Icarus 249 (2015) 62–73

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

Understanding the signature of rock coatings in laser-induced breakdown spectroscopy data

Nina L. Lanza [a,*], Ann M. Ollila [b], Agnes Cousin [a], Roger C. Wiens [a], Samuel Clegg [a], Nicolas Mangold [c], Nathan Bridges [d], Daniel Cooper [a], Mariek Schmidt [e], Jeffrey Berger [f], Raymond Arvidson [g], Noureddine Melikechi [h], Horton E. Newsom [b], Robert Tokar [i], Craig Hardgrove [j], Alissa Mezzacappa [h], Ryan S. Jackson [b], Benton Clark [k], Olivier Forni [l,m], Sylvestre Maurice [l,m], Marion Nachon [c], Ryan B. Anderson [n], Jennifer Blank [o], Matthew Deans [p], Dorothea Delapp [a], Richard Léveillé [q], Rhonda McInroy [a], Ronald Martinez [a], Pierre-Yves Meslin [l,m], Patrick Pinet [l,m]

[a] *Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, USA*
[b] *University of New Mexico, Department of Earth and Planetary Sciences, Albuquerque, NM 87131, USA*
[c] *Laboratoire de Planétologie et Géodynamique de Nantes, CNRS, UMR6112, Université de Nantes, 44322 Nantes, France*
[d] *Applied Physics Laboratory, Johns Hopkins University, 11100 Johns Hopkins Road, Laurel, MD 20723, USA*
[e] *Department of Earth Sciences, Brock University, 500 Glenridge Avenue, Saint Catharines, Ontario L2S 3A1, Canada*
[f] *Geological Sciences, University of Western Ontario, 1151 Richmond Street N., London, Ontario N6A 5B7, Canada*
[g] *Department of Earth and Planetary Science, Washington University, 1 Brookings Dr., Saint Louis, MO 63130-4899, USA*
[h] *Optical Science Center for Applied Research, Delaware State University, 1200 N. Dupont Highway, Dover, DE 19901, USA*
[i] *Planetary Science Institute, 1700 East Fort Lowell, Suite 106, Tucson, AZ 85719, USA*
[j] *School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85281, USA*
[k] *Space Science Institute, 4750 Walnut Street, Suite 205, Boulder, CO 80301, USA*
[l] *Université de Toulouse, 15 Rue de Lois, 31000 Toulouse, France*
[m] *CNRS IRAP, 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*
[n] *U.S. Geological Survey Astrogeology Science Center, 2255 N. Gemini Dr., Flagstaff, AZ 86001, USA*
[o] *Bay Area Environmental Research Institute, 596 1st St West, Sonoma, CA 95476, USA*
[p] *NASA Ames Research Center, Moffett Field, CA 94035, USA*
[q] *Department of Natural Resource Sciences, McGill University, St-Anne-de-Bellevue, Quebec H9X 3V9, Canada*

ARTICLE INFO

Article history:
Received 1 February 2014
Revised 13 May 2014
Accepted 25 May 2014
Available online 5 June 2014

Keywords:
Mars, surface
Spectroscopy
Geological processes
Experimental techniques

ABSTRACT

Surface compositional features on rocks such as coatings and weathering rinds provide important information about past aqueous environments and water–rock interactions. The search for these features represents an important aspect of the Curiosity rover mission. With its unique ability to do fine-scale chemical depth profiling, the ChemCam laser-induced breakdown spectroscopy instrument (LIBS) onboard Curiosity can be used to both identify and analyze rock surface alteration features. In this study we analyze a terrestrial manganese-rich rock varnish coating on a basalt rock in the laboratory with the ChemCam engineering model to determine the LIBS signature of a natural rock coating. Results show that there is a systematic decrease in peak heights for elements such as Mn that are abundant in the coating but not the rock. There is significant spatial variation in the relative abundance of coating elements detected by LIBS depending on where on the rock surface sampled; this is due to the variability in thickness and spatial discontinuities in the coating. Similar trends have been identified in some martian rock targets in ChemCam data, suggesting that these rocks may have coatings or weathering rinds on their surfaces.

