REMOVING CONTAMINATION FROM GENESIS SAPPHIRE COLLECTORS BY POLISHING.

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Introduction: The Genesis Solar Wind Sample Return Mission used a variety of materials as solar wind (SW) collectors. "Sapphire", which is single crystal corundum, was ~6.7% of the collector material flown. But, a much higher percentage of Genesis sapphire collectors (SAP) survived the crash of the sample-return capsule [1] as SAP is chemically inert, physically tough, and hard (MOHS 9, by definition). In fact, 39 sapphire fragments of bulk SW collector having areas ≥60mm^2 are available in JSC's Genesis online catalog, whereas only 1 similarly sized silicon fragment is available (accessed 1/1/2020). In spite of the ease of accessing larger fragments, sapphire has not been popular among Genesis researchers because it is an electrical insulator (making SIMS more difficult) and its chemical inertness, high melting point and high hardness precludes the use of many mass-spectroscopic techniques. Recently, as alternative techniques for measuring Genesis samples are developed (e.g., synchrotron TXRF, INAA, laser ablation mass spectroscopy), more researchers are choosing to analyze sapphire. Thus, a number of researchers are actively studying how to best remove contamination from the Genesis sapphire surfaces.

This report extends the task in Schmeling et al. ([2]) that used polishing compounds to remove contamination from Genesis sapphire and focuses on contaminants (welded silicon, aluminum) that current chemical methods find recalcitrant.

Experimental Methods, Materials and Tasks:

Methods. TXRF as a non-destructive and surface sensitive method is central to checking for increased surface roughness after grinding of Genesis collectors [3]. Additionally, it provides information about residues from the polishing compounds and contaminants from handling, etc., that will eventually require removal. Optical microscopy performed before and after polishing can detect physical changes / defects, whereas SIMS analyses of polished, H-damaged fragments can be used to evaluate (at the nm scale) the depth to which damaged SAP is removed by the polish.

Materials. The polishing compounds used in this study are listed in Table 1 and have MOHS hardness significantly less than that of corundum but, hopefully, hard enough to mechanically remove intractable surface contaminants from Genesis sapphire. All polishes were water soluble. Polishing was done on Texmet© polishing paper. Fragments of un-irradiated sapphire fragments were not from the Genesis flight vendor. Genesis flight-spare fragments were used for the irradiated sapphire. This irradiated sapphire had been coated with ~15 nm of e-beam evaporated of Al metal and had then been implanted using the PSII technique at Southwest Research Institute in 2007. Since 12 years had passed, the coating was no longer metallic; rather, it was greyish (although shiny in reflected light) and would no longer dissolve in ammonium hydroxide – an Al suboxide (schematic Fig. 1). Such suboxides of aluminum should be softer and more reactive than corundum, although the exact properties of the layer used here are not known.

Tasks. (1) polish fragments with undamaged surfaces and inspect for roughness and residues using TXRF. Note: task is complete; new results reported here, initial results in [2]. (2) Promising polishes from (1) are used on H-implanted flight-spare sapphire. Note: TXRF and optical observations are complete and reported herein, SIMS analyses were executed and results are being evaluated. (3) *If the SIMS is indeterminate*, then (2) will be repeated with new H implants containing a more easily tracked element, such as Mg. (4) The best polish(es) will be tested on Genesis-flown SAP.

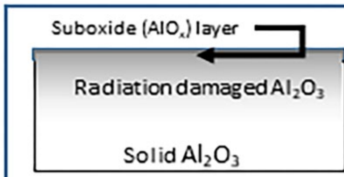


Fig. 1 Original geometry of Task (2) SAP

Results: TXRF results for Task (1) are given in Table 1 and Fig. 2. Except for garnet which did not completely remove the coating, no sample had more roughness than the unpolished control (blank) after polishing and no traces of residual cerium oxide, jeweler's rouge or garnet were seen in the TXRF spectra. TXRF results for

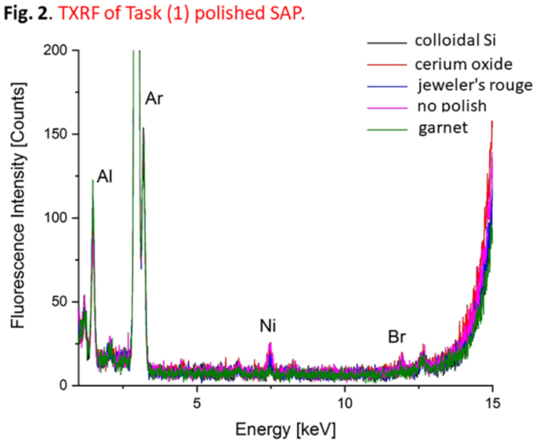
Table 1. Polishes and results on non-Genesis sapphire without damaged surfaces.

