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| Bob Anderson | University of Colorado |
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| Hunter Waite | University of Michigan |
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| Jan Toporski | Carnegie Institution of Washington |
| Janok Bhattacharya | Univ. of Texas, Dallas |
| Jennifer Biddle | Penn State |
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| Jim Garvin | Program Office--HQ |
| Marguerite Syvertson | Program Office--JPL |

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| **Source of Carbon** | **Carbon compounds. examples/comments** |
| Abiotic molecules from meteoritic / cometary influx | Amino acids, purines and pyrimidines, polycyclic aromatic hydrocarbons, chain hydrocarbons, fatty acids, sugars and sugar derivatives. |
| Prebiotic/abiotic molecules from synthesis reaction process on Mars | Amino acids, purines and pyrimidines, polycyclic aromatic hydrocarbons, chain hydrocarbons, fatty acids, sugars and sugar derivatives. |
| Terrestrial contaminating organics | Condensation products derived from rocket exhaust, lubricants, plasticizers, atmospheric contaminants |
| Terrestrial contaminating organisms | Whole cells, cell components (LPS, DNA, proteins, cytochromes) found on AFL itself. |
| Terrestrial like organisms – from Earth | Organisms not present on the craft measuring them, but had been previously transferred from Earth by either meteorite impact or contamination of previous spacecraft. Target molecules could include individual genes, membrane constituents, specific enzymes, and co-enzymes that would be expected to be over expressed or adapted in Martian conditions |
| Terrestrial-like organisms – evolved on Mars | Organisms that utilize terrestrial like biochemistries and have evolved on Mars Target molecules could include individual genes, membrane constituents, specific enzymes, and co-enzymes that would be expected to be over expressed or adapted in Martian conditions or organisms using metabolisms that would not be present on a space craft contaminant such as methanogens, psychrophiles endolithic survival mechanisms. |
| Non-terrestrial-like organisms | Utilizes an array of molecules for information storage, information transfer, compartmentalization and enzymatic activity that differ from those used by extant terrestrial life. Examples would be the use of novel amino acids and nucleotides or the use of novel nitrogen utilization strategies. |
| Fossil biomarkers | Detection of established terrestrial fossil biomarkers such as hopanes, archaeal lipids and steranes, for the detection of the diagenetic remains of terrestrial based life. Characterization of potential breakdown products that can be reasonably extrapolated from the detection of molecules comprising an extant Martian life form. Detection of the diagenesis products of extinct Martian organism based on carbon compositions consistent with biological fractionation of a narrow range of abiotic precursors. |

escence). The controversy mentioned earlier regarding the oldest fossils on Earth illustrate that it is difficult using all available analytical tools in a laboratory to unambiguously determine if something is truly of biological origin. Recognizing a fossil using the criterion of shape alone poses some challenges, particularly without actually being on the surface of Mars and knowing *a priori* whether it has a fossil record. In contrast, observing movement in extant life is easy. However, not all extant life moves, especially microbes, therefore making it difficult to determine if it is alive by shape alone. Interdisciplinary multi-instrument approaches have been shown to be effective for studies on deep subsurface ecosystems on Earth (e.g., Fisk et al., 2003; Steele et al., 2002; Toporski et al., 2002; Steele).

2. Biochemical analyses. A range of analyses based on either pure chemical or biochemical methods have proven to be useful on Earth in determining if a sample is of biological origin. However, in difficult cases it has usually taken several different methods of analyses to determine if a sample is unequivocally of biological origin. Carbon isotopes have successfully been correlated with individual Proterozoic microfossils (House et al., 2000) and FT-RAMAN spectra were obtained on presumed Proterozoic microfossils (Schopf et al., 2002). Furthermore, fossil and modern bacterial biofilms have been classified using a combination of bulk and spatially resolved measurements including XPS, EDX, XRD, Time of Flight – Secondary Ion Mass Spectroscopy (ToF-SIMS), pyrolysis GCMS, GCMS, GC-IRMS confocal laser microscopy and Raman and infrared microspectroscopy (Steele et al., 2001; Toporski, 2001; Toporski 2002; Toporski 2004, Hall-Stoodley et al, 2004; Benning et al 2004). Only the combination of a multiple-set of instruments lead to a unequivocal determination of the specific characteristics of biofilms.

