Martian Chronology and Atmospheric Composition: In Situ Measurements Versus Sample Return.

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Overview. I examine two significant issues of martian science from the point of view of in situ measurements by robotic spacecraft versus sample return and analysis in terrestrial labs. (1) To define martian history, ages of geological processes and surface features are required. Estimated ages from surface crater densities have limitations, and the ages measured for martian meteorites cannot be associated with specific martian locales. Whereas returned martian rocks could be accurately dated, some have suggested sending a robotic spacecraft to Mars to measure rock ages using the classical K-^{40}Ar technique, considered the easiest to implement. (2) To understand the evolution of the martian atmosphere and its interactions with the surface, requires precise measurements of atmospheric composition. A significant amount of information has derived from measurements by Viking and of martian meteorites. Instrumentation on the Mars Science Lander (MSL) spacecraft to be launched in the near future promises to determine atmospheric composition even more precisely. If MSL is successful, which questions about atmospheric composition will remain and thus will require atmospheric sample return to answer?

Meteorite Ages & Robotic Age Dating. At JSC we have measured ^{39}Ar-^{40}Ar ages of many martian meteorites. Essentially all of the shergottites, but not the nakhlites, contain excess ^{40}Ar that renders their K-Ar formation ages difficult to measure. We have argued that in many shergottite samples this excess ^{40}Ar was not acquired from the martian atmosphere, but is radiogenic ^{40}Ar contained in the basaltic magma and incorporated into the meteorites during crystallization. Fig. 1 gives an isochron plot of total K versus total ^{40}Ar for nine basaltic shergottites that show similar formation ages of ~170 Myr, as determined by other radiometric techniques. Data with high and very low [K] are feldspathic and pyroxene separates, respectively, and intermediate [K] data are whole rock. Such an isochron is the manner K-Ar data acquired robotically likely would be evaluated. The dashed lines all have the same slope and represent an isochron age of 170 Myr. It is obvious that none of the data are consistent with a K-Ar age as young as 170 Myr unless comparable amounts of excess ^{40}Ar (1-2.5 $\times 10^{-6}$ cm^{3}STP/g) is present in all samples. An analogous isochron plot of JSC data for three depleted shergottites having formation ages of ~470 Myr gives similar results.

A K versus ^{40}Ar isochron plot for whole rock and mineral separates of six martian nakhlites is strongly linear and defines a precise (R^2=0.9986) isochron age of 1325 ±18 Myr, in excellent agreement with the range in ages obtained on individual nakhlites by other chronometers. Further, because the isochron passes within error of the origin, these nakhlite samples contain essentially no excess ^{40}Ar.

The dilemma that would be faced in robotically dating *in situ* these meteorite samples by K-Ar is in knowing whether they did or did not contain excess ^{40}Ar. To answer this question clearly would require that a K-^{40}Ar isochron be produced from samples possessing sufficiently different [K] so as to define the isochron slope (Fig. 2). If the isochron slope is not defined, the presence or absence of ^{40}Ar$_{xs}$ and thus the K-Ar age cannot be determined. Even among six nakhlites, whole rock [K] varies less than a factor of three.

Martian Atmospheric Composition. The SAM FM mass and laser spectrometers aboard MSL have the potential of measuring the isotopic composition of several martian atmospheric species to precisions of ~0.2-1% (P. Mahaffy, pers. comm.., 2008). Measurement of lower abundance isotopes is expected to be less precise, yet these isotopes often constitute the most critical data for addressing science questions. Below I list major science questions associated with individual atmospheric species. Assuming that MSL will measure the isotopic abundance of these species to 1%. I then evaluate whether a strong rationale remains for returning to Earth an atmospheric sample of that species.

Xe and Kr. Isotopes of atmospheric Xe are strongly mass fractionated, ~40% across 124-136 amu, probably by early atmospheric loss. Kr composition, however, is close to solar Kr, but may be slightly mass fractionated. Relatively precise measurements of the extent of these fractionations are required to know the origins (e.g., solar, cometary, planetary) of original Xe and Kr acquired by Mars and of the atmospheric loss processes and timing. Further, the atmosphere contains large relative excesses of ^{129}Xe (^{129}Xe/^{132}Xe=2.6) from decay of extinct ^{129}I; likely small relative excesses of $^{80,\ 82}$Kr produced by neutron capture on bromine; fission Xe; and possibly gas produced by cosmic ray reactions. A 1% precision in measuring the total Xe isotopic composition would reasonably define both the fractionation pattern and the amount of excess ^{129}Xe, but would not accurately define the fission and spallation components. The small fractionation in Kr and the presence of neutron components would require precision greater than 1% to accurately define both effects. Thus, a strong case can be made for returning a sample of Kr, and a moderately strong case for returning Xe.

N_2, Ar, Ne Viking measured martian ^{15}N/^{14}N as 1.62 ±0.16 that of Earth. This value reflects fractionation during atmospheric loss over time, and is the major science issue associated with atmospheric ^{15}N/^{14}N. Measuring this ratio to 1% would be sufficient for modeling mechanisms of such loss. The ^{38}Ar/^{36}Ar ratio appears to have been increased by ~25% from the original by atmospheric loss over time, and is known to ~5-10%. Again, knowing this ratio to 1% would satisfy loss models. Because of uncertainties in loss models, it seems unlikely that precision greater than 1% in either ^{14}N/^{15}N or ^{36}Ar/^{38}Ar could address the original compositions before loss. The atmospheric ^{40}Ar/^{36}Ar ratio is ~1800 ±10%, and represents decay of ^{40}K in the crust and its degassing over time. Measuring this ratio to 1% is probably satisfactory in order to evaluate time evolution of the atmospheric ratio by comparison to older atmosphere trapped in solid samples. No precise measurements exist for Ne, which may be strongly fractionated due to loss. Again, a 1% isotopic precision is probably satisfactory.

CO_2. Viking measured the isotopic composition of C and O in atmospheric CO_2 to ~5-10%. These elements may not be significantly fractionated because of buffering by larger quantities of surface condensates. However, phase transitions and chemical reactions involving these elements produce small isotopic fractionations at the per mill level, and atmospheric CO_2 is likely to be an important part of these transitions. Thus, isotopic measurements of atmospheric CO_2 more accurate than those likely to be determined by MSL is important for a wide variety of science questions, including. temperatures involved in some reactions.

Minor Reactive Species. It is not apparent that minor, chemically reactive species in the martian atmosphere can be returned to Earth unaltered. Although they address interesting science questions, some of these species may be better measured *in situ*.

In summary, good rationale can be presented for return to Earth of martian atmospheric Kr, Xe, and CO_2, but the arguments are weaker for N_2, Ar, and Ne. This assumes that MSL actually measures these isotopic compositions to 1%. If MSL fails to accomplish this goal, good science rationale exists for measuring all these atmosphere species in terrestrial labs.

Lack of space prevents me from quoting many relevant references, for which I apologize.