Geochronology and Mars Exploration: Critical Measurements for 21st Century Planetary Science

Pamela G. Conrad[1], F. Scott Anderson[2], Robert C. Anderson[1], William J. Brinckerhoff[3], Peter Doran[4], Victoria E. Hamilton[2], Joel A. Hurowitz[1], Alfred S. McEwan[5], Douglas W. Ming[6], Dimitri A. Papanastassiou[1], Timothy D. Swindle[5]

[1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA; [2]Southwest Research Institute, Boulder, CO; [3]NASA Goddard Space Flight Center, Greenbelt, MD; [4]The University of Illinois, Chicago, IL; [5]The University of Arizona, Tucson, AZ, [6]NASA Johnson Space Center, Houston, TX

Executive Summary

Absolute dates are critical to the next level of understanding of the processes that differentiated the planet and shaped the Martian surface. To that end, we urge the Decadal Survey to recommend:

- Development of an architecture and schedule for implementing geochronology investigations on Mars within the next ten years
- Sustained funding to increase the technology readiness levels of instrumental approaches for measurements using multiple and complementary radiogenic isotopic systems, e.g., Rb-Sr and K-Ar geochronology.
- Funding to develop sample preparation approaches for unique challenges specific to in situ geochronology
- Development of requirements and procedures for selection of appropriate samples for chronology studies in samples to be returned from Mars

Introduction

Stunning data returned by recent orbital missions such as Mars Reconnaissance Orbiter, Mars Express, Mars Odyssey and Mars Global Surveyor have given us confidence in the hypothesis that Mars was once shaped by large amounts of water on its surface. The Mars Exploration Rovers have shown us glimpses of rocks that we recognize as indicative of particular paleoenvironments of deposition, and Phoenix has intrigued us with a tantalizing peek at potentially complex mineral alteration and geochemistry. As Mars Science Laboratory prepares to interrogate the surface of Mars, using an extraordinarily capable instrument payload to assess the planet's habitability potential, we are poised to move beyond the questions regarding characterization of contemporary Mars to achieving a quantitative understanding of the processes that have shaped it. The next steps in our understanding of Mars will come from insight into the rates of change for planetary processes such as the history of water, climate change, astrobiology, and the genesis of fundamental geologic structures. This requires us to begin building a foundation of absolute dates upon which to frame the relative dates of both geological and biological evolution. And beyond the importance of geochronology to Mars exploration, investigations into the evolution of other bodies in the solar system are also enabled profoundly by the capability to pinpoint events in absolute rather than relative time. Technical progress in this regard is now sufficient to position us to step from behind the declaration that in-situ geochronology is "just too hard" to the proposal of concrete and specific steps toward the dating of important events in the evolution of our solar system.

The search for life in the solar system is strongly dependent upon the success of searches for the right moments in planetary evolution. To the first order, life is not only what it eats, but also a reflection of several *environments*: where it originated, where it exists, where it declines, and where it is or is not preserved after death. Mars exploration is informed by Earth exploration, and vice versa. But on Earth, the furthest reach of our backward glance is made problematic by the continued dynamism of Earth's interior and the resultant plate tectonic movement, which has driven the subduction of Earth's history beyond about 3.8 billion years before present. On Mars, whatever the dynamic character may have been at one time, all appears quiescent now. To understand the nature and timing of events that have brought Mars and Earth to such markedly different present states could be critical to an understanding of our own origin.

The importance of establishing an absolute chronology for both Mars' surface and interior has already been established in the MEPAG goals document (Goal III - geology). MEPAG Goals I (life) and II (climate) are also dependent upon the determination of absolute timing of events in Mars' history. Doran et al. [11] provided a framework for the breadth of investigations in Mars science where improvements in geochronology are necessary. From among these target areas of inquiry are fundamental questions about Mars evolution:

What is the thermal and chemical evolution of Mars?
When did core convection cease to produce a protective magnetosphere?
What is the history of Martian tectonics?
What are the ages and rates of cratering on Mars?
What is the nature and timing of atmospheric evolution on Mars?
What is the history of the Martian water cycle?
What is the history of global climate change on Mars?