#### 5.2.2.2 What are the challenges for AFL in the search for biosignatures on Mars?

1. Tested Technologies. Of the techniques listed in table 1 those that have been shown to be successful during space missions include: gas chromatography, mass spectrometry, simple thermal analysis, Mossbauer and some types of interactive chemical techniques (e.g., the Viking biology experiments (see Mancinelli 1998 for review).

For Mars applications, it is necessary for the detector to be sensitive to the picogram level and capable of responding to a broad variety of compounds, i.e., have universal response. A flight proven detector that is both universal and sufficiently sensitive is the metastable ionization detector. The primary disadvantage of gas chromatography is the small margin of error associated with the column retention times for definitive identification of compounds, which can lead to mis-identification of compounds with similar retention times. This disadvantage should be minimized by use of multiple columns with different separation capabilities (i.e., different column coatings or packings) and calibration standards. A GC/MS has been used successfully on space missions, including the Viking mission The disadvantages are that the MS cannot be simultaneously tuned to be sensitive for the analysis of low and high molecular weight substances at the same time, and it is a bulky and heavy instrument*.* Various types of analytical instruments equipped with different pyrolytic devices have been used during space missions. These ranged from simple pyrolysis (combustion) to step-wise heating of samples and measuring the power input and temperature. Step-wise heating is usually followed by collecting any volatiles evolved from the sample during heating, and identifying and quantifying them by GC, or GC/MS. For example, heating samples of soil from earth in a step-wise fashion would first volatilize adsorbed water and gases (e.g., CO2, and lower molecular weight organic compounds) at the lower temperatures. At higher temperatures, water from mineral hydration, CO2 from carbonate decomposition, and volatiles from pyrolysis of higher molecular weight organics would be released. Although this technique allows one to analyze the evolved gases, it does not yield any direct information regarding the nature of the sample (e.g. clays vs. hydrated silicates). Mossbauer spectroscopy provides information on the valence state of specific elements (i.e., Fe, Sn, Sb, Ru, and Au), how these elements are combined in the structure of a compound, and the magnetic properties of the sample. Mossbauer spectroscopy can provide information about H2O only if it is associated with the elements Fe, Sn, Sb, Ru, or Au. This again is an area where micro total analytical systems and micromachining may allow significant weight and energy savings.

2. Non-tested technologies. Scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS), which maps electron intensities for identification of elements with atomic numbers greater than sodium, although windowless detection allows all elements heavier than boron to be detected. Electron spectroscopy for chemical analyses (ESCA) quantitatively determines the valence states and bonding energies of most naturally occurring elements (excluding hydrogen and helium). This technique is limited to analysis of the top 1-10 monolayers of the sample. X-ray diffraction (XRD) analysis directly and nondestructively probes atomic scale structural correlations of mineral samples yielding sample mineralogy along with information about the presence of H2O. X-ray fluorescence (XRF) analysis non-destructively provides information on the elemental composition of a sample for elements having atomic numbers greater than that of boron. However, no information is given about how those elements are combined in the sample. Rutherford backscattering spectrometry (RBS) maps the elemental composition and distribution measured on sample surfaces (the top 0.5 – 3 microns). Elements that can be analyzed by this non-destructive technique range from Li to U. Secondary ion mass spectrometry (SIMS) analysis has a very high sensitivity and can identify all elements including hydrogen and deuterium. A mass spectrometer (MS) provides information on elemental and molecular composition, including that of H2O, and the isotopic abundances found in a sample. Differential scanning calorimetry (DSC), in which the amount of heat required to maintain isothermal conditions between the sample and an inert reference placed in a continuously heating oven, is recorded, and the enthalpy provided directly. Sample identification is made by examination of the patterns of exotherms and endotherms along a temperature scale. The DSC provides quantitative data to ~700°C. For temperatures >700°C the signal-to-noise ratio becomes too great. Differential thermal analysis (DTA) is similar to DSC in that the sample and an inert reference are heated at the same rate, but to ~1200°C. The temperature of the sample and reference are monitored simultaneously. It differs from DSC in that when endothermic and exothermic events occur in the sample, no attempt is made to keep the sample and reference isothermal to each other. In DTA, the temperature difference between the sample and the reference is recorded as a function of oven temperature and provide the information for sample identification. The thermogram obtained from a DTA or DSC analysis provides information on the mineralogy and chemical composition of the sample. Where the DTA or DSC is coupled to a gas chromatograph (GC), the GC collects and analyzes the volatiles (including H2O) evolved from the sample as it is heated.

