YOUNG K-Ar AGE OF JAROSITE IN THE MOJAVE 2 SAMPLE AT GALE CRATER, MARS.

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Introduction: By combining the Sample Analysis at Mars (SAM [1]) instrument's capabilities with those of the alpha particle X-ray spectrometer (APXS [2]) on the *Curiosity* rover, radiometric K-Ar ages and ^{3}He, ^{21}Ne, and ^{36}Ar exposure ages have been measured on two samples as of sol 1430 [3,4]. The Cumberland mudstone was found to have a K-Ar age of 4.21 ± 0.35 Ga (all uncertainties here are reported in 1σ) [3], consistent with crater-counting estimates of the surrounding terrains [5]. A second geochronology experiment was undertaken on the potassium-rich Windjana sandstone [4], which resulted in the unreasonably young and unrepeatable ages of 627 ± 50 Ma and 1710 ± 110 Ma on two different aliquots. These results were attributed to incomplete Ar extraction arising from the coarse grainsize and Ar-retentive characteristics of sanidine, the major K-bearing mineral in the sample.

Recently, a drilled bedrock sample from the Murray mudstone formation (termed Mojave 2) was found by the CheMin instrument to contain approximately 3.1 wt% jarosite [6]. Jarosite is precipitated from acidic, sulfate-rich waters and is a suitable mineral for K-Ar dating [7]. On a large scale, jarosite has been thought to signal the aridification of Mars and a shift towards a cold, dry environment [4]. The small amount of jarosite in this sample prohibits generalization to a larger Martian context. However, since jarosite forms strictly through interaction with water, the K-Ar age of the jarosite in Mojave 2 puts a maximum age constraint on the last time liquid water was present at the sample site. By extension, it could also indicate the time of the very final stages of evaporation from the lake in Gale Crater.

A two-step heating experiment was designed to obtain the K-Ar age of the jarosite, which accounts for about 20% of the K_2O in the sample. The remainder of the K_2O exists in plagioclase, an amorphous component, and possibly a small amount in K-bearing phyllosilicates.

Methods: After drilling, samples are sieved to <150 μm and delivered to SAM's sample handling system. In the new two-step heating experiment, the sample is first preheated to ~135°C to remove contaminants introduced to the sample within SAM ("boil-off" step). The temperature is then ramped monotonically to 500°C. Evolved noble gases are purified by exposure to a scrubber and a getter, and measured by the quadrupole mass spectrometer (QMS) in high sensitivity semi-static mode (described in detail in [3]). The analyzed gas is then pumped away while still scanning with the QMS, enabling the background present in the instrument to be measured. The next sol, an identical procedure is followed on the same sample, except that the final temperature ramp reaches approximately 1000°C.

Results: The two-step heating experiment was attempted twice on Mojave 2. An over-pressure alarm was triggered during the first step and the gas released during heating was vented; as a consequence no data is available for this run. A second aliquot of the sample was available and the second two-step heating experiment was executed successfully.

Bulk K-Ar Age: Summing the two steps, a total of 4340 ± 580 pmol/g of ^{40}Ar was measured. Given a bulk K_2O of 0.73 wt%, an age of $1.72^{+0.34}_{-0.30}$ Ga is obtained. This low age suggests a youthful K-rich component in the sample, possibly the jarosite. By modeling the amount of K attributable to phases degassed in each heating step, the ages of low and high temperature components can be estimated independently (see discussion below).

Exposure Ages: While ^{3}He was measured successfully, measurement of ^{21}Ne was not successful in this run because of a radiofrequency shift near mass 21, which resulted in unreliable data in that area of the mass spectrum. Similarly, ^{36}Ar is not readily resolvable given the buildup of isobaric HCl (masses 36 and 38) in SAM over the course of *Curiosity's* mission. These cosmogenic isotope data may be recoverable, but are beyond the scope of the current project. Without validation of the ^{3}He results from these latter two isotopes, we defer discussion of the exposure age results to a later date.

Discussion: Interpretation of the K-Ar data requires a model of the potassium distribution within Mojave 2. The phases likely to host K are andesine, jarosite, the amorphous fraction (53% of the sample), and possibly phyllosilicates. The jarosite is thought to be approximately 1:1 K:Na-jarosite based on its XRD pattern [8], and andesine typically has ~0.3 wt % K_2O [9]. The K contents of the phyllosilicate and amor-

phous phases are less well known. By comparison to the K_2O content of other, more phyllosilicate-rich samples, the amount of K-bearing phyllosilicates (such as illite or K-nontronite, referred to hereafter as K-phyllosilicates) is thought to be at most a few wt% [10]. As any K-phyllosilicates would most likely not quantitatively retain [40]Ar [11], we propose a maximum of 1 wt% [40]Ar-retaining K-phyllosilicate in Mojave 2. By mass balance, the remainder of the K after assignment to the other phases must reside in the amorphous fraction.

