Rhönite in Luna 24 pyroxenes: First find from the Moon, and implications for volatiles in planetary magmas

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Abstract: Grains of rhönite have been discovered in magmatic inclusions in augite grains of the lunar regolith from Mare Crisium, returned to Earth by the Russian Luna 24 spacecraft. These rhönite grains are up to 8 micrometers long, pleochroic from tan to dark brown, and associated with ulvöspinel and silica-rich glass. Electron microprobe analysis gives a composition near end-member ferroan rhönite: (Ca$_{1.9}$Mn$_{0.0}$Na$_{0.1}$)(Fe$^{2+}$$_{4.5}$Mg$_{0.1}$Al$_{0.3}$Cr$_{0.0}$)Ti$_{1.0}$(Si$_{4.0}$Al$_{2.0}$)O$_{20}$. The Raman spectrum of these grains is like those of terrestrial rhönites, and distinct from titanian amphiboles. Compositionally, rhönite plus silica plus water or halogens (F, Cl) is equivalent to titanian amphibole plus pyroxene, so the presence of rhönite in lunar basaltic rock is consistent with the known low abundance of volatiles in the Moon. When calibrated, mineral reactions involving rhönite and titanian amphibole may provide quantitative constraints on fugacities of water, F, and Cl in basaltic magmas from the Moon and other planetary bodies.

Key Words:
LUNAR AND PLANETARY STUDIES: mare basalt, Luna 24
IGNEOUS PETROLOGY: moon, basalt, melt inclusion.
PETROGRAPHY: rhönite, melt inclusion.
Compared to the Earth, the Moon is strongly depleted in volatiles, and its interior is generally considered anhydrous (e.g., Heiken et al., 1991; Spudis, 2001). The internal volatile content of the Moon remains a critical control on its petrogenesis, and is being re-assessed in light of current interest in the Moon (e.g., Saal et al., 2007). One tool in this assessment is investigation of minerals that could contain volatile elements.

Amphibole is one such volatile-bearing mineral, as it can contain H$_2$O (as OH), F, and Cl. Amphiboles were reported in several lunar rocks (Gay et al., 1971; Mason et al., 1972), but these finds have not been verified. A report of amphibole in Luna 24 regolith olivine grains (Laz’ko et al., 1980) was the impetus for this study. I have not found amphibole, but have found the first lunar occurrence of the anhydrous mineral rhönite (Treiman, 2007), which has a composition similar to that of kaersutite amphibole. The rhönite is found in magmatic inclusions in pyroxene – the same setting for kaersutite amphibole in the shergottite Martian basalts (Treiman, 1985, 1997, 1998).

SAMPLES AND METHODS

Grain mount thin sections of Luna 24 regolith were examined optically at the ARES thin section library, Building 31, Johnson Space Center. Selected thin sections were borrowed for further analysis via a request to the CAPTEM lunar allocation subcommittee. The largest rhönite grain is in thin section 24105,15 – fortunately, it is exposed at the surface of the thin section. The allocated sections were examined optically at the Lunar and Planetary Institute, and then subjected to Raman and electron microprobe analyses at JSC.

Spot micro-Raman analyses were taken with the Horiba HR-LabRam Raman microscope at ARES (JSC) using red He-Ne laser light. We obtained several Raman spectra of the rhönite grain in 24105,15, and of the adjacent surrounding pyroxene, siliceous glass, and ulvöspinel. Raman scans were from 300 cm$^{-1}$ to 1100 cm$^{-1}$.

Chemical analyses are by electron microprobe (EMP), using the Cameca SX-100 at ARES, 15 kV accelerating potential, beam current 10 na, beam diameter 1 µm. Most elements were standardized against synthetic oxides. Other standards were: orthoclase for K; oligoclase for Na, fluorite for F, and tugtupite for Cl. Data were reduced in the Cameca PAP routine.
RESULTS

The L24 regolith includes mineral fragments, rock fragments, and glasses (Coish and Taylor, 1978). Most mineral fragments are pyroxenes and olivine, which are interpreted as fragments of crystalline basalts and gabbros emplaced in the Mare Crisium basin. Many of these pyroxene grains contain glassy inclusions (with or without crystalline phases) that are inferred to be melt inclusions – remnant of magma trapped in crystals as they grew (Roedder and Weiblen, 1978).

