Constraints on the U-Pb isotopic systematics of Mars inferred from a combined U-Pb, Rb-Sr, and Sm-Nd isotopic study of the Martian meteorite Zagami

LARS E. BORG,1,* JENNIFER E. EDMUNSON,1 and YEMANE ASMEROM2

1Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131, USA
2Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131, USA

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Abstract—Uranium-lead, Rb-Sr, and Sm-Nd isotopic analyses have been performed on the same whole-rock, mineral, and leachate fractions of the basaltic martian meteorite Zagami to better constrain the U-Pb isotopic systematics of martian materials. Although the Rb-Sr and Sm-Nd systems define concordant crystallization ages of 166 ± 6 Ma and 166 ± 12 Ma, respectively, the U-Pb isotopic system is disturbed. Nevertheless, an age of 156 ± 6 Ma is derived from the 238U-206Pb isotopic system from the purest mineral fractions (maskelynite and pyroxene). The concordance of these three ages suggest that the 238U-206Pb systematics of the purest Zagami mineral fractions have been minimally disturbed by alteration and impact processes, and can therefore be used to constrain the behavior of U and Pb in the Zagami source region. The μ value of the Zagami source region can be estimated, with some confidence from the 238U-206Pb isochron, to be 3.96 ± 0.02. Disturbance of the U-Pb isotopic systems means that this represents a minimum value. The μ value of the Zagami source is significantly lower than the μ values estimated for most basaltic magma sources from Earth and the Moon. This is surprising given the high initial 87Sr/86Sr ratio (0.721566 ± 82) and low initial eNd value (−7.23 ± 0.17) determined for Zagami that indicate that this sample is derived from one of the most highly fractionated reservoirs from any known planetary body. This suggests that Mars is characterized by a low bulk planet U/Pb ratio, a feature that is consistent with its relatively volatile-rich nature.

The leachates contain terrestrial common Pb that was probably added to the meteorite during handling, curation, or sawing. The mineral fractions, particularly those with significant amounts of impact melt glass, contain a second contaminant. The presence of this contaminant results in Pb-Pb ages that are older than the crystallization age of Zagami, indicating that the contaminant is characterized by a high 207Pb/206Pb ratio. Such a contaminant could be produced by removal of single-stage Pb from a relatively high μ martian reservoir before ~1.8 Ga, and therefore could be an ancient manifestation of hydrous alteration of martian surface material.

1. INTRODUCTION

The uranium-lead isotopic system provides powerful insights into both the timing of events occurring on planetary bodies and the geochemical behavior of U and Pb within planetary environments (e.g., Chen and Wasserburg, 1986a; Premo and Tatsumoto 1991; Borg et al., 1999). Although the timing of many events can often be gleaned from other isotopic systems such as K-Ar, Rb-Sr, and Sm-Nd, understanding the geochemical behavior of U and Pb in martian mantle and crustal reservoirs requires U-Pb isotopic analysis. Uranium-lead isotopic analysis can be used to constrain the relative abundances of these elements within a given planet, offer insights into how these elements are partitioned during planetary differentiation and magma production, and record how these elements are mobilized and redistributed on planetary surfaces. Despite its potential usefulness, the application of U-Pb chronology to samples from relatively large differentiated bodies is often hampered by the ease at which this system is disturbed by impact metamorphism, secondary alteration, and terrestrial contamination. As a result, the interpretation of U-Pb isotopic data from the Moon and Mars is seldom unambiguous unless additional constraints on the age of the sample, and/or

differentiation history of the planet, can be obtained from alternative sources (e.g., Unruh and Tatsumoto, 1977; Premo and Tatsumoto, 1991).

Here we present U-Pb, Rb-Sr, and Sm-Nd isotopic measurements completed on the same whole rocks, mineral fractions, and leachates from the basaltic martian meteorite Zagami. The goal of this study is to better understand the geochemical processes that influence the behavior of the U-Pb isotopic systematics on Mars by interpreting the U-Pb isotopic data in the context of the Rb-Sr and Sm-Nd crystallization ages of Zagami and in the context of the differentiation history of this planet. Although the disturbed nature of the U-Pb isotopic systematics preclude the derivation of clear age determinations from this system, the interpretation of the U-Pb data in the context of Rb-Sr and Sm-Nd crystallization ages helps define the nature of these disturbances, the composition and evolutionary history of Pb contamination in Zagami, and the initial Pb isotopic composition of the Zagami source region.

2. GEOCHEMICAL EVOLUTION OF MARS

The objective of this study is to constrain the geochemical evolution of Pb on Mars through U-Pb, Rb-Sr, and Sm-Nd isotopic analyses of the same mineral fractions derived from the basaltic meteorite Zagami. This is accomplished by dissecting this meteorite using detailed mineral separation procedures that permit the nature and extent of U-Pb isotopic disequilib-
rium to be better understood. To better interpret the U-Pb isotopic systematics of Zagami, it is necessary to review a few of the fundamental geochemical and isotopic systematics observed in the martian meteorite suite. These systematics provide a critical framework in which to interpret the new U-Pb isotopic data. The most germane issues in this regard are how the Rb-Sr and Sm-Nd isotopic systematics of the martian meteorite suite constrain (1) the extent and timing of planetary differentiation and (2) the relationship of Zagami to the other basaltic shergottites.

2.1. Extent and Timing of Planetary Differentiation

The martian meteorite suite displays an extreme range of geochemical and isotopic compositions. For example, chondrite-normalized REE patterns of bulk shergottites vary from almost flat ($^{147}$Sm/$^{144}$Nd = 0.18) to strongly light-rare-earth-element (LREE)-depleted ($^{147}$Sm/$^{144}$Nd = 0.50). There is also a very large range of initial $^{87}$Sr/$^{86}$Sr ratios (0.701 to 0.726) and $\varepsilon_{Nd}^{142}$ values (−8 to +46; Shih et al., 1982; Borg et al., 1997) forming a compositional continuum. One end of the continuum is represented by meteorites with trace element and isotopic compositions indicative of derivation from a highly depleted source region, whereas the other end of the continuum is represented by meteorites that appear to be derived from more evolved source regions that are more enriched in incompatible elements. These observations have been interpreted to reflect mixing of sources produced by an early martian planetary-scale differentiation event (e.g., Jones, 1989; Borg et al., 1997; Nyquist et al., 2001; Borg and Draper, 2003; Borg et al., 2003).

The presence of nonchondritic abundances of decay products of short-lived isotopic systems such as $^{142}$Nd and $^{182}$W have been observed in the martian sample suite (Harper et al., 1995; Nyquist et al., 1995; Nyquist et al., 2000). Therefore, although Zagami is mineralogically and texturally and mineralogically similar to the basaltic shergottites Shergotty and Los Angeles. Whole-rock Sr and Nd isotopic compositions of these three meteorites are also very similar (Shih et al., 1982; Nyquist et al., 1995; Nyquist et al., 2000). Therefore, although Zagami is mineralogically and texturally akin to many basaltic meteorites, it has incompatible element abundances and isotopic systematics typical of those meteorites that are derived from the most geochemically evolved reservoirs.

2.2. Relationship of Zagami to the Other Basaltic Meteorites

Zagami is a basaltic shergottite composed primarily of pyroxenes (70%–80%) and maskelynite (10%–25%), with 2 to 4% mesostasis, 2 to 3% oxides, 0.5 to 1.3% phosphates, 0.1 to 0.9% impact melt glass, and 0.2 to 0.6% sulfides (Stolper and McSween, 1979; McCoy et al., 1992). It has a cumulate texture, typical of the shergottites, and is composed of at least three distinct lithologies (McCoy et al., 1992). The two most voluminous lithologies are distinguished on the basis of grain size.