Argon is released from plagioclase only at high temperatures, and then only if it has a small grain size [3,4], so we associate the plagioclase-sourced Ar with the high T step. Similarly, jarosite releases Ar at ≤500°C [12], so its burden of Ar is assigned to the low-temperature step. The more poorly characterized amorphous and K-phyllosilicate fractions likely also release [40]Ar in the low temperature step. It is possible that some radiogenic Ar from these phases is not retained over geologic time either as a result of diffusion or as a result of dissolution/recrystallization in the case of the amorphous phase. Some additional Ar may also be lost from the amorphous fraction and/or K-phyllosilicates in the initial boil-off step [11].

High T Step: Taking the amount of andesine and its estimated K content, along with the amount of [40]Ar released, we estimate a K-Ar age of $4.04^{+0.32}_{-0.34}$ Ga for the high T step. We associate this age with the detrital feldspars in the sample. This age is well in line with previous results for detrital minerals in Gale Crater [3]. This agreement offers good evidence that the [40]Ar in this step was released only from the plagioclase fraction, and that it was released quantitatively.

Low T Step: By mass balance all K not associated with andesine is attributed to phases degassing in the low T step (jarosite, amorphous, and K-phyllosilicate). Jarosite is known to be Ar-retentive [7], while loss from the amorphous and phyllosilicate fractions in nature or in the boil off is possible.

Figure 1 illustrates the resulting mass balance implications for the estimated K-Ar age of the low temperature mineral components. If the amorphous and K-phyllosilicate fractions quantitatively retain their Ar until the low T step, then the combined age is $1.48^{+0.94}_{-0.48}$ Ga. In contrast, if neither the amorphous nor K-phyllosilicate phases retain any radiogenic [40]Ar, then the age of the jarosite (alone) would be $3.42^{+0.83}_{-0.63}$ Ga. This oldest age assumes no Ar retention in hypothetical K-rich phyllosilicates. If the maximum of 1 wt% K-phyllosilicates are present in the sample and no Ar is retained in the amorphous fraction, the bulk age of the low-T step is $2.81^{+0.90}_{-0.62}$ Ga. However, it is also unlikely that the amorphous material would be wholly unreten-
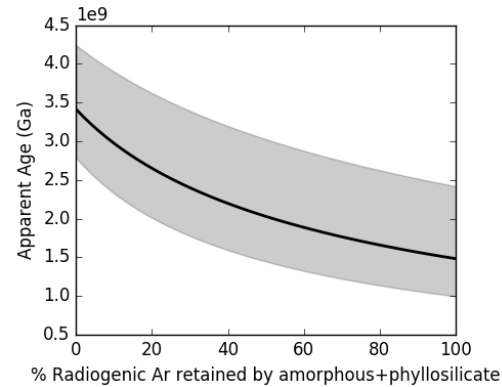

Figure 1: The calculated combined age of the phase releasing Ar at a low temperature. Uncertainty is shown in gray band.

tive. If the amorphous component retains 25% of its radiogenic [40]Ar, a bulk age of $2.26^{+0.90}_{-0.58}$ Ga results, assuming 1wt% K-phyllosilicate is also present. In the same scenario, if the amorphous phase is 50% retentive, an age of $1.92^{+0.90}_{-0.54}$ Ga is obtained.

Of these scenarios, those with a bulk age of ≳3 Ga are consistent with formation of jarosite by fluids associated with the lake in Gale Crater, while the younger ages would require far more recent activity of water to crystallize or recrystallize the jarosite +/- amorphous material. Without better constraints on the nature of the K-phyllosilicates and amorphous phase in Mojave 2, it is impossible to say which of these scenarios is most likely, except to say that quantitative retention or loss (the scenarios at 0% and 100% of Figure 1) of radiogenic Ar from these phases is unlikely. Despite the rather large uncertainty of these younger ages, the most likely scenario appears to be that the low-T phases were formed well after the plagioclase in the sample.

This younger authigenic age is potentially an indication of the most recent aqueous activity at the Mojave 2 drill site. Due to the implication of jarosite as an indicator of large-scale desiccation, obtaining a radiometric age on this component is a vital step towards understanding the absolute timing of Mars's evolution towards a cold, dry planet.

References: [1] Mahaffy P. R. (2012), *Space Sci. Rev.*, 170, 401-478 [2] Campbell et al. (2012), *Space Sci. Rev.*, 170, 319-340 [3] Farley K. A. et al. (2014), *Science*, 343.6169, [4] Vaconcelos P. M. et al. (2016) *JGR: Planets*, 121.10, 2176-2192, [5] Le Deit, L. (2013) *JGR: Planets*, 118.12, 2439-2473, [6] Rampe L. et al. (in prep), *EPSL* [7] Vaconcelos P. M. et al. (1994), *GCA*, 58.1, 401-420, [8] Morrison et al. (2017), Am. Min., submitted, [9] Bachmann et al. (2002) *J. Petrol.*, 43, 1469-1503, [10] Bristow T. et al. (2017), this meeting, [11] McDougall and Harrison (1999), *Oxford Press* [12] Waltenburg (2012), *thesis*, Univ. of Queensland