Spacecraft instrument technology and cosmochemistry

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Edited by Mark H. Thieme, University of California, La Jolla, CA, and approved February 4, 2011 (received for review September 22, 2010)

Measurements by instruments on spacecraft have significantly advanced cosmochemistry. Spacecraft missions impose serious limitations on instrument volume, mass, and power, so adaptation of laboratory instruments drives technology. We describe three examples of flight instruments that collected cosmochemical data. Element analyses by Alpha Particle X-ray Spectrometers on the Mars Exploration Rovers have revealed the nature of volcanic rocks and sedimentary deposits on Mars. The Gamma Ray Spectrometer on the Lunar Prospector orbiter provided a global database of element abundances that resulted in a new understanding of the Moon's crust. The Ion and Neutral Mass Spectrometer on Cassini has analyzed the chemical compositions of the atmosphere of Titan and active plumes on Enceladus.

Analyses of extraterrestrial materials performed by instruments on spacecraft have revolutionized our understanding of planets and planetesimals, and have driven significant advances in technology. Here we focus on mobile instruments that have made cosmochemical measurements, in keeping with the theme of this issue.

The adaptation of laboratory analytical instruments for flight on spacecraft missions poses many challenges. An obvious limitation for flight instruments is scale—mass and volume. Flight instruments must be crafted from light-weight materials, and miniaturization is required to fit into the confines of the spacecraft. Packing multiple instruments together can cause interferences which must be accommodated. Power limitations are often severe: instruments that use kilowatts in the laboratory might have to operate on watts in space. The storage and transmission capacities for data are limited, and onboard data compression may be required. Flight instruments must be durable to withstand the vibrations and g-forces encountered during launch and orbital insertion or landing. The instruments commonly experience extreme temperatures and irradiation by cosmic rays during long periods of interplanetary cruise. Environmental testing of flight instruments before and after they are integrated into the spacecraft system is expensive and time consuming, adding additional pressure to mission cost and schedule.

During the last decade, NASA and its international partners have launched numerous spacecraft, many carrying instruments capable of performing chemical analyses. Here we provide an illustrative sampling of three successful cosmochemistry flight instruments, along with discussions of how the data that they acquired have impacted science and technology. The data from these instruments are archived in NASA's Planetary Data System (PDS, <http://pds.nasa.gov/>) and are available to any interested investigators.

Examples of Cosmochemistry Flight Instruments

Alpha Particle X-ray Spectrometers (APXS). The Mars Exploration Rovers (MER) Spirit and Opportunity landed on Mars in 2004. Each rover carried an APXS (1), and these instruments together have analyzed hundreds of rocks and soils. The sensor head (Fig. 1), mounted on the rover arm, is brought into contact with the target whose surface is bombarded with energetic alpha

Fig. 1. Pancam image of the rover arm with APXS and RAT. Inset of APXS sensor head shows a collimator with X-ray detector behind in the center, surrounded by six radioactive alpha sources. The mass of the sensor head is 250 g and its diameter is 53 mm.

particles and X-rays produced by the decay of radioactive ²⁴⁴Cm. The α -particles and X-rays penetrate a few tens of microns into the sample, so that is the volume analyzed. The APXS utilizes two well established methods for chemical analysis: X-ray fluorescence and particle-induced X-ray emission. A detector registers the X-rays emitted at different energies and accumulates them in a histogram (Fig. 2). Each element generates X-rays at characteristic energies, and the abundances are determined from peak areas. The APXS is sensitive to elements ranging from Na (atomic mass = 23) to Br (atomic mass = 80). Analyses are carried out during the Martian night, because (i) the rover is stationary allowing long integration times, (ii) cold temperatures allow the X-ray detector to achieve maximum efficiency, and (iii) the APXS consumes relatively low power at a time when solar power is unavailable. APXS operation, calibration, and analysis are described fully by (2).

Characterizing rocks and regolith is critical for the geologic exploration of a planet's surface by rovers. Chemical analyses by APXS are among the tools used most frequently by the rovers. APXS-acquired data for both MER missions have been tabulated (3).