And these questions are key elements of inquiry about Martian life and habitability:

Did life ever arise on Mars?
If so, when? If not, why?

Significance of Mars Chronology

The existing understanding of Mars chronology is based primarily upon crater density and analogy with the Moon [1]. The rate of cratering (or bolide flux) and its fluctuations over time are incompletely constrained for both the Moon and Mars, which presents a problem when trying to infer absolute ages. There are models based upon the assumptions that (a) the lunar cratering history is understood, and (b) the Martian flux rates can be derived from the lunar rate. However, the models vary widely in their predictions of absolute age [3-11] so there are large uncertainties associated with these predictions. It is noteworthy that the assumption of lunar crater ages and implications were initially incorrect prior to actually dating returned Apollo samples and recognizing a non-linear impact rate [6, 7]. Additional confounding variables that contribute to the uncertainties associated with dating by crater density on Mars (and do not similarly impact interpretation of the lunar cratering record) are the contributions of persistent volcanism [12, 13, 14] and fluvial and aeolian weathering [1, 14, 15] to the preservation of impact craters on Mars. Crater counts on Mars provide crater retention ages, but that is only a lower limit to the age of the actual geologic units.

Why does this matter? There are at least two important reasons. First, the evolution of the Earth from its accretion to its present state with dynamic interior, robust biosphere, dense atmosphere and protective magnetic shielding was initiated at the same time as the evolution of Mars. With the two very different present outcomes, the two planets have either undergone different processes or different rates of similar processes. As we study both the evolution of Mars and the evolution of the Earth, the only opportunity to look at processes that occurred on Earth between the time our early history was subducted and the time of our formation may be by analog on Mars. Secondly, the ability to link large scale catastrophic events to moments in time will provide rich insight into how Mars moved from a potentially habitable planet, perhaps warmer and wetter, with denser atmosphere and dynamic interior with consequent magnetic protection from cosmic radiation, to its present desiccated and highly oxidized shell.

State of the Art on Earth and Sample Return

While the selection of the most appropriate chronometer(s) will still be driven by the nature and abundance of datable materials in a returned sample from Mars, the Earth laboratory has some clear advantages over the in situ laboratory: the entire arsenal of dating techniques can be applied to samples, or we can decide which techniques are applicable based upon cosmochemistry.

Modern Geochronology is a large, diverse and technically evolved field, but is based on a few well-defined principles and types of measurements; i.e, mass spectrometric analyses of the distributions of radiogenic isotopes and their parent nuclides. Chronometry based on isotopes of the noble-gases (e.g., K-Ar and U-He) principally involve heating of mg-sized samples, whereas the various lithophile-element chronometers (Rb-Sr, Sm-Nd, U-Pb, Re-Os) involve chemical separation of target elements from samples on the order of several milligrams, followed by isotopic analysis by thermal- or inductively-coupled-plasma ionization mass spectrometry. Successful, quantitative geochronology on Mars will surely involve either application of these laboratory techniques to samples returned from the Martial surface, or technical innovations that permit similar techniques to be simplified, automated, miniaturized and integrated into the analytical payload of an in situ platform.