The coarse lithology is composed of grains with an average size of 0.36 mm, whereas the fine-grained lithology contains grains that have an average size of 0.24 mm. Zagami has relatively high incompatible element abundances and a relatively light rare earth element enriched pattern. Thus, it is compositionally and mineralogically similar to the basaltic shergottites Shergotty and Los Angeles. Whole-rock Sr and Nd isotopic compositions of these three meteorites are also very similar (Shih et al., 1982; Nyquist et al., 1995; Nyquist et al., 2000). Therefore, although Zagami is mineralogically and texturally akin to many basaltic meteorites, it has incompatible element abundances and isotopic systematics typical of those meteorites that are derived from the most geochemically evolved reservoirs.

3. ANALYTICAL TECHNIQUES

A 2 g sample of the coarse-grained Zagami lithology was allocated from the meteorite collection at the University of New Mexico. This sample was adjacent to the sample allocated to L. Nyquist for isotopic analyses, making the Rb-Sr and Sm-Nd results of this study directly comparable to those of Nyquist et al. (1995). The unfractionated chip was first sonicated in 4x quartz-distilled water for 10 min. The sample was then crushed in a sapphire mortar and pestle and a whole-rock chip was then added to 0.5 M acetic acid (leachates designated L1) and 2 N HCl to leachate (leachates designated L2) for 10 min each. The residues (R) were then

FIG. 1. Flow diagram illustrating the mineral separation procedure used for Zagami. Residues (R), 2 N HCl leachates (L2), and 0.5 M acetic acid leachate (L1) in light gray have been analyzed for U-Pb, Rb-Sr, and Sm-Nd.
digested using a combination of hydrofluoric, nitric, and hydrochloric acids. Isotope dilution techniques were preformed on (−5%) aliquots of the digested samples to determine the concentrations of Sr and Nd in the samples and to ensure proper spike/sample ratios. The remaining −95% aliquots were spiked with mixed 235U-238U-205Pb, 146Sm-144Sm, and 149Sm-150Nd isotopic tracers. To minimize Pb contamination, the Rb-Sr and Sm-Nd isotopic tracers were prepared from stock solutions after Pb was removed using ion-exchange techniques. Uranium-lead, Rb-Sr, and Sm-Nd were sequentially separated from the same solutions. Uranium-lead was separated using 100 to 250 µL anion resin columns in HCl and HBr. The RREE were purified using RE-spec resin in 0.05N and from the anion chemistry washes using cation exchange columns in 2N HCl and HBr. Rubidium-strontium and RREE were separated and 149Sm-150Nd isotopic tracers. To minimize Pb contamination, the filaments. Mass fractionation of Rb was determined to be 0.6

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt (mg)</th>
<th>Rb (ppm)</th>
<th>Rb (ng)</th>
<th>Sr (ppm)</th>
<th>Sr (ng)</th>
<th>187Rb/186Sr</th>
<th>87Sr/86Sr</th>
<th>147Sm/150Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wr 1 (R)</td>
<td>24.66</td>
<td>6.61</td>
<td>163</td>
<td>29.21</td>
<td>720</td>
<td>0.6548 ± 0.066</td>
<td>0.723069 ± 0.010</td>
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</tr>
<tr>
<td>Wr 2 (L2)</td>
<td>14.44</td>
<td>7.52</td>
<td>109</td>
<td>36.74</td>
<td>531</td>
<td>0.5922 ± 0.059</td>
<td>0.722963 ± 0.010</td>
<td></td>
</tr>
<tr>
<td>Wr 2 (L2)</td>
<td>1.7</td>
<td>0.13</td>
<td>197</td>
<td>177.6</td>
<td>4198</td>
<td>0.1359 ± 0.014</td>
<td>0.721977 ± 0.010</td>
<td></td>
</tr>
<tr>
<td>Mask 1 (R)</td>
<td>23.64</td>
<td>8.34</td>
<td>90.1</td>
<td>0.18</td>
<td>123</td>
<td>0.08518 ± 0.019</td>
<td>0.721624 ± 0.010</td>
<td></td>
</tr>
<tr>
<td>Mask 2 (L2)</td>
<td>33.16</td>
<td>1.34</td>
<td>44.6</td>
<td>0.18</td>
<td>10.1</td>
<td>0.3973 ± 0.049</td>
<td>0.723995 ± 0.010</td>
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</tr>
<tr>
<td>Mg-Px (R)</td>
<td>70.53</td>
<td>2.67</td>
<td>188</td>
<td>4.27</td>
<td>298</td>
<td>1.810 ± 0.018</td>
<td>0.726028 ± 0.010</td>
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<tr>
<td>Mg-Px (L2)</td>
<td>0.6</td>
<td>2.67</td>
<td>188</td>
<td>4.27</td>
<td>298</td>
<td>0.02621 ± 0.026</td>
<td>0.721384 ± 0.010</td>
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</tr>
<tr>
<td>Fe-Px (R)</td>
<td>14.55</td>
<td>9.41</td>
<td>137</td>
<td>27.63</td>
<td>402</td>
<td>0.9848 ± 0.099</td>
<td>0.723908 ± 0.012</td>
<td></td>
</tr>
<tr>
<td>Fe-Px rej (R)</td>
<td>16.56</td>
<td>60.5</td>
<td>997</td>
<td>157.5</td>
<td>2592</td>
<td>1.117 ± 0.111</td>
<td>0.724159 ± 0.010</td>
<td></td>
</tr>
<tr>
<td>Mg-Px rej (R)</td>
<td>67.48</td>
<td>8.30</td>
<td>560</td>
<td>20.94</td>
<td>1413</td>
<td>1.147 ± 0.114</td>
<td>0.724178 ± 0.010</td>
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</tr>
<tr>
<td>Fe-Px rej (R)</td>
<td>33.38</td>
<td>8.18</td>
<td>273</td>
<td>14.52</td>
<td>485</td>
<td>1.630 ± 0.16</td>
<td>0.725326 ± 0.010</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Zagami Rb-Sr isotopic data.

*87Rb/86Rb ratio of six runs of the NBS-984 Pb standard = 2.624 ± 0.02 (2σp).
Ischrons are calculated using either 2σp (from standard runs) or 2σm (from measured isotopic ratios), whichever is larger.

1. Error limits apply to last digits and include a minimum uncertainty of 1% plus 50% of the blank correction for Rb and Sr added quadratically.
2. Normalized to 140Sm/86Sr = 0.1194. Uncertainties refer to last digits and are 2σm calculated from the measured isotopic ratios. 2σm = ([Σ(mi - m)^2]/[N(n - 1)])^1/2 for N measurements M with mean value m.
3. Uncertainties refer to last digits and are 2σp, 2σp = ([Σ(mi - m)^2]/[N(n - 1)])^1/2 for N measurements M, with mean value μ

4. Rubidium isotopic systematics

The results of Rb-Sr, Sm-Nd, and U-Pb isotopic analyses are presented in Tables 1, 2, and 3. The Rb-Sr and Sm-Nd isotopic data are discussed first because they constrain the crystallization age of Zagami, providing a basis in which to interpret the U-Pb data. The ages presented below are calculated using Isotol/Ex v. 2.49 (Ludwig, 2001).

