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Journal of Nuclear Materials 283–287 (2000) 1062–1067

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Effect of carbon pre-implantation on deuterium retention in tungsten

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Abstract

The effect of pre-implanted carbon on deuterium retention in tungsten was investigated using polycrystalline tungsten foils. Pre-implantation was performed with 1 keV C^+ ions to fluences of 10^{21} C^+/m^2 and 10^{22} C^+/m^2 at 300 and 500 K. Using this newly created W/C structure, a deuterium retention study with 1.5 keV D_3^+ (500 eV/D^+) ions was performed as a function of incident D^+ fluence and implantation temperature. For 1 keV C^+ implantations to 10^{21} C^+/m^2 at 300 K followed by 1.5 keV D_3^+ implantations to $<10^{23} D^+/m^2$ at 300 and 500 K, the amount of D retained was reduced by an order of magnitude compared with W specimens without a C^+ pre-implantation. At higher D^+fluences, $\geqslant 10^{24}$ D^+/m^2, the retention values were equivalent to those of D^+ on pure tungsten. For C^+ implantations to 10^{21} C^+/m^2 at 500 K, the amount of D retained tended to follow the behaviour of the pure W case. Carbon pre-implantations to a higher fluence (10^{22} C^+/m^2) resulted in D retention values higher than in pure W for D^+ fluences $<10^{23}$ D^+/m^2. At higher D^+ fluences, the retention behaviour differed significantly, depending on the D^+ implantation temperature. A possible mechanism is suggested to explain the observed results. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In next generation fusion reactors, particle-induced erosion of multi-material first wall and divertor structures will be inevitable, leading to cross-contamination of all surfaces. For example, in the International Thermonuclear Experimental Reactor (ITER) the first wall will be Be and the divertor will contain C and W. Erosion of carbon composites will give rise to C atoms and ions throughout the divertor region which will re-deposit and implant on nearby W surfaces. Since carbon is known to display significantly different hydrogen retention and recycling properties from tungsten, it is likely that the re-deposition or implantation of C on W will significantly alter its hydrogen recycling properties.

Very few results are available on the effects of C impurities on hydrogen retention in W. Sze et al. [1] used a deuterium plasma with carbon impurities to simulate co-bombardment at high flux, while others [2–4] have focused on the hydrogen interaction characteristics of tungsten carbide. It is thought that a tungsten carbide layer could be formed during the bombardment of W by C impurity ions, however, metallurgical methods of producing tungsten carbide are not necessarily representative of the new materials created in tokamaks. Rather than using prepared tungsten carbide specimens, we have chosen to initially implant C^+ into pure W to simulate the type of C–W interaction which may occur in the divertor region of a tokamak. Hydrogen retention studies were then performed on this newly created mixed material.

Retention measurements were also made on pure W foils exposed to a high-flux deuterium plasma in the Plasma Interactive Surface Component Experimental Station (PISCES) plasma device. This high-flux D^+ exposure also had an impact on subsequent D^+ retention measurements.

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PII: S0022-3115(00)00167-7

2. Experiment

2.1. Tungsten specimens

All of the experiments in the carbon pre-implantation study were performed with a piece of polycrystalline tungsten foil as the substrate (25 μm thick and 99.95 wt% pure from Rembar Co.). For each C^+-implantation/D^+-retention experiment, a new 8×10 mm^2 specimen was cut from a W foil sheet. Prior to implantation, all specimens were heated to 1473 K for 1 h to remove any residual stresses or residual bulk hydrogen.

2.2. PISCES specimens

To investigate the effect of a high-flux D^+ plasma exposure on subsequent D retention in tungsten, a pre-exposed W specimen (25 μm thick foil 99.92 wt% from Plansee) was obtained from the PISCES facility at UCSD. This specimen was annealed at 1400 K and then exposed to a D^+ plasma in PISCES-A at 973 K for 1 h to a flux of 10^{21} D/m^2 s at 100 eV/D^+. Due to the brittleness of the specimen, two fragments (each ~50 mm^2) were used for subsequent D retention experiments at UTIAS; the fragments were also annealed at 1473 K for one hour before starting the 500 eV/D^+ retention study.

