The potential for metal contamination during Apollo lunar sample curation

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Abstract

Curation and preparation of samples for chemical analysis can occasionally lead to significant contamination. This issue is of concern in the study of lunar samples, especially those from the Apollo sample collection, where available masses are finite. Here we present compositional data for stainless steels that have commonly been used in the processing of Apollo lunar samples at NASA Johnson Space Center, including a chisel and a vessel typically used to transfer Apollo samples to principal investigators. The Type 304 stainless steels are Cr-rich, with high concentrations of Mn (4000-18,000 $\mu\text{g g}^{-1}$), Cu (1000-22900 $\mu\text{g g}^{-1}$), Mo (1030-1120 $\mu\text{g g}^{-1}$) and W (72-193 $\mu\text{g g}^{-1}$). They have elevated highly siderophile element concentrations (up to 92 ng g^{-1} Os), $^{187}\text{Os}/^{188}\text{Os}$ ranging from 0.1310 to 0.1336, and negligible lithophile element abundances. We find that, while metal contamination is possible, significant ($>>0.01\%$ by mass) addition of stainless steel is required to strongly affect the composition of the highly siderophile elements (HSE), W, Mo, Cr or Cu for most Apollo lunar samples. However, careful appraisal on a case-by-case basis should take place to ensure contamination introduced through sample processing in the curation labs is at acceptably low levels. A survey of lunar mare basalts and crustal rocks indicates that metal contamination plays a negligible role in the compositional variability of the HSE and W isotopes preserved in these samples. Further work to constrain contamination on other properties of Apollo samples is required (e.g., organics, microbes, water, noble gases, magnetics), but the effect of metal contamination can be relatively well-constrained for the Apollo lunar collection.

1. Introduction

Collection and return of planetary materials to Earth requires significant curational capability. In the first instance, as with the Apollo lunar samples, there is a basic requirement that samples are quarantined while tests are conducted for possible pathogens and hazards (Allton et al., 1998). For Apollo samples, early curation also included the requirement of handling samples under vacuum. Cabinets for sample handling and the tools used for sample subdivision were developed rapidly, and materials that could come into contact with pristine lunar samples were restricted to Type 304 stainless steel, series 6100 aluminum alloy, and Teflon™ (Allen et al., 2011). After the Apollo 17 mission, in 1972, the concept of handling samples under vacuum was abandoned. Apollo samples were moved, within the NASA Johnson Space Center to a new sample facility in Building 31, where they still reside and are handled in a dry N₂ atmosphere (Papanastassiou et al., 2015) with less than 10 ppm H₂O (Allen et al., 2011).

Numerous forms of potential contamination can affect Apollo samples during curation and sample processing and include – but are not limited to – exposure to magnetic fields, organics, anaerobic microbes, water, nitrogen, noble gases, lithophile elements (of special concern are those used for non-traditional stable isotope research), Pb and the moderately siderophile and highly siderophile elements, including Mo, W and Os (e.g., Pearce et al., 1974; Papanastassiou et al., 2015; Verchovsky et al., 2017). Extensive research has recently taken place on siderophile element abundances and isotopic compositions in lunar samples, which was previously not possible for these elements using the earlier methods of neutron activation analysis (NAA). Significant improvements in sensitivity using negative ion thermal ionization mass spectrometry (N-TIMS) and the advent of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) have enabled studies of: 1) tungsten isotopes to understand the timing and origin of lunar formation (e.g., Touboul et al., 2015; Kruijer et al., 2015); 2) Mo, Os isotopes and highly siderophile elements to examine the chemical signatures of impactors that struck the Moon after its initial differentiation (e.g., Puchtel et al., 2008; Fischer-Gödde & Becker, 2012; Burkhardt et al., 2014); and 3) investigation of late-accretion highly siderophile element signatures in the lunar interior and crust to understand metal-silicate and late accretion processes acting on the Moon (e.g., Day et al., 2016).

In this contribution, we provide the first report on the potential for curatorial contamination during the handling of Apollo lunar samples, focused on the effect of metal contamination from specific batches of Type 304 stainless steel that were used during the period over which much of the recent HSE, W and Mo work on Apollo samples has occurred.