4.1. Rb-Sr Isochron

Figure 2 is a Rb-Sr isochron diagram of Zagami whole rocks, mineral fractions, and leachates analyzed in this study. The purest mineral fractions, Mask 1 (R), Mg-Px (R), and Fe-Px (R), yield an age of 176 ± 2 Ma with an initial Sr isotopic composition of 0.721556 ± 22 and a mean square weighted derivative (MSWD) = 1.1. The low uncertainties and MSWD, in large part, reflect the small number of fractions used to define this age. As a consequence, the most representative age is probably defined by all of the mineral fractions. The silicate and oxide mineral and reject fractions define a Rb-Sr age of 166 ± 6 Ma and an initial 87Sr/86Sr ratio of 0.721566 ± 82 (MSWD = 17). The age and initial Sr isotopic composition of the coarse-grained Zagami lithology determined by Nyquist et al. (1995) and Shih et al. (1982) are 183 ± 6 Ma, 0.721604 ± 57 and 180 ± 4 Ma, 0.72145 ± 5, respectively, and are in good agreement with the results presented here for the same lithology. Our mineral fractions define a larger range of 87Rb/86Sr ratios and somewhat less scatter, most likely reflecting their greater purity. The maskelynite mineral fractions analyzed in
this study have $^{87}$Rb/$^{86}$Sr ratios near zero, and therefore place relatively tight limits on the initial Sr isotopic composition of Zagami. The Rb-Sr isotopic compositions of the L2 leaches were also determined. All but one of the leaches lie below the isochron defined by the silicate mineral fractions and whole rocks, indicating that they contain a relatively unradiogenic Sr component that is not indigenous to, that is, in isotopic equilibrium with, the Zagami silicate fractions.

It is important to note that deviations of mineral, whole-rock, and leachate fractions from individual Rb-Sr (and Sm-Nd; Fig. 3) isochrons are a ubiquitous feature of basaltic martian meteorites (e.g., Nyquist et al., 1979; Shih et al., 1982; Nyquist et al., 1995; Borg et al.; 1997; Nyquist et al., 2000; Borg et al., 2002; Borg et al., 2003). This is a result of these samples having undergone varying degrees of thermal metamorphism associated with shock and having been subjected to alteration on Mars and Earth. Compared to most martian meteorites, however, Zagami demonstrates minimally disturbed isotopic systematics as demonstrated by Rb-Sr (and Sm-Nd) ages that are defined by all but a few of the analyzed fractions. Never-

### Table 2. Zagami Sm-Nd isotopic data.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt (mg)</th>
<th>Sm (ppm)</th>
<th>Sm (ng)</th>
<th>Nd (ppm)</th>
<th>Nd (ng)</th>
<th>$^{147}$Sm</th>
<th>$^{144}$Nd</th>
<th>$^{148}$Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wr 1 (R)</td>
<td>24.66</td>
<td>1.947</td>
<td>48.0</td>
<td>4.830</td>
<td>119</td>
<td>0.24347</td>
<td>± 0.024</td>
<td>0.51231</td>
</tr>
<tr>
<td>Wr 2 (R)</td>
<td>14.44</td>
<td>0.250</td>
<td>3.6</td>
<td>0.371</td>
<td>5.4</td>
<td>0.40665</td>
<td>± 0.055</td>
<td>0.51289</td>
</tr>
<tr>
<td>Wr 2 (L2)</td>
<td>1.6</td>
<td>0.063</td>
<td>1.5</td>
<td>0.143</td>
<td>3.4</td>
<td>0.26468</td>
<td>± 0.074</td>
<td>0.51218</td>
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<tr>
<td>Mask 1 (L2)</td>
<td></td>
<td>2.2</td>
<td>5.6</td>
<td>0.23325</td>
<td>± 0.45</td>
<td>0.51283</td>
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<td></td>
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<tr>
<td>Mask 2 (L2)</td>
<td></td>
<td>23.64</td>
<td>0.672</td>
<td>41.7</td>
<td>0.110</td>
<td>0.29206</td>
<td>± 0.080</td>
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<tr>
<td>Mg-Px (R)</td>
<td>33.16</td>
<td>0.316</td>
<td>10.5</td>
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<td>15.5</td>
<td>0.40858</td>
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<td>Mg-Px (L2)</td>
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<td>3.0</td>
<td>8.2</td>
<td>0.22058</td>
<td>± 0.31</td>
<td>0.51294</td>
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<tr>
<td>Fe-Px (R)</td>
<td>70.53</td>
<td>0.263</td>
<td>18.5</td>
<td>0.375</td>
<td>26.4</td>
<td>0.42338</td>
<td>± 0.42</td>
<td>0.51299</td>
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<tr>
<td>Fe-Px (L2)</td>
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<td>23.3</td>
<td>62.3</td>
<td>0.22549</td>
<td>± 0.23</td>
<td>0.51301</td>
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<tr>
<td>Ox (R)</td>
<td>14.55</td>
<td>1.890</td>
<td>27.5</td>
<td>4.820</td>
<td>70.1</td>
<td>0.23706</td>
<td>± 0.24</td>
<td>0.51230</td>
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<tr>
<td>Mask 1–2 rej (R)</td>
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<td>16.46</td>
<td>0.068</td>
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<td>0.152</td>
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<td>0.2700</td>
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<td>Mg-Px rej (R)</td>
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<td>67.48</td>
<td>0.309</td>
<td>20.8</td>
<td>0.465</td>
<td>31.4</td>
<td>0.40165</td>
<td>± 0.40</td>
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<td>Fe-Px rej (R)</td>
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<td>33.38</td>
<td>0.335</td>
<td>11.2</td>
<td>0.513</td>
<td>17.1</td>
<td>0.39490</td>
<td>± 0.39</td>
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<tr>
<td>LaJolla Nd (N = 12)</td>
<td></td>
<td></td>
<td>2–10</td>
<td>0.51187</td>
<td>± 0.17</td>
<td></td>
<td></td>
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</table>

### Table 3. Zagami U-Pb isotopic data.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt (mg)</th>
<th>U (ppm)</th>
<th>Pb (ppm)</th>
<th>$^{238}U$</th>
<th>$^{206}Pb$</th>
<th>$^{235}U$</th>
<th>$^{207}Pb$</th>
<th>$^{234}Pb$</th>
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<tbody>
<tr>
<td>Wr (R)</td>
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<td>0.126</td>
<td>0.837</td>
<td>13.0</td>
<td>23.0</td>
<td>8.427</td>
<td>35.075</td>
<td>13.742</td>
<td>17.1</td>
<td>14.937</td>
<td>± 15</td>
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<tr>
<td>L1</td>
<td>11.7</td>
<td>0.575</td>
<td>35.46</td>
<td>5.57</td>
<td>10.09</td>
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<td>13.199</td>
<td>13.515</td>
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</tr>
<tr>
<td>Mask 1 (R)</td>
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<td>9.36</td>
<td>0.118</td>
<td>0.626</td>
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<td>26.4</td>
<td>10.09</td>
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<td>13.199</td>
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<td>± 14</td>
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<td>Mask 1 (L2)</td>
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<td>0.405</td>
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<td>32.8</td>
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<td>13.182</td>
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<tr>
<td>Ox (R)</td>
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<td>13.63</td>
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<td>± 16</td>
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<td>18.344</td>
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<tr>
<td>Mg-Px rej (R)</td>
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<td>0.379</td>
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<td>27.3</td>
<td>20.59</td>
<td>33.347</td>
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<td>33.484</td>
<td>± 33</td>
</tr>
<tr>
<td>Fe-Px rej (R)</td>
<td></td>
<td>33.38</td>
<td>0.179</td>
<td>0.456</td>
<td>25.0</td>
<td>16.4</td>
<td>21.08</td>
<td>33.884</td>
<td>13.300</td>
<td>18.816</td>
<td>± 16</td>
</tr>
<tr>
<td>NBS-981 (N = 17)</td>
<td></td>
<td></td>
<td>36.505</td>
<td>0.72</td>
<td>15.438</td>
<td>21.965</td>
<td>± 16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Notes

\( a \) Error limits refer to last digits and include a minimum uncertainty of 0.5% plus 50% of the blank correction for U and Pb added quadratically.

