Review of terrestrial laihunite and stilpnomelane analogs, identified as potential secondary alteration phases in MIL 03346. K. E. Kuebler, A. Wang, and Brad Jolliff Dept. of Earth & Planetary Sciences and the McDonnell Center for Space Sciences, Campus Box 1169, One Brookings Drive, Washington University, St. Louis, MO 63130, kuebler@levee.wustl.edu

Introduction: [1] indicated that laihunite might be present in MIL and [2] identified stilpnomelane and laihunite as secondary alteration phases in MIL 03346. These identifications are rather unusual so we present our supporting evidence here: Raman and XRD spectra for the stilpnomelane, Raman spectra for the laihunite, and EMP data for both.

The laihunite standard is from the personal collection of Alian Wang, and is from the type locality in Lai-He, China (a magnetite mine). These grains were originally identified by XRD, although we do not have access to this data. Our stilpnomelane standard is from Fredericke von Weilburg, Nassau, Germany (a locality mentioned by Dana) and once belonged to the mineral collection of the Michigan School of Mines.

Analysis of the standards: We mounted and polished a single grain of the laihunite standard in epoxy (AW #73, see the reflected light image in Fig. 1: laihunite is the brighter phase in reflected light, fayalite is darker). We collected two Raman traverses across the contact between the fayalite and laihunite domains and acquired EMP data on both phases. We do not have access to this data. Our stilpnomelane standard is from Fredericke von Weilburg, Nassau, Germany (a locality mentioned by Dana) and once belonged to the mineral collection of the Michigan School of Mines.

Raman spectrum of the Excalibur sample best matches stilpnomelane schist hand to the personal collection of Alian Wang, and is from the type locality in Lai-He, China, the Jade XRD database. The five peaks highlighted in red correlate with the quartz spectrum and the twelve in green correlate with the stilpnomelane spectra.

Figure 4 shows Raman spectra of all three of our stilpnomelane standards along with the stilpnomelane spectrum with the fewest peaks from other phases acquired in vein 2 of traverse 3 on MIL 03346,177. All three of the standards have a broad Si-O-Si (bridging oxygen) peak centered between 590 and 600 cm⁻¹ with a shoulder near 505 cm⁻¹, the breadth of the peak is attributed to the large size of the unit cell and modulated structure. The Si-O-Si (non-bridging oxygen) peaks above 900 cm⁻¹ and lattice vibrations below 400 cm⁻¹ vary between samples but the Excalibur standard provides the best match to the MIL vein-filling materials.

Fig. 1) Reflected light photo of standard #73 from Lai-He, China. The more reflective phase is laihunite and the darker phase fayalite. Tick marks on cross-hairs are 10 µm apart. Fig. 2) Raman spectra suggest that a minor phyllosilicate may also be present, see text.

<table>
<thead>
<tr>
<th>Raman shift (cm⁻¹)</th>
<th>laihunite</th>
<th>bsl10171033</th>
<th>bsl10171034</th>
<th>bsl10171036</th>
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<td>200</td>
<td>355</td>
<td>185</td>
<td>186</td>
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<td>400</td>
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<tr>
<td>1200</td>
<td>687</td>
<td>687</td>
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<tr>
<td>1400</td>
<td>785</td>
<td>785</td>
<td>718</td>
<td>902</td>
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EMP data of laihunite and stilpnomelane. Representative EMP data are shown for the laihunite and fayalite in the Chinese standard and averaged analyses for the stilpnomelane standards. The low total of the laihunite reflects the presence of Fe$_{3}^{3+}$ and could be reduced using the published laihunite formula [Fe$_{2+}^{3+}$Fe$_{3}^{3+}$(SiO$_{2}$)$_{2}$]. The stilpnomelane also have low totals (consistent with their inferred H$_{2}$O contents) and both standards are consistent with analyses published in [4].


**Table 1. EMP analyses of standards.**

<table>
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<tr>
<th>phase id.</th>
<th>laihunite</th>
<th>fayalite</th>
<th>stilpnomelane</th>
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<tr>
<td>see spectrum</td>
<td>10101025</td>
<td>10101004</td>
<td>10101004</td>
<td>10050020</td>
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<td>spot size</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>SiO$_{2}$</td>
<td>32.23</td>
<td>29.98</td>
<td>44.60</td>
<td>45.67</td>
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<tr>
<td>TiO$_{2}$</td>
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<td>0.00</td>
<td>0.04</td>
<td>0.03</td>
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<tr>
<td>Al$<em>{2}$O$</em>{3}$</td>
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<td>0.00</td>
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<td>5.12</td>
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<tr>
<td>CaO</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
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<tr>
<td>FeO</td>
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<td>70.02</td>
<td>0.02</td>
<td>34.38</td>
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<tr>
<td>MgO</td>
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<td>0.34</td>
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<td>1.04</td>
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<tr>
<td>MnO</td>
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<td>0.00</td>
<td>0.28</td>
<td>0.02</td>
</tr>
<tr>
<td>Na$_{2}$O</td>
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<td>0.00</td>
<td>0.01</td>
<td>1.11</td>
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<td>K$_{2}$O</td>
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<td>0.00</td>
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<tr>
<td>Fe$_{2+}^{3+}$</td>
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<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
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<tr>
<td>F</td>
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<td>100.87</td>
<td>89.02</td>
<td>89.65</td>
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<tr>
<td>Fe$_{2+}^{3+}$</td>
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<td>0.00001</td>
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<td>FeO</td>
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<td>Fe$^{3+}$</td>
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<td>2.21</td>
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<td>Mg</td>
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<td>0.04</td>
<td>0.28</td>
<td>0.58</td>
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<tr>
<td>Ca</td>
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<td>0.00</td>
<td>0.02</td>
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<td>K</td>
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<td>0.00</td>
<td>0.05</td>
<td>0.12</td>
</tr>
</tbody>
</table>

For olivine:

| sum oct | 3.14 | 2.00 |
| sum tet | 1.86 | 1.00 |
| Mg# of ol | 1.92 | 2.03 |

For stilpnomelane:

| Si+Al+P+S | 3.93 | 3.91 |
| Fe$^{2+}$/Fe$^{3+}$+Mg+Ti+Cr+Ni | 2.49 | 2.56 |
| Ca+Na+K | 0.08 | 0.29 |

Total cations: 5.00 3.00 6.50 6.75

**Fig. 3** Raman spectra of our three stilpnomelane standards; two from the collection of A. Wang, the third purchased from Excalibur. A Raman spectrum from the second vein of traverse 3 on MIL 177 is shown for comparison. **Fig. 4** XRD spectrum of the Excalibur standard with one quartz and two stilpnomelane spectral matches from the Jade XRD database; the red lines highlight quartz peaks and green lines highlight stilpnomelane peaks.