ABSOLUTE COOLING RATES OF LUNAR ROCKS BASED ON THE KINETICS OF ZR DIFFUSION IN OPAQUE OXIDES: APPLICATIONS TO APOLLO 15 ROCKS FROM ELBOW CRATER


An important query about the lunar rocks is: what are the absolute cooling rates of these rocks? Our approach to this problem is based on the study of the kinetics of Zr partitioning between coexisting ilmenite and ulvöspinel in the lunar rocks. Since the partitioning is solely a function of temperature, as the experimental investigation of Taylor & McCallister (1) has shown, and was found to be relatively constant for a given lunar sample, Taylor et al. (2) used it as a geothermometer with which differences in cooling rates of mineralogically and texturally similar rocks could be discerned qualitatively.

In order to apply the partitioning data for quantitative estimation of cooling rates, kinetic experiments were performed by Taylor & Williams (3) to determine the rate at which a Zr partitioning formed at some high temperature will reequilibrate upon cooling. Figure 1 shows the results of the reequilibration runs at 10000°, 9000° and 8000°C, starting with an 11000°C Zr-saturated charge (1.1 wt.% Zr) and using the Zr content of the ilmenite as the indicator of the reequilibration process.

Although lunar samples are found to have characteristic Zr(iil)/Zr(usp) ratios, the partitioning data obtained from isothermal laboratory experiments cannot be applied directly to these rocks because thermal histories of lunar rocks are nonisothermal, and they cannot be expected to have attained equilibrium. However, by combining the experimentally determined partitioning data with the measured concentration ratio in a lunar rock, it is possible to estimate, with simplifying assumptions, the cooling rate.

The salient features of the partitioning process between two coexisting phases (diffusivities \(D_1\) & \(D_2\)) should be reasonably well elucidated by solution of the diffusion problem in a composite sphere with phase 2 forming a concentric shell uniformly around a core of phase 1. Solution to this problem is presently being addressed both analytically and numerically. For the present, a more approximate analysis which seems capable of providing at least order-of-magnitude estimates is obtained as follows:

1) Approximate values of \(D_1(T)\) and \(D_2(T)\) for a particular temperature \(T\) are obtained from isothermal experiments by assuming that a particle of diameter \(\chi_0\) reaches 1/e of its equilibrium solute concentration in time \(t_0 = \chi^2/2D_1(T)\).

2) An Arrhenius form, \(D_1(T) = D_0 \exp(-A/T)\), is assumed for the lower diffusivity which is likely to be the controlling factor in determining the partitioning ratio at \(T\). From the data in Figure 1, one obtains \(D_0 = 1.6 \times 10^{-5}\) cm²/sec and \(A = 2.1 \times 10^4\) K.

3) The characteristic diffusion distance \((\chi_1)\) in time \(t\) is given by \(\chi_1^2 = \int_0^t D(t')dt'\). Assuming a linear cooling rate, \(T = T_0 - \Delta(T<T_0/a)\), where \(T_0\) is the characteristic temperature in °K (based on isothermal experiments) of
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Fig. 2  Per Cent Zr in Uivspinei

The concentration ratio measured in the lunar sample (nonisothermal process) and \( t \) is the final time taken to reach 0 K so that \( t = T_0/a \). The cooling rate, \( a \) (°K/sec), is given by the relation:

\[
x_1^2 = \int_0^{T_0} \frac{D_a}{a} \left[ \frac{T(\tau)}{T_0} \right] \text{d}t = \frac{D_a}{a} \left[ \frac{T(\tau)}{T_0} \right]^{T_0} \exp \left( -\frac{A}{T_0} \right) + E_i \left( -\frac{A}{T_0} \right)
\]

Typically, \( A/T_0 = 20 \), so an asymptotic form can be used for the exponential integral function, \( E_i \). The equation then reduces to

\[
x_1^2 \approx \left( \frac{D_a}{a} \right) \left( y - 2e^{-y} \right)
\]

where \( y = A/T_0 \), and is accurate to 10%. It can be assumed that for thermal history of lunar rocks below \( T_0 \), \( x_1 \) is the "effective" size of the ilmenite-ulvöspinel composite. We can now solve for \( a \) using discrete values of \( x_1 \). Taking \( x_1 = 15 \) as a typical case for the Apollo 15 rocks in question, we obtain:

\[
\log a = -2.7 + 2 \log T_0 - 9120/T_0
\]

where \( T_0 \) is the characteristic temperature obtained from the Zr data and \( a \), the cooling rate, is in °K/sec.