\( b \) Normalized to \(^{146}\text{Nd}/^{144}\text{Nd} = 0.7219.\)

\( c \) Error limits refer to last digits and are \( 2\sigma_p = \sigma_{up} = \sqrt{\frac{\sum(M_i - \mu)^2}{n(n-1)}} \) for N measurements \( M_i \) with mean value \( \mu \).

All samples and standards run as NdO\(^6\).

\( W_r \) = whole rock; \( P_x \) = pyroxene; \( M_{ak} \) = maskelynite; \( O_x \) = oxide; \( L_2 \) = HCl leachate; \( R \) = residue; \( rej \) = portion of mineral fraction rejected after handpicking.

Values are weighted averages of \( N = 1 \)–10 mass spectrometry runs. Error limits refer to last digits and include a minimum of 0.02% per annum for uncertainty of fractionation correction plus the weighted average of \( 2\sigma_p \) added quadratically. \( 2\sigma_p = \sqrt{\frac{\sum(M_i - \mu)^2}{n(n-1)}} \) for N measurements \( M_i \) with mean value \( \mu \).
Nyquist et al. (1995) completed Rb-Sr isotopic analyses on both the coarse and fine-grained portions of Zagami. They noted that the crystallization ages from the coarse and fine-grained fractions were within uncertainty of one another, but the initial Sr isotopic compositions were not. They interpreted this to reflect slightly different source regions for the parental magmas of the two lithologies. Note, however, that the variable presence of an unradiogenic leachable component in the coarse and fine-grained lithologies could account for the different initial Sr isotopic compositions of the two lithologies. To account for its higher initial Sr isotopic composition, the fine-grained lithology is expected to contain less of this component. Interestingly, the fine-grained mineral fractions analyzed by Nyquist et al. (1995) were leached in HCl, whereas the coarse-grained mineral fractions were not. The differences in the initial Sr isotopic compositions of the coarse and fine-grained lithologies could therefore reflect removal of an unradiogenic Sr component from the fine-grained mineral fractions by leaching.

The Zagami age and initial \( \frac{\text{Sr}}{\text{Sr}} \) ratio are very similar to those determined for Shergotty (165 ± 8 Ma and 0.72260 ± 12; Nyquist et al., 1979) and Los Angeles (166 ± 11 Ma and 0.720997 ± 51; Nyquist et al., 2000). The initial \( \frac{\text{Sr}}{\text{Sr}} \) ratio of these meteorites is significantly higher than the initial Sr isotopic compositions determined on all other martian meteorites, some of which have \( \frac{\text{Sr}}{\text{Sr}} \) ratios as low as 0.7013 (Borg et al., 1997). If the Zagami source formed from a planet with the initial Sr isotopic composition of best achondrite basaltic initial (BABI \( \frac{\text{Sr}}{\text{Sr}} = 0.69898 \)) at 4.558 Ga, then the Zagami source is required to have a \( \frac{\text{Sr}}{\text{Sr}} \) ratio of 0.356. In comparison, the source regions of terrestrial basalts as well as lunar basalts have significantly lower \( \frac{\text{Sr}}{\text{Sr}} \) ratios.

Instead, the \( \frac{\text{Sr}}{\text{Sr}} \) ratio of the Zagami source region is similar to the composition of terrestrial continental reservoirs (e.g., Newsom, 1995). Thus, the \( \frac{\text{Sr}}{\text{Sr}} \) isotopic systematics of Zagami suggest that it is derived from a highly evolved source region.

### 4.2. Sm-Nd Isochron

Samarium-neodymium isotopic analyses were also completed on the whole rocks, mineral fractions, and L2 leachates. A Sm-Nd isochron plot of the Zagami fractions is presented in Figure 3 and yields a crystallization age of 166 ± 12 Ma and an initial Nd isotopic composition of \( e_{\text{Nd}} = -7.23 ± 0.17 \) (MSWD = 3.7). The Sm-Nd age is defined by all of the leachates with the exception of Wr 2 (L2) and Mask 1 (L2) and is consistent with the Rb-Sr age. Unfortunately, the Mask 1 (R) fraction failed to run, making a direct comparison with the Rb-Sr age defined by the purest mineral fractions Mask 1 (R), Mg-Px (R), and Fe-Px (R) impossible. The fact that several of the leachates lie on the Sm-Nd isochron but off the Rb-Sr isochron is typical of how the Rb-Sr and Sm-Nd isotopic systematics of shergottites respond to alteration. The Sm-Nd systematics of the leachates that lie on the isochron are most likely dominated by Nd derived from igneous phosphates known to be present in Zagami (Wadhwa et al., 1994). In contrast, leachates that lie below the isochron are most likely dominated by alteration products. Alteration agents such as water, and alteration products such as calcite and Ca-sulfate, are characterized by low REE abundances, but have elevated Sr abundances. Thus, alteration may affect the Sr isotopic systematics more dramatically than the Nd isotopic systematics. Nevertheless, the fact that some leachates have Nd isotopic compositions that lie significantly below the isochron suggests that

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**Fig. 2.** Rb-Sr isochron plot of Zagami whole-rock, mineral, and leachate fractions. The purest mineral fractions, Mask 1 (R), Mg-Px (R), and Fe-Px (R) yield an age of 176 ± 2 Ma with an initial Sr isotopic composition of 0.721556 +/− 22 and a MSWD = 1.1. The most representative age, defined by all of the silicate and oxide mineral and reject fractions (filled circles), is 166 ± 6 Ma and an initial \( \frac{\text{Sr}}{\text{Sr}} \) ratio of 0.721566 ± 82 (MSWD = 17). Most leachates do not lie on the isochron (open circles). Inset represents deviation of individual fractions from the isochron, in epsilon units.

**Fig. 3.** Sm-Nd isochron plot of Zagami whole-rock, mineral, and leachate fractions. The best age is defined by all silicate and most leachate fractions (filled circles) with the exception of the Mask 1 (L2) and Wr 2 (L2) (open circles). This isochron yields an age of 166 ± 12 Ma and an initial \( e_{\text{Nd}} \) value of −7.23 ± 0.17 (MSWD = 3.7). Inset represents deviation of individual fractions from the isochron, in epsilon units.
alteration resulted in the addition of unradiogenic Nd. Although this Nd could be of either terrestrial or martian origin, it is difficult to imagine how terrestrial Nd could have been added to this meteorite given that it is a fall. If this scenario is correct, it implies that the martian surface contains a component characterized by $e_{Nd} < -7$ and $\delta^{143}$Sm/$\delta^{144}$Nd ratio $< 0.721$, and is therefore isotopically similar to terrestrial crustal sources (e.g., Goldstein and Jacobsen, 1988; Ben Othman, 1989).