Specifically for extant life detection interactive chemical methods were performed as part of the Viking mission. This approach is fraught with problems. It assumes prior knowledge of Martian organism metabolism. Using these culturing methods only detect 1-2% of the microbes in earth soil can be detected. A distribution mass peaks obtained by a mass spectrometer of alkanes showing a decrease in concentration with increasing carbon number would indicate abiotic processes. Similarly a predominance of biogenic amino acids with an excess of the L isomer would indicate extant or recently extinct life. Whereas, a suite of racemized biogenic amino acids may indicate fossil life. Detection of hopanes by Time of Flight Mass Spectrometry may also be indicative of life. Field ATP luminometry measurements of the cryptoendolithic communities may provides a rapid method of detecting relative amounts of metabolic turnover in microbial communities. None of these techniques would provide definitive evidence of life during the MSL mission. Clearly, multiple approaches need to be done on samples to determine if they contain viable extant organisms. For example, if organic mass gas chromatography spectrometry analyses combined with deep UV florescence, SEM and RAMAN all point toward life, then there is a high probability that the sample may contain life.

## 5.3 Preservation Potential

A biosignature preservation model, guided by data from AFL, will be critical to long term Martian life detection strategy. That is to say that AFL in detecting carbon chemistry in various sites of possible habitability (see definition) can indicate whether such niche areas could preserve clues of Martian life. This must be modeled by suitable experimentation in laboratories before suitable interpretation of any data can be undertaken. We still do not know the exact composition of the mysterious Martian oxidant postulated in the Viking experiments.

Long-range Astrobiological exploration of Mars will require an understanding of the preservation potential of biosignatures. This is an important part of the scientific logic of going from possible biosignature to confirmed biosignature.

Lessons from Earth

•Life processes produce a range of biosignatures, and geological processes progressively alter and ultimately destroy them.

•Understanding the potential for preservation has been a key part of biosignature interpretation.

Application to Mars

•We don’t know the biosignatures of Martian life forms (if they exist).

•However, with appropriate data, it should be possible to postulate a preservation model relating biosignatures as we understand them on Earth to various Martian geologic environments. This model will likely have important predictive value in guiding future search strategy. Models predict that biomolecules and organisms can survive in simulated conditions such models need refinement and to address diagenetic processes in predicted conditions (Scheurger et al., 2003).

# 6.0Precursor Discoveries

Relevant data may already be available but two major classes of discovery would be of essential relevance to AFL mission planning:

MRO

•Sending AFL to a hydrothermal site is impossible with present knowledge, because none are known. However, the CRISM spectrometer on MRO is very powerful, and it has potential to discover the mineralogic expression of hydrothermal zones.

Phoenix

•Phoenix will be the first lander designed to acquire and analyze ice-bearing samples.

•It will collect data of relevance to each of the three primary components of habitability (water, carbon, energy), and thus is capable of returning a result which significantly improves or reduces our interest in sending AFL to an ice-related site.

Table 3 A summary of types and amounts of biomolecules present in a single bacterial cell and compared to known preservation potential for such molecules.