Author contributions: T.H.P. designed research; H.Y.M., R.L.M., and T.H.P. performed research; H.Y.M., R.L.M., and T.H.P. analyzed data; and H.Y.M., R.L.M., and T.H.P. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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Fig. 2. APXS X-ray spectrum of Mars rock Peace. “RAT” and “brushed” refer to surfaces that were abraded or brushed, respectively. Characteristic peaks are labeled with element symbols; other unlabeled peaks are spurious signals from elastic and inelastic scattering.

The Spirit landing site (4) is covered with boulders of basaltic lava, identified using a plot of the abundances of alkali oxides vs. silica (Fig. 3), a diagram used to classify volcanic rocks on Earth. Prior to the MER missions, there was considerable controversy about whether great swaths of the Martian surface were covered with andesite, another volcanic rock type, but APXS analyses helped demonstrate that Mars is basalt-covered (5). Gusev Crater, in which Spirit landed, has now become the most thoroughly documented igneous province on Mars. The higher abundance of alkalis, relative to the compositions of Martian meteorites (Fig. 3), demonstrates that the mantle that partially melted to produce basaltic magmas on Mars must be heterogeneous. Used in conjunction with the Rock Abrasion Tool (RAT), APXS analyses reveal that the rocks are coated with thin alteration rinds, thought to have been formed through leaching by acidic aqueous fluids (6). During its traverse, Spirit also used its APXS to analyze pyroclastic rocks formed by explosive eruptions (7) and altered rocks including carbonates (8). The chemical compositions of soils at this site are similar to basaltic rocks (Fig. 3), suggesting that they formed primarily by the physical degradation rather than by chemical reactions, as on Earth (9). Nickel abundances of 240–680 ppm in the soils constrain the addition of a meteorite component to ~1–3%. Some subsurface soils excavated by the rover wheels have high contents of sulfates or silica, reflecting precipitation from groundwater or leaching by hydrothermal fluids.

Fig. 3. Plot of alkali oxides ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) vs. SiO_2 used to classify volcanic rocks. APXS-measured compositions of RAT-abraded or -brushed rocks from Gusev Crater indicate they are mostly basalts, and are distinct from Martian meteorites.

The Opportunity rover (10) encountered sedimentary rocks shown by APXS to have high contents of S, Cl, and Br (11). These deposits formed by evaporation of salt-laden brines (12) that precipitated sulfates and other salts and cemented sand grains. Chemical analyses of stratigraphic layers within the walls of craters in Meridiani Planum revealed a correlation of S with Mg (Fig. 4), suggesting the presence of magnesium sulfate. This sulfate anticorrelates with Cl, presumably present as chloride. The varying ratio of salts indicates that fluids changed composition. APXS analyses, used in conjunction with Mössbauer spectra, were also important in understanding hematite (Fe_2O_3) spherules—concretions formed as groundwater circulated through the sediments and mobilized Fe. The spherules (“blueberries”) weathered out of rocks and now form a layer on the surface of Meridiani Planum. Identified from orbital spectra (13), hematite’s origin was not understood at the time. The geologic picture that has emerged is of a region of sand dunes and playa lakes that intermittently were filled with saline water. The APXS documentation that liquid-water existed in vast quantities on ancient Mars has implications for the planet’s geologic history and the possible life (10).

APXS technology has been so successful that improved versions have been carried on every Mars rover since Mars Pathfinder in 1996, and it will be part of the instrument package for the next rover, the Mars Science Laboratory.

Gamma-Ray Spectrometer (GRS). The Lunar Prospector (LP) mission used nuclear spectroscopy to make the first global maps of the Moon’s elemental composition. The LP payload included both a gamma-ray spectrometer (GRS) and a neutron spectrometer (NS), both mounted on booms to minimize background from the spacecraft. Data were acquired in high- (100 km) and low-altitude (30 km) circular polar mapping orbits for accumulation times of 300 and 220 d, respectively. The GRS and NS data produced maps of H abundance, neutron number density, and major and a few trace or radioactive elements. While the LP mission ended in 1999, the data continue to be utilized in research on lunar cosmochemistry and other areas (14). The LP dataset has been supplemented by γ -ray spectroscopy data from the Japanese SELENE (Kaguya) and Chinese Chang’E-1 lunar missions. An overview of planetary nuclear spectroscopy is provided by (15).