The Sm-Nd age determined in this study is concordant with the Sm-Nd age defined for Zagami by Nyquist et al. (1995). However, the isochron defined by the data presented here demonstrates less scatter and results in a more precise age determination. For example, the best Sm-Nd age determined by Nyquist et al. (1995) is 180 ± 37 Ma and uses mineral fractions from both the coarse and fine grained lithologies. Several mineral fractions analyzed by Nyquist et al. (1995) from both the coarse and fine-grained lithologies fall significantly off the Sm-Nd isochron presented here. This may reflect uncertainties associated with analysis of relatively small amounts of Nd, or the presence of a component in Nyquist’s chip that was not present in our chip.

The negative initial $e^{143}$Nd value of $-7.23 ± 0.17$ indicates that Zagami is derived from a source region with a long-term LREE enrichment. This source region has an inferred $147$Sm/$144$Nd ratio of 0.184, assuming it formed at 4.52 Ga (Borg et al., 2003; Borg and Drake, 2005; Foley et al., 2005) from an initially chondritic reservoir. The source region for Zagami has Sm/Nd ratios that are very similar to the source region for Shergotty ($147$Sm/$144$Nd = 0.182) and Los Angeles ($147$Sm/$144$Nd = 0.186). Therefore, the source region of Zagami is characterized by Sm/Nd and Rb/Sr ratios that are typical of the most incompatible element-enriched martian source regions.

5. U-Pb ISOTOPIC SYSTEMATICS

5.1. U-Pb Isochrons

Uranium-lead isotopic analyses have been completed on the same whole-rock, mineral, and reject fractions, as well as L2 leachates that Rb-Sr and Sm-Nd isotopic analyses have been completed on. The 0.5 M acetic acid whole-rock leachate, Wr 1 (L1), was also analyzed for U-Pb. The U-Pb isochrons are presented in Figure 4a.b. As demonstrated below, the U-Pb isotopic compositions of Zagami are highly disturbed. Therefore, the goal of the U-Pb analyses is not to define the crystallization age of the sample; this is defined by the Rb-Sr and Sm-Nd isochrons. Instead, the U-Pb isotopic systematics of martian samples are used in the context of the Rb-Sr and Sm-Nd ages to constrain the behavior of U and Pb on Mars. As a consequence, the most reliable U-Pb data are those defined by mineral fractions which yield isochron ages that are concordant with Rb-Sr and Sm-Nd isochron ages.

The best $238$U/$206$Pb age and initial $206$Pb/$204$Pb isotopic ratio is defined by the purest mineral fractions, which include Mask 1 (R), Mg-Px (R), and Fe-Px (R). This isochron yields an age of 156 ± 6 Ma and an initial $206$Pb/$204$Pb ratio of 13.268 ± 0.018 (MSWD = 1.3). This age is younger than the Rb-Sr age determined on the same fractions (176 ± 2 Ma), but concordant with the preferred Rb-Sr (166 ± 6 Ma) and Sm-Nd (166 ± 12 Ma) ages defined by all silicate and oxide mineral fractions. Al-

![Fig. 4. U-Pb isochron plots of Zagami whole-rock, mineral, and leachate fractions.](image-url)
weak acids at room temperature for a relatively short period of time. Gaffney et al. (2005) reached the same conclusion regarding leached mineral fractions from uncontaminated Apollo 11 basalt 10017. These authors demonstrated that leachate-residue fractions lie on the same U-Pb isochron, that recombined leachate-residue pairs define the same age and initial Pb isotopic composition as the residue fractions, and that the \(^{238}\text{U}-^{206}\text{Pb}\) age agrees with Rb-Sr and Sm-Nd ages determined on the same fractions.

The oxide mineral fraction as well as the leachate L1 and L2 fractions do not lie near the \(~156\text{ Ma}\) isochron, however. The Ox (R) mineral fraction lies to the right of the isochron, possibly due to Pb removal by the light leaching in 0.5 M acetic acid, which would raise the \(^{238}\text{U}/^{204}\text{Pb}\) ratio (\(\mu\) value) of the mineral fraction. This explanation has been invoked to account for apparently high \(\mu\) values observed in leached oxide-rich mineral fractions from Apollo basalt 15085 (Unruh and Tatsumoto, 1977). If this scenario is correct, \(~75\%\) of the Pb must be removed from the oxide mineral fraction by leaching. A more likely explanation for the high \(\mu\) values of the Ox (R) fraction is that the oxides may not retain Pb efficiently during impact metamorphism. In either case, the Ox (R) mineral fraction appears to have lost Pb relatively recently.

The U-Pb isotopic systematics of the leachate fractions, like the Rb-Sr isotopic systematics, appear to contain a contaminant that is not in isotopic equilibrium with the silicate fractions. This contaminant is characterized by a more radiogenic Pb isotopic composition than the mineral fractions, suggesting that it is derived from a source region with a longer-term U/Pb ratio than the Zagami source region. Although it is not impossible, it seems unlikely that surface contaminates on Mars will be derived from sources with higher, more fractionated U/Pb ratios than the Zagami source because the Zagami source is one of the most fractionated. We therefore speculate that the Pb contamination is of terrestrial origin and was, perhaps, added to the sample during sawing of the initial meteorite. This is supported by the Pb isotopic compositions of the leachates that approach, or are identical to, terrestrial common Pb values (Table 3). The Rb-Sr, Sm-Nd, and U-Pb isotopic compositions of the leachates suggest that the Sr and Nd contamination could be derived from Mars, whereas the Pb contamination is derived from Earth. This requires the terrestrial contaminant to have relatively high Pb, but low Sr and Nd abundances, whereas the opposite is required for the martian contaminant. Alternatively, all of the Sr, Nd, and Pb contamination observed in the leachates could be derived from Earth.

The \(^{235}\text{U}-^{207}\text{Pb}\) isochron plot is presented in Figure 4b. Although this plot yields no age information, a line corresponding to an age of \(312 \pm 1300\text{ Ma}\) and an initial \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio of \(13.20 \pm 0.89\) is defined by Mask 1 (R), Fe-Px (R), and Mg-Px (R), the purest mineral fractions. A more restricted reference age of \(360 \pm 220\text{ Ma}\) with an initial \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio of \(13.15 \pm 0.14\) is defined if all of the silicate mineral fractions are included in the calculation. The large amount of uncertainty in the \(^{235}\text{U}-^{207}\text{Pb}\) age compared to the \(^{238}\text{U}-^{207}\text{Pb}\) age is not unexpected, because a small amount of Pb contamination will have a large effect on the limited abundance of radiogenic \(^{207}\text{Pb}\) produced by the small proportion of \(^{235}\text{U}\) present (<1\% \(^{238}\text{U}\)) in the rock when it formed. Like the \(^{238}\text{U}-^{207}\text{Pb}\) system, the leachates lie above the isochron, reflecting the presence of terrestrial contamination, whereas the oxide fraction lies to the right of the isochron most likely reflecting Pb loss.

