RESEARCH ARTICLE

Astrobiological applications of μ-mapping X-ray fluorescence spectrometry

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Abstract

In situ elemental imaging of planetary surface regolith at a spatial resolution of 100s to 1000s of microns can provide evidence of the provenance of rocks or sediments and their habitability, and can identify post-depositional diagenetic alteration affecting preservation. We use high-resolution elemental maps and XRF spectra from MapX, a flight prototype in situ X-ray imaging instrument, to demonstrate this technology in rock types relevant to astrobiology. Examples are given for various petrologies and depositional/diagenetic environments, including ultramafic/mafic rocks, serpentinites, hydrothermal carbonates, evaporites, stromatolitic cherts and diagenetic concretions.

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Introduction

The value of microscale in situ observations of planetary surfaces

Many low-temperature planetary surface processes leave traces of their actions as features in the size range from 0.01 mm to several mm. Syn-sedimentary, authigenic and diagenetic features at the higher end of this size range include varves, vesicles, precipitates and concretions that can be used to decipher depositional and diagenetic processes. On the Earth, microbial life is known to exploit microscale disequilibria at boundaries where valence, chemical potential, pH, Eh, etc., vary on a length scale commensurate with the organisms themselves – tens to thousands of micrometres. These disequilibria can exist within cracks or veins in rocks and ice, at inter- or intra-crystalline boundaries, at sediment/water or sediment/ atmosphere interfaces, or within fluid inclusions trapped inside minerals. Larger organized sedimentary structures such as stromatolites can provide macroscale evidence of biogenic influence, but abiogenic examples are known as well and detailed study at the microscale is required for confirmation of biogenicity. Detection of accumulations of the biogenic elements C, N, O, P and S at appropriate concentrations on or in a mineral substrate could constitute permissive evidence of life, but context is also necessary. Does or did the putative biosignature exist in a habitable environment? Under what conditions of P, T and chemical potential was the host mineralogy formed? Most importantly, post-emplacement alteration (taphonomy) resulting from variations in temperature, pressure or fluid chemistry after deposition has the capacity to preserve evidence of biogenicity or its processes, or to erase such evidence completely.

In the characterization of solids (rocks, soil or planetary regolith), three fundamental properties can be used to elucidate conditions of formation and post-formational processing history: crystal structure, elemental composition and morphology. Based on these measurable properties, it is possible to determine provenance (useful in evaluating habitability or biogenicity) and taphonomy (useful in evaluating preservation potential).

Micro-mapping X-ray fluorescence spectroscopy (μ-mapping XRF)

The Mars Exploration Rovers Spirit and Opportunity each had instruments capable of elemental analysis (Alpha Particle X-ray Spectrometer (APXS); Rieder et al., 2003; Gellert et al., 2006), iron mineralogy (Mössbauer Spectrometer; Morris et al., 2006), IR imagery (Miniature Thermal Emission Spectrometer (Mini-TES); Christensen et al., 2003; Ruff et al., 2006) and contextual hand-lens imagery (Athena Microscopic Imager (MI); Herkenhoff et al., 2003; Herkenhoff et al., 2008). The spatial resolution of all but the microscopic imager is on the order of centimetres, with the result that imaged features can rarely be related to elemental chemistry or mineralogy. The Mars Science Laboratory rover Curiosity (Grotzinger et al., 2012) is capable of landed optical imagery of rocks or soil with an ultimate spatial resolution of tens of microns (Mars Hand Lens Imager (MAHLI); Edgett et al., 2012), and quantitative compositional data can be obtained from quite larger surface areas of 2–3 cm diameter using APXS (Campbell et al., 2012). Occasionally, smaller features of a few mm have been characterized by comparing data from areas of regolith on and off a feature of interest (VanBommel et al., 2016). The Laser-Induced Breakdown Spectrometry (LIBS) instrument on Curiosity (Maurice et al., 2012) is capable of acquiring sub-mm qualitative to semi-quantitative elemental information, but these data are limited to individual spots and 1D or 2D arrays of analyses that are rudimentary at best when compared to companion optical information. Mineralogical data from the Chemistry and Mineralogy (CheMin) instrument (Blake et al., 2012) and the Surface Analysis at Mars (SAM) instrument (Mahaffy et al., 2012) represent a homogenized volume of soil collected by a
scoop, or a powdered drill core 1 cm in diameter and 3–6 cm deep (Sample Acquisition, Sample Processing and Handling (SA/SPaH) instrument; Anderson et al., 2012).

The PIXL instrument on the Mars 2020 rover Perseverance (Allwood et al., 2020) for the first time provided a capability to X-ray map and quantitatively analyse a small portion of Mars regolith with 125 μm lateral spatial resolution (see e.g. Liu et al., 2022; Tice et al., 2022; Scheller et al., 2023). PIXL is a scanning instrument in which a focused 125 μm diameter X-ray beam is moved in X and Y across a regolith surface. Two silicon drift detectors (SDD) collect the fluoresced X-rays as the beam is moved, to produce point analyses, transects or X, Y elemental maps. The ultimate resolution of the analysis is defined by the distance between the X, Y positions.