Element abundances were mapped on different spatial scales, depending on statistical precision and spacecraft altitude. The intrinsic spatial resolution of the LP spectrometers was about 1.5 times the orbital altitude, e.g., 45 km full width at half maximum or about 1.5° of arc length on the surface; however, for elemental abundances with high precision, e.g., Th, forward modeling spa-

Fig. 4. Measured concentrations of S, Cl, and Mg, normalized to the top sample, show significant variations with depth in Endurance Crater.

tial deconvolution was used to characterize features at higher spatial scales (16, 17).

The LP GRS consisted of a bismuth germanate (BGO) scintillator surrounded by a boron-loaded plastic (BLP) scintillator, which served as an anticoincidence shield to veto cosmic-ray interactions (18). The BLP and BGO scintillators were read out by separate photomultiplier tubes (Fig. 5). The high atomic number and density of BGO enabled efficient γ -ray detection. The size of BGO crystal was selected to achieve ample detection efficiency over a wide energy range in order to measure the lunar leakage spectrum of γ -rays produced by neutron reactions and radioactive decay (Fig. 6). The low mass of local materials surrounding the active elements of the spectrometer minimized background from cosmic-ray interactions and induced radioactivity. LP orbited closer to the surface and accumulated counting data for a longer period of time (>500 days) than any other lunar mission, enabling precise determination of element abundances (19–21).

A complicating factor in the analysis of elemental abundances was the relatively low pulse height resolution of BGO. Early results were obtained for Th and Fe, which have well resolved full energy γ -ray peaks at 2.6 million electron volts (MeV) and 7.6 MeV, respectively (22, 23). Accurate determination of the other elements required the development of spectral unmixing techniques (24) (Fig. 7). The production of γ -rays by neutrons depends on the flux of neutrons within the regolith. For each map pixel, the spectral components for neutron-induced γ -rays were adjusted using parameters determined by neutron spectroscopy. The background spectrum used in unmixing was determined by assuming an average composition of the lunar highlands was represented by anorthositic lunar meteorites (25, 26). This approach avoided the use of data from landing sites, which are heterogeneous and small in scale compared to the pixel size used in the unmixing analysis. The assumptions and calibration were independently confirmed by comparing GRS-derived thermal neutron absorption cross sections to those measured independently by the NS.

Significant results from LP included discovery of H at the lunar poles associated with cold, permanently shadowed craters believed to contain trapped water ice (27). The form of H as water was confirmed by the NASA LCROSS mission (28). Global geochemical data fully documented the compositional asymmetry of the Moon, which can be divided into at least three geological terranes (29). LP further revealed variability in the compositions of mare basalts, indicating that changes in basaltic volcanism occurred over time (e.g., 29, 30). Abundances of the best-determined elements (24), compared to sample data (Figs. 8 and 9), are superimposed on a lunar shaded relief base map (Fig. 10).

Fig. 5. Cutaway view of GRS shows BGO and BLP scintillators, photomultiplier tubes (PMT) and read out electronics. The cylindrical GRS sensor head has a mass of 8.6 kg, diameter of 16.7 cm, and length of 55.4 cm. (S. Storms, Los Alamos National Laboratory).

Fig. 6. Production and leakage of neutrons (blue) produced by interaction of regolith with cosmic rays, and γ -rays (black) made by the decay of naturally radioactive elements and by neutron reactions. Leakage flux of neutrons and γ -rays conveys information about composition of the outer meter of regolith.

Volatile K and refractory Th are not easily incorporated into crystallizing minerals, so their relative abundances are unaltered from the source material that formed the Moon. The slope of the GRS data (Fig. 8A) gives a K/Th ratio that is low compared to the inner planets, indicating that the Moon is depleted in volatile elements, as expected if the Moon formed by a giant impact (31). The global Th map (Fig. 10) shows that radioactive materials are concentrated on the near side in association with mare basalts. Decay of radioactive elements may have provided heat that drove mare volcanism.

Th and FeO abundances discriminate three major types of lunar rocks returned by the Apollo missions: ferroan anorthosites, mare basalts, and rocks rich in K, rare earth elements, and P (called KREEP). Most GRS data are contained within a triangle formed by these end members (Fig. 8B); however, a portion of GRS data falls outside and cannot be explained by compositional mixing of lunar samples. Those data are concentrated in Procellarum and Imbrium, which contain the youngest basalts whose compositions are not well represented by returned samples. Regions with high FeO are generally associated with the maria (Fig. 10). The distinct composition of these regions indicates that the composition of basalts changed with time, with later eruptions containing greater amounts of FeO (23, 24, 30).