There can be little doubt that dates measured on returned samples will be higher in quality than those measured by any easily imagined in-situ instrument. Modern geochronologic labs are able to process samples in clean environments that permit confident analysis of the isotopic compositions of pg-quantities of most elements. And, the mass spectrometric instruments in such laboratories routinely achieve precisions for isotope ratio measurements on the order of parts per million; when applied to the various common lithophile-element chronometric systems (Rb-Sr; Sm-Nd; U-Pb) this level of precision translates into dates with uncertainties of 0.1 % or less, relative (though modern laboratory methods of geochronology on materials we are likely to encounter on Mars —mafic igneous rocks, authogenic sulfates and oxides — typically yield data with external errors on the order of 1 % because the most precise chronometric systems are not easily applied to them). Finally, terrestrial labs include several capabilities for dating by surface analysis techniques, based on ion-microprobe, laser-ablation-inductively coupled plasma mass spectrometry (ICPMS) and electron probe techniques that can yield dates with precisions on the order 1-2 %, relative, for select materials and isotopic systems. Ion probe U-Pb on zircons is typically 0.1% or better. These techniques consume very little material (typically $\leq$1 μg) and provide dates with petrographic context, so they have great potential for the study of the small, precious materials that would be returned to Earth by a sample-return mission. However, it should be recognized that established in-situ dating techniques are generally useful only for dating by the U-Pb system on phases that are exceptionally rich in U and poor in Pb (e.g., zircon, monazite and badelyite). Such phases are rare in the Martian (SNC) meteorites and may be rare on the surface of Mars.

Despite the many obvious strengths of laboratory dating of returned Martian materials, the dating of returned samples from Mars is also challenging. Even leaving aside obvious hurdles such as cost and the technical challenge associated with a robotic launch from another planet and return of uncompromised samples to Earth, there are even some scientific challenges. A sample return mission would not permit iteration between sample selection and analysis, and so its scientific impact would depend strongly on the soundness of the initial sampling plan. The MER mission has been pleasantly surprised by discoveries to which the science and technical teams could respond in near real time; much of this flexibility would be lost without the ability to respond in situ. Also, the interrogation of many samples will be necessary to statistically constrain results. Once we are ready to proceed with a sample return mission, there are several scientific problems that must be addressed beforehand. For example, much of our interest in the surface evolution of Mars centers on aqueously deposited and aqueously altered materials that provide evidence for past water-rich environments. We now know that some of these materials are rich in authogenic sulfates and oxides that are not common targets for terrestrial geochronology, though they have been done with robust interpretations [28]. It is critical that we develop a sophisticated understanding of just how one approaches the geochronology of such materials. This will require studies of terrestrial analogues for these phases and experimental studies of trace-element partitioning and mobility within them.

The state of the art on Earth is not an argument for sample return geochronology to the exclusion of in situ geochronology on Mars, but rather it is an important aspect of what should be focused and complementary programs that advance our capability to ask planetary science questions that require absolute dates.

In Situ Dating

Doran et al [11] argued that the large uncertainties associated with the placement of the Martian epochs, allows for considerable relaxation of the requirements for precision on in situ measurements that can still produce important science.

Significant study has been invested in identifying viable methods for producing absolute dates on the surface of Mars [c.f. 16, 17, 18, 19, 20]. The relatively high abundance and simplicity of sampling and analysis strategies for ^{40}K-^{40}Ar and ^{87}Rb-^{87}Sr methods have led to their proposal to flight programs and PIDDP [18, 19, 20, 21, 22]. Three potential in-situ methods appropriate for long-term chronology (that we know of) are currently under investigation:

1) Noble gases: A single broad-spectrum analysis of the noble gases can be used for a wide range of chronometers (e.g., ^{40}K-^{40}Ar dating, U-Th/^{4}He dating, and ^{3}He and ^{21}Ne exposure ages). Noble gas chronometry has a number of potential advantages. The type of mass spectrometers one might use for such analyses have already been built and flight-certified (e.g., the quadrupole mass spectrometer that is a component of the Sample Analysis at Mars experiment that will fly on the upcoming Mars Science Laboratory). The magnitudes of isotopic variations resulting from radioactive decay are relatively large (tens of % and more), so mass spectrometric measurements can require relatively less precision. Efficient methods of extracting gases from solids and of ionizing gases in a mass spectrometer are well understood and previously used in space missions. The ^{40}K-^{40}Ar approach requires a three step process in which the elemental abundance of ^{40}K in a powdered sample is determined using XRF or LIBS, followed by the measurement of ^{40}Ar noble gas using an 1100-1600° oven and mass spectrometry technique. To accurately assess the gas output, the mass of the sample also needs to be accurately determined. Published designs for dating using the ^{40}K-^{40}Ar system may require multiple measurement stations and a transport system. Analysis and interpretation of SNC meteorites using K-Ar have been the subject of debate regarding their interpretation due to the need to correct for excess ^{40}Ar in the Martian atmosphere and the Martian interior. The atmospheric $^{40}Ar/^{36}Ar$ ratio is well known, but the interior $^{40}Ar/^{36}Ar$ ratio is unclear, and is likely to be variable and difficult to correct [23, 24, 25]. When the Mars Science Laboratory's SAM instrument conducts its noble gas measurements, these variables will have better constraints. Development of the sample transport and oven systems have been initiated, with hopes to redesign and integrate existing mass spectrometry instruments (SAM) and XRF or LIBS approaches, though the oven system remains a design issue [25].