A second method of X-ray mapping utilizes a flood of X-rays/γ-rays/α-particles to irradiate the entire sample at once, and an X-ray lens to focus the fluoresced photons from the sample onto a charge coupled device (CCD) detector. This method is called full-frame X-ray fluorescence imaging (FF-XRF). FF-XRF instruments have been demonstrated in space (Mercury Imaging X-ray Spectrometer (MIXS); Fraser et al., 2010) in the laboratory (Price et al., 2004), as planetary instrument prototypes (Mapping X-ray Spectrometer (MapX); Blake et al., 2015; Sarrazin et al., 2016, 2018; Thompson et al., 2017; Walroth et al., 2019) and as portable field instruments (MapX-II (Cartix); Walter et al., 2018; Sepúlveda et al., 2020).

Irrespective of how X-rays are detected and imaged, with a full characterization of the excitation source and source–sample–detector geometry, it is possible to calculate spatially resolved quantitative compositional information using the fundamental parameters method (Solé et al., 2007; Pia et al., 2009; Schoonjans et al., 2012).

Here we present elemental imaging results from a variety of sample types relevant to astrobiology, collected at ∼125 μm lateral resolution in MapX-III, a FF/XRF planetary instrument prototype. These data are compared with imaging results collected at 50 μm lateral spatial resolution in a commercial scanned beam X-ray imaging instrument (EDAX Orbis).

Materials and methods

Hand samples, thin sections and thin section stubs were selected that represent a range of habitable environments, diagenetic fabrics and biologically meditated structures. Bulk samples were trimmed to petrologic thin-section size (19 × 26 mm) and thin sections were prepared. The prepared slides are intended to represent the smooth and dust-free abrasion targets typically studied by the Mars 2020 Perseverance rover’s X-ray fluorescence (PIXL) and Raman (SHERLOC) microscale mapping instruments (Hickman-Lewis et al., 2022; Razzell et al., 2022). In addition, thin sections allow for a petrographic characterization of the samples, useful for relating underlying microstructures with X-ray fluorescence maps. Representative portions of each sample were powdered and analysed by X-ray diffraction to determine the quantitative mineralogy of the samples.

Samples were first imaged and analysed in a commercial EDAX Orbis X-ray spectrometer in vacuum under a standard set of conditions: accelerating voltage 30 keV, beam current 350 μA (10.5 W), rhodium anode, 30 μm spot size polycapillary optic, 80 mm² SDD detector. Samples were scanned with a step size of 50 μm, and a dwell time of 0.2 s. In a typical analysis of a 19 × 26 mm thin section, a matrix of 380 × 520 spots is collected, requiring ~11 h and 115 Watt hours (Wh) total beam energy.

The geometry of the MapX instrument used in this work is illustrated in Fig. 1. Sources bombard the sample with X-rays or α-particles/γ-rays, resulting in sample X-ray fluorescence (data for all figures in this paper were collected in MapX-III, a prototype having X-ray tube sources). X-ray photons emitted in the direction of an X-ray sensitive CCD imager pass through a 1:1 lens (X-ray Micro-Pore Optic (MPO)) that focuses a spatially resolved image of the X-rays onto the CCD. The CCD is operated in single photon counting mode (meaning that the imager is read often enough so that in the vast majority of cases, each pixel in the array contains either the charge generated by a single photon, or background). Under these conditions, both the energies and X, Y positions of individual X-ray photons are recorded. In a single analysis, several thousand frames are collected and processed in real time.
MapX-III (Fig. 2) is comprised of custom flight-qualifiable camera electronics that drive a flight-qualified e2v frame-transfer front illuminated CCD-224. The camera is interfaced to a high vacuum enclosure that contains the CCD-224 imager, a Photonis MPO lens and sample stage. Two Newton Scientific Au target transmission window X-ray tubes, operated at 15 keV and 25 μA (0.750 W total) illuminate the sample through ports in the chamber.

The overall geometry of the instrument (distances between sample, MPO and CCD, and the characteristics of the MPO) was optimized through the testing of MPO lenses at Stanford Synchrotron Radiation Light Source Beam Line 2–3 (Sarrazin et al., 2018) and by ray-tracing simulations (Gailhanou et al., 2018). The measured lateral spatial resolution of the instrument is 100 μm with a depth of field of ±5 mm with minimal loss of resolution.