2. Samples and Methods

We analyzed two metals that commonly come into direct contact with Apollo samples during sample processing or transport. We analyzed a Type 304 stainless-steel fragment of a chipping implement used for breaking fragments of lunar samples, and we took a fragment of a standard stainless-steel container (9-6465), in this case used to ship a sample of the ‘rusty rock’ sample 66095 used in a previous study (Day et al., 2017). Samples were prepared using a slow speed, high-precision cutting diamond saw, and sawn surfaces were then sanded using corundum paper and cleaned with distilled water. The stainless steels used for both objects are generally of Type 304, but the major, minor, and trace element compositions of Type 304 stainless steel varies substantially depending on the supplier and the raw materials used. To characterize the composition of the metals, we undertook a systematic procedure of laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), to document elemental variations in the metals at <0.1 mm scales and with limited total sample mass, and on larger mass aliquots by solution ICP-MS, to obtain precise major and trace element concentrations, and isotope dilution determination of highly siderophile elements, followed by N-TIMS analyses of Os isotopes. We also characterized our in-house reference materials, the iron meteorites Hoba, Filomena and Coahuila, to ensure accuracy, precision and consistency with prior work (e.g., Petaev & Jacobsen, 2004; Cook et al., 2004; Walker et al., 2008). All work was done at the Scripps Isotope Geochemistry Laboratory.

Analysis by LA-ICP-MS was performed using a *New Wave Research UP213* (213 nm) laser-ablation system coupled to a *ThermoScientific iCAP Qc* ICP-MS. Analyses were done using ~ 0.5 mm long rasters with a 100 μm beam diameter, a laser repetition rate of 5 Hz, and a photon fluence of ~ 3 to 3.5 J/cm². Ablation analysis took place in a 3 cm³ ablation cell. The cell was flushed with a He-gas flow to enhance production and transport of fine aerosols and was mixed with an Ar carrier-gas flow of ~ 1 L/min before reaching the torch. Each analysis consisted of ~ 60

s data collection. Backgrounds on the sample gas were collected for ~20 s, followed by ~40 s of laser ablation. Washout time between analyses was >120 s. Data were collected in time-resolved mode so effects of inclusions, mineral zoning and possible penetration of the laser beam to underlying phases could be evaluated. Plots of counts per second versus time were examined for each analysis, and integration intervals for the gas background and the sample analysis were selected. Standardization was performed using reference material iron meteorites Hoba, Coahuila and Filomena, used by us and by other groups (e.g., [McCoy et al., 2011](#)).

Major- and trace-element abundances were determined using solution ICP-MS. Samples and the reference material metal standards Hoba, Coahuila and Filomena were digested at 150°C in Optima grade concentrated HF (4 mL) and HNO₃ (1 mL) for >72 hrs on a hotplate, with total analytical blanks and standards. Samples were sequentially dried and taken up in concentrated HNO₃ to remove fluorides, followed by dilution and doping with a 1 ppm indium solution to monitor instrumental drift during analysis. Trace-element abundances were determined with a *ThermoScientific iCAP Qc* quadrupole ICP-MS in standard mode. Analyses were standardized versus reference material BHVO-2 that was measured throughout the analytical run. In addition, reference materials were analyzed as “unknowns” (BHVO-2, BIR-1, BCR-2, Hoba, Filomena, Coahuila) to assess matrix matching, external reproducibility and accuracy. Special attention was taken to circumvent the effect of potential interference from polyatomic species, and potential interferences were monitored using the iron meteorite reference materials. For trace-elements, reproducibility of the reference materials was generally better than 10% (RSD) and in line with standard data measured in our laboratory (e.g., [Day et al., 2017](#)).