* Corresponding author.
E-mail addresses: nlanza@lanl.gov (N.L. Lanza), aollila@unm.edu (A.M. Ollila), rwiens@lanl.gov (R.C. Wiens), sclegg@lanl.gov (S. Clegg), nicolas.mangold@univ-nantes.fr (N. Mangold), nathan.bridges@jhuapl.edu (N. Bridges), dcooper@lanl.gov (D. Cooper), mschmidt2@brocku.ca (M. Schmidt), jberge44@uwo.ca (J. Berger), arvidson@wunder.wustl.edu (R. Arvidson), nmelikechi@desu.edu (N. Melikechi), newsom@unm.edu (H.E. Newsom), rltokar@psi.edu (R. Tokar), chardgrove@gmail.com (C. Hardgrove), amezzacappa09@students.desu.edu (A. Mezzacappa), rjacks04@unm.edu (R.S. Jackson), bclark@spacescience.org (B. Clark), olivier.forni@irap.omp.eu (O. Forni), sylvestre.maurice@irap.omp.eu (S. Maurice), marion.nach@gmail.com (M. Nachon), rbanderson@usgs.gov (R.B. Anderson), jgblank@gmail.com (J. Blank), matthew.deans@nasa.gov (M. Deans), ddelapp@lanl.gov (D. Delapp), rich.leveille@gmail.com (R. Léveillé), rhondam@lanl.gov (R. McInroy), rkmartinez@lanl.gov (R. Martinez), pmeslin@irap.omp.edu (P.-Y. Meslin).

http://dx.doi.org/10.1016/j.icarus.2014.05.038
0019-1035/

1. Introduction

1.1. The importance of rock surface alteration

The goal of the NASA Mars Science Laboratory rover 'Curiosity' is to determine the past and present habitability of the martian surface (Grotzinger et al., 2012). A key criterion for habitability is the presence of liquid water, including evidence for water-formed materials and rock textures indicative of aqueous alteration. On Earth, the physical and chemical breakdown of rocky materials occurs through interactions with the atmosphere, soil, biological processes, and aqueous solutions. Alteration frequently occurs on rock surfaces or in joints—areas that are directly exposed to the environment—leaving distinctive morphologies and chemistries that provide information about the processes that have acted on the rock. The goal of this study is to better understand the signature of such surface alteration with the payload of Curiosity, with a focus on the element manganese.

Chemical weathering modifies rock compositions by either adding or removing material through aqueous alteration. This can produce coatings and rinds, two distinct types of alteration features on rock surfaces that form in similar environments but that provide different types of information about the weathering environment (e.g. Coleman and Pierce, 1981; Dorn, 1998; Dixon et al., 2002; Salvatore et al., 2013). Coatings are composed of materials emplaced on and cemented to the rock surface. The composition of the coating is frequently unrelated to the host rock, with the constituent materials coming from external sources. The transition between the coating and the rock is sharp, and the coating may not be continuous, especially if the rock surface is rough. In contrast, rinds are alteration horizons near the rock surface that show a chemical gradient with the host rock. Although rinds can be regions of accumulation, they are frequently associated with element removal by mineral dissolution. Cations with greater mobility will be preferentially removed, leaving behind a rind with a composition similar to the rock but depleted in certain elements. Coatings and rinds often form concurrently in the same rock and may even interact with one another. Minerals may be dissolved from the rock interior and reemplaced closer to the rock exterior to form a rind, or a surface coating may dissolve and permeate into the rock interior in a process known as case hardening (e.g. Dorn, 1998; Conca and Rossman, 1982).

Through coatings and rinds, rock surfaces record information about the physical environment to which they have been exposed. In particular, rock surface alteration can provide significant details about the amount and types of fluids with which a rock has interacted. Characteristics of the fluids such as pH and Eh will influence the style of alteration a rock experiences. Thus, the composition and thickness of coatings and rinds can provide details about both the climate and the presence and abundance of water in the surface environment (e.g. Dorn, 1998).