Samples were imaged and analysed in MapX-III under the conditions noted in the text for each analysis. The equivalent of ≤3 h of analysis time is considered as a nominal baseline for a deployed planetary instrument. MapX can be equipped with either an X-ray tube source or a radioisotope source to fluoresce the sample. For an X-ray tube sourced instrument, we modelled 25 KeV accelerating voltage and 200 μA beam current (5 W total power in the beam, 15 Wh total energy per analysis). For a radioisotope sourced instrument, we modelled 30 mCi of $^{244}$Cm, equivalent to that used in the APXS instruments (Rieder et al., 2003; Gellert et al., 2006; Economou, 2011). The radioisotope $^{244}$Cm produces 14 and 18 KeV γ-rays (suitable for fluorescing Kα lines from calcium through zirconium) and 5.8 MeV α-particles (suitable for fluorescing Kα lines from oxygen through potassium).
Whether from the EDAX instrument or MapX-III, once data are collected, they are processed identically. In MapX-III, the individual images (frames) collected by the CCD are binned by energy and combined into an $X \times Y \times$ photon energy hdf5 data cube (see Supplementary Information and Fig. S1). The data cube is commonly hundreds of megabytes in size, too large for routine downlink from a spacecraft. Software was developed to generate reduced data records more suitable for downlink. Single-element maps, Mg–Ni are computed from the hdf5 file using custom python code. These maps are qualitative only in that fluorescence efficiency, absorption effects, detector efficiency, etc., are not accounted for. In a 3 h nominal analysis, single-pixel spectra lack sufficient counting statistics to be quantified. However, qualitative single-element maps are the highest resolution and highest sensitivity data products produced by the instrument.

We use an unsupervised machine learning program to identify regions of similar composition (regions of interest or ‘ROI’) in the hdf5 data cube. ROI are identified by finding element–element correlation clusters in $N \times N$ dimensional space where $N$ is the number of relevant elements (see Supplementary Information and Fig. S2). These clusters are then applied to the 2D image to generate a map of ROI. The XRF spectra from the individual pixels contained in each ROI are summed to generate high signal-to-noise quantifiable XRF spectra for ground processing. The hdf5 data cube is reduced to a set of single-element maps, a set of ROI (composition maps) having unique element compositions and XRF spectra from each ROI. If necessary, the hdf5 data cube can be reprocessed to generate additional data products on the basis of the initial quick-look elemental images and ROI.

Results

Examples are organized by rock type and depositional/diagenetic environment (ultramafic/mafic rocks, serpentinites, hydrothermal carbonates, evaporites, stromatolitic cherts and diagenetic concretions). All raw hdf5 files, element maps, ROI, ROI spectra, etc., for the samples shown here and many others are archived in and downloadable from the Planetary X-ray Fluorescence Petrography database: https://doi.org/10.48484/R7WV-3T89.
Ultramafic xenoliths from Spitsbergen, Norway; analogues of the ALH84001 meteorite

Xenoliths of mantle material comprise as much as 20% by volume of several quaternary volcanic centres in Spitsbergen, Norway. The xenoliths include spinel lherzolites and pyroxenites having mineralogies broadly similar to that of the Mars meteorite ALH84001, purported to show evidence of microbial life on ancient Mars (McKay et al., 1996).

While the preponderance of available evidence now supports an abiotic origin for the carbonate globules in ALH84001 (e.g. see Treiman et al., 2002), this meteorite nevertheless represents an important rock type for Mars. The mineralogy/petrology of ALH84001 demonstrates that deep-seated volcanism occurred \( \sim 4.1 \) Gy before the present, influenced by a low-temperature near-surface or surface hydrothermal event predating a shock that caused the ejection of ALH84001 from the planet’s surface. The hydrothermal event was brief enough, or at low enough temperature (\(<200^\circ\)C) that the ultramafic minerals, unstable in the presence of water, were not altered to serpentine.

Figure 3 illustrates a partial EDAX and MapX-III dataset from AMASE08 UI-3, one of several ultramafic xenoliths from Spitsbergen, Norway that were analysed by X-ray diffraction, electron microprobe and optical point counting (Treiman et al., 2010). The highest resolution data returned by the instrument are the individual elemental images. ROI representing regions of the sample having common compositions were calculated from the hdf5 data cube using an unsupervised machine learning algorithm (see Supplementary Information and Figs S1 and S2). In this example, ROI are seen to represent three minerals plus basalt: clinopyroxene (cpx, ROI 1), orthopyroxene (opx, ROI 3), chrome spinel (csp, ROI 4) and host basalt (bas, ROI 2). Mineral identifications were made separately on UI-3 thin sections and powder separates using optical point counting, electron microprobe and X-ray diffraction data (enstatite 26.09 wt.%, forsterite 7.79 wt.%, augite 59.22 wt.%, albite 4.05 wt.%, spinel 2.85 wt%) (Treiman et al., 2010). XRF spectra returned for each ROI can be quantified using fundamental parameters methods, and in favourable cases, it is possible to relate the compositions of ROI to specific minerals using the RRUFF database (Lafuente et al., 2015). Total beam power: 9 Wh, equivalent to 120 min of analysis with a nominal X-ray tube or \(^{244}\)Cm radioisotope-based spacecraft instrument.

It is interesting to note that one of the first rock types imaged in Jezero crater by the PIXL instrument (Farley et al., 2022; Liu et al., 2022) has a similar fabric and mineralogy to the ultramafic xenoliths analysed from Spitzbergen (Treiman et al., 2002, 2010) and illustrated in Fig. 3.

Serpentinization of mafic and ultramafic rocks: a source of energy for chemosynthetic ecosystems

Serpentinization is the process by which ultramafic rocks containing olivine and pyroxene react with water to form magnetite, serpentinite and hydroxide minerals. As a consequence of this reaction, molecular hydrogen is released, a potential source of chemical energy for life (McCollom and Shock, 1997; Sleep et al., 2004). Serpentinitizing systems are regarded as important analogues for potential early ecosystems on Earth and Mars, where highly reducing mineralogy was likely widespread in an undifferentiated crust (Kelley et al., 2005; Schulte et al., 2006).