|  |  |  |  |
| --- | --- | --- | --- |
| **Component** | **% Total Weight (or mass C x10-13 g)** | **Number of Types** | **Preservation** |
| **Water** | 70 (NA) | 1 | Unknown in Organic and mineral phases |
| **Proteins** | 15 | ~2000 | 1000’s without protection by a mineral matrix. ~45Ma with protection?. |
| **Nucleic Acids** |  |  |  |
| DNA | 1 | 2+ | Oldest ? ~350,000 |
| RNA | 6 | (see below) | Days – Months (studies on longevity of RNA other than in clinical settings have not been performed. |
| *rRNA* | 5.5 | 3 | Days – Months |
| *tRNA* | 0.1 | ~32 | Days – Months |
| *mRNA* | 0.3 | 1000’s | Days – Months |
| *Non coding RNA* | 0.1 | 1000’s | Days – Months |
| **Polysaccharides** | ~1 | Uncounted | Chitin - 25Ma. Exopolymer sheaths ~2Ga |
| **Lipids** | 2 | ~50 | Cell wall components - Hopanes 2.7Ga |
| **Amino acids** | 0.4 | ~100 (20 main ones) | As protein diagenesis – Ma.  Chiral signal in fossils lost after ~ 1 Ma. |
| **Sugars** | ~3 | ~200 | Days to weeks (see polysaccharides) |
| **Other small organics** | 0.2 | ~200 | Porphyrins ~ 2 Ga |
| **Inorganic species (C, H, N, O, Fe, P, S etc).** | 1 (~100% dry weight) | ~20 – 30 (including inorganic complexes) | Isotopes may preserved for ? 3.5 Ga for C.  Research is continuing to define other isotope systematics for preservation of a biogenic signature. |
| **Diagenetic Macromolecular material** | Total cell breakdown products (100% dry weight of cells) | Kerrogens (4 types)  Melanoidins (100’s) | Kerrogens – ? 3.5Ga for biogenic (Type 1-3). Type 4 indicative of meteoritic input.  Melanoidins conbination of sugar and proteins, ~50 Ma. |

? – debate over the data. Total mass of the organic inventory is based on the assumption that most terrestrial prokaryotes contain approximately 10-13 g of carbon per cell.

# 7.0Mission Site Selection

Four subgroups were founded to begin to address the need for AFL to respond to the discoveries and requirements for as yet to be determined site. Through this process a core mission concept was arrived at and presented to the engineers for costing.

There are four obvious general types of site in which the overall scientific goal of AFL (major advance in A/B) can be pursued:

•The sedimentary record.

•Fossil (inactive) hydrothermal systems

•Sites with ice

•Sites where it may be possible to sample liquid water

We do not have enough information as of this writing to know how these four options would be prioritized by a future SDT. Future discoveries could have a major effect on planning. At the time of writing this document all of the above sites may be postulated to currently exist on Mars. The sedimentary record has been explored by at Gusev and Meridiani by Spirit and Opportunity respectively (Squyres et al., 2004; Grant et al., 2004; Morris et al., 2004; Kerr 2004c (commentary); Arvidson et al., 2004; Bertelsen et al., 2004; Herkenhoff et al., 2004; Gellert et al., 2004). Fossil (slightly active) hydrothermal systems may be concluded from initial papers outlining the concurrence of water vapour, shallow ground ice and methane at Arabia Terra, Elysium Planum and Arcadia Memnoma, (See Kerr 2004a,b and c for commentary). Sites with ice and the obvious poles or shallow “dirty” ice sites such as Phoenix proposes to explore. Sites with possible hydrothermal activity represent a chance to sample liquid water, although this may be at some distance below the surface. To remain flexible to current and future discoveries we

Figure 3 Shows the antecedent discoveries that will impact and guide the choice of sites and final payload of the AFL mission

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## 7.1 Sediments

Here we present a mission concept with the overall goal of finding evidence for past or present life in the Martian stratigraphic record in an environment that is highly likely to have formed from the subaqueous deposition of sediment in a shallow marine or lacustrine environment such as exposed in craters at both the Spirit and Opportunity sites (Squyres et al., 2004; commentary by Kerr 2004c).

Objectives

Specific supporting objectives that support this goal are to:

Assess spatially resolved changes in mineralogy with depth on a scale consistent with the depth of individual strata.

Determine the abundance and nature of organic chemicals at the same scales as above.

Seek information regarding water cycling from the strata, eg. is there free or bound water in any of the layers? Ice? Hydrous mineral phases?

Confirm the depositional environment.