4) The cooling rates estimated using equation (1) for characteristic temperatures of 110°, 1000° and 900°C are 75°, 20° and 4°C/day, respectively.

APPLICATIONS  Six rocks collected from Station 1 at Elbow Crater were selected for study. Samples 15065, 15075, 15076 and 15085 are coarse-grained gabbros; 15082 and 15086 are fine-grained, well-consolidated breccias. The Zr contents of coexisting ilmenite and ulvöspinel grains were determined by EMP analyses and the results are shown in the composite diagram in Figure 2.

Based on the isothermal partitioning data of Taylor & McCallister (1), an equation relating the partitioning ratio and \( T_0 \), the characteristic temperature, can be given:

\[
\frac{0.1350 \times 10^4}{1.3787 - \log r} = T_0 (°K)
\]

where \( r = Zr(\text{il})/Zr(\text{usp}) \). Table 1 shows a compilation for each sample of: the mean Zr ratio \( \bar{r} \), \( \sigma_1 \), \( T_0 \) calculated from equation (2) and \( a \), the cooling rate, calculated from equation (1).

Table 1. Cooling Rates of Elbow Crater Rocks

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \bar{r} )</th>
<th>( \sigma_1 )</th>
<th>( T_0 ) (°C)</th>
<th>( a ) (°C/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15065</td>
<td>1.70</td>
<td>0.16</td>
<td>903</td>
<td>4</td>
</tr>
<tr>
<td>15075</td>
<td>1.76</td>
<td>0.15</td>
<td>918</td>
<td>5</td>
</tr>
<tr>
<td>15076</td>
<td>2.58</td>
<td>0.24</td>
<td>1122</td>
<td>95</td>
</tr>
<tr>
<td>15082</td>
<td>1.91</td>
<td>0.31</td>
<td>957</td>
<td>10</td>
</tr>
<tr>
<td>15085</td>
<td>1.93</td>
<td>0.22</td>
<td>962</td>
<td>11</td>
</tr>
<tr>
<td>15086</td>
<td>2.16</td>
<td>0.55</td>
<td>1020</td>
<td>25</td>
</tr>
</tbody>
</table>

The much greater cooling rate for 15076 is anomalous in view of the similar coarse-grained textures, with large (2-4 mm) prismatic pyroxenes, in the rest of the gabbros that would normally indicate similar cooling rates. One possible explanation is a two-stage crystallization of 15076 -- of coarse pyroxenes at depth, much...
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of which were carried in suspension onto the lunar surface and preserved through crystallization under relatively rapid cooling conditions. The coarse grained texture of the other gabbros could be entirely the result of slow cooling within the interior of the flow(s) in which they formed.

The composition of the titanian chromite and chromian ulvöspinel phases in Figure 3 seem to support this idea. The lack of chromite in 15076, compared with the rest of the gabbros, may well be due to its crystallization and gravitational settling at depth.

The FeNi metal grains in the gabbros (Fig. 4) are characterized by high Co (>1.0%) uniformly very low P (<0.03%) and a significant spread in Ni between the different samples, up to a maximum of 58.2% in 15085. The Ni-Co plot (Fig. 5) of metals in breccias 15082 and 15086 shows a scatter that suggests disequilibrium. This is in agreement with the wide variance in their Zr(II)/Zr(usp) ratios (Fig. 1 & Table 1), not unlikely situations for lunar breccias.

In conclusion, we have demonstrated the development and use of the Zr partitioning between coexisting ilmenite and ulvöspinel as an indicator of absolute cooling rates. This study and the data presented should find numerous applications in the study of lunar rocks.

REFERENCES