Osmium isotope and HSE abundance analyses were determined from metal aliquots that were digested in sealed borosilicate Carius tubes, with isotopically enriched multi-element spikes (⁹⁹Ru, ¹⁰⁶Pd, ¹⁸⁵Re, ¹⁹⁰Os, ¹⁹¹Ir, ¹⁹⁴Pt), and 11 mL of a 1:2 mixture of multiply Teflon distilled HCl and HNO₃ that was purged with H₂O₂ to remove Os. Samples were digested in Carius tubes to a maximum temperature of 240°C in an oven for 72 hours. Osmium was triply extracted from the acid using CCl₄ and then back-extracted into HBr, prior to purification by micro-distillation, with the other HSE being recovered and purified from the residual solutions using anion exchange separation ([Day et al., 2016b](#)). Isotopic compositions of Os were measured in negative-ion mode

on a *ThermoScientific* Triton thermal ionization mass spectrometer. Rhenium, Pd, Pt, Ru and Ir were measured using an Cetac Aridus II desolvating nebulizer coupled to a *ThermoScientific* iCAP Qc ICP-MS. Offline corrections for Os involved an oxide correction, an iterative fractionation correction using $^{192}\text{Os}/^{188}\text{Os} = 3.08271$, a ^{190}Os spike subtraction, and finally, an Os blank subtraction. Precision for $^{187}\text{Os}/^{188}\text{Os}$, determined by repeated measurement of the UMCP Johnson-Matthey standard was better than $\pm 0.2\%$ (2 St. Dev.; 0.11372 ± 22 ; $n = 9$). Measured Re, Ir, Pt, Pd and Ru isotopic ratios for sample solutions were corrected for mass fractionation using the deviation of the standard average run on the day over the natural ratio for the element. External reproducibility on HSE analyses using our method was better than 0.5% for 0.5 ppb solutions and all reported values are blank corrected. The total procedural blanks ($n = 2$) run with the samples had $^{187}\text{Os}/^{188}\text{Os} = 0.171 \pm 0.003$, with average quantities (in picograms) of 3.9 [Re], 73 [Pd], 2.5 [Pt], 11 [Ru], 2.5 [Ir] and 0.7 [Os]. All data are blank corrected, with the blanks representing between less than 0.5% of Re, Pt, Ir and Os, less than 1.2% of Ru and less than 2% of Pd.

3. Results

The two metals that we analyzed are Type 304 austenitic stainless steels with between 75 to 82 wt.% Fe, 13.4 to 14.7 wt.% Cr and 4 to 8 wt.% Ni (**Table 1**, *Table S1*). The container steel used for shipping is Mn-rich (1.9 wt.%), whereas the Type 304 stainless steel chipping implement used for sample processing is Cu-rich (2.3 wt.%). Other notable elements with elevated abundances include Co (480-1260 $\mu\text{g g}^{-1}$), Mo (1030-1120 $\mu\text{g g}^{-1}$), and high Nb in the chipping implement (2600 $\mu\text{g g}^{-1}$). For the trace elements, concentrations of W, Zn, Ga, Se, Pb and Sn are $< 200 \mu\text{g g}^{-1}$, whereas the rare earth elements (REE) and large ion lithophile elements (LILE) are $< 50 \mu\text{g g}^{-1}$, or are at the limits of detection.

The highly siderophile elements (HSE: Os, Ir, Ru, Rh, Pt, Pd, Re, Au) were measured by both LA-ICP-MS and isotope dilution methods (**Table 2**). The new isotope dilution HSE abundances determined for the aliquots of Hoba, Coahuila and Filomena that we use for LA-ICP-MS study agree well with previously reported values (Petaev & Jacobsen, 2004; Cook et al., 2004; Walker et al., 2008; McCoy et al., 2011). For the austenitic stainless steels we find that results for both isotope dilution and LA-ICP-MS are broadly similar, although the individual laser ablation rasters for each sample ($n = 4$) indicate at least 20% variability in the distribution of the HSE within

the metals at <0.1 mm resolution is possible. The metals have elevated (10's ng g⁻¹) and fractionated chondrite-normalized HSE patterns (**Figure 1**) and ¹⁸⁷Os/¹⁸⁸Os (0.1310-0.1336) ratios that are above the chondritic range (0.126-0.128; Day et al., 2016).

