

STANDARDS FOR ANALYSIS OF Ce, La, Pb, Rb, Se, Sr, Y, AND Zr IN ROCK SAMPLES USING LASER-INDUCED BREAKDOWN SPECTROSCOPY AND X-RAY FLUORESCENCE. Jason Mackie¹, M. Darby Dyar², Caroline Ytsma³, Kate Lepore², Caleb I. Fassett⁴, Avery Hanlon², Carlie Wagoner², and Allan Treiman⁵, ¹Dept. of Geology, Amherst College, 220 South Pleasant St., Amherst MA 01003, USA, jmackie17@amherst.edu, ²Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, ³Dept. of Chemistry, Smith College, Ford Hall, 100 Green Street, Northampton, MA 01063, ⁴NASA Marshall Space Flight Center, Huntsville, AL 35805, ⁵Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058.

Introduction: Analytical geochemistry has long depended on the availability of robust suites of rock standards with well-characterized compositions. Standard rock powders for wet chemistry and x-ray fluorescence were initially characterized and supplied to the community by the U.S. Geological Survey, which continues to distribute a few dozen standards. Many other rock standards have subsequently been developed by organizations such as the Centre de Recherches Pétrographiques et Géochimiques (CRPG) and Brammer Standard Company, Inc.

Because these standards are nearly all naturally-occurring, they represent a range of concentrations in terrestrial rocks that may not cover what is present on other bodies. For example, Ni is a primary constituent of meteorites, and thus may be abundant in ancient surface materials of planetary bodies with impact craters [1-3]. Yet no terrestrial standards come close to covering the possible extremes of Ni concentration that would result under those conditions. Moreover, chemical analysis techniques that depend on specific peaks for individual elements may have their accuracies reduced by the presence of overlapping peaks from other elements. To mitigate these issues, standards with varying concentrations of the same dopant are desirable for development of calibration curves. Such standards are labor-intensive to prepare and expensive to characterize accurately. However, the need for such materials will continue to expand as landers and rovers with geochemical analysis instruments explore new and diverse targets in the solar system.

The current study is part of an ongoing project focusing on the creation of laboratory calibration standards for analytical techniques used in the exploration of planetary surfaces. Previously, we studied five rock matrices doped with Ni, Mn, Zn, Cr, Co and S using LIBS spectroscopy [4,5]; these standards are now being shared with XRF users, x-ray absorption spectroscopy facilities at Argonne National Laboratory, and the Planetary Instrument for X-Ray Lithochemistry (PIXL) science team on *Mars 2020* for potential use in calibration. This study adds four matrices and eight additional dopants to the suite of existing standards, which now numbers over 290 samples. Here, we describe the newest additions to our standard suite.

Geochemical Rationales for Dopant Selection: Eight different dopants (Ce, La, Pb, Rb, Se, Sr, Y, and Zr) were chosen to complement our previous standards

discussed above. Elements were chosen to be useful indicators of processes in igneous rocks on planetary surfaces, in order to maximize their usefulness on multiple planets (Mars, Venus) as well as some asteroids. Their occurrences are well-summarized in [6] and the classic references by Mielke [7] and Wedepohl [8]. Rationales for choosing them as dopants useful for planetary science problems listed below.

Ce^{3+,4+} is the most abundant rare earth element (REE), and can be used (in igneous rocks) as a general proxy for REE abundances and more specifically the light REE. Ce is concentrated in minerals such as allanite, apatite, zircon, and sphene [6]. Felsic igneous rocks are commonly far richer in Ce (and) REE than are basalts (although there are exceptions).

La³⁺ is the second-most abundant REE, and can serve (like Ce) as a proxy for light REE abundances. La (and Ce) is refractory during planetary accretion, so that ratios like K/La and Rb/La can indicate planetary depletions in volatile elements. La can also serve as a monitor of Ce oxidation ($3+ \Rightarrow 4+$); because Ce⁴⁺ can be fractionated away from La³⁺ during aqueous and oxidizing processes.

Pb²⁺ is incompatible in igneous processes, and so becomes enriched in fractionated (felsic) igneous rocks. It can substitute for K in alkali feldspar, also be enriched in zircons. On Venus, Pb may be mobile in the atmosphere and could be concentrated in so-called “heavy metal frost” [9].

Rb¹⁺ is a “large ion lithophile” incompatible element in igneous systems, like K¹⁺, and is enriched in late-stage differentiated magmas. The Rb/K ratio in basalts can constrain planetary composition, because Rb is more volatile during accretion than K but behaves otherwise identically. Rb¹⁺ is strongly adsorbed onto clay minerals, which then commonly have higher Rb/K ratios than their source igneous rocks.