The second and third samples collected and analysed by the MSL Curiosity rover during its investigation of Gale crater on Mars were of a \( \sim 3.7 \) G-year-old mudstone interpreted to be a lithified sediment deposited in a lacustrine environment (Grotzinger et al., 2013; Vaniman et al., 2013; Bristow et al., 2015). When compared to the elemental composition of global soil (used as a proxy for average Martian basalt) collected during Curiosity’s first analysis on Mars (Bish et al., 2013; Blake et al., 2013), the elemental composition of the mudstone (now principally comprised of secondary minerals) is a close match, suggesting that the mudstone was similar in its initial mineralogy and experienced a closed-system diagenetic event. On the basis of mass-balance calculations, Bristow et al. (2015) propose a mechanism akin to serpentinization in which original mafic minerals (e.g. olivine), unstable in the presence of water, transformed into a stable assemblage including clay minerals (ferrian saponite; Treiman et al., 2014) and magnetite. Hydrogen would have been released in such a reaction, and on the
basis of the mineral assemblage and its sedimentological context, this ancient lakebed was identified as a habitable environment for chemosynthetic organisms (Grotzinger et al., 2013).

Orbital spectral observations made by the CRISM instrument on Mars Reconnaissance Orbiter have identified serpentine and serpentine-like minerals in many locations on Mars, suggesting the presence
of widespread and deep-seated serpentinization reactions in the crust of Mars, creating potential habitable environments early in Mars history (Ehmann and Edwards, 2014 and references therein).

The most widespread serpentinizing environment on the Earth is the seafloor, where mafic and ultramafic oceanic crust interacts with seawater (Deming and Baross, 1993; McCollom and Shock, 1997; Kelley et al., 2001a, 2001b). ‘Ophiolite sequences’, slivers of oceanic crust thrust upward into the shallow continental crust as a result of plate tectonics, are found in northern California and southern Oregon (Coleman, 2000). These rocks, in contact with connate fluids at moderate to low temperatures (∼200°C), are presently undergoing serpentinization (Barnes et al., 1967; Barnes and O’Neil, 1969; Blake and Peacor, 1985).

Schulte et al. (2006) analysed hand samples of olivine-rich rocks from actively dewatering outcrops in the Coast Range Ophiolite in N. California. Figure 4 illustrates a partial dataset from a thin section

Figure 4. Thin section stub of a partially serpentinized cobble from Complexion Springs, California. (a) Optical image, white rectangle shows area imaged in MapX-III; (b) RGB element map from EDAX-Orbis instrument (50 μm resolution), Red = Fe, Green = Ca, Blue = Cr, white rectangle shows area imaged in MapX-III; (c) RGB element map from MapX-III (∼125 μm resolution), same colour scheme as in b; (d–g) element images from MapX-III; (h) ROI selected by elemental correlation cluster analysis from EDAX hdf5 data cube (numbers refer to individual ROI also shown in (i) from the MapX-III instrument; (i) ROI selected by elemental correlation cluster analysis from MapX-III hdf5 data cube; (j) MapX-III XRF spectra from individual ROI, numbers refer to ROI labelled in (i) (total MapX-III beam power = 2.25 Wh (30 min analysis)).
stub of one such sample described in Schulte et al. (2006). The modal proportions of minerals in the original rock prior to serpentinization were estimated to be 70% olivine, 20% orthopyroxene, 7% clinopyroxene and 3% other minerals. Primary olivine and pyroxene account for about half of the present mineralogy, with a fine-grained groundmass representing the remaining bulk (and comprised of serpentine minerals, fine-grained magnetite and Fe-rich brucite). Despite the fact that most mineral phases are below the resolution of both the EDAX and MapX-III, the mafic-ultramafic elemental composition of ROI and the rock fabric displayed in element images (secondary veining and the absence of large crystals) strongly suggest that this rock is a serpentinite, and represents a potentially habitable environment.

**Carbonates on Earth and Mars**

Carbonates are important rock-forming minerals on early Earth and should have been on early Mars as well. On early Mars, a dense, CO$_2$-rich atmosphere in the presence of surface and near-surface water would promote the dissolution of mafic minerals by carbonic acid and the precipitation of Ca-Fe-Mg carbonates at near-normal pH.