2.3. Ion implantation

All implantations were performed in an ultra-high vacuum system, using a mass analyzed ion accelerator. The experimental procedures for these experiments were very similar to those followed in previous studies, Refs. [6,7].

Ion implantation was carried out in two stages. First, 1 keV C^+ ions were implanted into the pure W specimen. The C^+ ions were generated by feeding CO gas into the accelerator's duoplasmatron source and extracting the mass filtered C^+ at 2.5 keV. The specimen was biased at +1500 V to obtain the desired 1 keV C^+ energy; the ion flux was $\sim5\times10^{18}$ C^+/m^2 s. In the present study, the implanted C fluence was fixed at either 10^{21} or 10^{22} C^+/m^2. These fluences were chosen based on implantation time considerations; however, as shown in the results, these particular fluences happen to also represent significantly different C–W interaction behaviour. X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS) were performed on some specimens subsequent to C^+ ion implantation.

For the second stage, 1.5 keV D_3^+ (500 eV/D^+) ions were implanted into the W/C specimen without any intermediate treatment. Again, the ions were extracted at 2.5 keV but a +1000 V bias was applied to the specimen to obtain the desired ion energy. The deuterium ion flux was $\sim1.7\times10^{19}$ D_3^+/m^2 s, corresponding to $\sim5\times10^{19}$ D^+/m^2 s, allowing D^+ fluences of $\sim10^{22}$–3×10^{24} D^+/m^2 to be reached (D^+ is used to represent the D atoms in the *incident* D_3^+ molecular ion). Both sets of ion implantations were carried out at room temperature (300 K) and 500 K to explore temperature effects, if any. The same D^+ beam parameters were also used in the D retention study with the PISCES specimens.

2.4. Thermal desorption spectroscopy (TDS)

The amount of D trapped in the W/C system was measured using TDS; for procedure see [6,7]. TDS was performed in a separate vacuum system, with delays of 16–72 h between the final implantation and desorption such that only trapped D (no solute) was measured [5]. Temperature ramping rates during TDS were ~10 K/s with specimen temperatures reaching ~2000 K. The amount of D retained in the specimens was determined by integrating the quadrupole mass spectrometer (QMS) signals for D_2, HD, and CD_4 during thermal desorption. The QMS was calibrated in situ during each run using a D_2 calibrated leak bottle.

3. Results

3.1. Low C^+ fluence cases

The effect of the low carbon fluence (10^{21} C^+/m^2) pre-implantation on subsequent D retention in W was studied for four temperature/ion combinations: (i) both C^+ and D_3^+ implantations at 300 K; (ii) C^+ at 300 K followed by D_3^+ at 500 K; (iii) C^+ at 500 K followed by D_3^+ at 300 K; and (iv) both C^+ and D_3^+ implantations at 500 K. The D^+ fluence dependence results for these cases are shown in Fig. 1. Also included for reference are the

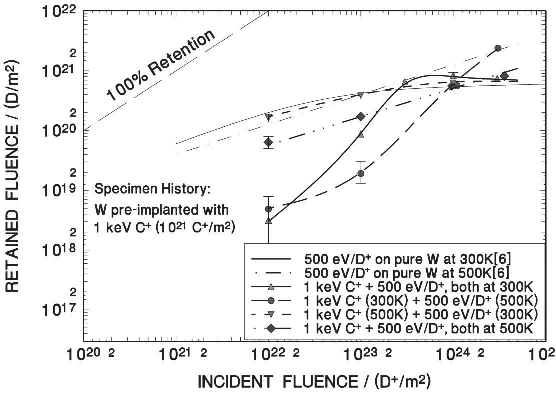

Fig. 1. Deuterium retention as a function of incident D^+ fluence for a W foil pre-implanted with 1 keV C^+ to 10^{21} C^+/m^2 (low C fluence). Lines are drawn through data corresponding to different C^+ and D_3^+ implantation temperatures. Reference curves for 500 eV D^+ implantation in pure W [6] are shown for comparison.

