CREEPY (not KREEPy) GOLD-INDIUM INTERMETALLIC COMPOUNDS ON SECONDARY ION MASS SPECTROMETRY SAMPLES.

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Introduction: A series of Secondary Ion Mass Spectrometry (SIMS) sessions to measure hydrogen (H) in Martian meteorite minerals [1-3] was completed using the Cameca 6f SIMS and NanoSIMS 50L at Arizona State University (ASU). During these sessions, a "creeping" phenomenon has occurred, where the edges of samples pressed in indium are covered by a metal alloy. We summarize these observations herein, present a collection of preliminary data, and discuss explanations and concerns for future SIMS work. We conclude the report with a research plan for further study.

SIMS/NanoSIMS Sample Preparation: Routine preparation of samples and standards for low-blank H analysis by SIMS requires a variety of special preparatory methods including dry polishing on lapping film (1 μm) without water, an acetone and isopropanol wash, and careful pressing into a 1-in aluminum mount of indium [1-4]. Microanalysis of a non-conductive material requires a thin (typically 15-30 nm) conductive coat to be deposited at the sample surface. Gold (Au) coating is often preferred for NanoSIMS analysis due to its high conductivity and ease of sputter-removal during analysis. However, carbon (C) provides a suitable alternative for the higher beam currents used in SIMS. Thus, our observations are documented from multiple sessions where mounts were coated with C for SIMS and Au for NanoSIMS.

Observations: In all of the Au-coated SIMS sessions, and none of the C-coated SIMS sessions, a "creeping" phenomenon occurred where a layered ring was observed on mineral surfaces (Fig. 1). What appear to be layers were observed starting at the point of contact with indium (at sample edges and within cracks), and with varied widths (0 to 100 μm). A challenge to mounting in In is that imperfect or incomplete pressing can leave gaps around samples that are difficult to fill. Adjacent to these gaps, the phenomenon was not observed (Fig. 1).

Hypothesis and Concerns: The following Au-In intermetallic (IMC) compounds have been documented in experiments at room temperature: $AuIn_2$, $AuIn$, Au_7In_3, Au_4In [5]. Work on thin film deposition and interactions between Au and In within the materials chemistry industry demonstrates that interdiffusion between Au and In thin films is temperature dependent [5-7] and occurs over laboratory timescales even at temperatures as low as -50 °C [7]. We hypothesize, that the metallic films appearing on our Au-coated samples, are multiple Au-In IMCs that have formed through a continuous reaction of indium with the overlying Au coat. Their formation is likely induced by the environment (T and/or P) of the SIMS/NanoSIMS sample chamber.
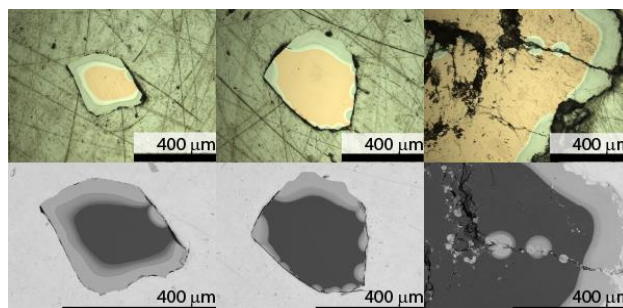

Fig. 1. Reflected light (top) and corresponding BSE images (bottom) of 3 samples exhibiting Au-In layered films at their surfaces and cracks. All were co-mounted in indium and coated with 30 nm of gold for the same SIMS session. *Left to right, NWA5789 olivine 1, NWA5789 olivine 2, RBT 04262 section.*

When samples are large these surficial layers are small enough that they only cover sample edges and have been easily avoided during analysis. However, work with astromaterials is often limited to small (micron to submicron) grains and particles due to sample availability, preparation methods, and preservation of precious samples. Additionally, analysis targets are often pre-planned and analyzed by electron microprobe for compositional information at specific locations (e.g. diffusion experiments). In recent sessions, we have experienced multiple challenges where targets and surface markings used for identification were covered, and small samples were entirely engulfed, making analysis difficult or even impossible.

Less obvious and general concerns include (1) matrix effects of Au-In IMCs on SIMS/NanoSIMS analysis (2) effects on surface conductivity (3) contamination of extraterrestrial samples (4) added adsorbed terrestrial H (for H analysis specifically) and (5) inconsistency between measurements on affected and unaffected surfaces.

We approach these concerns with 2 initial questions: (1) What are the layers composed of (2) How do they form?

Methods: Upon identification, all affected grains were photographed under reflective light. The JEOL 7600F SEM at NASA-JSC was used to look for variation in back-scatter electron (BSE) images, and to generate X-ray maps of 1 affected olivine grain from Martian meteorite Northwest Africa 5789 (NWA 5789). The SX100 Cameca electron microprobe at NASA-JSC was used to quantify the relative abundance of Au:In across the same sample. This EMPA analysis was guided by the SEM generated X-Ray maps, and measurements were programmed as transects to encapsulate the stratification depicted in the reflected light and BSE images (Fig. 1) from rim to center.