**Meteoritic Carbonates**

Carbonates were described in the Martian meteorites Nakhla (Bridges and Grady, 2000; Bridges and Schwenzer, 2012) and in ALH84001 (McKay et al., 1996). While these carbonates comprise a volumetrically small fraction of the overall mineralogy in these meteorites, they are nevertheless important because detailed information about their paragenesis has been obtained with laboratory-based instrumentation. In all cases, carbonate formation can best be explained by surface or near-surface hydrothermal activity in mafic or ultramafic rocks (Bridges et al., 2018 and references therein). Treiman et al. (2002) describe carbonate globules contained within ultramafic xenoliths from the Sverrefjell volcano (Spitsbergen, Norway) that are nearly identical to those found in the ALH84001 meteorite and present evidence that the globules are hydrothermal precipitates formed within a shallow sub-surface volcanic complex. Figure 5 shows data from ultramafic xenolith AMASE08 UI-6. X-ray diffraction analysis shows it to be comprised of 15.7% enstatite, 81.1% olivine, 1.9% augite and 1.2% albite. In this case (unlike AMASE08 UI-3 shown in Fig. 3), only a small amount of Ca-containing clinopyroxene is present, so that carbonate globules are identifiable based on Ca element images. Treiman et al. (2010) describe the secondary mineralization shown in (Fig. 5(f)) as partial melts and products of aqueous alteration near and around spinels, the alteration products including zoned spherules of (CaMg,Fe)CO$_3$.

**Martian Carbonates**

Orbital observations of Mars with the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument have identified volumetrically significant deposits of carbonate in Nili Fossae (Ehlmann et al., 2008) and elsewhere. Morris et al. (2010) report the discovery of carbonate-rich basaltic outcrops in Gusev crater, Mars using instruments aboard the Mars Exploration Rover Spirit. Comanche Spur is an apparent volcaniclastic deposit with a fracture filling comprised of Mg-Fe-Ca carbonate. The composition of the carbonate is reported to be Mg$_{0.62}$Fe$_{0.25}$Mn$_{0.02}$Ca$_{0.11}$CO$_3$ based on Mossbauer, APXS and Mini-TES instrumental data. The closest terrestrial analogue to the Comanche carbonate is from Spitsbergen, Norway in carbonate-cemented, breccia-filled volcanic pipes associated with late-stage hydrothermal activity. Morris et al. (2011) describe this occurrence (see also Treiman et al., 2010; Blake et al., 2011). The Sverrefjell volcanic province is quaternary in age and manifests itself as volcanic cinder cones which on the basis of pillow basalts exposed on their flanks, must have erupted under water (Treiman et al., 2002). Laboratory and field evidence
Figure 5. Ultramafic xenolith AMASE UI-6, an orthopyroxenite comprised principally of orthopyroxene and olivine with minor chrome spinel and carbonate. (a) Petrographic thin section, small black rectangle shows area of thin section magnified in (f); (b) RGB element map from EDAX-Orbis instrument, Red = Fe, Green = Ca, Blue = Cr, large white rectangle shows area imaged in MapX-III; (c) RGB element map from MapX-III, colour scheme same as in (b); (d) Ca element image from EDAX instrument; (e) Ca element image from MapX-III instrument; (f) optical micrograph of portion of thin section outlined in figures a–e, g, h, showing carbonates (C) and other secondary mineralization surrounding chrome spinel (S), Opx = orthopyroxene, Ol = olivine; (g) ROI map from EDAX instrument; (h) ROI map from MapX-III instrument; (i) XRF spectra from MapX-III ROI labelled 1 and 3 in (h) (total beam power = 9 Wh (120 min analysis)).
suggest that the carbonates were deposited by hydrothermal fluids, likely heated by the volcanic rock itself, flowing through pre-existing volcanic pipes in a hydrothermal cell. Figure 6 shows EDAX and MapX results from a thin section of a carbonate-cemented basalt breccia from this locality. At the 50 μm spatial resolution of the EDAX instrument, the prismatic texture of the cement is evident, as are void spaces, demonstrating rapid crystal growth in a surface or shallow sub-surface aqueous environment. At the 125 μm resolution of MapX-III, void spaces are evident, but not the prismatic texture. Elemental maps document changes in carbonate chemistry during cement deposition, and the predominance of the divalent cations Ca-Mg-Mn suggest that the carbonate is rhombohedral. In fact, XRD analyses of these cements (Blake et al., 2011) reveal a wide variety of rhombohedral carbonates, including Mg-calcite (Mg_xCa_{1-x}CO_3), huntite (Mg_3Ca(CO_3)_4), magnesite (MgCO_3), dolomite/ankerite (Ca(Mg,Fe)(CO_3)_2), siderite (FeCO_3) and in some cases late-stage aragonite (orthorhombic CaCO_3). From these data, it appears that specific carbonate mineral chemistries (e.g. thin rind of Mn, calcium core, magnesium rim in the cement) are reflective of changing hydrothermal conditions and what divalent cations are present in the solution.