results of the fluence dependence study [6] for 1.5 keV D_3^+ (500 eV/D^+) at 300 and 500 K on pure tungsten. For C^+ pre-implantations at 300 K and low D^+ fluences ($\leqslant 10^{23}$ D^+/m^2), the amount of D retained is over an order of magnitude lower than the pure W data. For C^+ pre-implantations at 500 K, and low D^+ fluences, the decrease in retention compared with pure W is much smaller. For example, for both C^+ and D^+ implantations at 500 K, the reduction is only a factor of 2 to 3; for the C^+ pre-implantation at 500 K followed by a D^+ implantation at 300 K, one sees no difference from the pure W case. At high D^+ fluences ($\geqslant 10^{24}$ D^+/m^2), the specimens exhibit the same retention behaviour as pure W, except when both C^+ and D^+ implantations are at 500 K. In this latter case, the retained amounts, as a function of D^+ fluence, follow the same slope as the pure W at 500 K, but the whole retention curve is lower by a factor of three.

3.2. High C^+ fluence cases

With the high C^+ fluence (10^{22} C^+/m^2) pre-implantation, a D^+ implantation fluence dependence study was performed using only two cases: (i) both C^+ and D^+ implantations at 300 K, and (ii) both C^+ and D^+ implantations at 500 K. The results of these experiments are shown in Fig. 2, together with pure W data [6]. For the 300 K implantation, one sees a significant increase in D retention over the pure W case for D^+ fluences $\sim 10^{22}$ D^+/m^2, but at the higher D^+ fluences ($\geqslant 10^{23}$ D^+/m^2), the specimens follow the same D retention behaviour as pure W. With both C^+ and D^+ implantations at 500 K, the specimens also show increased retention over pure W at low D^+ fluences ($\sim 10^{22}$ D^+/m^2), but exhibit a very different behaviour at the higher fluences ($> 10^{23}$ D^+/m^2). At a fluence of $\sim 10^{24}$ D^+/m^2, a large drop in D retention is observed – an order of magnitude less than in pure W at 500 K. Then as the incident D^+ fluence increases to 3×10^{24} D^+/m^2, the retention also increases, but the amount retained is still about five times lower than the pure W case.

3.3. PISCES specimen

The 500 eV/D^+ fluence dependence results for the PISCES specimens at 300 and 500 K are shown in Fig. 3. Again, pure W data are also shown [6]. Considering the possible effect of implantation history on trapping [7], it is possible that a high fluence ($\geqslant 10^{23}$ D^+/m^2) implantation, even at 500 eV/D^+ with no displacement damage, could alter the 100 eV D^+ high-flux-induced surface modification produced in PISCES. Thus, one of the two PISCES fragments was exposed to high fluence implantations ($\geqslant 10^{23}$ D^+/m^2), while the other was exposed to lower fluence implantations ($< 3 \times 10^{22}$ D^+/m^2) only. The same specimen was exposed to D^+ at both 300 and 500 K.

At 300 K, the D retention characteristics of the PISCES specimens are the same as the pure W foil. However, at 500 K, very different results are seen at low D^+ fluences. For fluences $> 10^{23}$ D^+/m^2 at 500 K, the PISCES specimen follows the same D retention characteristics as seen in pure W, namely, the D retention values follow a 0.5 slope, indicating a diffusion-limited trapping mechanism. However, for fluences $< 10^{23}$ D^+/m^2 at 500 K, the amount of D retained in the PISCES specimen is more than an order of magnitude lower than in pure W. These results indicate that the 100 eV D^+ high-flux exposure in PISCES had a significant effect on subsequent D retention at 500 K (at UTIAS), while no

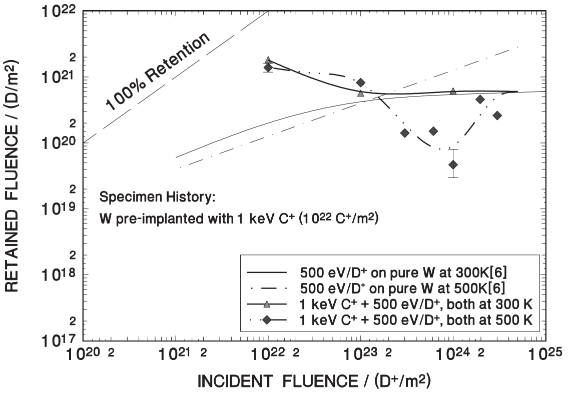

Fig. 2. Deuterium retention as a function of incident D^+ fluence for a W foil pre-implanted with 1 keV C^+ to 10^{22} C^+/m^2 (high C fluence). Lines are drawn through data corresponding to different implantation temperatures. Reference curves for 500 eV D^+ implantation in pure W [6] are shown for comparison.

