primary zonations during solidification if the distribution coefficient is known as a function of temperature. Such modified conditions can readily be handled by the program used to solve
FE - MG DIFFUSION IN OLIVINE

Taylor et al.

the diffusion problem. Equation (1) has been solved by replacing it with its finite difference analog, applying the boundary conditions, and solving the set of simultaneous equations found by the Thomas tridiagonal method. Due to the non-linearity of the equation, it was necessary to iterate the procedure to approach the correct solution. Concentration profiles were calculated for several cooling rates and sets of initial conditions. The values of \( X_1, X_2, C_1 \) and \( C_2 \) indicate possible solidus conditions in the lunar samples under investigation. These parameters could not be changed independently. Mass balance and size of the grain had to be maintained.

For cooling rates larger than about 5°C/day, there was little change in the forsterite profile at temperatures below about 750°C. Cooling rates smaller than about 1°C/day allowed diffusion to be effective at lower temperatures. Since the diffusion coefficient depends on concentration, each case (i.e. olivine grain) must be considered separately. The absolute concentrations, as well as the concentration gradient, are important parameters for specifying the minimum cooling rates.

APPLICATION: Two lunar samples were chosen (15555, 147 and 12002, 02) for which cooling rates have been experimentally determined (2, 3). The choice of these samples provides a means of comparison between our theoretical approach and the empirical studies conducted by experimentalists. These lunar specimens are compositionally and texturally different, and different cooling rate estimates should be obtained from compositional gradients in the olivines.

The applicability of the kinetic model is dependent upon a well-defined choice of phases for which a diffusion couple can be described. In the case of lunar samples 15555 and 12002, this entailed finding and measuring the compositions of olivines which had compositionally different cores and rims. Compositional profiles were determined on selected olivines (Figs. 1 & 2) by EMP.

The calculated concentration profile after cooling was compared to the measured profile. The results indicate a minimum cooling rate for 12002 of about 20°C/day (0.8°C/hr) and a minimum cooling rate for 15555 of about 10°C/day (0.4°C/hr). These cooling rates compare favorably with those estimated, experimentally, by Walker et al. (< 1°C/hr) and Bianco and Taylor (slightly less than 1°C/hr), respectively. The cooling rate estimates for 15555 from this investigation are lower than for 12002 - a reasonable result since 15555 is a coarser-grained, equigranular, more siliceous (quartz-normative basalt composition) lunar sample than the porphyritic, 12002 (an olivine-normative basalt composition).

The kinetic modelling technique used in this study has a general applicability provided the basic criteria for its use are met. For the lunar samples 15555 and 12002, it has been demonstrated that this technique gives reasonable minimum cooling rate estimates slightly less than but similar to those obtained from crystallization studies.

PRIMARY CHEMICAL COMPONENTS IN THE HIGHLAND CRUST; S. R. Taylor, Research School of Earth Sciences, The Australian National University, P. O. Box 4, Canberra A.C.T. 2600, Australia, and A. E. Bence, Dept. of Earth and Space Sciences, State Univ. of New York, Stony Brook, N. Y. 11794.

The chemical composition of the highlands crust has proven difficult to model through conventional terrestrial differentiation processes. Several important observations are pertinent. First, the highland lithologies show a spectrum of compositions from anorthosites to norites to dunites with distinctive chemical characteristics. The Apollo Soil Survey identified several preferred major element groupings among the glass compositions, which were identified with the following rock types: anorthosite, gabbroic anorthosite, highland basalt (or anorthositic gabbro) and three types of Fra Mauro basalt [low, medium, and high K]. Frequency estimates and mixing models indicate that low-K Fra Mauro basalt and highland basalt are the two most abundant compositions and many breccia compositions can be interpreted principally as a consequence of mixing of these two types. The parallel nature of the REE patterns indicates that mixing is an important process in producing the observed spectrum of compositions.

The close proximity of the average compositions of the low-K Fra Mauro and medium-K Fra Mauro basalts to peritectic points on the SiO₂-01-An diagram (1) indicate a crystal-liquid control at low pressures on these compositions at some stage in their evolution. Two possibilities exist. Small degrees of partial melting of an Mg-rich component [of "whole moon composition"] will generate the high Mg numbers required for some of the observed compositions (2). High concentrations of REE are derived from the mixing of a KREEP component. An alternative model produces Fra Mauro basalts by partial melting of "average highland" composition (approximated by Highland basalt) produced by mixing of the three initial components. Partial melting at about the 30% level is required to obtain the high Mg/Mg+Fe ratios. The high concentrations of REE are obtained from the "KREEP" component.

Another observation is that the Mg content of olivine increases with increasing Na content of coexisting plagioclase (3). This important effect is the reverse of that observed in fractional crystallization in natural or experimental systems. Average highland crustal compositions show a high content of MgO (8.6%) and Cr (600 ppm) with very low indigenous Ni contents, high Mg/Mg+Fe number (0.70), coupled with average REE contents about 20-30 times chondritic values. The HKFM samples show extreme enrichments up to 500 X chondritic values. Some of these characteristics, such as the high REE contents, are characteristic of extreme degrees of fractional crystallization. Others, such as the high Mg and Cr contents, indicate a primitive unfractuated composition. The high abundance of plagioclase indicates the presence of a high Ca-Al parental liquid.