2) The second approach uses laser desorption followed by electron impact of the secondary neutrals and measurement in a mass spectrometer. This approach has advantages of being comparatively simple, with history of published results for generally similar laboratory based instruments using this technique. However, a challenge for all Rb-Sr measurements is the separation, and high precision

measurement, of ^{87}Rb from ^{87}Sr. This instrument approach measures the net abundance of mass 85 (^{85}Rb) and 87 ($^{87}Rb+^{87}Sr$), then uses the amount of ^{85}Rb to estimate ^{87}Rb, with the difference being ^{87}Sr. Similar methods using LA-ICP-MS to determine the ^{87}Rb and ^{87}Sr have been used to date a some terrestrial rocks [e.g. 26], however, there are significant sample dependent issues including problems with: a) accurate estimates of ^{87}Rb and ^{87}Sr when the Rb abundance is large, b) laser induced isotopic & elemental fractionation, and c) molecular isobaric interferences [27]. Development of the mass spectrometry portion of the instrument is highly advanced, and current work focuses on integration, testing of the ion source, and refinement of the technique to produce data.

3) The third approach uses Laser Desorption Resonance Ionization Mass Spectrometry (LDRIMS) for ^{87}Rb-^{87}Sr, requiring a single measurement station, and enabling the separate, interference free measurement of Rb and Sr [16, 19], avoiding the issues described in #1-2. The LDRIMS approach requires little sample preparation, and the surface can be cleaned via laser desorption before measurements begin. LDRIMS prototype development is extensive enough to produce initial isotopic measurements of rubidium (easy) and strontium (hard), using only low power lasers, in a package consistent with future flight opportunities. LDRIMS is currently producing data consistent with in-situ geochronology, specifically, Rubidium and Strontium can be detected to part-per-trillion levels, and a measurement precision of 0.5% on net 10 ppm Sr samples (in under 1 minute) has been repeatedly attained. Because LDRIMS measurements can be made much more quickly than traditional geochronology methods, and bypass the need for chemical separation of Rb and Sr, many more points can be measured, significantly mitigating the effects of lower precision. For example, 1000 measurements, sufficient to date 4-billion-year-old Martian meteorite, ALH84001, to better than ±100 Ma, can be achieved in under 6 hours using the present instrument. The LDRIMS technique has not previously been used for geochronology, though it has long been recognized that the approach is well suited for Rb-Sr measurements. This instrument builds on a mass spectrometer twice proposed for flight, though the resonance lasers need further development.

Conclusions and Specific Requests

While challenging, a detailed strategy for how to approach the development of geochronology investigations on Mars is scientifically important. We argue for inclusion of a geochronology experiment on the next landed Mars mission, and that this investigation is essential to our understanding of both Mars in specific and planetary science beyond the Earth in general. It is important to develop in the very near future flight instruments for the promising chronometers and analytical approaches discussed in this paper. There are specific steps toward flight qualification and operational readiness for such an experiment, and we urge the decadal survey to recommend the following:

- Development of an architecture and schedule for implementing geochronology investigations on Mars within the next ten years
- Sustained funding to increase the technology readiness levels of instrumental approaches for measurements using multiple and complementary radiogenic isotopic systems, e.g., Rb-Sr and K-Ar geochronology.
- Funding to develop sample preparation approaches for unique challenges specific to in situ geochronology
- Development of requirements and procedures for selection of appropriate samples for chronology studies in samples to be returned from Mars

The sophistication and complexity of the questions that are emerging as the basis for planetary exploration mission objectives require that we anchor the relative dates and rates of planet-changing processes such as the emergence of life and dramatic alteration of surface climate. Understanding the nature and timing of such events has profound implications that go beyond interpretation of where Mars presently resides in its life cycle to possible glimpses into the future of Earth.