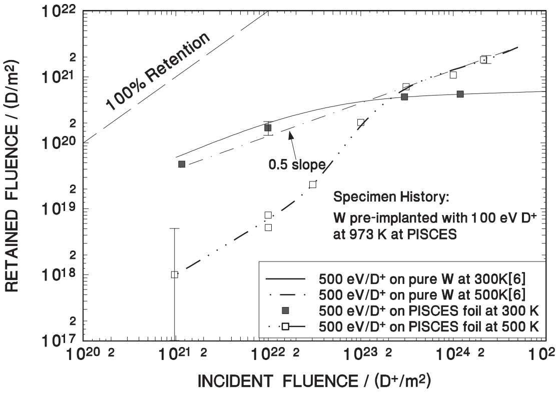

Fig. 3. Deuterium retention as a function of incident D^+ fluence for the PISCES specimens at 300 and 500 K. Lines are drawn through data corresponding to difference implantation temperatures. Reference curves for 500 eV D^+ implantation in pure tungsten [6] are shown for comparison.

effect was seen at 300 K. The D retention values between the high and low fluence regimes suggest a smooth transition from one to the other, thus eliminating the possibility that the differences are due to different specimens being used for each regime.

4. Discussion

4.1. Effect of C^+ pre-implantation – low C^+ fluence cases

To aid in an explanation of how C^+ implantation could affect D retention in tungsten, XPS and RBS surface analyses were performed subsequent to C^+ implantations. XPS shows increasing surface C concentrations with increasing C^+ fluence from 38% C for the pure W reference to 53% C for the 300 K low C^+ fluence case. However, the differences in surface concentrations of graphite, carbide and atomic W were even more pronounced. The pure W area had ~22% atomic W on the surface with negligible amounts of graphite and tungsten carbide; most of the C was in the form of hydrocarbons. With XPS analysis of the low C^+ fluence beam spot, it was evident that WC was formed at the surface (~10% WC), but the low C^+ fluence was also sufficient to form a significant amount of graphite (21% graphite) with only small amounts of atomic W (4%) left on the surface. The C^+ pre-implantation has obviously caused a change in surface chemistry, even for a low fluence C^+ implantation at 300 K which had no visual evidence of a beam spot.

RBS surface analysis of a low C^+ fluence implantation at 300 K shows $\sim 5.3 \times 10^{20}\ \mathrm{C/m^2}$ in the near surface, which suggests that about half of the implanted C was at or near the surface. Because XPS can only scan the top 3 nm of the surface, it is possible that more WC ($>10\%$) exists beyond the first 3 nm of the specimen. With a low C^+ fluence implantation at 500 K, less C was measured on the surface, $\sim 3.3 \times 10^{20}\ \mathrm{C/m^2}$, suggesting the possibility of significant C diffusion into the bulk.

4.2. Effect of C^+ pre-implantation – high C^+ fluence cases

From visual examinations of the W surface after a high fluence C^+ pre-implantation ($10^{22}\ \mathrm{C^+/m^2}$) at 300 K, a definite beam spot was visible. XPS elemental analysis of the beam spot revealed a C concentration of 90%, with chemical analysis showing almost half the surface (48%) made up of graphitic carbon with very little WC ($<1\%$) and negligible amounts of atomic W in the top 3 nm of the surface. These results clearly show the formation of a graphitic surface layer. Further surface analysis by RBS confirmed the formation of a carbon layer. As with the low C^+ fluence case, just over half of the implanted carbon, $\sim 5.7 \times 10^{21}\ \mathrm{C/m^2}$, was measured in the surface layer. Assuming zero porosity, this would lead to a graphitic layer of ~43 nm thickness. RBS analysis also shows the possible existence of up to 19 at.% tungsten carbide just below the C–W interface. This is considerably higher than the ~1% WC seen by XPS in the top 3 nm layer, implying that WC exists beyond the XPS analysis range. Thus, it would appear that the C^+ pre-implantation may initially lead to the formation of WC, but above a certain C^+ fluence, the near-surface becomes saturated with C and a graphite layer begins to build. RBS also showed a tail of C, ~2 at.%, extending 170 nm into the specimen, indicating a significant amount of C diffusion. With high C^+ fluence implantations at 500 K, visual inspection and RBS analysis yielded results similar to the high fluence C^+ pre-implantation at 300K: a definite beam spot with $\sim 4.8 \times 10^{21}\ \mathrm{C/m^2}$ in the surface layer, and a tail of C, ~1 at.%, extending 300 nm into the bulk.