Preliminary Results: Data from all 3 techniques appear to be correlated. SEM images show a stratification in BSE that coincide with the surface features observed in reflected light (Fig. 1), and the SEM X-Ray map of In abundances (Fig. 2). EMPA transects are used to derive Au:In ratios, with the distribution of ratios indicating clear populations at Au:In of 2:3, 1:1, and 3:1 (grain rim to center). Backscattered electron data indicate the presence of other, less voluminous phases with different backscatter intensities possibly indicating additional AuIn phases.
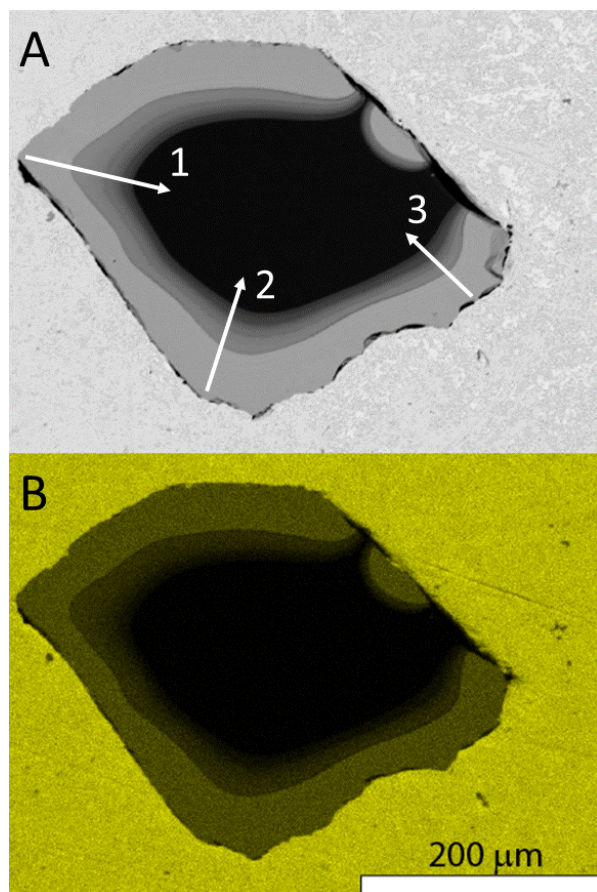

Fig. 2. SEM generated (A) BSE and (B) indium X-Ray maps of *NWA5789 olivine 1*. Image (A) is labeled with EMPA transect locations (line 1, 2, and 3).

Discussion and Research Plan: Some of the Au:In ratios estimated by EMPA are similar to the expected formulae of other Au-In IMCs that have been reported [5, 8-9]. However, it is plausible, that the stratifications observed in the BSE images and X-Ray maps reflect varied film thickness in addition to composition. Since the amount of gold deposited at the sample surface is limited to the 30 nm added by coating, the signal from the underlying substrate (the sample) likely contributes to the contrast between light and dark layers to some degree. According to a literature survey of Au-In compounds, cubic and hexagonal crystal structures have been documented for Au-In IMCs elsewhere [8-9]. Future crystal structure identification and thickness measurements may be necessary to constrain the cause(s) of the stratification.

Although the data gathered from the affected samples has been useful for preliminary investigation of Au-In IMCs, less-precious samples allow greater flexibility for analysis. Analogue experiments in which an Au-coated indium mount will be exposed to varied T and P will be presented at the meeting.

Conclusions: Layered Au-In thin films have been observed in In-filled sample mounts that were coated with Au for NanoSIMS analysis. The cause of film formation needs to be investigated, but is likely a result of Au-In IMC formation, possibly induced by the temperature and/or pressure conditions within the SIMS sample chamber. Further study of affected samples and experiments are needed, and discussion of sample preparation practices within the SIMS/NanoSIMS community is encouraged. Alternative SIMS sample preparation/coating may need developing.

References: [1] Dudley J. M. et al. (2019) *LPSC L,* Abstract #2971. [2] Dudley J. M. et al. (2019) *Goldschmidt 2019*, Abstract #863. [3] Dudley J. M. et al. (2020) *LPSC LI*, this meeting [4] Peslier A. H. et al. (2019) *Geochim. Cosmo-chim. Acta, 266,* 382-415. [5] Simic V. and Marinkovic Z. (1977) *Thin Solid Films 41,* 57-61. [6] Finstad T. G. et al. (1975) *Thin solid Films 29*, 145. [7] Bjontegaard J. et al. (1983) *Metallurgical and Protective Coatings 101,* 253-262. [8] Massalski T. B. (1957) Acta Metallurgica 5, 541-547. [9] Hiscocks S. E. R. and Hume-Rothery W. (1964) *Proc. R. Soc. Lond. A. 282,* https://doi.org/10.1098/rspa.1964.0235.