4. Discussion

During any form of curation or preparation/processing of rock samples, there exists the potential to contaminate. For example, contamination or modification of rocks can take place in the form of interaction and modification by fluids, gases, or microbes, thermal processes that alter the nature of the rock, such as sawing, or physical inclusion of foreign material by abrasion or impact. For lunar samples curated at NASA Johnson Space Center, whether collected by astronauts or collected as meteorites in Antarctica, these forms of modification are all possible. In the discussion, we focus on the potential of these processes to modify the Apollo samples, although many of the arguments applied here can equally be transplanted to understanding contamination of meteorite samples. In so doing, we use evidence that obvious metal smearing has occurred on the outside surfaces of at least some 1 to 2 g impact melt breccia fragments (Papanastassiou et al., 2015) and during sawing (e.g., Figure S8 of Tikoo et al., 2014), and that chipping implements with brittle steels might lead to particulate contamination. The analyzed metals have negligible levels of elements used in lithophile radiogenic and non-traditional stable isotope studies, like Sr (<0.45 µg g⁻¹), Nd (<0.024 µg g⁻¹), Hf (<0.16 µg g⁻¹), Pb (<3.35 µg g⁻¹), Rb (<0.68 µg g⁻¹), Zr (<3.5 µg g⁻¹), Zn (<19 µg g⁻¹), Ga (<25.3 µg g⁻¹), so we do not consider these elements further in the present study.

4.1 Potential for contamination of osmium and the highly siderophile elements

A primary goal of this study is to define the effect of possible metal contamination on the highly siderophile elements (HSE) due to curatorial processing at NASA Johnson Space Center. The HSE have been particularly powerful tracers of late accretion to the Moon, including within the lunar interior (e.g., Walker et al., 2004; Day et al., 2007; 2010; Day & Walker, 2015), as well as within lunar impact breccias and melt-rocks (e.g., Higuchi and Morgan, 1975; Hertogen et al., 1977; Korotev, 1994; Norman et al., 2002; Puchtel et al., 2008; Fischer-Gödde & Becker, 2012; Sharp et al., 2014; Liu et al., 2015; Day et al., 2017; Gleißner & Becker, 2017). A persistent concern is potential metal contamination during curation and curatorial sample processing, due to

the significant leverage of high HSE abundances (10's-100's ng g⁻¹) in the stainless steel tools compared with pristine crustal rocks or mare basalts (0.001-0.1's ng g⁻¹), or impact melt rocks (1-10's ng g⁻¹).

Previously, ¹⁸⁷Os/¹⁸⁸Os, a proxy for long-term Re/Os, and the relative and absolute abundances of the HSE have been used as sensitive indicators to detect and constrain levels of meteoritic contamination (Day et al., 2010). In addition to having highly elevated HSE abundances, chondritic materials (as well as some iron meteorites) are characterized by limited variations in the relative and absolute abundances of these elements (<40%; Horan et al., 2003; Day et al., 2016). Osmium isotopic composition is especially diagnostic because the limited range in Re/Os among chondrites and some irons leads to a restricted range in ¹⁸⁷Os/¹⁸⁸Os (e.g., Smoliar et al., 1996; Horan et al., 2003). The diagnostic capability of Os isotopes assumes that magmatic processes under most conditions should lead to rocks with non-chondritic relative HSE abundances, including Re/Os. The ¹⁸⁷Os/¹⁸⁸Os of a truly pristine crustal sample should therefore evolve away from a chondritic growth trajectory, even if it formed from a melt with chondritic isotopic composition. This presumption is supported by (1) variably fractionated HSE abundances for most mare basalts (Day & Walker, 2015), (2) data for terrestrial igneous rocks indicating highly variable HSE partitioning characteristics (Day, 2013), and (3) distinctly non-chondritic ¹⁸⁷Os/¹⁸⁸Os and relative HSE abundances in some lunar crustal rocks (Day et al., 2010). Lunar non-mare samples with chondritic or near-chondritic ¹⁸⁷Os/¹⁸⁸Os and relative HSE abundances are presumed to have HSE dominated by one or more exogenous component(s).