4.3. D retention in C^+-implanted specimens

The progressive surface evolution, from pure W to WC, to a graphitic surface layer, with increasing C^+ fluence, can be used to explain our D retention results for the C^+-implanted specimens.

With a low fluence C^+ pre-implantation and low incident D^+ fluences, one would expect WC to be prevalent at the surface. Using this as a basis, we suspect the decrease in D retention values below the levels of pure W (Fig. 1) to be due to WC formation. Atsumi and Tanabe [3] have observed that H retention decreases with progressive carbide formation, but they did not observe retention values that were lower than the case of pure W. With a high fluence C^+ pre-implantation and a low incident D^+ fluence, we expect the presence of a graphite layer on the surface. For these conditions, we find that D retention is greater than the pure W case (Fig. 2). Since graphite displays much higher D retention than tungsten [6–9], the higher retention values, relative to pure W, can be attributed to retention of D in the graphitic layer. Higher D trapping in carbon films has been used to explain why D retention increased in carbon-contaminated tungsten samples [1]. In fact, our retention values for the high C^+ and low D^+ fluence implantations are comparable to D retention in pure graphite [8,9].

So far, we have only described the formation of C structures with increasing C^+ fluence; however, the subsequent D^+ bombardment will lead to preferential erosion of C atoms from the surface. This process will first remove the graphitic layer (formed during high fluence C^+ implantation), leaving a WC interface, and eventually a pure W surface. This implies that a high fluence C^+ pre-implantation followed by an appropriate D^+ bombardment can yield the same results as a low fluence C^+ pre-implantation, or even the same results as pure W if the D^+ fluence is high enough. So, basically, we have three different domains for D retention. (i) D impact on a graphitic surface layer formed by high-fluence C^+ pre-implantation; (ii) D impact on a WC surface formed either by low-fluence C^+, or high-fluence C^+ pre-implantations followed by D^+ bombardment to remove the graphite layer; and (iii) D^+ implantation into pure tungsten when all the carbon structures are removed from the surface. All of these three domains can be seen on the curve with high-fluence C^+ pre-implantation at 500 K in Fig. 2.

4.4. Retention and recycling mechanisms

One may notice a similarity between the results for the low-fluence (10^{21} C/m^2) C^+ pre-implantation cases and the PISCES specimens pre-exposed to a D^+ plasma. Specifically, the case of 1 keV C^+ pre-implantation at 300 K followed by 500 eV/D^+ at 500 K (Fig. 1) closely mirrors the 500 eV/D^+ at 500 K PISCES results (Fig. 3). At low incident D^+ fluences, the retained D in both cases is an order of magnitude lower than the pure W case. The only difference between the PISCES specimen and pure W is a high-flux 100 eV D^+ pre-exposure for the former. It has been suggested [10] that the high-flux pre-exposure heavily damages the surface to create a network of open porosity, thus promoting a high D_2 release rate and lower D retention. However, for the 300 K retention experiments, we find no difference between the PISCES and the pure W foil results, suggesting that the high-flux plasma pre-exposure has no effect at this temperature. We suspect that the differences between the 300 and 500 K retention results are due to differences in D diffusion. At 500 K, D diffusion may be enhanced such that the surface recycling rate is limited by the rate of surface recombination, but at 300 K, the rate of D diffusion may be much lower such that surface recycling is limited by diffusion. In such a scenario, one would not see any decrease in retention for the diffusion-limited regime (lower temperatures), but at higher temperatures, back diffusion to the surface may be fast enough such that increased recycling can lead to decreased D retention.

