STANDARDS FOR GEOCHEMICAL ANALYSIS OF MAJOR, MINOR, AND TRACE ELEMENTS IN ROCK POWDERS. M. Darby Dyar[1], Cai R. Ytsma[1], and Kate Lepore[1], [1]Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, mdyar@mtholyoke.edu.

Introduction: Analytical geochemistry has long depended on availability of robust suites of rock standards with well-characterized compositions. Standard rock powders 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.

Existing standards from terrestrial rocks contain concentration ranges that may not cover what is present on other bodies. Notably, Ni is a primary constituent of meteorites, and thus may be abundant on ancient surfaces with impact craters [1,2]. Yet no commercial terrestrial rock standards come close to covering the possible extremes of Ni concentration that could result from impact contamination. Moreover, accuracy of chemical analysis techniques that depend on specific peaks for individual elements may diminish due to the presence of overlapping peaks from other elements. To mitigate these issues, calibration curves can be calculated using standards with varying concentrations of the same dopant. Such standards are labor-intensive to prepare and expensive to characterize. But once created, they can be used for many geochemical techniques such as laser-induced breakdown spectroscopy (LIBS), x-ray fluorescence (XRF; e.g., the Planetary Instrument for X-Ray Lithochemistry, or PIXL, on *Mars 2020)*, and x-ray absorption. This paper summarizes the Mount Holyoke College (MHC) standard suite.

Samples: This sample suite currently includes 2,483 natural rock powders and 484 rock powders doped with minor and trace elements. A majority of the samples came from the XRF laboratory of J. Michael Rhodes at the nearby University of Massachusetts [3]. Pure minerals came from Dyar's collections. Rocks were contributed to this collection by Cal Barnes, Mark Brandriss, Marshall Chapman, Todd Feeley, Fred Frey, Mike Garcia, Wes Hildreth, Tony Irving, Barry Maynard, Alex McBirney, Scott McLennan, Damon Teagle, Dick Tollo, Peter Robinson, and Meg Thomson. Distribution of rock types is roughly 70% igneous, 25% sedimentary, and 5% metamorphic rocks. Minerals are largely common rock-forming silicates.

The doped samples used eight matrices with different bulk compositions (blue in Table 1), including:

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);
4. washed SiO_2 sea sand (Fisher Scientific);
5. Columbia River continental flood basalt collected in Moscow, Idaho by Mickey Gunter;
6. rhyolite from Newberry Volcano in Oregon;
7. a 50:50 by weight mixture of diopside and forsteritic olivine to simulate an ultramafic rock; and
8. granite from the Vinalhaven intrusive complex, Maine collected by Sheila Seaman.

For dopants, we used reagent-grade chemicals in the form of BN, $CBaO_3$, C, CeO_2, CoO, Cr_2O_3, Cs_2TiO_3, CuO, Ga_2O_3, La_2O_3, LiCl, MnO_2, MoS_2, Nb_2O_5, NiO, OPb, RbCl, $CaSO_4$, Sc_2O_3, SeO_2, SnO_2, SrO, Y_2O_3, ZnO, and ZrO_2. Rock powders were shatter-boxed to grain sizes <25 µm prior to weighing into mixtures.

Methods: Preparation of doped samples used a protocol developed for creation of XRF standards. We weighed out 9:1 ratios of matrix to dopant (chemical or element) and shatter-boxed them together to get ~10 wt% mixtures for each dopant. Those powders were then diluted with additional aliquots of matrix to create nine more mixtures of approximately 5, 1, 0.5, and 0.1 wt.% and 500, 250, 100, 50, and 10 ppm of dopant, depending on the concentration of the original mixture. At higher concentrations, only a single dopant was used in each matrix to minimize interactions between the dopant and the matrix. At lower concentrations, all dopants were mixed into the same matrix to reduce analytical costs. Each new mixture was then shatter-boxed for one minute to homogenize it and reduce the grain size <<25 µm.

Powders of each doped mixture were sent to Bureau Veritas Mineral Laboratories, (Vancouver BC, Canada) for analysis by XRF for major elements and ICP-MS for trace elements using their LF202, LF300, LF600, and MA250 packages. Fused glass disks were prepared for XRF. Replicate analyses (up to 7 for each matrix) and, in some cases, as-weighed compositions were averaged to create the penultimate reference data and outliers were discarded. All other un-doped rock standards use either literature values or analyses from the laboratory of Dr. J. Michael Rhodes at the University of Massachusetts [3] using his standard protocols.