Previously, Chen and Wasserburg (1986a) reported U-Pb isotopic analyses on a whole rock and two leachates of Zagami. Although an “isochron” defined by the residue, leachate, and calculated total (recombined residue plus leachates) yields a \(^{238}\text{U}-^{206}\text{Pb}\) age of \(231 \pm 3\text{ Ma}\), the similarity to the Rb-Sr, Sm-Nd, and \(^{235}\text{U}-^{208}\text{Pb}\) crystallization ages that have been determined here, and previously (Shih et al., 1982; Nyquist et al., 1995), appears to be fortuitous. This is because the samples analyzed by Chen and Wasserburg (1986a) have somewhat more radiogenic Pb than the samples that define the 156 Ma \(^{238}\text{U}-^{206}\text{Pb}\) age in this study (Fig. 4a). Thus, the fractions analyzed by Chen and Wasserburg (1986a) appear to contain some of the radiogenic Pb contaminant that is present in our leaches. Note that the leachates of Chen and Wasserburg (1986a) are less radiogenic than the leachates presented here, implying that they contain less contamination. As a result, the whole-rock residue of Chen and Wasserburg (1986a) could contain a greater proportion of terrestrial contamination than the residues analyzed in this study.

The initial \(^{206}\text{Pb}/^{204}\text{Pb}\) and \(^{207}\text{Pb}/^{204}\text{Pb}\) isotopic ratios determined from the isochrons (Fig. 4a,b) indicate that Zagami was derived from a source region with a fairly low \(\mu\) value. An initial \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio of \(13.268 \pm 0.018\) corresponds to a source region with a \(\mu\) value of 3.96 \pm 0.02, assuming growth in a reservoir that formed at 4.558 Ga with the initial Pb isotopic composition of the Canyon Diablo meteorite (\(^{206}\text{Pb}/^{204}\text{Pb} = 9.307\); Tatsumoto et al., 1973; Chen and Wasserburg, 1983). Although there is significantly more uncertainty associated with the initial \(^{207}\text{Pb}/^{204}\text{Pb}\) ratio (as a result of the poorly defined isochron), the most precise \(\mu\) value calculated from an initial \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio of \(13.15 \pm 0.14\) is 4.49 \pm 0.22 (using the initial \(^{207}\text{Pb}/^{204}\text{Pb}\) ratio of the Canyon Diablo meteorite of 10.294; Tatsumoto et al., 1973; Chen and Wasserburg, 1983). The observations that the only way to obtain a \(^{238}\text{U}-^{206}\text{Pb}\) isochron age that is concordant with the Rb-Sr and Sm-Nd crystallization ages is to select the purest mineral fractions, and that the \(^{235}\text{U}-^{207}\text{Pb}\) system yields no coherent linear regression indicates that the U-Pb systematics of Zagami are disturbed. Whereas the purest mineral fractions yield a \(^{238}\text{U}-^{206}\text{Pb}\) age that is concordant with the Rb-Sr and Sm-Nd ages, the \(^{235}\text{U}-^{207}\text{Pb}\) system demonstrates significantly more scatter. If both systems were disturbed to the same degree, similar amounts of scatter are expected on both plots, resulting in significantly greater uncertainty associated with the \(^{235}\text{U}-^{207}\text{Pb}\) age because of the low modern production rate of \(^{207}\text{Pb}\). Furthermore, the \(\mu\) value calculated for the Zagami source region using the initial \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio is higher than the \(\mu\) value calculated from the initial \(^{206}\text{Pb}/^{204}\text{Pb}\) ratio. In fact, the initial \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio of Zagami predicted on the basis of the measured initial \(^{206}\text{Pb}/^{204}\text{Pb}\) ratio is 12.81 (inset Fig. 4b), differing from the best value of 13.15 \pm 0.14 determined from the \(^{235}\text{U}-^{207}\text{Pb}\) isochron. Consequently, all of the mineral fractions lie above a 156 Ma isochron with an initial \(^{207}\text{Pb}/^{204}\text{Pb}\) ratio of 12.81 in Figure 4b (inset). These observations indicate that the disturbance in the U-Pb system is most clearly manifest in the \(^{235}\text{U}-^{207}\text{Pb}\) isotopic systematics.
5.2. Disturbances of the U-Pb Isotopic System

To interpret the disturbed U-Pb isotopic systematics of Zagami, it is necessary to discuss idealized Pb growth in an undisturbed martian system. Gale (1972) and Gale and Mussett (1973) have pointed out that undisturbed geologic systems that have experienced lead growth in two stages yield linear arrays on Pb-Pb, U-Pb concordia, and U-Pb isochron plots. Although the Rh-Sr and Sm-Nd isotopic systematics of the basaltic martian meteorites indicate that their source evolved in two stages, isotopic growth in the rocks derived from these sources once they crystallized represents a third stage of evolution. Thus, stage one represents growth in an undifferentiated primordial reservoir; stage two represents growth in a differentiated reservoir presumably produced in association with core, mantle, and crust formation; and a third stage represents isotopic growth in the rocks and minerals derived from the melting of reservoir two. Gale (1972) and Gale and Mussett (1973) also note that three-stage Pb growth forms linear arrays on these U-Pb diagrams under specific circumstances. One case is when the time interval between stages is of limited duration. As noted above, \( e^{142}_{\text{Mg-Px}} - e^{142}_{\text{Mg-Px}} \) systematics of the martian meteorite suite are consistent with silicate differentiation occurring \( \approx 30 \) Ma after planetary formation. This represents the latest time that U and Pb are likely to be fractionated from their primordial ratio in the martian meteorite source regions. The \( \approx 30 \) Ma time span between planet formation and silicate differentiation will have negligible effect on the growth of radiogenic Pb. Consequently, U-Pb isotopic evolution of mineral fractions derived from martian basalts, such as Zagami, is expected to approximate two stages of growth. The first stage is from the time of silicate differentiation (\( \approx 4.52 \) Ga) to source melting and melt crystallization (\( \approx 166 \) Ma), and the second is from 166 Ma to present.

5.2.1. Concordia diagram

A concordia diagram in which radiogenic Pb is calculated by subtracting primordial Pb composition is presented in Fig. 5. The discordia presented on this diagram is defined by all of the whole-rock, mineral, and leachate fractions and yields a discordia that intercepts concordia at 4584 ± 100 Ma and 70 ± 160 Ma. In a two-stage Pb evolution model, the upper intercept reflects the time in the history of the planet when it had a primordial lead isotopic composition (Gale, 1972). There is no way to equate this age with any evolutionary phase in the planet’s history (Gale and Mussett, 1973). In a two-stage model of Pb evolution, the lower intercept represents the time when U and Pb were first fractionated from a primordial reservoir. In a two-stage Pb evolutionary model for a basalt, this represents the crystallization age of the sample.

The scatter of data points on the U-Pb isochron plots presented in Figure 4a,b clearly indicate that the U-Pb system has been disturbed, most likely through the addition of Pb. As a consequence, models in which terrestrial Pb (206Pb/204Pb = 18.2, 207Pb/204Pb = 15.5) and martian Pb (206Pb/204Pb = 13, 207Pb/204Pb = 14) is mixed with the Wr (R) fraction are plotted on Figure 5. These mixing models demonstrate that contamination of individual fractions by extraneous Pb raises their 207Pb/204U and 206Pb/204U ratios along a line that approximates the discordia defined by the mineral, whole-rock and leachate fractions. As a result, it is probable that the U-Pb isotopic systematics displayed on the concordia diagram represent the combined effects of Pb contamination and more or less two stages of Pb growth. It is not possible, therefore, to unambiguously interpret the lower (or upper) discordia intercepts in the context of geochronology.