Se²⁻ is important on planetary surfaces because it substitutes for S in sulfide minerals like pyrite and sphalerite. Thus the ratio of Se/S could be valuable in assessing surface/atmosphere reactions on Venus.

Sr²⁺ substitutes readily for Ca²⁺ in feldspar but not in pyroxene and thus is a good tracer of the presence of plagioclase, both in the source magma, and as a fractionating phase. For instance, rocks enriched in plagioclase, like anorthosites, have high Sr abundances.

Y³⁺ is a useful as a proxy for heavy REEs, with

which it shares charge and ion size. Alone, it is an indicator of the degree of igneous fractionation. La/Y is a proxy for light REE enrichment, as occurs during fractionation & mantle metasomatic processes.

Zr⁴⁺ is incompatible (a high-field-strength element) in igneous processes, and so is generally enriched in fractionated (felsic) magmas. Zr is refractory in planetary accretion, so that the Na/Zr can indicate planetary depletions in the volatile element Na.

Table 1. Major element concentrations in matrices

Element	Holyoke	Mexico	Hawaii	Sea sand
SiO ₂	52.01	75.68	51.56	97.69
TiO ₂	1.04	0.14	2.50	0.49
Al ₂ O ₃	13.74	11.18	13.98	0.35
Fe ₂ O ₃ *	13.44	2.80	12.49	1.34
MgO	5.46	0.02	6.68	0.01
CaO	9.34	0.17	10.93	0.01
Na ₂ O	2.82	5.04	2.49	0.01
K ₂ O	0.71	4.39	0.44	0.12
P ₂ O ₅	0.13	0.01	0.24	0.01

*Fe reported as total Fe in terms of Fe₂O₃.

Samples and Methods: This project used four matrices with very different bulk compositions (Table 1). They include:

1. Weathered basalt from Holyoke, MA that is part of the Lower Jurassic basalt in the Newark Supergroup, Massachusetts;
2. Rhyolitic volcanic glass from Mexico; locality unknown, but likely from Tequila Volcano;
3. Hawaiian basalt collected from Kīlauea by Tim Orr (USGS, HVO); and
4. Sea sand purchased from Fisher Scientific.

For dopants, we used reagent-grade chemicals in the form of CeO₂, La₂O₃, PbO, RbCl, SeO₂, SrO, Y₂O₃, and ZrO₂. Rock powders were shatterboxed to grain sizes <25 μm prior to weighing into mixtures.

Preparation of doped samples used a protocol established for creation of x-ray fluorescence standards. Exactly 10.000 g of each dopant oxide or chloride (individually) were shatterboxed with 90.000 g of each powdered matrix, each with 10 wt.% dopant (**Figure 1**). Those powders were then diluted with additional aliquots of matrix to create mixtures of approximately 10, 1, 0.5, and 0.1 wt.% and 500, 250, 100, 50, and 10 ppm of dopant, depending on the molecular weight of the dopant. At higher concentrations of 10%, 1% and 0.5%, only a single dopant was used in each matrix to minimize interactions between the dopant and the matrix (3 concentrations × 8 elements × 4 matrices = 96 samples total). At lower concentrations, all dopants were mixed into the same matrix, yielding an additional (6 concentrations × 4 matrices) 24 samples. Each mixture was then shatterboxed for one minute to homogenize it and reduce the grain size <<25 μm.



Figure 1. JM weighing out 9:1 mixtures of matrices to dopants.

Powders of each mixture were sent to Bureau Veritas Mineral Laboratories, (Vancouver BC, Canada) for analysis by x-ray fluorescence (XRF) for major elements and ICP-MS for trace elements using their LF600 package. Fused glass disks were prepared for XRF. Replicate analyses (up to 7 for each matrix) were averaged to create the penultimate reference data. All samples were subsequently pressed into pellets using 1.5 cm diameter aluminum cups for LIBS analysis; their initial results are given in [10].

Conclusions: These and our previously-created standards will form the basis for useful cross-comparisons of analytical techniques to be flown on future missions to planetary surfaces. Integration of data on these standards for use in bulk rock analysis techniques will increase our understanding of quantitative analyses and produce improvements in accuracy of predicting these elements. Limited amounts of powdered samples and XRF glass disks are available for loan from the second author, along with complete chemical analyses for all samples.

Acknowledgments: Research supported by NASA grants NNX14AG56G and NNX15AC82G and NSF grants CHE-1306133 and CHE-1307179.

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