Determine provenance of the sediment

Assess the fossil preservation potential of the environment. Factors which might be considered are temperature, rock type, local weather, UV flux, depositional regime as suggested by sedimentary structures

Approach

Central to this mission is the selection of a landing site that possesses multiple outcrops of layered sedimentary rock. We would use remote sensing methods that possess sufficient spatial resolution to resolve individual layers to acquire information from several outcrops. Subsequently, a rover would visit at least one 3D outcrop of layered sedimentary rock, measuring variation in chemistry, mineralogy and texture of the strata for at least 100 meters along the strike and ten meters in the dip of the outcrop. Subsurface penetration would be an important feature of this mission for the acquisition of subsurface samples that are from depths great enough to extend beyond the level of surface oxidation. This may mean accessing a depth of one meter in a horizontal area, though it would be desirable to penetrate the exposed bedding along the slope of an outcrop in a larger feature such as the wall of a crater. Examining the subsurface of such beds would only require a relatively shallow penetration (perhaps a few centimeters), and we would then have access to the primary sediment without having to go through the more recent Aeolian deposits.

Required measurements for meeting the scientific objectives must be conducted at multiple spatial scales, and we recommend three suites of instruments that can provide integrated measurements *a la* the remote sensing, non-contact/contact and analytical suite designations originally suggested by the MEPAG PSIG for the MSL mission. Both spectroscopy and imaging will be key to an integrated science package, and we assume technical progress in science autonomy before the launch of AFL that optimizes science operations on the Martian surface.

There are several engineering /science trade issues associated with taking a large number of measurements from a large outcrop in three dimensions. Some of them are:

“Go to” mobility is required. The degree of mobility will be complementary to the degree of precision of the landing.