Fig. 7. Least squares fit of elemental spectral components to a γ -ray spectrum acquired by GRS. The spectrum is a histogram of pulse heights that, when calibrated, are proportional to γ -ray energy. This spectrum was determined by averaging many spectra acquired during the high-altitude mapping orbit as Lunar Prospector repeatedly passed over a 5° equal area pixel. A spectral unmixing algorithm was used to fit spectral components for major oxides and radioactive elements to the background-subtracted spectrum.

Fig. 8. Comparison of element abundances determined by GRS (24) with laboratory analyses of Apollo and Luna samples. The 1,790 GRS data points are for equal area pixels covering the entire lunar surface. (A) Covariation of K and Th. (B) A mixing triangle, defined by end members from the sample data, is superimposed on the plot of Th vs. FeO.

TiO₂ abundances in mare basalts form a bimodal distribution (32), but the LP data form a continuous distribution (24, 33), with most GRS data concentrated at low values (Fig. 9A). The abundance of TiO₂ in basalts is highly variable (Fig. 10), and is used to classify lunar lava flows from distinct mantle sources. The discrepancy between samples and GRS data is thought to reflect insufficient sampling of surface rocks.

Rocks in the lunar highlands can be characterized by a plot of Al₂O₃ vs. Mg number (molar Mg/[Mg + Fe]) (34). The GRS data in Fig. 9B generally follow the sample trend. A few unusual Apollo rock types, including primitive rocks such as troctolite and evolved rocks such as granite, were not detected at the coarse spatial scale sampled by GRS; however, a trend towards lower Mg number for high Al₂O₃, characteristic of ferroan anorthosite, is evident (Fig. 9B). The global map of Mg shows high abundances in association with Th (Fig. 10). This association could result from gravitational overturn that mixed Mg-rich and incompatible element-rich components in the lunar mantle (24). The impact that excavated the huge South Pole Aitken basin is expected to have exposed mantle rocks; however, the average Mg abundance determined by GRS within the basin is lower than expected for the lunar mantle. This result does not exclude the possibility that the basin floor may represent a mixture of mantle and crustal materials.

Ion and Neutral Mass Spectrometer (INMS). The Ion and Neutral Mass Spectrometer (INMS) is one of six in situ-sensing instru-

ments on the Cassini-Huygens spacecraft (Fig. 11). The INMS includes closed and open ion sources, electrostatic focusing lenses, a quadrupole switching lens, a radiofrequency quadrupole mass analyzer (35, 36), two secondary electron multiplier (SEM) detectors and the associated electronics (37). The instrument runs in three modes: a neutral closed-source mode, wherein an antechamber creates a density enhancement for nonreactive neutral species to improve measurement accuracy, background, and field of view; a neutral open-source mode used for reactive neutral species; and an ion mode, also using the open-source aperture but without the electron impact ionization filaments turned on. Only one mode can be used at a time, so careful planning is required for each observation sequence. The instrument has a sampling integration period of 34 ms and provides a science data rate of 1,498 bps.

Electrons supplied by a filament are accelerated and ionize incoming neutral atoms and molecules. Depending upon the impact energy, neutral molecules “break” into characteristic “cracking” patterns. By quantitatively analyzing the ions associated with these patterns, the incoming neutral molecular composition can be deduced. These ions, in turn, are accelerated into a region of alternating electric field at radiofrequencies. Ion velocity varies with mass, and only those with the resonant speed are collected to produce a signal.

INMS has mass-per-unit charge ranges of ~1–8 and ~12–99 u/e (unified atomic mass units per electron charge) (or Da/e) and can be run in 1 u/e or 1/8 u/e steps with either

Fig. 9. (A) Comparison of GRS element abundances (21) with analyses of lunar samples, obtained as described for Fig. 8. Superimposed on (B) are the compositional ranges for lunar rock types (29).