Due to the similarity in results for the PISCES and the C^+ pre-implanted specimens, it is also possible that the surface damage due to the 1 keV C^+ beam leads to an increase in surface recycling, either by roughening the surface to increase the effective surface area, or by ion-induced damage which promotes a higher release rate. TRVMC [11] calculations with 1 keV C^+ ions on pure W show significant displacement damage (>1000 dpa) within the first 5 nm with almost no damage beyond 10 nm. It may also be possible that the presence of WC in the system somehow decreases D retention below the levels seen for pure tungsten, perhaps acting as a catalyst for surface recombination of deuterium.

An alternate explanation for the observed decrease in D retention after C^+ pre-implantation is that the implanted C atoms occupy the trap sites where the D would normally be trapped, reducing the number of trapping sites available for the D. Once trapped in the lattice, the C atoms bond with the adjacent W atoms forming WC. It has been suggested [3], that tungsten co-existing with carbon has low bulk hydrogen retention if it is converted into well-reacted carbides, thus removing the dangling C bonds by forming bonds with tungsten atoms. In this manner, the total trap concentration available to D is reduced and D retention is decreased.

4.5. Temperature effects

From Figs. 1 and 2, it is apparent that D retention in the W/C system is very much dependent on the implantation temperature of the 1 keV C^+. This suggests that the observed decreases in D retention may not be solely due to ion beam effects, but also to the presence of C in the pure W foil.

Assuming that the presence of WC leads to a decrease in D retention, either by competing for trap sites, or by increasing surface recombination, the following hypothesis is proposed to explain the effect of temperature on D retention in C^+ pre-implanted tungsten. Based on RBS analysis, the implanted C was found to diffuse deeper into the bulk at 500 K than at 300 K. The case of higher diffusivity (at 500 K) could lead to two main effects.

(i) The formation of WC extends deeper into the bulk, requiring a much higher D^+ fluence to remove C from the bulk. If the C is trapped beyond the D^+ range, its removal may not be possible, and hence the pure W case may not be recoverable even at high D^+ fluences. In the high C^+ fluence case, the enhanced diffusion at 500 K might lead to the formation of some WC below the graphitic surface (as evidenced by RBS analysis). Thus, when the graphitic layer is removed, the specimen might exhibit a decrease in retention due to the presence of WC. This effect was indeed observed in our experiments; a drop in D retention at an incident fluence of $\sim 10^{24}$ D/m^2 at 500 K is evident in Fig. 2.

(ii) The second effect of a higher C diffusivity is to decrease the local concentration of WC. With the C atoms diluted, or dispersed throughout a greater volume, the local carbide concentration will decrease, thus reducing the effectiveness of the carbides on D retention. This effect can be seen in Fig. 1, where effects of the C^+ pre-implantation are much less pronounced for C^+ pre-implantations at 500 K than at 300 K.

5. Conclusions

Deuterium retention in C^+-implanted W was found to have a strong dependence on the magnitude of the C^+ fluence and the implantation temperature. With a high C^+ fluence (10^{22} C^+/m^2) and low D^+ fluences, the presence of a graphitic surface-layer increases D retention above the pure W case. With a lower C^+ fluence (10^{21} C^+/m^2), no graphitic layer, but rather, WC was formed at the surface, leading to decreased D retention at low D^+ fluences, compared to the pure W case. With increasing D^+ fluence, preferential sputtering removes both the graphitic surface layer and the implanted C from the bulk such that the D retention behaviour of the specimen tends towards that of pure W (with no C^+ pre-implantation) at high D^+ fluences.

We suggest that the formation of WC leads to a reduction of the retained D – either through occupation of trapping sites by the implanted C atoms and subsequent removal of these 'free' C atoms by carbide formation, or by altering surface recombination, as hypothesized with the D retention measurements on the pre-exposed specimens from PISCES. At elevated C^+ implantation temperatures, higher C diffusion rates may lead to a 'dilution' of the formed WC, and thus to a reduced effect on D retention. One cannot directly compare our results with published data on D retention in WC because we are not measuring D retention in WC. Rather, our results focus on the effects of implanted C^+ on W, of which the formation of WC leads to a reduction in the amount of D retained.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada. We wish to thank Dr Russ Doerner at UCSD for providing the PISCES specimens, Ross Davidson at Surface Science Western for the XPS analysis, and Dr Jacob Kleiman at UTIAS for his surface analysis advice. Also, many thanks to Dr Rick Macaulay-Newcombe for providing us with the RBS surface analysis.

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