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| **Table 8- Techniques Suggested for AFL by SSG Members** | | | | | | | | | | | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | Measurement Tier | | | Example Target/Sample Information | | |  | Example Technique Characteristics (instrument implementation) where appropriate | | | | | | | |  | Discovery/Follow-up per Table 7 | | | |  |  |  |
| Technique | Data/ Signatures Sought | Mmnt Reqts Addessed (Section 7) | Remote Sensing/Standoff | Contact or Close Range | Analytical Lab | Physical Form (Solid, Gas, Liquid) | Example Origin/Host Material | Processing Required/ (Desired) | Sample Mass/ Volume | Distance to Target | Size of Area Probed/ FOV | Target Feature Scale | Selectivity | Detection Limits | Resolution | Precision | Mass Range | Other | Recent Surface Water | Hydrous Mineral Phases | Organic Molecules | Sedimen. Structures | Sedimen. Rocks | Evidence for Fossil Life | Microbes |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| stereo optical imaging | identify targets, evidence of weathering, sedimentation, alteration, etc. | A | x |  |  |  | sedimentary rocks/ structures | n |  | 1m - 10+km | 10cm - 1+km |  |  |  |  |  |  |  | 1 | 6 |  | 1,2,3,4 | 4 | 1,2,3,6,8 | 3 |
|  | identify surface samples | A |  |  |  |  |  |  |  | 10-100 m | 1-10 m | 10cm-1m |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | identify distant sedimentary outcrops | A |  |  |  |  |  |  |  | 1 km | 10-100 m | 1-10 cm |  |  | 10 cm @ 1 km | |  |  |  |  |  |  |  |  |  |
| VIS/NIR Spectroscopy | surface mineralogy, texture | B | x | x |  | s | rocks, fines | n (abr) |  | cm - m |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| mini TES | mineralogy | B | x |  |  | s |  | n (abr) |  | m - km |  |  |  |  |  |  |  |  |  |  |  |  | 1 |  |  |
| long focal length imaging | identify distant sedimentary outcrops | A | x |  |  |  |  | n |  | 10m - km | cm-10m | cm |  |  |  |  |  |  |  |  |  |  |  |  |  |
| laser ranging | distance to target | A | x |  |  |  | boulders, vertical faces | n |  | 100m - km | cm spot |  |  |  | cm @ 100 m | |  |  |  |  |  |  |  |  |  |
| LIBS | elemental composition | B | x |  |  | s | boulders, slopes | n |  | 1 - 25m | mm - cm spot |  | low (l absorb.) | ppmw |  | ~ 10% | elements | laser ablation | | 2,4 |  |  | 2,5 | 3 |  |
| ground penetrating radar | ice, H2O, other | B, C | x |  |  | s | subsurface | n |  | m - 10s m |  |  |  |  |  |  |  |  | 3 |  |  |  |  |  |  |
| seismic sounding | ice, H2O, other | B, C | x | x |  | s | subsurface | n |  | 100's m - km |  |  |  |  |  |  |  |  | 3 |  |  |  |  |  |  |
| neutron spectroscopy | ice, hydrated minerals | B | x | x |  |  | drill cores, fines | n (acq) |  | 10's cm - m's |  |  | high | variable <%-% | |  |  |  |  |  |  |  |  |  |  |
| gamma ray spectroscopy | elemental composition | B | x | x |  |  | any | n |  | 10's cm - m's |  |  | med | variable <%-% | |  |  |  | 5 |  |  |  |  |  |  |
| x-ray spectroscopy | elemental composition | B, E2 |  | x |  |  | any | n (acq) |  | cm | cm+ |  | med | variable <%-% | |  |  |  |  |  |  |  |  |  |  |
| Raman spectroscopy | mineralogy, some geochemical/organic | B, E | x | x |  |  | rocks | n (abr) |  | cm - m | cm+ |  | med |  |  |  |  |  |  | 1,5 | 1,4 |  | 2 | 1 |  |
| micro-Raman spectroscopy | mineralogy, some geochemical/organic | B,D,E |  | x | x |  | rock chips | n (acq, abr) | | mm - cm | < mm |  | med |  |  |  |  |  |  | 1,5 | 1,4 |  | 2 | 1 |  |
| micro-LIBS | elemental composition | B,D |  | x | x | s | rocks, chips | acq,pos |  | mm - cm | < mm |  | low (l absorb.) | |  |  |  |  |  | 2,4 |  |  | 2,5 | 3 |  |
| hand-lens-scale imaging | phase texture/identity | D |  | x |  | s |  | n (abr) |  | cm - m's | 0.1-10 mm | grains |  |  |  |  |  |  |  |  |  |  |  |  |  |
| optical microscopy | fine morphology | D,E |  | x | x | s |  | n (abr) |  | mm - cm | 0.001-1 mm | subgrain |  |  |  |  |  |  |  |  | 2 |  |  | 1,2,3,6,8 |  |
| confocal microscopy |  | D,E |  |  | x | s |  |  |  | mm | 0.001-1 mm | subgrain |  |  |  |  |  |  |  |  | 2 |  |  | 1,2,3,6,8 |  |