**Figure 6.** Carbonate-cemented basalt breccia from Spitsbergen, Norway. (a) Petrologic thin section; (b) RGB element map from EDAX-Orbis instrument (50 μm resolution), Red = Fe, Green = Ca, Blue = Mg, white rectangle shows area imaged in MapX-III; (c) RGB element map from MapX-III, same colour scheme as b; (d–g) Element images from EDAX (l) and MapX-III (r); (h) ROI map from EDAX (l) and MapX-III (r) note that ROI 1 from MapX is blue while the same ROI in EDAX is yellow; (i) ROI XRF spectra for MapX-III, ROI labelled in (h) (total beam power = 9 Wh (120 min analysis)).
Ancient cherts: fine-scale early preservation of evidence of life and habitability

On the early Earth, Proterozoic silica deposition (abiotic silica precipitation as either a primary chemical sediment or as an early diagenetic cement in the marine environment) is a predominant mechanism for fine-scale preservation of primary depositional fabrics, early diagenetic features and remnants of the earliest microbial life (cellular processes and organic biosignatures). Original silica was emplaced as amorphous and/or sparingly crystalline opal-A and opal-CT from a silica-saturated ocean (or from silica-rich ground water). These original components have been recrystallized into microcrystalline quartz (i.e. chert) in the rock record. Knoll (1985) suggests that well-preserved stromatolytic occurrences such as the Gunflint Chert (Tyler and Barghoorn, 1954; Barghoorn and Tyler, 1965; Awramik, 1976) were formed in peritidal environments in which evaporation and heightened salinity played a role in silica deposition. It appears that the presence of organic material is a common feature in early silicification, and petrographic observations of cement fabric suggest that initial opal-A or opal-CT nucleation occurs on individual microbial sheaths and processes. A second type of early silica deposition with fine-scale preservation involves the replacement of pre-existing carbonate completely or partially by silica.

Silica deposition as a chemical sediment or an early diagenetic replacement cement should have been common on early Mars, where water interacted with mafic rocks, dissolving olivine, pyroxene and other minerals with the liberation of aqueous silica (McLennan, 2003). Tosca and Knoll (2009) and references therein document numerous detections of hydrated silica on the surface of Mars from both in situ and remote observations. For example, evaporative sedimentary rocks at Meridiani Planum contain as much as 20 wt.% hydrated silica (McLennan et al., 2005), and opaline silica was identified in the Columbia Hills of Gusev Crater, interpreted as the product of aqueous activity, possibly related to hydrothermal processes (Squyres et al., 2008). Remote observations from MRO/CRISM have identified opaline silica (Milliken et al., 2008) as well.

The discovery of amorphous and crystalline silica in ~3.5 Ga Murray formation lacustrine mudstone sequences in Gale crater on Mars (Morris et al., 2016; Rampe et al., 2017) raises the possibility that retention of depositional/early diagenetic features in silica (including preservation of organic biosignatures, if present) is possible and even likely on Mars. Silica-rich sequences of the Murray formation (and of other similar sedimentary deposits found elsewhere on Mars) may have the highest probability of retention of evidence of biogenicity (or of abiotically produced endogenous/exogenous carbon) and may offer a taphonomically favourable window into the biologic potential of early Mars.

Figure 7 shows a thin section stub of finely preserved stromatolitic material from the 2.1 Ga Gunflint Chert, Schrieber Beach locality. The chert preserves carbonate features that were likely the original material of the stromatolitic structures. However, abiotically precipitated silica is ubiquitous in the Precambrian, and locations such as Schrieber Beach were only found through extensive fieldwork by paleontologists (and indeed, much of the Gunflint formation was subject to extremes of diagenesis that would have overprinted the features preserved in the Schrieber Beach locality). As shown in the figure, spatially resolved element images can be highly useful in identifying the small fraction of chert samples that may contain evidence of early preservation and of potential biogenicity. It is interesting to note that there are no mineral phases in this sample that are large enough to be resolved by the 125 μm spatial resolution of MapX-III or even the 50 μm spatial resolution of the EDAX instrument (e.g. the Ca-Fe-Mn rich regions in this sample were found by optical microscopy to be comprised of clusters of ~10 μm carbonate rhombs, and the fabric of the microcrystalline chert is only resolvable in a petrographic microscope). The key feature of this sample that would separate it from others is the apparent chemical disequilibrium and heterogeneous distribution of elements in the images and the composition of the ROI at mm- and larger scales.

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Figure 7. Gunflint Chert, Schrieber Beach locality stromatolite. (a) Polished thin section stub; (b) RGB element maps from EDAX-Orbis and MapX-III instruments, Red = Fe, Green = Ca, Blue = Mg; (c–f) comparison element images from EDAX (l) and MapX-III (r) for Si, Ca, Fe and Mn; (g–j) ROI maps from EDAX instrument; (k–m) ROI maps from MapX-III; (n) XRF spectra for EDAX ROI; (o) XRF spectra for MapX-III ROI (total beam power = 9 Wh (120 min analysis)).
Evaporites

On early Mars, volcanic sulphur emanations combined with the presence of surface water suggest that sulphates of all kinds should be present on the surface. Indeed, on the basis of extensive observations of sulphates from orbit by the OMEGA instrument (Bibring et al., 2006), sulphate deposits are known in the Vallis Marineris (Juventae Chasma), Terra Meridiani (Squyres et al., 2006) and many other places on the Mars surface. In Juventae Chasma, these deposits are over 2 km thick and have an unknown origin (Bishop et al., 2009). MSL’s landing site in Gale crater was chosen in part because the central mound of the crater (Mt. Sharp) is comprised of flat-lying phyllosilicate-rich sediments overlain by a sulphate layer (Milliken et al., 2010). During MSL’s traverse, gypsum, bassanite and anhydrite have been detected in secondary diagenetic veins and fillings during its entire traverse of the crater. Most recently, the mineral Starkeyite (MgSO₄·4H₂O) and an amorphous Mg-sulphate were identified by the CheMin XRD instrument on the Curiosity rover (Chipera et al., 2023). Starkeyite was seen to dehydrate to amorphous Mg-sulphate in the low relative humidity environment of the instrument, and it is likely that much of the detected amorphous Mg-sulphate was originally crystalline. However, the paragenesis of these sulphates is unknown.