Using the same logic, taking the composition of the Type 304 chipping implement stainless steel as contaminant yields a mixing curve that begins at a factor of ~5 to 7 times less Os concentration and more radiogenic ¹⁸⁷Os/¹⁸⁸Os compared with a chondritic impactor contaminant (Figure 2). The curve for the stainless steels does not pass through the main cluster of pristine crustal rocks or mare basalts, but does pass through the most radiogenic ¹⁸⁷Os/¹⁸⁸Os for some lunar impact melt breccias. However, to account for the Os isotope composition of these rocks would require between 1 to 100% by mass contamination by the stainless steel implements, which is far in excess of any realistic contamination levels. Critically, the strongly fractionated HSE pattern of the steels (Figure 1) would, in turn, strongly impact the HSE patterns of lunar samples that, to

date, has not been observed. For example, contamination by stainless steel would lead to equal effects on all the HSE. The metals have Os/Ir of 3.3 ± 1.9 and Ru/Ir = 4.2 ± 2.4 , but no mare basalt (Os/Ir = 1.4 ± 0.8 ; Ru/Ir = 3.1 ± 2.9 [Day & Walker, 2015]), or lunar crustal rock (Os/Ir = 0.8 ± 0.4 ; Ru/Ir = 3.7 ± 2.7 [Day et al., 2010]) has Os/Ir and Ru/Ir characteristics that match this signature. While mixing curves in **Figure 3** might be taken to imply contamination of 0.001 to 0.1% of stainless steel from curatorial processing to affect the Os isotopic composition of some mare basalts and lunar pristine crustal rocks, the collateral effects on Os/Ir or Ru/Ir would be severe and detectable. Our results imply that, while metal contamination can affect some lunar rocks during curatorial processing, the potential for impact on the HSE abundances of samples is low.

4.2 Potential for contamination of W, Mo, Cr and highly chalcophile elements

The stainless steels used in the lunar curatorial facility contain a range of slightly (SSE), moderately siderophile elements (MSE), and highly chalcophile elements (HCE). These elements, which include Cr (SSE), Mo, W (MSE) and Se (HCE) are of significant interest, both for isotopic tracing of materials (e.g., Warren, 2011; Kruijer et al., 2015) and for investigating volatile-siderophile element delivery to the Moon (e.g., Wang & Becker, 2013). While the Cr, Mo and W isotopic compositions of the stainless steels should ultimately be determined by interested parties, we note the magnitude of element addition possible at low mass addition ($\sim 0.1\%$) is generally minor ($\sim 100 \mu\text{g g}^{-1}$ Cr, $\sim 30 \mu\text{g g}^{-1}$ Cu, $< 1 \mu\text{g g}^{-1}$ Mo, $< 0.2 \mu\text{g g}^{-1}$ W, $\sim 0.003 \mu\text{g g}^{-1}$ Se; **Figure 3**). The concentrations of SSE, MSE and HCE are high enough in the stainless steels, however, that some key ratios used for investigating volatile processes (e.g., Cu/Ag or Se/Te) might be affected, as would some lunar rocks that have low Cu, Se, Mo or W contents.

Given that terrestrial metal is likely to have ‘normal’ isotopic compositions of Cr, Mo, and W, the magnitude of effect on original isotopic composition assuming, at most, 0.1% mass addition would be quite limited. For example, both Touboul et al. (2015) and Kruijer et al. (2015) note small ^{182}W excess ($\sim 21\text{--}28$ ppm) measured in lunar rocks, compared to the silicate Earth, consistent with disproportional late accretion, as also inferred from the HSE (Day et al., 2007; Day & Walker, 2015). To generate a shift of this magnitude, from metal contamination alone, would require up to 10% by mass contamination of a metal with $^{182}\text{W}/^{184}\text{W}$ characteristics like early-formed, Hf-

depleted planetesimal iron cores (e.g., [Horan et al., 1998](#)). As noted for the HSE, this amount of mass addition during curatorial processing is highly unlikely and would be visually detectable.