Polish	Br	Fe	Ni	Ti	roughness
colloidal Si		x	x		
cerium oxide	x	x	x		X
jeweler's rouge	x		x		
Garnet		x	x		
Blank	x	x	x	?	x

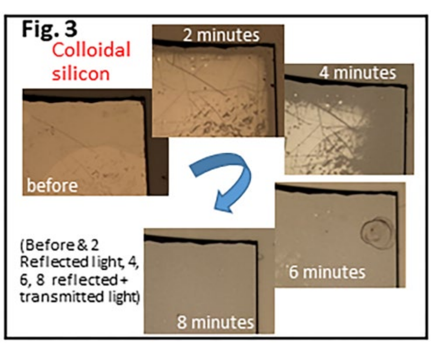
The increase in surface roughness with garnet may have been just the scratched coating.

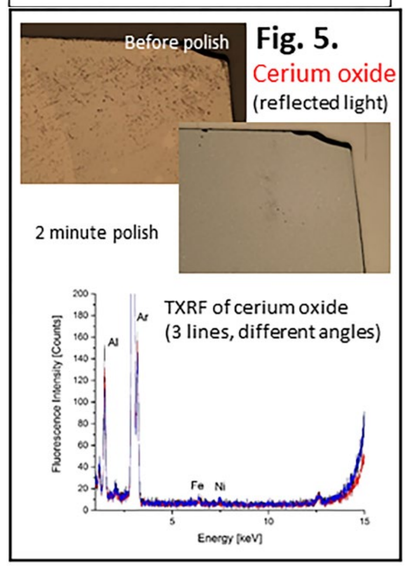
Note that the different polishes took different amounts of time to remove the Al-suboxide coating: most of the coating was still present after 6 minutes with garnet; colloidal silicon finished in 8 minutes; cerium oxide in 2 minutes (Figs. 3, 4, 5) and jeweler's rouge was a nasty mess and disqualified. Note: polishing with garnet and colloidal silicon was extended in increments of 2 minutes to see how the coating was affected. Although garnet was the highest-hardness abrasive, the ~15 nm coating was nearly intact (except for scratches) after 6 minutes of polishing. Colloidal silicon removed the coating after 8 minutes, suggesting a removal rate of the coating of ≤2 nm/minute. Cerium oxide was faster.

Fig. 2. TXRF of Task (1) polished SAP.



Discussion: The hardest of the abrasives scratched the sub-oxide coating but did not remove it, so any polish used for cleaning Genesis SAP must be reactive as well as abrasive. That is, garnet likely would not completely remove the occasional "aluminum" spots on flown sapphire surfaces, but either colloidal silicon or cerium oxide would. No adhering polish was observed. TXRF was not expected to detect a signal from colloidal silicon directly (due to low concentration and poor detection limits for lighter elements), but there was no increase in roughness (cf., adhering alumina in [2]). Moreover, SiO_2 is of low importance to most analyses. Cerium oxide residue below TXRF detection limits (DL





~$8.5x10^{10}/cm^2$) is possible. Cerium oxide is not recommended for SAP used for REE or related analyses. For SAP polished with colloidal silicon and cerium oxide, SIMS analysis is being done to insure that the H implant underlying the Al-coating hasn't been removed.

Summary and Conclusion: The surface-roughness check using TXRF is necessary in this and future studies of cleaning SAP with abrasives. Exposure to SW *may* have (1) reduced the hardness of the surface and/or (2) increased the reactivity of the surface. Both could be indicated as roughness in TXRF – a lesson from studying alumina polish [2]. Yet, any polish useful for cleaning Genesis sample will need to be reactive as well as abrasive. Thus far, the two most promising candidates are colloidal silicon and cerium oxide.

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