Melt inclusion in many pyroxene grains contain tabular brown crystals – approximately 20 such grains have been found in the three investigated grain-mount sections (L24105,15; L24149,41; L24174,64). These grains may have been noted before by Roedder and Weiblen (1978) as “… roughly tabular, transparent, yellow-brown daughter crystal[s], presumably a spinel….” The two largest brown crystals are ~10 µmeters in length, and one in L24105,15 is cut by the thin section surface (Figure 1); all optical and chemical data are for that grain. The brown grains are optically anisotropic, length-slow, pleochroic from pale greenish brown to reddish brown (in the slow direction), and with inclined extinction ($Z\wedge c = 58^\circ$ for the grain of Figure 1). These optical properties are not consistent with previously reported lunar minerals, but are consistent with kaersutite amphibole (as is found in similar magmatic inclusions in Martian meteorite pyroxenes; Treiman, 1985) and with rhönite (Anthony et al., 2003). Other minerals in the melt inclusions are ulvöspinel, silica-rich glass (Table 1), and Fe-sulfide (not analyzed). Iron metal was not noted.

Fortuitously, the largest grain is exposed at the surface of the thin section, and is big enough (~ 8 µmeter long) for multiple chemical analyses by EMP. The EMP analyses are all within analytical uncertainty of each other, so an average is given in Table 1. The brown grain contains ~ 25% SiO₂ – far too little silica to be kaersutite or other amphibole, but consistent with the mineral rhönite (Söllner, 1907). The EMP chemical analysis normalizes properly for rhönite stoichiometry as $(Ca_{1.88}Mn_{0.02}Na_{0.09})(Fe^{2+}_{4.56}Mg_{0.12}Al_{0.31}Cr_{0.01})Ti_{0.99}(Si_{4.02}Al_{1.98})O_{20}$, which is close to the ideal formula: $Ca_2M^{2+}_5Ti(Al_2Si_4)O_20$. Ferric iron is not required for charge balance in the L24 rhönite; in fact, its chemical normalization has a slight excess of cation charge, which
could suggest the presence of some Ti$^{3+}$ (as reported in some asteroidal rhönites: e.g., Nazarov et al., 2000).

The grain’s identity as rhönite is confirmed by its Raman scattering spectrum, Figure 2. Its Raman spectrum shares major scattering peaks with a literature rhönite spectrum, a grain from the Eifel district, Germany (Downs, 2006). Specifically, both rhönite spectra have Raman scattering peaks near 540, 670, 720, 840, and 980 cm$^{-1}$ (Fig. 2). Differences between the rhönite spectra are ascribed to their widely differing chemical compositions (ferric absent for L24; ferric rich for Eifel; Rondorf, 1989). Raman spectra of kaersutite amphiboles are completely distinct from those of rhönite (Fig. 2).

**DISCUSSION**

**Rhönite**

Rhönite is a mineral in the aenigmatite group of branched single-chain silicates (Cosca et al., 1988; Kunzmann, 1999), which accommodate a wide range of elemental substitution. Rhönite is a widespread but uncommon accessory mineral in terrestrial basaltic rocks, particularly silica-undersaturated varieties, and are commonly rich in ferric iron. In basalts, rhönite occurs as microphenocrysts, and as larger grains in late-stage differentiates (e.g., Johnston and Stout, 1985; Cosca et al., 1988; Grapes et al., 2003; Nédli and Tóth, 2003; Cosario et al., 2007). Rhönite is also found occasionally in magmatic inclusions, as reported here for the Luna 24 sample (Kothay et al., 2003; Jannot et al., 2005; Timina et al., 2006). Rhönite also is present among the breakdown products (in ‘opacite’ rims) of kaersutite and related amphiboles (O’Connor et al., 1996; Monkawa et al., 2003; Grapes et al., 2003; Kovács et al., 2004; Alletti et al., 2005; Corsaro et al., 2007).