Fig. 10. Compositional maps (in color) superimposed on shaded relief base map of the Moon, displayed as cylindrical projections (21). Maps of Fe, Ti, and Th were made from γ -ray spectra from the low-altitude mapping orbit and binned on 2° equal area squares. Map of Mg is based on high-altitude mapping data binned on 5° equal area squares. All maps were smoothed for visualization. Apollo and Luna landing sites are marked by aqua circles and diamonds.

survey or selected-mass modes. In neutral mode the average power usage is 23.3 W, as compared with 20.9 W in ion mode and 13.1 W in sleep mode. A 4 W replacement heater is used when the instrument is off. The instrument mass is 10.3 kg, including ~ 1.4 kg of Ta that was added around the SEMs to mitigate the radiation background in Saturn's magnetosphere. The entrance is protected with a metal ceramic breakoff cap with a pyrotechnic actuator. From Cassini's launch in 1997 until arrival at Saturn in 2004, the instrument remained sealed to prevent contamination during orbit insertion when significant propellant was burned by the orbiter's main engine. Measurements made following cap jettison discovered an ionosphere over the A-ring (38).

Multiple flybys through Titan's upper atmosphere have revealed a host of data on atmospheric structure, temperatures, waves, isotopic compositions, and minor constituents including C-nitrile compounds (39). Measurements in the ion mode have revealed a similarly rich ionospheric composition with the major ion HCNH^+ , as had been predicted, but also with hydrocarbon-ion C_nH_m^+ and nitrile $\text{C}_n\text{N}_k\text{H}_m^+$ families, which had not. Mass spectrometer measurements by INMS have been key to our current and evolving understanding of Titan, its atmosphere, and their interaction with each other and with Saturn's magnetosphere (40).

In addition to studying Titan's atmosphere, the source of plasma to Saturn's magnetosphere has been a target for investigation (41 and references therein). Initial estimates of the

Fig. 12. Time-integrated mass spectrum showing first compositional results from INMS for Enceladus plumes (37). Figure shows counts per integration period (IP) as a function of mass per charge measured by the quadrupole mass analyzer. Schematic at the top shows cracking patterns of various molecules detected, with red arrows indicating dominant contributions. For these signal levels, the INMS cannot discriminate between N_2 and CO .

neutral density in the magnetosphere and near the icy satellites due to energetic-particle sputtering were low, and there was doubt as to whether neutral material would be detectable. The discovery of active cryovolcanism at Enceladus, and the subsequent direct measurement of the composition of the plumes have been the major serendipitous discovery of the Cassini mission. INMS showed that the plumes are primarily H_2O , with an admixture of CO_2 and hydrocarbons (42) (Fig. 2). In particular, the detection of NH_4 greatly added to evidence for the plumes originating from a liquid-water reservoir (43) (Fig. 12). Recent work has led to detection of neutral material and water-group ions in Saturn's magnetosphere associated with the plumes of Enceladus (44), now known to be the source of Saturn's E-ring (41).

The Cassini INMS continues to play a vital role in understanding Titan's atmosphere, the material in the active plumes of Enceladus, and the interaction of neutral material with Saturn's magnetosphere during the ongoing, extended Cassini mission.

Future Challenges for Cosmochemistry by Spacecraft

To date, cosmochemical flight instruments have focused on analyses of major element and stable isotope abundances and identification of minerals and the simplest organic molecules. Significant development is required to enable semiautonomous

Fig. 11. INMS detector and schematic. The instrument maximum envelope (cruise configuration) is $20.3 \times 42.2 \times 36.5$ cm (32), and its mass is 10.3 kg.

sample manipulation, analyses of radiogenic isotopes and trace elements, radiometric age determination, and characterization of complex organic matter, all while maintaining low instrument mass and power requirements. The evolution of instruments to image and analyze ever-smaller samples would provide advantages now available only in the laboratory. Another challenge is designing instruments that can function in extreme environments of temperature, pressure, and radiation.

Instruments on orbiting and landed spacecraft are mobile laboratories that provide context for, and complement laboratory

analyses of returned samples and meteorites, as well as allow extrapolation from local to global and evolutionary conclusions. Continued instrument development is a critical aspect of cosmochemistry.

ACKNOWLEDGMENTS R.L.M. acknowledges conversations on the workings of the INMS instrument with H. B. Niemann, W. T. Kasprzak, and J. H. Waite Jr. Research on these missions was carried out at University of Tennessee (UT), Johns Hopkins University Applied Physics Laboratory (JHU/APL), and Planetary Science Institute (PSI) under the auspices of NASA.

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