These characteristics are not readily explicable by a single conventional petrologic process. The high degree of brecciation and mixing exhibited by the breccias, together with the presence of impact melt rocks (e.g., 14310, 68535) adds to the obscurity of the primary processes responsible for the generation of the highland crust.

Although these processes have destroyed most evidence of primary textural features, the chemistry does not appear to have been altered to a degree that
Chemical Components in Highland Crust

Taylor, S. R. et al.

precludes recognition of highland crustal genesis. It is the purpose of this study to attempt to unravel the chemical composition observed in the breccias and interpret them in terms of the three components for the highland crust proposed in the Taylor-Jakes-Bence models.

The Plagioclase Component

The plagioclase component is the only one of the three components for which primary crystalline rocks are recognized, with any degree of certainty, in the returned samples. These are the anorthositic rocks which have been recognized at all sites including the mare soils. They are characterized by high Ca, Al, Sr, and Eu, low incompatibles, Mg, Cr, etc., and high Fe/Fe+Mg ratios. Those samples most closely approaching the ideal end-member consist of > 95% modal calcic plagioclase (An92-96) and less than 5% ferromagnesians with generally high, but quite variable, ratios of Fe/Fe+Mg. Its origin as an ancient component formed early in the Moon's evolutionary history (4.4-4.6AE) is suggested by extremely low 87Sr/86Sr. Excavation ages in excess of 4.0AE are indicated by 40Ar/39Ar incremental heating ages. The coexistence of iron-rich ferromagnesians with highly calcic plagioclase is consistent with the formation of the highland crust by the crystallization and flotation of plagioclase in a sodic-deficient magma ocean during an advanced stage of crystallization following the extensive removal of high-Mg ferromagnesian phases (primarily olivine) through crystal settling.

The KREEP Component

The KREEP component is characterized by very high concentrations of K, REE, P, other incompatible elements, and iron. It is low in Mg, Ca, Al, Sr, Eu, Ni, Cr, etc. Mechanisms for the origin of a rock with a high KREEP component are model dependent but the elements that characterize it can be concentrated either in fractional crystallization or partial melting sequences. In the Taylor-Jakes model, this component is concentrated in the late-stage residual liquids at the base of the crust. We purposefully refrain from the designation of KREEP as a rock type to avoid the semantic entanglements of KREEP basalt, KREEPless KREEP, with the low-, medium-, and high-K Fra Mauro basalts, etc. The KREEP component is present in varying proportions in the majority of the highland breccias and soils.

The Mg-Rich Component

The Mg-rich component is an enigma for most lunar evolutionary models—especially those involving extensive early melting followed by fractional crystallization. This component is characterized by high ratios of Mg/Mg+Fe, high Cr, Ni, etc., and is depleted in the incompatible components. Large rocks with these characteristics include 72415-417 (dunite), 76535 (troctolite), and 67435 (pink spinel troctolite). The Apollo 17 soil fraction contains another lithologic component with these characteristics—the spinel cataclasites (4, 5, 6). Geological processes that could account for these elemental relationships include: (a) crystal cumulation from a melt, (b) residuum in a partial melting process, (c) an ultramafic magma generated by extensive partial melting in the deep lunar interior, (d) a chilled crustal component of whole moon composition, or (e) late infall of planetesimals of whole moon composition. Combinations of these processes are quite possible. The very old Rb-Sr age reported for the dunite 72415-417 (7), if interpreted correctly, suggests that, for this particular rock, processes a, b, and c are unlikely. The 4.2AE 40Ar/39Ar...
Chemical Components in Highland Crust

Taylor, S. R. et al.

The plateau age reported for the spinel troctolite (8) is most likely an excavation age and does not constrain the possibilities.

Studies of the Apollo 15, 16 and 17 highland soils, as well as the orbital γ-ray experiments, indicate that these three components are heterogeneously distributed in the lunar highland crust. The plagioclase component indicated both by the proportions of the anorthositic component in the soils and by the Al2O3 content of the soils differs markedly between the 16 and 17 sites.

**Apollo 16 and 17 Highlands Samples**

A suite of 18 petrographically described 2-4 mm soil fragments have been analyzed for trace elements. The data for the REE are shown in Fig. 1. Several features may be noted. The REE patterns are subparallel and the La/Yb ratios are uniform. There is slight evidence of a positive Ce anomaly, but this may be within the precision limits of the data. The range in REE abundances in these samples covers almost the entire range reported for previous highland samples. The samples with highest REE are similar to medium-K Fra Mauro basalts. There are several low-K Fra Mauro basalts. With decreasing REE abundances, examples of gabbroic anorthosites and anorthositic gabbros appear. As the plagioclase component increases, the Eu anomaly becomes positive. Finally, examples of true anorthosites with large positive Eu anomalies appear. These are the first reported anorthosites from the Apollo 17 site.

**References**


![Fig. 1](image-url.com)