Availability: At a minimum, mixtures containing roughly 50-100 g of each powder were created. Sam-

ples with reactive ingredients are being stored in a dry-box, while a majority are stored in air. Aliquots of all samples have also been prepared as pressed-powder pellets contained in 1.6 cm-diameter aluminum cups with flat surfaces.

Visitors to the laboratory are welcome to bring their instrumentation with them to analyze the samples in this suite *in situ*. Requests for the loan of small sample masses will be considered by first author on a case-by-case basis. These samples represent a precious geochemical calibration suite, the need for which will continue to expand as we explore new and diverse targets in the solar system with in situ instrumentation.

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References: [1] Yen A. S. et al. (2005) *Nature*, 436, 49-54. [2] Yen A. S. et al. (2006) *JGR*, 111, E12S11. [3] Rhodes J. M. and Vollinger M. J. (2004) *Geochem. Geophys. Geosyst.,* 5, Q03G13.

Table 2. Compositions of Geochemical Standards (Pressed Pellets and Powders) Available in Dyar's Laboratory ay Mount Holyoke College

Element & Form	Units	# of Standards	Concentration		Element & Form	Units	# of Stand-ards	Concentration	
			Max.	Mean				Max.	Mean
SiO_2	wt%	3035	100.0	58.5	**In**	ppm	107	0.6	0.1
TiO_2	wt%	3031	17.5	1.2	**La**	ppm	2485	85268	192.7
Al_2O_3	wt%	3035	100.0	13.5	**Li**	ppm	568	81881	571.7
Fe_2O_3*	wt%	3022	95.8	8.0	**Lu**	ppm	752	4.9	0.5
MnO	wt%	2851	31.9	0.2	**Mo**	ppm	733	100000	644.4
MgO	wt%	3027	49.4	5.6	**Nb**	ppm	2718	100050	193.8
CaO	wt%	3032	55.6	6.0	**Nd**	ppm	948	688.0	31.2
Na_2O	wt%	3031	11.4	2.7	**Ni**	ppm	2688	82998	397.6
K_2O	wt%	3027	13.0	2.2	**P**	ppm	2535	203057	1190.3
Ag	ppm	402	14.0	**0.2**	**Pb**	ppm	2493	92832	189.0
As	ppm	438	115.0	2.3	**Pr**	ppm	747	192	7.2
Au	ppm	293	336.2	2.5	**Pt**	ppm	30	55.1	19.2
B	ppm	293	100000	1853.2	**Rb**	ppm	2696	70683	157.3
Ba	ppm	2657	100453	618.1	**SO_3**	ppm	1146	99974	1146.0
Be	ppm	599	35.6	2.0	**Sb**	ppm	411	14.8	0.4
Bi	ppm	510	52.5	0.4	**Sc**	ppm	939	87633	346.5
Br	ppm	41	440	67.4	**Se**	ppm	346	71165	970.3
CO_2	wt%	94	64.9	3.5	**Sm**	ppm	962	119.0	6.5
Cd	ppm	373	6	0.2	**Sn**	ppm	742	100009	633.1
Ce	ppm	2550	81409	220.7	**Sr**	ppm	2764	84560	411.2
Co	ppm	922	78723	749.5	**Ta**	ppm	756	49.8	1.7
Cr	ppm	2624	68522	459.6	**Tb**	ppm	915	20.5	1.0
Cs	ppm	872	100006	542.7	**Te**	ppm	85	23.0	2.1
Cu	ppm	979	100061	555.3	**Th**	ppm	2473	245.0	7.9
Dy	ppm	840	29.0	5.0	**Tl**	ppm	411	16.0	0.3
Er	ppm	824	31.7	3.3	**Tm**	ppm	448	2.6	0.5
Eu	ppm	995	19.6	1.1	**U**	ppm	2383	80.0	1.8
F	ppm	122	54500	1534.3	**V**	ppm	2703	1333.0	149.4
Ga	ppm	2581	100020	198.7	**W**	ppm	550	842.2	84.2
Gd	ppm	831	77.1	5.8	**Y**	ppm	2802	78744	163.9
Ge	ppm	50	4.9	1.4	**Yb**	ppm	930	40.7	3.3
Hf	ppm	887	54.5	6.2	**Zn**	ppm	2692	82605.0	33.9
I	ppm	26	380	58.6	**Zr**	ppm	2799	74032.2	327.9