Rhönite and related minerals are present in a few extraterrestrial samples, notably from calcium-aluminum-rich inclusions (CAIs) in carbonaceous chondrites (e.g., Fuchs, 1971; Simon et al., 1999, Nazarov et al., 2000). Aenigmatite has been found in chondritic breccias (Ivanov et al., 2003; Bischoff et al., 2006), and its original source may also have been CAIs or related material. Rhönite might also be expected in angrite meteorites, asteroidal basalts rich in calcium and aluminum; it has recently been found in one (NWA 4950; Kuehner and Irving, 2007) and has been produced in laboratory experiments on angrite compositions (Lofgren et al., 2006). A sin-
gular occurrence of rhönite in a ureilite meteorite is as small euhedra in an Al-rich glassy en- 
clave, which could have affinities to the angrite basalts (Warren et al., 2006).

Geologic Setting

The L24 rhönite grains are all in multi-phase inclusions in augite pyroxenes. Many of the 
augite grains are distinctly zoned, with inclusion-rich pink-colored zones and inclusion-free pale 
zone. All pink-colored pyroxenes contain multiphase inclusions, but not all such pyroxenes con- 
tain rhönite-bearing inclusions. The proxene adjacent to the rhönite grain of Figure 1 is ferrohe- 
denberge (Wo26En06Fs68) with a lunar Fe/Mn ratio (Table 1; Papike et al., 2003), and is rich in 
Al and Ti and poor in Cr. Formula normalizations show slight charge excesses, which could in- 
dicate that some Ti in the augite is Ti$^{3+}$ rather than Ti$^{4+}$. Pyroxenes like those hosting the rhönite- 
bearing inclusions are common in the Luna 24 regolith in fragments of very-low-titanium (VLT) 
basalt and as isolated grains ascribed to VLT basalt or VLT-derived ferro-gabbro (e.g., Bence et 
al., 1977; Coish and Taylor, 1978; Papike and Vaniman, 1978; Roedder and Weiblen, 1978; Lu 
et al., 1989).

Significance

This is the first report of rhönite from a lunar sample. Beyond being a mineralogical odd- 
ity, this find shows that the returned lunar samples have not been ‘mined out’ scientifically – 
much remains to be discovered and learned with modern techniques and new minds!

The petrologic significance of this rhönite occurrence is its implications for volatiles in 
lunar magmas. Lunar magmas have been considered essentially anhydrous (e.g., Heiken et al., 
1991; Spudis, 2001), but some lunar basalt glasses contain tens of ppm $\text{H}_2\text{O}$ (Saal et al., 2007) 
and some reports of amphiboles suggested abundant water or other volatiles (Gay et al., 1971; 
Mason et al., 1972). The find here of rhönite suggests that the Luna 24 basalts were quite poor in 
volatile, because rhönite is a common dehydration/devolatilization product of titanian amphi- 
bole (O’Connor et al., 1996; Monkawa et al., 2003; Grapes et al., 2003; Alleotti et al., 2005; Co- 
sario et al., 2007). Production of rhönite from titanian amphibole can be modeled by the reaction:

$$\text{Ca}_2(\text{M}^{2+}_4\text{Ti})(\text{Al}_2\text{Si}_6)\text{O}_{22}(\text{OH})_2 + \text{M}^{2+}\text{SiO}_3 = \text{Ca}_2\text{M}^{2+}_5\text{Ti}(\text{Al}_2\text{Si}_4)\text{O}_{20} + 3 \text{SiO}_2 + \text{H}_2\text{O}$$

titano-tschermakite pyroxene rhönite
where $M^{2+}$ represents $\text{Fe}^{2+}$ and $\text{Mg}^{2+}$, titano-tschermakite is a model for kaersutitic amphibole, and the silica and water might reside in silicate melt (Table 1). Comparable reactions can be written for fluor- and chlor-amphiboles, with the implication that rhönite should form only in volatile-poor systems. Unfortunately, the locations these and other reactions involving rhönite are poorly known (e.g., Boivin, 1980; Cosca et al., 1988; Kunzmann, 1999), so ‘volatile-poor’ cannot yet be quantified.