References

[1] Tanaka, K. L., Scott, D. H., and Greeley, R. R., 1992, Global Stratigraphy, in, Mars, Kieffer, H.H., Jakosky, B. M., Synder, C. W., and Matthews, M. S., editors, University of Arizona Press, p. 345-382.

[2] Doran, P.T., Clifford, S.M., Forman, S.L., Nyquist, L., Papanastassiou, D.A., Stewart, B.W., Sturchio, N.C., Swindle, T.D., Cerling, T., Kargel, J., McDonald, G., Nishiizumi, K.. Poreda, R., Rice, J.W. and K. Tanaka, 2004, Mars chronology: assessing techniques for quantifying surficial processes. *Earth Science Reviews* **67**, p 313 – 337.

[3] Strom, R. G., and Neukum, G., 1988, The Cratering Record on Mercury and the Origin of Impacting Objects, In Mercury, eds., Villas, F., Chapman, C. R., and Matthews, M. S., University of Arizona Press, p. 336-373.

[4] Hartmann, W. K., 1973, Martian Cratering. 4. Mariner 9 Initial Analysis of Cratering Chronology, J. Geophys. Res., 78, p. 450-452.

[5] Soderblom, L. A., Condit, C. D., West, R. A., Herman, B. M., and Kriedler, T. J., 1974, Martian Planet Wide Crater Distribution: Implications for Geologic History and Surface Processes. Icarus. 22, p. 239-263.

[6] Neukum, G., and Wise, D., 1976, Mazrs: A Standard Crater Curve and Possible New Time Scale, Science, 194, p. 1381-1387.

[7] Neukum, G., and Hiller, K., 1981,Martian Ages, J. Geophy. Res., 86, p. 3097-3121.

[8] Neukum, G., and Ivanov, B. A., 1994, Crater Size Distribution and Impact Probabilities on Earth and lunar, Terrestrial Planets, and Asteroid Cratering Data, in Hazards Due to Comets and Asteroids, Gehrels, T., ed., University of Arizona Press, p.359-416.

[9] Neukum, G., Ivanov, B. A., and Hartmann, W. K., 2001 Cratering Record in the Inner Solar System in Relation to the Lunar Reference System, Chronology and Evolution of Mars, 96, p. 105-164.

[10] Hartmann, W. K., Strom, R. G., Weidenschilling, S. J., Blasius, K., R., Woronow, A., Dence, M.R., Grieve, R. A. F., Diaz, J., Chapman, C., R., Shoemaker, E. M., and Jones, K. L., 1981, Chronology of Planetary Volcanism by Comparison Studies on Planetary Cratering, in Basaltic Volcanism on the Terrestrial Planets, Pergamon Press, 1049-1127.

[11] Hartmann, W.K. and G. Neukum, 2001, Cratering Chronology and the Evolution of Mars, *Space Science Reviews*, 96, 165-194.

[12] Malin, M.C., Carr, M.H., Danielson, G.E., Davies, M.E., Hartmann, W.K., Ingersoll, A.P., James, P.B., Masursky, H., McEwen, A.S., Soderblom, L.A., Thomas, P., Veverka, J., Caplinger, M.A., Ravine, M.A., Soulanille, T.A., and Warren, J.L., 1998, Early Views of the Martian Surface from the Mars Orbiter Camera of Mars Global Surveyor, *Science* **279**, 1681.