Along with providing information about aqueous alteration, coatings and rinds may also be important indicators for extant life. On Earth, there is an association between many rock coatings and microbes. In some cases it appears that the coating formed first and was then colonized by microbial communities (e.g. Wierzchos et al., 2011), while other coatings may be formed in part by the metabolism of microbes (e.g. Northup et al., 2010; Parchert et al., 2012). Coatings and rinds may also provide habitats for microorganisms in environments that are otherwise extremely hostile to life. Rock varnish coatings in the hyperarid Atacama Desert have been found to contain viable microbial colonies despite a general lack of microbes in the surrounding soils (Kuhlman et al., 2008). Weathering rinds may similarly provide shelter from a harsh environment. Microbial colonies have also been found in the porous exteriors of ignimbrite rocks in the Atacama Desert to a depth of ~1 mm, which offers significant protection from UV radiation and retains moisture long after wetting events (Wierzchos et al., 2013).

1.2. Previous in situ observations of surface alteration on martian rocks

The most definitive in situ observation of a rock coating on Mars was made by the Mars Exploration Rover (MER) Spirit on a rock called Mazatzal near Bonneville crater. Before analysis, Mazatzal was a partially buried, relatively light-toned rock with a ventifacted surface (Haskin et al., 2005). It was brushed and then abraded with the Rock Abrasion Tool (RAT) twice in a single location (Arvidson et al., 2004; Haskin et al., 2005). Measurements from Mössbauer on both the undisturbed and brushed surfaces suggest the presence of a dark oxide material similar to hematite, likely formed by alteration (Morris et al., 2004). Measurements by Mini-TES of the brushed surface of Mazatzal are consistent with a basalt covered by a coating of oxides $<\sim 50\ \mu m$ thick (Christensen et al., 2004), although models of Mössbauer element detections by depth based on laboratory studies of layered materials suggest that the oxide coating is $\sim 10\ \mu m$ thick (Fleischer et al., 2008a, 2008b). After the second abrasion activity in the same location, mineral grains were discernible in the rock surface (Herkenhoff et al., 2004), suggesting that the coating had been removed. The observation of a Fe-oxide coating on Mazatzal demonstrates that micron-scale metal-rich coatings can form on Mars.

The apparent lack of coatings on other rocks in the vicinity of Mazatzal emphasizes the spatial variability in coatings in a given region; coatings are not necessarily ubiquitous in areas in which they are observed. Rock coatings have been shown to be regionally variable on Earth (e.g. Palmer, 2002) so this result from Mars is not unexpected. Spatial variability is also important when examining individual rock targets. Terrestrial rock varnish is well known to be highly discontinuous at the hand sample and micron scale (e.g. Dorn, 1983; Northup et al., 2010; Lanza et al., 2012).

Iron is not the only element that has appeared as a constituent in a putative surface alteration feature on Mars. In Gale crater, the landing site of Curiosity, there is evidence for enhancement in rock surfaces of some fluid mobile trace elements, particularly in the target Bathurst Inlet (sol 55). ChemCam data show that mobile elements Li, Rb, K, and Na are more abundant at the surface of Bathurst compared to its interior, with the strongest decreasing gradient occurring in Li (Ollila et al., 2014). It is not yet clear why this particular rock expresses surface alteration when most other rocks do not, although wind abrasion may play a role in removing alteration features like coatings and rinds (Bridges et al., 2014). Other rock targets, most notably Caribou (sol 342) show similar decreasing trends in Mn, as discussed later in this paper. These observation of chemical trends with depth suggests that at least some rock surface alteration (whether coatings or rinds) is present in Gale crater.

1.3. Goals of the current study

In light of previous observations of rock surface alteration on Mars and the implications such alteration has for understanding habitability, it is important for Curiosity to recognize the signatures of these features if and when they are encountered on the martian surface. In this study, we examine a terrestrial basalt with a rock varnish (Mn-rich) coating in the laboratory and compare these results to data from ChemCam taken in the first 360 sols of the mission. The goal of this work is to analyze a known and well-studied coating from Earth with LIBS to better understand the general signature of coatings as seen by ChemCam. Rock