| near-field microscopy | very high res imaging | D,E |  |  | x | s | flat chip | acq, pos |  |  |  | subgrain |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Mossbauer | Fe-bearing mineralogy | B |  | x | x | s |  |  |  | mm - cm |  | avg |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Fe-NMR |  | B |  | x |  | s |  |  |  | mm - cm |  |  | high |  |  |  |  |  |  |  |  |  |  |  |  |
| XRD/XRF | mineralogy | B,D |  |  | x | s | drill cores, fines | acq, pow | mg's | 0 | whole sample | avg or grains | |  |  |  |  |  |  | 1 |  |  | 1,5 |  |  |
| FTIR | mineralogy, some geochemical/organic | B |  |  | x | s |  |  |  |  |  |  |  |  |  |  |  |  |  | 1,5 | 1,4,6 |  | 2,5 | 3 | 4 |
| VCD |  |  |  |  | x | s |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| deep UV fluorescence | organics: identity, oxidation state, … | B,D,E |  | x | x | s |  | n (abr) | surface? | mm - m |  | grain scale+ | |  |  |  |  |  |  |  | 1 |  |  | 3 |  |
| pyrolysis/GCMS | organic and some mineralogical/inorganic composition; isotopes | B,E |  |  | x | s,g,l |  | acq, pos, vac | mg-10's mg | 0 | whole sample | avg | low |  |  |  |  |  | 4 |  | 1,5 |  | 5 |  |  |
| chemical derivatization | less-tractable organics | E |  |  | x | s,l |  | liq |  | 0 | whole sample | avg |  |  |  |  |  |  | 4 |  | 1,4,7 |  | 5 |  |  |
| isotope ratio MS (IRMS) | C and other isotopes for bio-fractionation, age dating | E2 |  |  | x | s,l |  | acq, pos, vac | | 0 | whole sample | avg |  |  |  |  |  |  | 2 |  |  |  |  |  |  |
|  | compound-specific IRMS using sampling selectivity | E2 |  |  |  |  |  |  |  |  | whole sample | avg | cmpd isolated w/pyr, GC,or other proc. | | | |  |  |  |  |  |  |  |  |  |
| chiral GC | enantiomeric excess (ee) | E3 |  |  | x | s,g,l |  | acq, pos, gas | | 0 | whole sample | avg |  |  |  |  |  |  |  |  | 3 |  |  |  |  |
| circular dichroism | enantiomeric excess (ee) | E3 |  |  | x |  |  |  |  | 0 |  | avg |  |  |  |  |  |  |  |  | 3 |  |  |  |  |
| liquid chromatography (LC) | organics, ee | E |  |  | x | s,l |  | liq |  | 0 | whole sample | avg |  |  |  |  |  |  | 4 |  | 1,3,5 |  | 5 |  |  |
| 2D GCMS/TOF-MS | organic and some mineralogical/inorganic composition; isotopes | B,E |  |  | x | s,g,l | rocks/cores, fines | acq, pos, vac | 10's mg | 0 | whole sample | avg | low |  |  |  | ~1E3-1E5+ | | 4 |  | 1,5 |  | 5 |  |  |
| electrospray ionization MS (ESI/IMS/CIT-MS) | | E |  |  | x | s,g,l |  | acq, pos, vac | g's | 0 | whole sample | avg | low |  | Dm/m 1E2-1E3+ | |  | contact w/ fluidized sample | | |  |  |  |  |  |
| laser ablation TOF-MS | local elemental/isotopic composition | B,D |  |  | x | s | rock chips, fines | acq, pos, vac | surface | 0 | 10mm - 1 mm | grain scale+ | low (l absorb.) | ppbw-ppmw | Dm/m 1E2-1E3 | 5-25% | ~ 300 |  | 4 | 2,4 |  |  | 2,5 | 1,3 |  |
| LD/MALDI-TOF MS | high-MW organics; some inorganic molecules | D,E |  |  | x | s | rock chips, fines | acq, pos, vac (pow, liq) | surface/prep film | 0 | 100mm - 1 mm | grain scale+ | med (l absorb.) | fmol-pmol | Dm/m 1E3-1E4 | | ~1E3-1E5+ | |  |  | 1,2,4,7 |  |  | 3 | 4 |
| REMPI-MS/RIMS | organics, elements (trace) | E |  |  | x | s |  | acq, pos, vac | | 0 | 10mm - 1 mm |  | very high (l absorb.) | s. atom - pmol | Dm/m 1E2-1E4 | | ~ 1E3 |  |  |  |  |  |  |  |  |
| AP-MALDI-MS (TOFMS or ITMS) | organic, inorganic molec. | D,E |  | x | x | s | rocks, ices | vac | surface | mm | 10mm - 1 mm | grain scale+ | med (l absorb.) | fmol-nmol | Dm/m 1E3-1E4+ | | ~ 1E3-1E5 |  |  |  |  |  |  |  |  |
| electrospray TOF-MS | high-MW organics | E |  |  | x | s,l | rocks/cores, fines | acq, liq, pos, vac | | 0 | whole sample | avg | med |  | Dm/m 1E2-1E4 | | ~1E4-1E5+ | |  |  | 1,2,7 |  |  | 3 | 4 |
| TOF-SIMS | chemical imaging | B,E |  |  | x | s | rock chips | acq, pos, vac | surface | 0 | 50nm-50mm | sub-grain+ | low |  | Dm/m 1E3-1E4 | | ~1E3-1E4 |  |  |  |  |  |  |  |  |
| ICP-MS | trace elements | B |  |  | x | s,g,l | rock chips, fines | acq, pos, vac, gas | | 0 | whole sample | avg or grains | low | pptw-ppbw | Dm/m 1E3+ | 0.1-10% | ~ 300 |  | 2,4 |  | 1,3,5 |  | 5 |  |  |
| TIMS | isotope ratios (~IRMS) | B,E2 |  |  | x | s |  | acq, pos, vac | | 0 | whole sample | avg | low | pptw-ppbw | Dm/m 1E3+ | 0.1-1% | ~ 300 |  | 2 |  | 5 |  |  |  |  |