[13] Keszthelyi, K., McEwen, A.S., and Thordarson, T., 2000, Terrestrial Analogs and Thermal Models for Martian Flood Lavas, *J. Geophys. Res.* **105**, 15,027–15,050.

[14] Hartmann, W.K., and Berman, D.C., 2000, Elysium Planitia Lava Flows: Crater Count Chronology and Geological Implications, *J. Geophys. Res.* **105**, 15,011–15,025.

[15] Greeley, R., Kuzmin, R.O., and Haberle, R.M.:2001, Aeolian Processes and Their Effects on Understanding the Chronology of Mars, *Space Sci. Rev.*, 96.

[16] Perera I.K., I.C. Lyon, and G. Turner, Isotope Ratio Measurements in Strontium Using Two photon Two-colour Resonance Ionization Mass Spectrometry, J. Anal. Atomic Spectroscopy, 10, 273-279, 1995.

[17] Doran, P. T., T. E. Cerling, S. M. Clifford, S. L. Forman, L. Nyquist, D. A. Papanastassiou, B. W. Stewart, N. C. Sturchio, and T. D. Swindle, 2000, Martian Chronology: Goals for Investigations from a Recent Multidisciplinary Workshop, Concepts and Approaches for Mars Exploration, LPI abstract 6208

[18] Swindle, T. D., Bode, R., Boynton, W. V., Kring, D. A., Williams, M., Chutjian, A., Darrach, M. R., Cremers, D. A., Wiens, R. C., Baldwin, S. L., AGE (Argon Geochronology Experiment): An Instrument for In Situ Geochronology on the Surface of Mars, 34th Annual Lunar and Planetary Science Conference, League City, Texas, abstract no.1488, March 17-21, 2003.

[19] Cardell, G., Taylor, M.E., Stewart, B.W., Capo, R.C. & Crown, D.A., 2002, A combined laser ablation-resonance ionization mass spectrometer for planetary surface geochronology [Abstract]. *Abstracts of Papers, 33rd Lunar and Planetary Science Conference,* Houston, TX. Abstract #2047.

[20] Stewart, B.W., Cardell, G., Taylor, M.E., Capo, R.C., and Crown, D.A., 2001, In situ geochronology of planetary surfaces: Application of the rubidium-strontium isotope system, in *Eleventh Annual V. M. Goldschmidt Conference*, Abstract #3891, LPI Contribution No. 1088, Lunar and Planetary Institute, Houston (CD-ROM).

[21] F. S. Anderson, T. Whitaker, G. Miller, D. Young, J. Mahoney, and M. Norman, L. French, A Laser RIMS Instrument To Date Igneous Rocks Using Rb-Sr and Measure Elemental Chemistry, 2005, abstract no. 1843, *LPSC XXXVI.*

[22] Anderson, F.S., et al., A LASER RIMS Instrument to Date Igneous Rocks, Measure Geochemistry, & Characterize Alteration in-situ on Mars, 2002, American Geophysical Union, Fall Meeting.

[23] Bogard and Garrison, 1999, Meteoritics Planetary Sci. 34, 451-473.

[24] Bogard and Park, 2008, Meteoritics Planetary Sci. 43, 1113-1126.

[25] Bogard, 2009, Meteoritics Planetary Sci. 44, 3-14.

[26] Ramos, F, et al., 2004, Measuring 87Sr/86Sr variations in minerals and groundmass from basalts using LA-MC-ICPMS, Chemical Geology 211, 135–158.

[27] Vroon, PZ, & B. van der Wagt & J. M. Koornneef & G. R. Davies, 2008, Problems in obtaining precise and accurate Sr isotope analysis from geological materials using laser ablation MC-ICPMS, Anal Bioanal Chem, 390:465–476

[28] Glodny, J., B, Bingen, H. Austrheim, J. Molina and A. Rusin, 2002, Precise eclogitization ages deduced from Rb/Sr mineral systematics: The Maksyutov complex, Southern Urals, Russia, *Geochim. et Cosmochim. Acta.* **66**, 1221 – 1235.