

EXTENDED CALIBRATIONS FOR THE APXS FOR THE MARS SCIENCE LABORATORY MISSION. P. L. King^{1,2}, R. Gellert³, J. L. Campbell³, B. C. Hyde², C. D. M. Schofield², G. Perrett³, W. Brown-Bury³, M. S. Spilde¹, N. Boyd³, A. Ollila¹, N. Lanza¹, T. Aran¹, W. McCutcheon¹, and H. Newsom¹ Inst. Meteoritics, Univ. New Mexico, Albuquerque, NM USA. ²Dept. Earth Sciences, Univ. Western Ontario, London, ON Canada. ³Guelph-Waterloo Phys. Inst., Univ. Guelph, Guelph, ON Canada.

Introduction: The Alpha Particle X-ray Spectrometer (APXS) is part of the payload for the Mars Science Laboratory (MSL) mission [1]. Like previous missions (Pathfinder, Mars Exploration Rover mission), the APXS will analyze the bulk chemistry of martian materials. The MSL APXS will use a ²⁴⁴Cm source and an x-ray detector that are housed in a head that is brought into contact with the sample. The incident x-rays and alpha particles cause x-ray excitation in the sample of the elements Na to Sr. For MSL, the APXS has been modified to have a Peltier-cooled detector for day use; a shorter sample-detector distance for higher count rates and shorter integration times; no alpha detector; and a calibration target. The flight APXS (FEU) has passed qualification tests and we are now using a laboratory MSL APXS to test aspects of the instrument capabilities.

Extended calibration dataset: To ensure that the calibration standards are relevant to martian compositions, we created a database of certified geostandards including igneous (109) and sedimentary (233) rocks and minerals (129). We examined the range of compositions measured on Mars and with that information we chose 28 additional geostandards for extended calibrations. Because the certified geostandards did not encompass the range of martian compositions, we synthesized additional calibration materials using USGS BHVO-2 mixed with known masses of 'additives' of dried, reagent grade NiO, ZnO, S, FeS₂, FeS, Fe, Fe₂O₃, NaCl, CuCl, KBr and HgBr₂. Within this group, sample additives were chosen based on variations in density to test if density affects the x-ray attenuation coefficient. Samples were made with similar total S and Fe contents, but S and Fe were added in different forms: S (2.06gcm⁻³)+Fe (7.87gcm⁻³); S+Fe₂O₃ (5.2gcm⁻³); FeS (4.84gcm⁻³); and FeS₂ (~5gcm⁻³). We also added halides in constant concentration with different densities: NaCl (2.17gcm⁻³), CuCl (2.54gcm⁻³), KBr (2.75gcm⁻³) and HgBr₂ (6.05gcm⁻³). These samples will be analyzed with the laboratory MSL APXS and compared to bulk analyses (ICP-MS).

Sample texture and crystallographic effects: One of the assumptions of APXS analysis is that the sample is homogeneous [2]. To test this assumption we are analyzing samples with different textures and crystallographic orientations.

Rocks vs. powders. We have analyzed several rock samples (polished, cut, and uncut slabs) versus pow-

dered samples with APXS. Powdered samples have been prepared both as dried powders in sample cups and as pressed pellets (XRF-style, but without any binder). Our results for the basaltic calibration target rock versus unpressed powder produced concentrations that agree within 5% rel. for all elements, except Cr which was ~30% rel. higher in the powder. This preliminary data suggests that the effects of bulk sample density on APXS results are minor.

Phenocryst size effects. To evaluate grain size effects on APXS analyses we are synthesizing basaltic rocks with Gusev-like compositions (excepting Mg#) from 75% USGS BCR-2 and 25% San Carlos olivine. Five olivine size fractions will be used: <45 µm, 90-180 µm, 180-297 µm, 500-710 µm, and 1-3 mm.

Crystallographic orientation effects will be measured using muscovite, biotite, phlogopite, and lepidolite, both perpendicular and parallel to the (001) face.

Martian analog rocks and coated rocks: To ground truth APXS analyses from the Mars Exploration Rover mission and to test the laboratory MSL APXS we synthesized martian analog rocks from minerals. The greatest challenge was finding volumes of minerals (>10g each), that were relatively homogeneous to prepare sufficient volumes of analog rocks for APXS and complementary analyses (ICP-MS and analyses with other MSL instruments). Candidate minerals were chosen using a custom-made database of 174 minerals (from literature and spectral databases). We then obtained candidate minerals, hand-picked appropriate material, and analyzed them on the electron microprobe. The final minerals chosen include: olivine-San Carlos AZ; augite- Kilbourne Hole NM; labradorite- Sonora Mexico; apatite- Durango Mexico; magnetite- Peña Colorado Mexico; hematite- Minas Gerais Brazil; selenite- Eddy Co., NM; jarosite- Peña Blanca NM; natroalunite- Quartzite AZ; opal- Mojave Desert, CA; and reagent NaCl.