The mixing models demonstrate that relatively large amounts of contamination are required before individual points move significantly along the discordia (Fig. 5). The addition of terrestrial contamination moves individual fractions slightly above the discordia defined in Figure 5, whereas addition of martian Pb, characterized by a higher 207Pb/206Pb ratio, drives the fractions slightly below the discordia. Interestingly, the fractions that lie below the discordia are those that would be most disturbed by impact processes, that is, those fractions that contain impact-produced glasses (maskelynite and reject mineral fractions). The lower intercept of a line regressed through these glass-rich fractions also intercepts concordia near the crystallization age of Zagami (116 Ma), indicating that even these partially contaminated mineral fractions retain some vestige of the crystallization age of the sample. The upper intercept lies to the right of the concordia curve (4750 Ma), suggesting...
that the contaminant present in the impact melt glasses is characterized by an elevated $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (mixing model B, Fig. 5). In contrast to the impact glass-rich fractions, the leachates tend to lie above the discordia in Figure 5, consistent with the presence of Pb with an isotopic composition that is more similar to terrestrial Pb (mixing model A, Fig. 5).

5.2.2. $^{206}\text{Pb}$/$^{207}\text{Pb}$ isochron diagram

The relatively large amount of disturbance observed in the $^{235}\text{U}$/$^{207}\text{Pb}$ system compared to the $^{238}\text{U}$/$^{207}\text{Pb}$ system is also illustrated on the $^{206}\text{Pb}$/$^{207}\text{Pb}$ isochron plot (Fig. 6). If the Pb isotopic systematics were not disturbed, and Pb growth occurred in two stages, the mineral fractions are expected to lie on a line with a slope corresponding to an age of ~166 Ma. Furthermore, since isotopic growth of martian meteorite sources is approximated by two stages of growth, this would result in a single-stage growth curve of primordial Pb with a $\mu$ value near 4 (the $\mu$ value calculated on the basis of the initial $^{206}\text{Pb}/^{204}\text{Pb}$ ratio). Note, however, that all of these mineral fractions are shifted to higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, indicating that the initial $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of the mineral fractions is higher than expected if the U-Pb isotopic system was undisturbed. In contrast to the mineral fractions, the leachates analyzed in this study as well as those from Chen and Wasserburg (1986a) fall along a line in Figure 6 with a slope corresponding to an age of ~4 Ga. The fact that both terrestrial common Pb and the initial Pb isotopic composition of Zagami determined from the U-Pb isochrons lie along this line further suggests that the leachates are mixtures of Pb that is derived from leachable igneous sources, presumably phosphates, and Pb derived from terrestrial contamination.

The U-Pb isotopic disturbances observed in Zagami are typical of disturbances observed in the U-Pb isotopic systematics of other basalitic martian meteorites. Although U-Pb isotopic analyses have been completed on several whole rocks and leachates of basalitic meteorites (EET79001, ALH77005, LEW88516, Zagami) by Chen and Wasserburg (1986a, 1986b), analyses of mineral separates have only been completed on Shergotty and Y793605 (Chen and Wasserburg, 1986a; Misawa et al., 1997). Nevertheless, all of the samples analyzed so far demonstrate U-Pb isotopic disturbances that are similar to those discussed above for Zagami. Thus, the $^{207}\text{Pb}$/$^{206}\text{Pb}$ and $^{235}\text{U}$/$^{207}\text{Pb}$ ages of these samples are significantly older than their Rb-Sr, Sm-Nd, and $^{238}\text{U}$/$^{206}\text{Pb}$ ages. Furthermore, the $^{230}\text{U}$/$^{206}\text{Pb}$ ages are also often disturbed (Chen and Wasserburg, 1986a; Misawa et al., 1997). It is therefore probable that the U-Pb isotopic systematics of all of the basalitic shergottites have been disturbed by the same mechanism.

5.3. Mechanisms to Disturb the U-Pb Isotopic Systematics of the Shergottites

5.3.1. Pb isotopic composition of the contaminants

The U-Pb isotopic data discussed above demonstrate that there are at least two contaminants present in Zagami. The first is easily removed by leaching and appears to have the isotopic composition of terrestrial common Pb. As argued above, this contaminant was probably added to the sample during handling, curation, or sawing. The second contaminant appears to be present in the silicate mineral fraction residues and is characterized by a relatively high $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. This contaminant is physically associated with the mineral fractions that are most disturbed by impact processes, that is, those containing significant amounts of impact melt (the maskelynite and reject fractions). This suggests that this contaminant is present in the impact melt glasses and has been added to them through the shock process. Rao et al. (1999) demonstrated that elevated sulfur abundances in impact glass from EET79001 was likely to reflect the presence of martian soil added to these glasses during impact. Therefore, the fact that the reject mineral fractions containing relatively large proportions of impact melt glass have the highest $^{207}\text{Pb}/^{206}\text{Pb}$ ratios suggests that the contaminant present in the Zagami mineral fractions may ultimately be derived from martian surface material.

The Pb isotopic composition of this contaminant cannot be tightly constrained from the Zagami U-Pb isotopic data. However, several reject mineral fractions that lie off the U-Pb and Pb-Pb isochrons have elevated $^{207}\text{Pb}/^{206}\text{Pb}$ ratios up to 0.98 (Table 3), indicating that the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of the contaminant must be at least 1. The contaminant must also have a $^{207}\text{Pb}/^{206}\text{Pb}$ ratio that is in excess of 13.15, the initial $^{207}\text{Pb}/^{204}\text{Pb}$ ratio determined from the isochron. This is because the best-measured initial $^{207}\text{Pb}/^{204}\text{Pb}$ ratio is higher than the value predicted on the basis of the minimally disturbed $^{238}\text{U}$/$^{208}\text{Pb}$ isochron. Thus, the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of the contaminant must have a Pb isotopic composition that, when added to the mete-
orite, results in higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of the mineral fractions.

5.3.2. Mechanisms to produce a contaminant with an elevated $^{207}\text{Pb}/^{206}\text{Pb}$ ratio

Modern Pb with a $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of $\geq 1$ and a $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of $\geq 13.15$ cannot be produced by a single stage of growth in a reservoir with a constant $\mu$ value since 4.56 Ga. Instead, at least two stages of growth are required in reservoirs with differing $\mu$ values. The first stage of growth must occur in a reservoir with a relatively high $\mu$ value to produce an enrichment of $^{207}\text{Pb}$ relative to $^{206}\text{Pb}$. Continued decay of U in this reservoir will lower its $^{207}\text{Pb}/^{206}\text{Pb}$ ratio because its $^{238}\text{U}/^{235}\text{U}$ ratio is increasing through time. Thus, to preserve high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in martian materials until the present, Pb must be fractionated from U early in the evolutionary history of the system.

The timing of this fractionation event can be partially constrained. The shaded area in Figure 6 represents single-stage Pb that has a $^{207}\text{Pb}/^{206}\text{Pb}$ ratio greater than 1, and $^{207}\text{Pb}/^{206}\text{Pb}$ ratio that is greater than 13.15. Lead removed from a reservoir that formed at 4.56 Ga with a $\mu$ value greater than ~5 (before ~1.8 Ga ago) will satisfy the minimum isotopic criteria of the contaminant. This scenario requires U and Pb to be fractionated completely, that is, formation of a second reservoir with a $\mu$ value of 0. The extreme U-Pb fractionation required by this scenario ultimately suggests that this is a minimum age and that U-Pb fractionation likely occurred before 1.8 Ga.