On the other side of this equation, kaersutite amphibole (Ti-rich) is found in magmatic inclusions in many Martian basaltic meteorites (Floran et al., 1978; Treiman, 1985, 1997, 1998; Ikeda, 1997, 1998; Mikouchi and Miyamoto, 2000; Sautter et al., 2006). These kaersutites have been used to suggest that the Martian basalts contained abundant water (Johnson et al., 1991; McSween and Harvey, 1993); however, these amphiboles are oxy-kaersutites and contain nearly no OH (Watson et al., 1994). The oxy-kaersutite in the Martian meteorites could have formed by dehydrogenation/oxidation of hydrous kaersutite, or could be a primary igneous composition (Popp et al., 1995; Mysen et al., 1998; McCubbin et al., 2006). If the latter, it is not clear why oxy-kaersutite might form instead of a $\text{Fe}^{3+}$-bearing rhönite. So, knowing the relative stabilities of titanian amphiboles and rhönite-group minerals would provide important constraints on the volatile contents of lunar, Martian, and some terrestrial magmas (Cosca et al., 1988).

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Figure 1. The largest L24 rhönite grain, in a magmatic inclusion within a grain of augite; top images are plane light, rotated 90° to each other, to show pleochroism. Rhönite is brown, ulvöspinel is opaque, colorless material between rhönite and augite is silica-rich glass. Bottom image is crossed polars with host pyroxene near extinction, showing the birefringence of the rhönite.
Figure 2. Raman scattering spectrum of the L 24 rhönite grain (Fig. 1), compared with spectra of a terrestrial rhönite and a terrestrial kaersutite amphibole (RRUF spectra 060316 & 070128 respectively, unoriented grains, 785 nm excitation; Downs, 2006). Intensity axis scaled arbitrarily for presentation.
Table 1. EMP chemical compositions of rhönite and adjacent materials in L24105,15.

<table>
<thead>
<tr>
<th></th>
<th>rhönite average</th>
<th>pyroxene</th>
<th>ulvöspinel</th>
<th>glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>27.40</td>
<td>45.81</td>
<td>0.07</td>
<td>66.9</td>
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<tr>
<td>TiO$_2$</td>
<td>8.99</td>
<td>1.17</td>
<td>30.90</td>
<td>0.10</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>13.27</td>
<td>3.22</td>
<td>5.12</td>
<td>14.0</td>
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<tr>
<td>Cr$_2$O$_3$</td>
<td>0.07</td>
<td>0.05</td>
<td>0.56</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>37.21</td>
<td>37.04</td>
<td>60.35</td>
<td>2.78</td>
</tr>
<tr>
<td>MnO</td>
<td>0.16</td>
<td>0.46</td>
<td>0.35</td>
<td>0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>0.56</td>
<td>2.00</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>CaO</td>
<td>11.96</td>
<td>11.01</td>
<td>0.32</td>
<td>8.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.36</td>
<td>0.06</td>
<td>0.00</td>
<td>0.87</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>1.85</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.05</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>F</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>sum</td>
<td>99.99</td>
<td>100.83</td>
<td>97.94</td>
<td>94.9</td>
</tr>
</tbody>
</table>

Fe/Mg 37 10 374 -
Fe/Mn 237 79 170 -

Rhönite values are average of three individual analyses, all within analytical uncertainty of each other. Low total for ulvöspinel reflects a small proportion of ferric iron. Low total for glass reflects use of non-ideal standards, and should not be construed to indicate an abundance of volatiles.