4.3 Other possible sources of contamination for Apollo lunar samples

In this study, we considered the effects of metal contamination during the curation and processing of the Apollo samples at NASA Johnson Space Center. Despite the painstaking and careful approach taken by astronauts and curatorial staff, since their collection on the Moon, the Apollo samples have been subjected to a range of collection, curatorial and processing materials. From the outset, during collection, the samples were taken from the conditions of collection into lunar modules, where the indium edges on the sample container boxes did not remain hermetically sealed. They have been preserved in terrestrial N₂ gas, within stainless steel boxes or containers, wrapped in Teflon. The samples experienced exposure to magnetic fields, affecting both acquisition of isothermal and viscous remnant magnetization ([Pearce et al., 1974](#)). Many of the samples have also been sawn with diamond blade materials, which can heat samples and have magnetic as well as chemical contamination effects. Our results confirm that, for metal, typically significant physical addition (>0.1% by mass) of terrestrial materials would need to occur to have a strong measurable effect on HSE, MSE, SSE or HCE in the Apollo samples. The only area of curatorial processing where we have not done a detailed investigation is during cutting of the Apollo samples at the NASA curatorial facility, including the use of saw blades, bands and wires for wire saws. Saw blade material has been recognized on some lunar sample materials previously, and the composition of the metal smears (Fe_{0.75}Ni_{0.05}Cr_{0.15}; [Tikoo et al., 2014](#)) is similar in composition to the stainless-steel implements reported here. Nonetheless, the exact compositions of these materials that could potentially contaminate the samples should ultimately be assessed. Overall, we consider the likelihood of significant contamination of lunar samples during curation and curatorial processing for most elements by metal contamination to be low.

Conclusions

Our results imply a generally negligible contribution from metal contamination during curation and sample processing in the NASA Johnson Space Center curatorial facility. While further work to constrain contamination on other properties of Apollo samples is required (e.g., magnetism, organics, anaerobic microbes, water, nitrogen, noble gases), the effect of metal

contamination can be constrained for the Apollo lunar collection. Our results do not preclude contamination effects from saw-blades or from the handling of samples by lunar principal investigators after they have received samples.

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Figures and Figure Captions

Figure 1: Images of tools, sample containers and other metal curation devices used during Apollo sample preparation.

Figure 2: CI-chondrite normalized highly siderophile element patterns for NASA stainless steel curational materials, measured by isotope dilution TIMS/ICP-MS and LA-ICP-MS. CI-chondrite normalization from the compilation in [Day et al. \(2016\)](#).

Figure 3: Osmium concentration (pg g^{-1}) versus $^{187}\text{Os}/^{188}\text{Os}$ for Apollo 12, 15 and 17 lunar mare basalts (Day et al., 2007; Day & Walker, 2015), lunar pristine crustal rocks (Day et al., 2010; grey filled circles), lunar impact-melt breccias (LIMB; e.g., Puchtel et al., 2008; Fischer-Godde & Becker, 2012), and ordinary, carbonaceous, enstatite and rumuruti chondrites (Horan et al., 2003; Fischer-Godde et al., 2010). The solid curve shows mixing between a hypothetical mare basalt parental melt composition, from Day & Walker (2015), with very low Os ($^{187}\text{Os}/^{188}\text{Os} \sim 0.22$; $\text{Os} = 1 \text{ pg g}^{-1}$), and the NASA curatorial Type 304 stainless steel ($^{187}\text{Os}/^{188}\text{Os} = 0.1336$; $\text{Os} = 92,100 \text{ pg g}^{-1}$). The dashed curve shows mixing between the hypothetical mare basalt parental melt and an averaged chondritic contaminant ($^{187}\text{Os}/^{188}\text{Os} = 0.127$; $\text{Os} = 600,000 \text{ pg g}^{-1}$). Percentages (by mass) of the various components along the mixing lines are labelled.

Figure 4: Concentration of an element added to a sample as a function of physical mass addition for Se, W, Mo, Cu and Cr for lunar curational stainless steels.

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