The Castile Formation evaporite on Earth is a cm-to-mm scale laminated deposit of gypsum/dolomite (CaSO₄·2H₂O/CaMg(CO₃)₂) couplets that is 400–500 m thick that filled portions of the Permian basin of southeast New Mexico (∼250 MYa). The deposit is thought to have formed in a shallow basin after reef growth cut off the influx of marine water, causing the basin to fill with gypsum and carbonate (Kirkland et al., 2000). The carbonate–gypsum couplets are thought to represent annual changes in sedimentation, with gypsum layers forming during high evaporation (summer), and carbonate layers forming during low evaporation (winter). Some variants also include halite. Figure 8 shows X-ray mapping results from a petrologic thin section of Castile Formation evaporite, illustrating the sulphate and carbonate diurnal varves. Varves are plainly visible at both 50 μm resolution (EDAX) and 125 μm resolution (MapX-III) corresponding to alternating sulphate and carbonate layers. In the MapX ROI generated by machine learning, the varves could not be discriminated. However, the h5 data cube stored on the instrument is available for reprocessing and new algorithms could be devised (e.g. ‘identify the locus of X, Y pixels containing Ca and Mg’), the data cube reprocessed and quantifiable XRF spectra generated from the newly calculated ROI.

Hematite/goethite diagenetic crystallization

Clastic, sand-sized particles deposited in aeolian, lacustrine, fluviatile and sabkha type environments quite commonly retain their porosity and permeability after deposition. Syn-sedimentary or early diagenetic events caused by fluid migration and oxidation/reduction of soluble species can be characterized by the nature of infilling cement, precipitates, secondary crystallizations, etc. These secondary products provide a window into the pH/Eh, etc., conditions that were present when diagenetic processes were active. Figure 9, for example, shows a quartz sandstone decorated by iron oxide crystals (identified by XRD to be goethite, in all likelihood a pseudomorphic replacement of primary hematite) from Spitzbergen, Norway. The identification of secondary crystallization of Fe-oxide phases points to the early influx of soluble Fe²⁺ and its oxidation and precipitation in place. Taphonomic alteration in this case would have likely destroyed evidence of the provenance of the sediment or of original habitability.

Over the course of a 10-Earth year, 30 km transect across the central mound of Gale crater (Aeolus Mons, informally known as Mt. Sharp), the MSL Curiosity rover has identified hundreds of examples of secondary concretions, crystals and crystal pseudomorphs in the ancient sediments of Gale lake. Knowledge of the compositions of these features will allow an evaluation of the nature of the taphonomic changes experienced by the sediments and ultimately the potential for preservation of evidence of habitability. Bristow et al. (2021), for example, describe Vera Rubin Ridge, an Fe-oxide rich prominent feature on lower Mt. Sharp, Gale crater, as depositionally equivalent to the immediately
adjacent and clay-rich Glen Torridon region. Brine-driven destruction of clay minerals caused by silica-poor diagenetic fluids is proposed as the mechanism for destruction of the original mineralogy, and under these taphonomic conditions, any evidence of habitability present in the original mudstone would likely have been erased.

Discussion

Much of what we interpret is based on images. In the case of Mars, orbital imagery prior to the arrival of the Mars Express orbiter provided information that was largely morphological in nature. Fluvial, deltaic and lacustrine features and processes were identified based on their shapes and context, analogous to similar features and processes on Earth. With orbital remote data returned from the Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) instrument...
on the Mars Express orbiter (Bibring et al., 2005, 2006, 2007), these features could be overlain with mineralogical/compositional information, resulting in the identification of clay minerals, sulphate minerals, iron oxide minerals, etc., in spatially resolved chemical features that in many cases validated and refined earlier morphology-based interpretations. The juxtaposition of clay mineral, sulphate mineral and oxide mineral layers in sedimentary sequences on a global scale was seen to correlate with a notional understanding of the history of the planet (‘Phyllosian’, loosely correlated with the Noachian, 4.5–3.6 Ga; ‘Theiikian’, loosely correlated with the Hesperian, 3.6–2.6 Ga; and ‘Siderikian’, loosely correlated with the Amazonian, 2.6 Ga–present) (Bibring et al., 2006; Grotzinger and Milliken, 2012).