Martian analog rocks made from minerals. Four Martian analog rocks have been synthesized from the minerals listed above. We synthesized a Clovis-like powder (composition similar to Clovis-Case 1 from [3]) using mineral modes similar to those proposed by [3]. We synthesized an Adirondack-like powder [2] using minerals in similar abundances to the calculated CIPW norm [4]. We also wished to synthesize sulfate rich material like Arad Samra [5] and Paso Robles [2]; however, unstable hydrous sulfates are not compatible

with the APXS vacuum. Because we were unsuccessful at completely dehydrating Mg- and Fe-sulfate minerals (consistent with other workers observations of their hygroscopic nature, e.g., [6]), we substituted gypsum and jarosite for Mg- and Fe- sulfate in these rocks. We made a gypsum-rich rock with mineralogy similar to that inferred for Arad Samra [5] except the only sulfate was gypsum so the rock had a relatively Ca-rich, Mg-Fe-poor composition. Also, we made a jarosite-rich rock with mineralogy similar to that calculated for Paso Robles [3], but the only sulfate was jarosite and the composition was relatively K-rich. We will compare the APXS analyses of these analog rocks with those made from fired chemical reagents.

Coated rocks. Thin coatings/rinds are common on rocks on Mars [e.g., 7], and such coatings affect APXS analysis (e.g. compare unbrushed, brushed, and abraded analyses in [2]). Coatings particularly affect determining the concentrations of light elements (e.g., Mg and Na) that have low X-ray yields due to attenuation. We plan to test the theoretical models for the effects of coatings versus measurements of coated samples.

As a first step, we have set up a technique to coat materials with halides. Reagent grade halide (e.g., NaCl) is melted and then large pieces of halide are vaporized in a vacuum coating system and deposited on a flat, substrate sample that sits on a rotating platform. The average thickness of the halide coating is calculated using the mass and area of the substrate plus coating minus the substrate alone. The calculated thickness for a 1 μm coating was within ~20% relative of thicknesses measured using a scanning electron microscope (SEM). Because the APXS measures over a diameter of 1.2 cm, the average calculated thickness is a reasonable measure of the coating thickness.

We will measure APXS spectra on the following samples to examine the effect of variable thickness coatings on chemistry, especially the Mg and Na contents: Mg-poor rhyolitic obsidian coated with MgCl_2 and basaltic rock (BT-2) coated with different thicknesses of NaCl or MgCl_2 .

Analyzing very light elements: Campbell et al. [9] developed a method to determine very light element (atomic no. < 10) contents by modeling the Pu-scatter peaks in the x-ray spectra in a selection of geochemical reference materials. The approach may be used to estimate H_2O content in rocks on Mars [10].

We tested this method using well-characterized Fe-H-C-S-O minerals, a standard XRF sealed ^{244}Cm source ($E > 10\text{keV}$), and controlled relative humidity conditions (see [10] for details). The minerals were analyzed for cations and anions (ICP-OES, IC and electron microprobe), for O, H and C (vacuum-line

mass spectrometry), and mineralogy (XRD) [10]. They included hematite, magnetite, jarosite, szomolnokite, rhomboclase, schwertmannite, melanterite, ferrocopiapite, paracoquimbite, and siderite. Where necessary, during APXS analysis the sulfates were kept sealed with thin Kapton film to maintain stable mineralogy and their mineralogy was confirmed after APXS analysis by XRD. APXS-deduced O contents are in reasonable agreement with actual values, in spite of the large uncertainties imposed by the column of air and Kapton film between the sample and detector (Fig. 1).

Our next step is to analyze the vacuum-compatible Fe-H-C-S-O minerals with the laboratory MSL APXS. We will also analyze phyllosilicates, carbonate rocks, and basalt- H_2BO_3 mixtures.

Conclusions: The extended calibrations of the laboratory MSL APXS will provide information on instrument response and calibration that may be used for the MSL and prior missions. We are testing the assumption of homogeneity using materials with different textures and crystallographic orientation. We have synthesized or obtained calibration materials with compositions within the range of martian compositions. We will examine how the density of the phase hosting an element affects APXS analyses. We will also examine the effect of coatings, concentrating on Mg and Na analysis. Finally, we will continue to investigate the Pu-scatter peak method for determining very light element concentrations.

References: [1] Gellert R. et al. (2009) *LPS* 40, 2364. [2] Gellert et al. (2006) *JGR* 111, doi:10.1029/2005JE002555. [3] Ming et al. (2006) *JGR* 111, doi:10.1029/2005JE002560 [4] McSween et al. (2008) *JGR* 113, doi:10.1029/2007JE002970 [5] Yen et al. (2008) *JGR* 113, doi:10.1029/2007JE002978. [6] Wang et al. (2009) *JGR* 114, doi:10.1029/2008JE003266. [7] Kraft & Greeley (2000) *JGR* 105, 15107. [8] Osterloo et al. (2008) *Science* 319, 1651. [9] Campbell J.L. et al. (2008) *JGR* 113, doi:10.1029/2007JE002959. [10] Hyde, B.C. (2009) MSc, Univ. West. Ontario.

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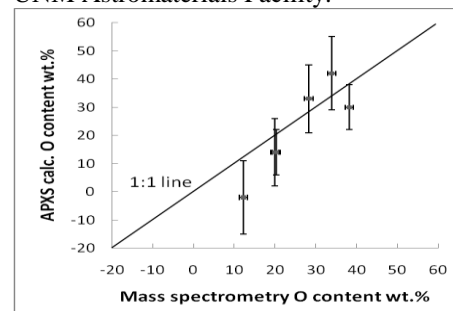


Figure 1: APXS calculated O content versus mass spectrometry O content for Fe-H-C-S-O minerals from [10].