Igneous processes involving pyroxene and olivine cannot strongly fractionate U from Pb. However, U is significantly more mobile than Pb in some fluid-dominated weathering conditions. Asmerom and Jacobsen (1993) demonstrated that U is removed in preference to Pb in modern terrestrial weathering environments as a result of the increased solubility of U relative to Pb. In fact, they found that the $\mu$ values of crustal weathering residues could be lowered from their original values by a factor of ~2. If the low U/Pb of the source of the Zagami contaminant reflects U removal by weathering, a U-rich surface material is expected to be present in Mars. Alternatively, chemical precipitates formed from aqueous solutions may have low U/Pb ratios as a result of a greater compatibility of Pb compared to U in these precipitates. Martian surface materials such as soils could therefore represent material from which U was removed, and/or Pb concentrated, by water. Thus, it is possible that fluid-based weathering of surface materials occurring before 1.8 Ga could strongly fractionate U/Pb ratios, accounting for the Pb isotopic systematics of the contaminant. If this material is present in the impact melt glasses in Zagami, as suggested for EETA79001 by Rao et al. (1999), it could explain the U-Pb isotopic disturbances observed in the Zagami mineral fractions. Production of the Pb isotopic systematics of the contaminant by fluid-based weathering processes is consistent with a soil origin for the contaminant. If the contaminant Pb observed in the martian meteorites is derived from the soils, then the soils are likely to have been geochemically altered by ancient fluid-based weathering processes.

5.4. $^{238}\text{U}/^{204}\text{Pb}$ Ratio of Planetary Reservoirs

5.4.1. Comparison of reservoirs from Earth, the Moon, and Mars

Estimations of the $\mu$ value of planetary mantle and crustal reservoirs on Earth, the Moon, and Mars are constrained to varying degrees on each body. Because U and Pb are not strongly fractionated by igneous processes, the $\mu$ values of these reservoirs in turn constrain the $\mu$ values of the bulk planet. For example, the $\mu$ values of the Earth’s mantle and crust are estimated to be 8 to 10 and 11 to 12, respectively (e.g., Zartman and Haines, 1988; Asmerom and Jacobsen, 1993), suggesting that bulk silicate Earth has a $\mu$ value of 10 ± 2. In contrast to terrestrial samples, the ancient age and impact metamorphosed nature of many lunar samples, combined with their very low Pb abundances, has resulted in much more uncertain estimations of $\mu$ values of lunar sources (e.g., Tera and Wasserburg, 1972; Tera and Wasserburg, 1974; Tera et al., 1974). Nyquist and Shih (1992) noted that the $\mu$ values estimated for mare basalt source regions ranged from ~0 to 650, with most estimates between 100 and 400. Unruh and Tatsumoto (1977) argued that the $\mu$ values for mare source regions should be representative of the bulk Moon, concluding that the bulk Moon has a $\mu$ value between 100 and 300. Finally, the $\mu$ value for the Zagami source is estimated to be 3.96 ± 0.02. This is the only internally consistent estimate of the $^{238}\text{U}/^{204}\text{Pb}$ of any martian source. The Rb-Sr, Sm-Nd, and Lu-Hf (Blichert-Toft et al., 1999) isotopic systematics of Zagami indicate that it is derived from one of the most highly fractionated and evolved reservoirs on any sampled differentiated body (Borg et al., 2003), suggesting that the $\mu$ value of the Zagami source is likely to represent a near maximum value for any martian mantle or crustal reservoir.

Despite the uncertainties, it is evident that the $\mu$ value for bulk Moon is greater than the $\mu$ value for bulk Earth, which is in turn greater than the $\mu$ value for bulk Mars. This could reflect differences in U/Pb ratios of the bulk planet, or removal of Pb from the silicate portion of the body by core formation. Chen and Wasserburg (1986a) noted that the U-Pb isotopic systematics of martian meteorites indicated derivation from low $\mu$ sources and speculated that this was consistent with higher volatile element (e.g., K, Rb, and Pb) abundances for Mars (Dreibus and Wänke, 1985). This is also supported by the observation that the bulk $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of the Moon (0.042; Renan and Jacobsen, 2005), Earth (0.083), and Mars (0.16; Borg et al., 1997) inversely correlate with estimates of their bulk $\mu$ values. Because Rb is not fractionated from Sr by core formation, this inverse correlation suggests that variations of U/Pb ratios in the silicate portions of the Moon, Earth, and Mars reflect variations in the volatile element budgets of these bodies.

5.4.2. U/Pb ratios of martian meteorite source regions

It is difficult to estimate the $\mu$ value of the source regions of the basaltic martian meteorites other than Zagami because their U-Pb isotopic systematics are clearly disturbed. Some of the meteorites, however, yield $^{238}\text{U}/^{206}\text{Pb}$ ages that are concordant with their Rb-Sr and Sm-Nd ages (Chen and Wasserburg, 1986a; Chen and Wasserburg, 1986b; Fig. 7) and are therefore
Fig. 7. 238U/206Pb isochron plot of basaltic meteorites which yield ages that are roughly concordant with their Rb-Sr and/or Sm-Nd ages (i.e., ~170 Ma). The U-Pb isotopic systematics of these samples appear to be the least affected by impact metamorphism and alteration. EETA79001A (open diamonds), ALH77005 (filled triangles), Zagami (open squares) are leachate whole-rock tie lines, whereas Shergotty (filled circles) are whole-rock, mineral, and leachate data (Chen and Wasserburg, 1986a; Chen and Wasserburg, 1986b). Filled squares are Zagami mineral fraction residues from this study. There is no correlation between the initial 206Pb/204Pb (Ipb) determined from these isochrons and initial Sr and Nd, suggesting that the initial 206Pb/204Pb ratios determined from leachate whole-rock tie lines are not reliable despite yielding appropriate crystallization ages.

Altogether, the Pb isotopic systematics of Mars are probably required before potential variations in the U/Pb ratios of their source regions can be rigorously evaluated.

6. CONCLUSION

The crystallization age of Zagami is well-defined by concordant Rb-Sr, Sm-Nd, and 235U-207Pb ages of 166 ± 6 Ma, 166 ± 12 Ma, and 156 ± 6 Ma, respectively. The concordance of these ages suggests that the 238U-206Pb isotopic system of the most pure mineral fractions has not been significantly disturbed by postcrystallization processes. In contrast, the 235U-207Pb systems demonstrate more disturbance as manifested by discordant or imprecise ages derived from chronometers that incorporate the 215U-207Pb decay series. The isotopic disturbances observed in the silicate and reject mineral fractions are interpreted to be the result of the addition of Pb characterized by an elevated 207Pb/206Pb ratio. This Pb must ultimately be derived from an ancient high μ martian source that was subsequently fractionated to a lower μ value before 1.8 Ga. This fractionation of U from Pb early in martian history probably requires aqueous processes to efficiently separate U from Pb, indicating the contaminant could be derived from martian surface material. The initial 206Pb/204Pb ratio determined from the 238U-206Pb isochron is 13.268 and corresponds to a source region with a μ value of 3.96. Although this is a maximum value, given the disturbance of the U-Pb isotopic system, it is significantly lower than estimates for terrestrial or lunar sources regions. The initial 87Sr/86Sr ratio and 166Nd value of Zagami are 0.721566 ± 0.000082 and ~7.23 ± 0.17, respectively, and indicate that this meteorite is derived from one of the most highly evolved martian source regions. It is therefore probable that the μ value estimated for Zagami represents a near maximum martian value. The low μ value of the Zagami source likely reflects the high volatile element content of Mars relative to other terrestrial bodies.

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