Figure 9. Goethite crystals on quartz sandstone (Spitzbergen, Norway). (a) Hand specimen, scale bar = 1 cm; (b) RGB element map from EDAX-Orbis instrument, Red = Fe, Green = Si, Blue = Ca; (c) RGB element map from MapX-III instrument, Red = Fe, Green = Si; (d) Fe map, MapX-III; (e) Si map, MapX-III; (f–h) ROI maps from MapX-III; (i) XRF spectra from ROI-1 and ROI-2, MapX-III (total beam power = 9 Wh (120 min analysis)).
Optical in situ high-resolution images of planetary regolith (e.g. from the MAHLI imagers on MER Spirit and Opportunity and MSL Curiosity rovers) far exceed the lateral spatial resolution of companion elemental analysis instruments such as APXS (lateral spatial resolution about 2 cm), resulting in a similar quandary: depositional and diagenetic events can be inferred from optical images, but spatially resolved elemental images are needed to fully characterize them. This has been remedied to the \( \sim 125 \) micron level with the development of in situ X-ray fluorescence imaging and the arrival of the PIXL instrument at Mars (Allwood et al., 2020).

Microscale morphological information combined with elemental composition provides for a much improved interpretation of small-scale features. Principal igneous textures (flow structures, crystal fabrics) and primary sedimentary depositional fabrics (varves, ripples, etc.) can be more confidently interpreted, providing insight into modes of formation and the provenance of the source materials. Diagenetic features (concretions, secondary crystals, crystal pseudomorphs, vein fillings, alteration haloes, etc., can be used to interpret the timing and chemistry of secondary fluids that altered rocks and primary fabrics. In returned sample science as is being initiated by Mars 2020 Perseverance rover, the spatially resolved elemental chemistry of features in candidate rocks is useful in evaluating samples prior to caching. Microscale chemistry informs two important questions for sample triage prior to sample return: (1) Does the original environment, as evaluated on the basis of morphology and chemistry have the potential to harbour life, and (2) Does post-depositional diagenetic change (taphonomy) preserve or destroy such features (or, did the diagenetic environment itself support habitability)?

Not surprisingly, nature doesn’t obey arbitrary size constraints or specific chemistries. There is nothing unique about 125 \( \mu \)m resolution or even 5 \( \mu \)m resolution in returned images, although improvements in spatial resolution will always allow for more confident interpretations. Nearly all of the sedimentary rocks imaged during MSL Curiosity’s traverse in Gale crater had grain sizes smaller than fine sand (<125 \( \mu \)m) and were in many cases below MAHLI resolution (\( \sim 15 \mu \)m). Fortunately, in many cases, compositionally distinct features (element images, ROI) can be compelling if not diagnostic at spatial scales larger than the dimensions of individual mineral grains. Images of rock fabric combined with elemental chemistry tell a compelling story.

The Mars Science Laboratory rover Curiosity identified the first habitable environment on ancient Mars in 2013 based on the mineralogy of the ancient lake sediment found in the Sheepbed member of the Yellowknife Bay formation (Grotzinger et al., 2013; Vaniman et al., 2013). The presence of significant quantities of clay minerals in the John Klein and Cumberland drill samples, key to habitability, was unexpected because they were not identified in orbital spectra. This has been the case for much of Curiosity’s transit through more than 600 vertical meters of flat-lying sedimentary rocks; clay minerals and habitable environments were found through nearly the entire traversed section despite the absence of orbital evidence for clay minerals. There are two notable exceptions: aeolian sandstones that were porous and permeable in which water was apparently never present long enough to induce diagenetic change in the original basaltic sediments, and original basaltic sediments that were diagenetically altered by late-stage fluids to the extent that evidence of habitability (or even of provenance) has been erased (e.g. Bristow et al., 2021). High spatial resolution elemental images can identify and discriminate such occurrences.

Conclusions

In situ X-ray imaging instruments such as PIXL or MapX are capable of analysing the microstructure and elemental composition of rock types relevant to astrobiology rapidly and in many cases with minimal surface preparation. In searching for evidence of life or of habitable environments, the most important consideration aside from the nature of the original depositional environment is the degree of post-depositional taphonomic alteration (i.e. if evidence of life or conditions of habitability were originally present, to what extent were they preserved?). Over the past decade, MSL Curiosity has documented hundreds of post-depositional diagenetic features – veins, concretions,
recrystallizations, alteration halos, etc., most in the mm-size range or larger that are useful in evaluating taphonomic change.

Dozens of geologically diverse and scientifically compelling landing sites have been identified and characterized from orbit as a result of the MER, MSL and Mars 2020 site selection workshops (Grant et al., 2004, 2011, 2018). In order to characterize the full geological diversity of Mars, its early habitability and its potential to support in situ resource utilization (ISRU) and eventual human exploration, comprehensive in situ science investigations need to be performed at many diverse sites. A small fleet of MER-class rovers could serve such a purpose (Blake et al., 2021a), equipped with smaller, more powerful next-generation analytical instruments (e.g. Blake et al., 2021b; Rampe et al., 2021). If future human exploration of Mars is to be contemplated, a comprehensive understanding of the diversity of its many environments is a necessary prerequisite.

Supplementary material. The supplementary material for this article can be found at https://doi.org/10.1017/S147355042400003X

Data availability statement. The data that support the findings of this study are openly available in the Planetary X-ray Fluorescence Petrography database: https://doi.org/10.48484/R7WV-3T89

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