| AFM | nanoscale imaging | D, E3 |  |  | x | s | flat chip | acq, pos | chips |  | 1nm-1mm | sub-micron | |  |  |  |  |  |  |  |  |  |  |  |  |
| TEM/SEM | nanoscale imaging | D |  |  | x | s | flat chip | acq, pos, vac | chips |  | 1nm-1mm | sub-micron | |  |  |  |  |  |  |  |  |  |  |  |  |
|  | image microbes in ice cores | D,E3 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| XPS | chemical comp. and bond state | B,C |  |  | x | s,l |  | vac | 100's mg |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Auger spectroscopy | bond state of elements | B,C |  |  |  | s,l |  | vac | 100's mg |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| amino-acid sensors (eg MOD) | detection of amino acids | E |  |  | x | s,l |  | acq | 100's mg |  | whole sample |  | high |  |  |  |  |  |  |  | 1,3 |  |  |  |  |
| oxidant sensors | detection of oxidants | C |  |  | x | s,l |  | Acq, dry | 100's mg |  | whole sample |  | high |  | per sample weight | |  |  |  |  | 6 |  |  |  |  |
| bio-assay chip lab |  | E |  |  | x | s,l |  | liq | 100's mg | 0 | whole sample |  | high | pptw | per sample weight | | Kda |  |  |  | 7 |  |  | 1,5,6 | 1,5,6 |
| micro-array sensors |  | E |  |  | x | s,l |  | Liq | 100's mg |  | whole sample |  | high | pptw | per sample weight | | Kda |  |  |  | 7 |  |  | 1,5,6 | 1,5,6 |
| MORD |  |  |  |  | x | s |  |  | 100's mg | 0 | whole sample |  | high |  | per sample weight | |  |  |  |  |  |  |  |  |  |
| fluorescence staining | organics | E |  | x | x | s,l |  | Liq | 100's mg |  | whole sample | avg | high | single cell | per sample weight | |  |  |  |  | 7 |  |  |  |  |
|  | SYBR gold, SYTO, DAPI nucleic acid stains for counting microbes | E |  |  | x | s,l |  | Liq | 100's mg |  | whole sample |  | Medium | single cell | per sample weight | |  |  |  |  |  |  |  |  | 1.5.6 |
|  | CTC, tetrazolium salt redox stains for individual cells | E |  |  | x | s,l |  | Liq | 100's mg |  | whole sample |  | Medium | Single cell | per sample weight | |  |  |  |  |  |  |  |  | 1,5,6 |
| isotopic labelling | 14CO2 or 3H for total population activity | E |  |  | x | s,g,l |  | Lig | 100's mg |  | whole sample | avg | medium | single cell | per sample weight | |  |  |  |  |  |  |  |  | 1,5,6 |
| flow-cytometry |  | E |  |  | x | s,l |  | liq | 100's mg |  | whole sample | avg | medium | single cell | per sample weight | |  | If have required media | | |  |  |  |  | 1,5,6 |
| culturing/cell-growth assays |  | E |  |  | x | s,l |  | liq | 100's mg |  | whole sample | avg | high | single cell | per sample weight | |  | If have required media | | |  |  |  |  | 1,5,6 |
| ATP and LAL enzyme assays |  | E |  |  | x | s,l |  | liq | 100's mg |  | whole sample | avg | high | pptw | per sample weight | |  |  |  |  |  |  |  |  | 1,5,6 |
| DNA extraction/PCR |  | E |  |  | x | s,l |  | liq | 100's mg |  | whole sample | avg | high | 100 cells | per sample weight | |  | with correct primers | | |  |  |  |  | 5,6 |
| capillary electrophoresis (CE) |  | E |  |  | x | s,l |  |  | 100's mg |  | whole sample | avg | high | pptw | per sample weight | |  |  |  |  | 7 |  |  |  | 1,5,6 |
| microcalorimetry |  |  |  |  | x |  |  |  | 100's mg |  | whole sample | avg | medium | pptw | per sample weight | |  |  |  |  | 7 |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **KEY:** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| n - can be operated with no sample acquisition/processing | | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| abr - abrasion to remove surface layers | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| acq - sample acquisition from host matl (via whatever means) | | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| pow - powdering of solid sample | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| pos - sample positioning (e.g., manipulation to oven, point of focus or extraction) | | | | | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| vac - vacuum processing |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| liq - liquid processing |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| gas - gas processing |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |