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Title: Observations on 3He Release from ErT2 films

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Observations on ^3He release from ErT_2 films

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Abstract:

We have loaded thin (500nm) films of erbium to a stoichiometry of ErT_2, and have been observing their ^3He release characteristics. The films are stored in vacuum-tight metal vessels and the headspace helium is analyzed after accumulation for times ranging from a day to several months. Analysis is performed with very high sensitivity using a static noble gas mass spectrometer. For the first several years, ^3He release is a fairly constant function of helium generation, and does not depend on the substrate or the amount of helium accumulated in the film. We find a somewhat higher helium release (up to 3%) at very early times, decreasing over 6 months to a fairly consistent value (0.8%). This observation is consistent with a bubble nucleation and growth mechanism. The very early release behavior does not appear to be dependent upon the presence or growth of surface oxide layers. We also observed that, despite the very low vapor pressure of ErT2, our vacuum system became contaminated with low levels of tritium, representing perhaps a few ppm of the tritium in a sample.

Purpose:

To better define ^{3}He early release characteristics of metal tritides, specifically ErT_2 films, using static noble gas mass spectrometry (1000x more sensitive than previous techniques).

Background:

Previous investigators have looked at release of ^{3}He from metal tritides by standard analytical techniques (pressure buildup or measuring ^{3}He by mass spectrometry, Ref 1,2,3,4). They have defined two characteristic regimes: early release (low level), and accelerated release (released at ^{3}He generation rate or above). Various models have been proposed to explain the release behavior, involving formation of bubbles and release either along grain boundaries (conduits to the surface) or the exposed surface (Ref. 5,6,7,8). In the case of erbium, a persistent oxide, and some hydroxide forms on the surface (9, 10, 11, 12, 13, 14) and may influence ^{3}He release behavior from thin samples.

Experimental:

Samples:

Samples of Er (500 nm thick) are hydrided under UHV system conditions to produce ErD_2, with variable D/T ratio (up to 99% T). In most cases, the erbium is deposited on a molybdenum substrate, and yields $ErD_{2.08}$. In some cases, the erbium is deposited on Kovar, which yields a nominal $ErD_{1.95}$ ratio. A few samples were heated after hydriding, which should eliminate any tri-hydride that might have been formed, and, from visual appearance, may also have thickened the surface oxide layer. Samples are placed in all-metal UHV sample vessels, evacuated to 10^{-7} Torr and stored for variable amounts of time before analysis (ranging from minutes to several months). The samples are stored without pumping during this time and, although there is insignificant air in-leakage (<10-10 cc/sec), there is a buildup to a few millitorr of pressure (<10-5 atm) inside the storage container, due to degassing of the unbaked stainless steel of the storage vessel. Two samples of ErDT were stored in gold-coated storage vessels in an attempt to minimize this degassing.

Table 1

Sample Type	# of Samples
ErT2 on Mo	5
ErT2 on Kovar	3
ErDT on Mo	2

For Jane

Who proposed models
Lundin reference

ErDT on Mo (gold coated vessels)	2
ErDT on Mo (heated 500 C)	2

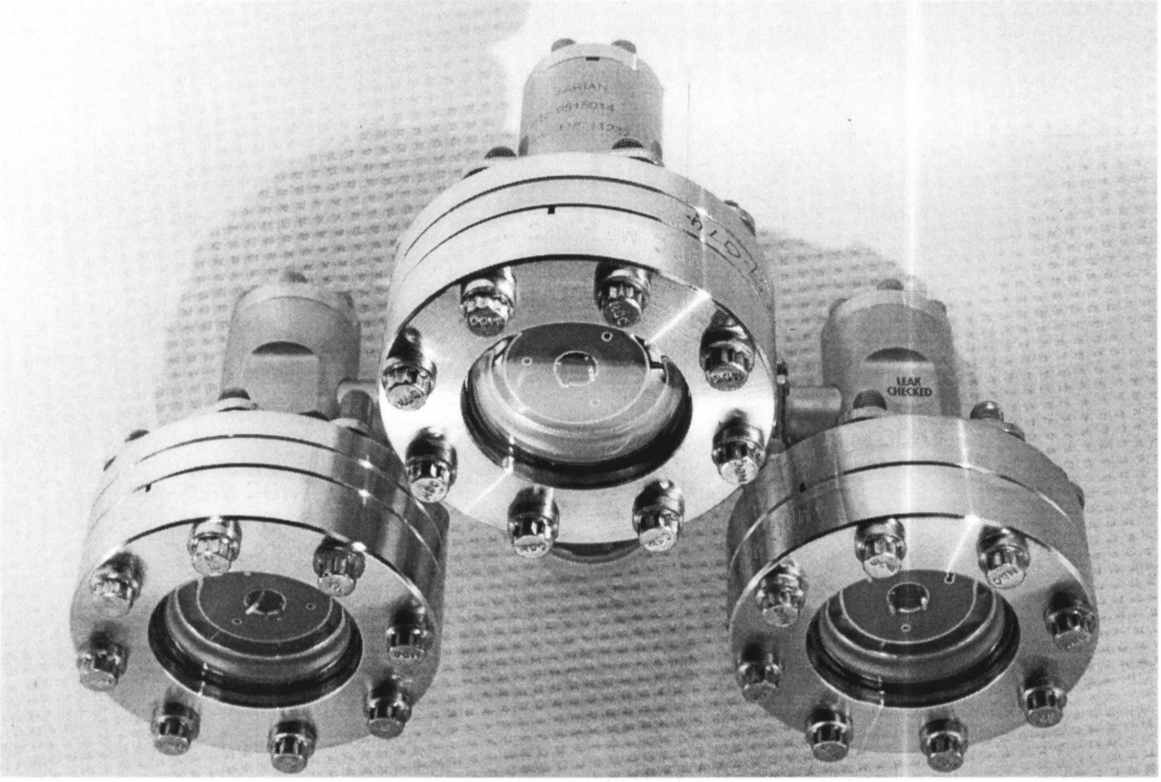

Figure 1: Erbium tritide films in storage vessels

Analysis:

To quantify the ^{3}He that has accumulated in the headspace of the sample vessel during storage, the gas is expanded into an ultra-high vacuum system on-line to the mass spectrometer. First, the gas is exposed to an ST-707 getter to remove reactive gases (including hydrogen). A tiny aliquot of this gas is further purified by exposure to three additional getters and activated charcoal at -196 C, before introduction into the mass spectrometer. Absolute uncertainty in ^{3}He amounts is about +/-10%, although aliquots and standards reproduce to better than +/-5%. Blanks are performed on the gas handling system, on a storage vessel containing a film of ErD_2, and on a storage vessel containing a molybdenum substrate that had been through the tritiation process. In all cases these blanks are negligible.

Samples are analyzed using static noble gas mass spectrometry, where the gas is equilibrated into the volume of the mass spectrometer with no active pumping. This give 1000x greater sensitivity than the more usual dynamic gas mass spectrometry. Only the noble gases are analyzed -- ^{3}He for this experiment, as well as ^{4}He and ^{20}Ne to monitor air in-leakage during storage (extremely low or undetectable in all samples). The detection limit for ^{3}He with this system is about 10^6 atoms. The mass spectrometer body was made at the University of Minnesota (ref 15).

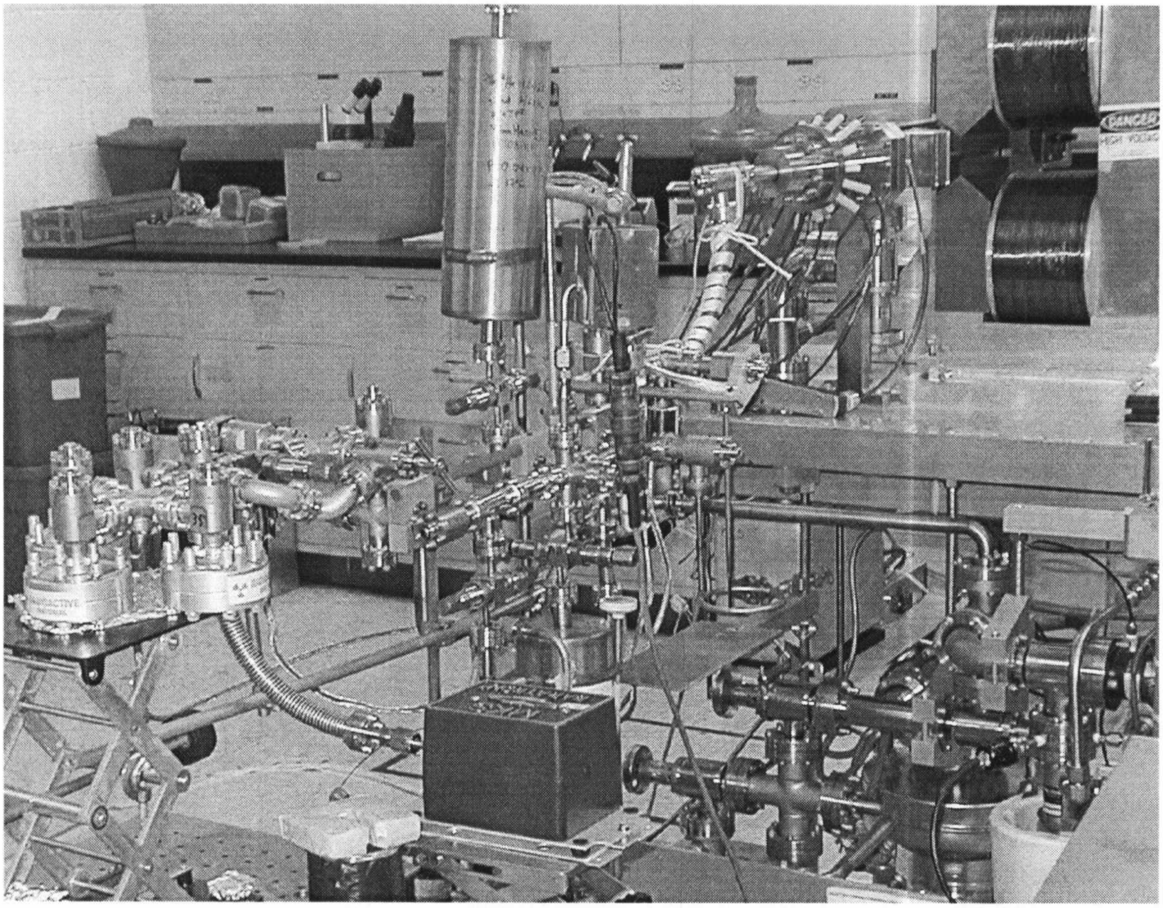

Figure 2: Gas handling system with Minn-Mass-3 mass spectrometer in the background.

Results and Discussion:

Our **definition** of **^{3}He release fraction** is the amount of ^{3}He accumulated in the headspace of the storage vessel, divided by the number of tritium decays in the film during that storage time. It does not include any ^{3}He that has previously accumulated in the film. All of our discussion focuses on the "early release" portion of the release curve, where releases are generally low.

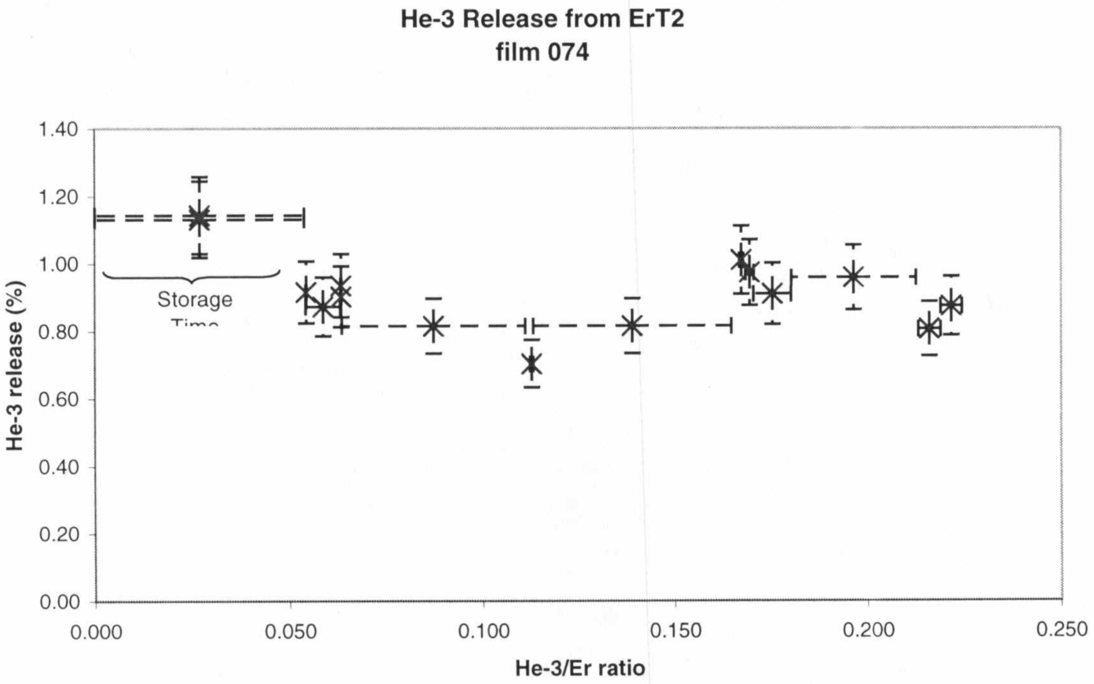

Figure 3. ^{3}He Release Fraction for a single ErT2 film on molybdenum substrate. The horizonal "error bars" represent the storage time of the sample. The vertical error bars are the estimated uncertainty for ^{3}He amount (+/-10%).

We find ^{3}He release within the range previously reported: around 1% of the ^{3}He generated during the storage is released during that time (Fig. 3). During subsequent storage periods, the release rate is similar or lower, implying that the past stores of ^{3}He do not contribute to the release rate.

Our initial surprise was the constancy of helium release between samples (figure 4). Previous data had typically shown considerably more scatter than the differences of <10% between 5 "sister" samples, produced in a single batch. Samples hydrided at different times also show similar results, as do samples on different substrates and samples hydrided with mixed deuterium and tritium (Fig. 8).

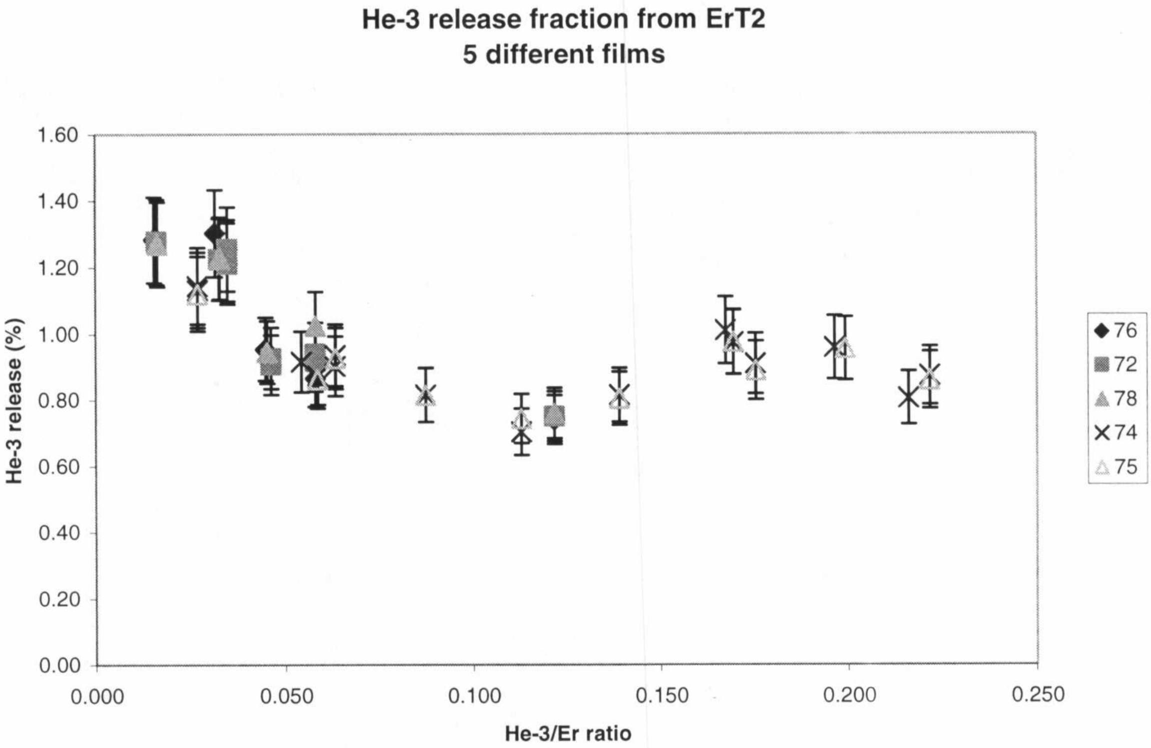

Figure 4. ^{3}He release from 5 "sister" sample of ErT_2 on Mo. Storage times ranged from 5 minutes to several months. The consistency between samples is striking.

The general pattern is that ^{3}He release is higher at the initial stages of helium accumulation, and then slowly decreases over several months to a plateau that is about 65% of the initial value. Storage time had little influence on the sample release rate -- 5 minutes, 1 day, and several months all give the same release rate in fig. 4, as expected if it reflects rapid trapping or release at time of tritium decay.

Very Early Release:

Hydriding of erbium films with mixed DT allows us to examine the ^{3}He release fraction at very low ^{3}He/Er ratios (Figure 5). We find that the release rates are significantly higher at ^{3}He/Er ratios less than about 0.007 -- up to 2.5 or 3%. We see some scatter in the data outside of analytical uncertainty, but with few data points do not attribute particular significance to this variability. This observation of increased release fraction at early times supports models where initial release comes from generation of single ^{3}He atoms near surfaces or grain boundaries. As helium accumulates in the crystal, bubbles can nucleate, grow, and provide trapping sites (Refs.? 5, 6, 7, 8).

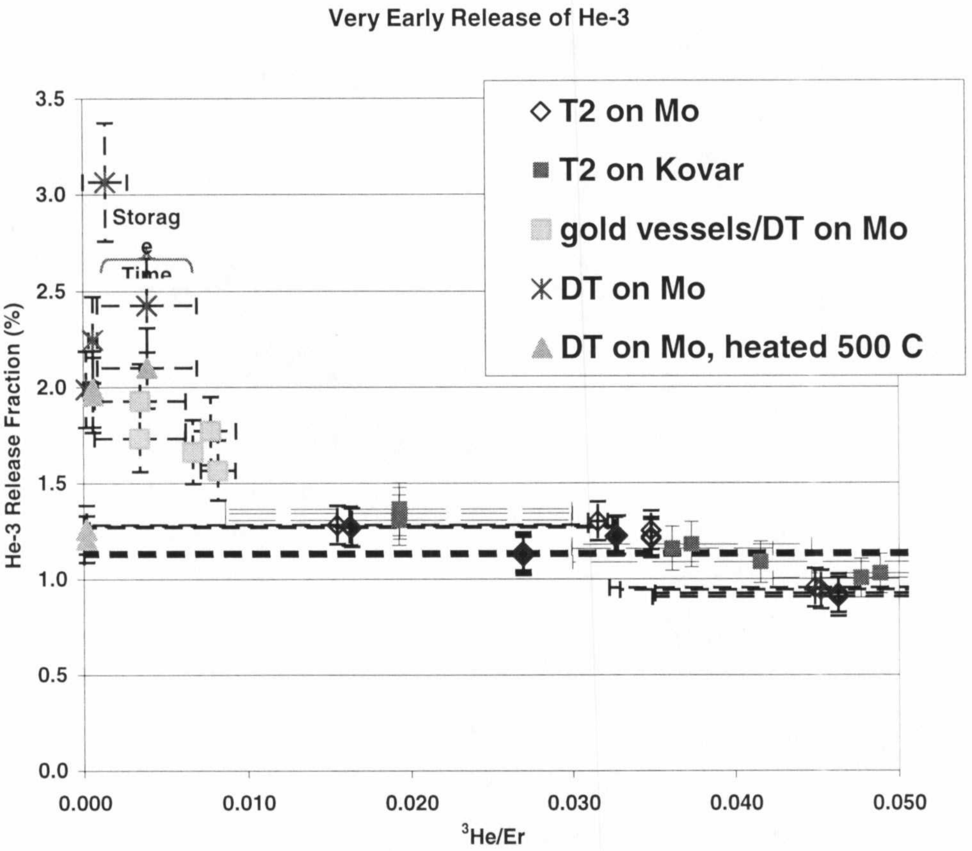

Figure 5. ^{3}He Release Fraction for ErT2 films of various types. The horizonal "error bars" represent the storage time of the sample. For very early, short storage times the release fraction increases significantly.

Mo vs. Kovar substrate

RMS roughness for Mo were 3x that of Kovar, leading us to believe that the surface roughness for the ErT$_2$ on Mo should be significantly higher than for ErT$_2$ on Kovar. This is one of the observations that suggests that the He release mechanism is not extremely surface dependent. Another difference is that the T to Er ratio is 2.08 for Er on Mo, whereas it is 1.95 on Kovar. It is interesting that we see no influence from these factors on the helium release rates (Fig. 5).

Heated Samples:

The one exception that we found to earliest ^{3}He release being the highest is for ErDT that had been heated after hydriding. For two samples, the ^{3}He release fraction initially increased from about 1.25 to about 2%, where it then falls into the trend for the other ErDT samples at early time (Figures 6 and 8). We speculate that heating may have driven off some labile (oxide surface layer?) tritium (leading to labile ^{3}He). Perhaps this is related to the "unexpected" tritium that is released from the storage vessels into the analysis system (see below). The effect of heating is only apparent at extremely early times: by the analysis at an average ^{3}He/Er ratio of 0.0006, the heated samples are closer to the unheated sister sample than it is to a second unheated sample. It is further speculative to note that even the unheated sister sample (#1), shows an upward trend for the first three points, although just about at the precision of the data. If this is a real trend, it may reflect nothing more than increasing influence of the accumulated background gases during longer storage times (see below).

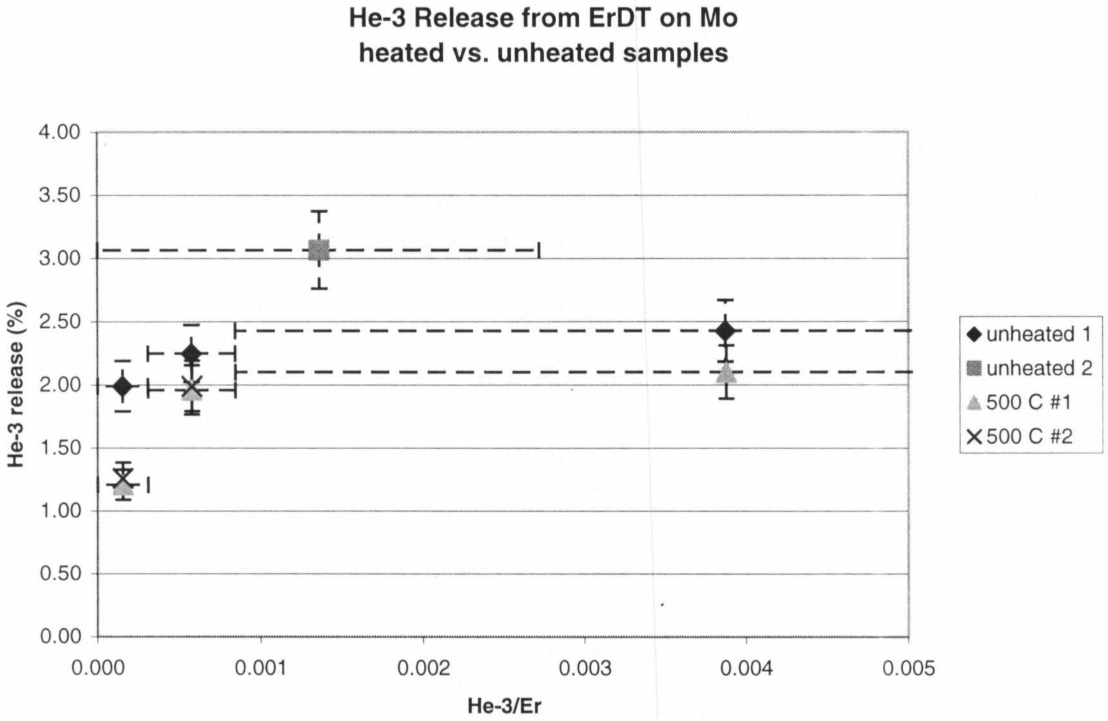

Figure 6. Very early ^{3}He release rates for heated (& oxidized?) vs. unheated samples of ErDT on Mo. Horizontal "error bars" represent the storage time. Although the first analysis of two heated samples is well below the unheated sister sample, by the second and third analyses, the heated samples are only slightly below the unheated sample.

Vessel Atmosphere/Tritium Exchange/Gold Coating

Because the storage vessels are held statically, gas accumulates in the unbaked stainless steel container. The pressure in the storage vessel builds up to <10^{-5} atm. over a few months. Its composition (figure 7, below) is as expected under these conditions -- H_2, CO_2, N_2, and some CO and CH_4.

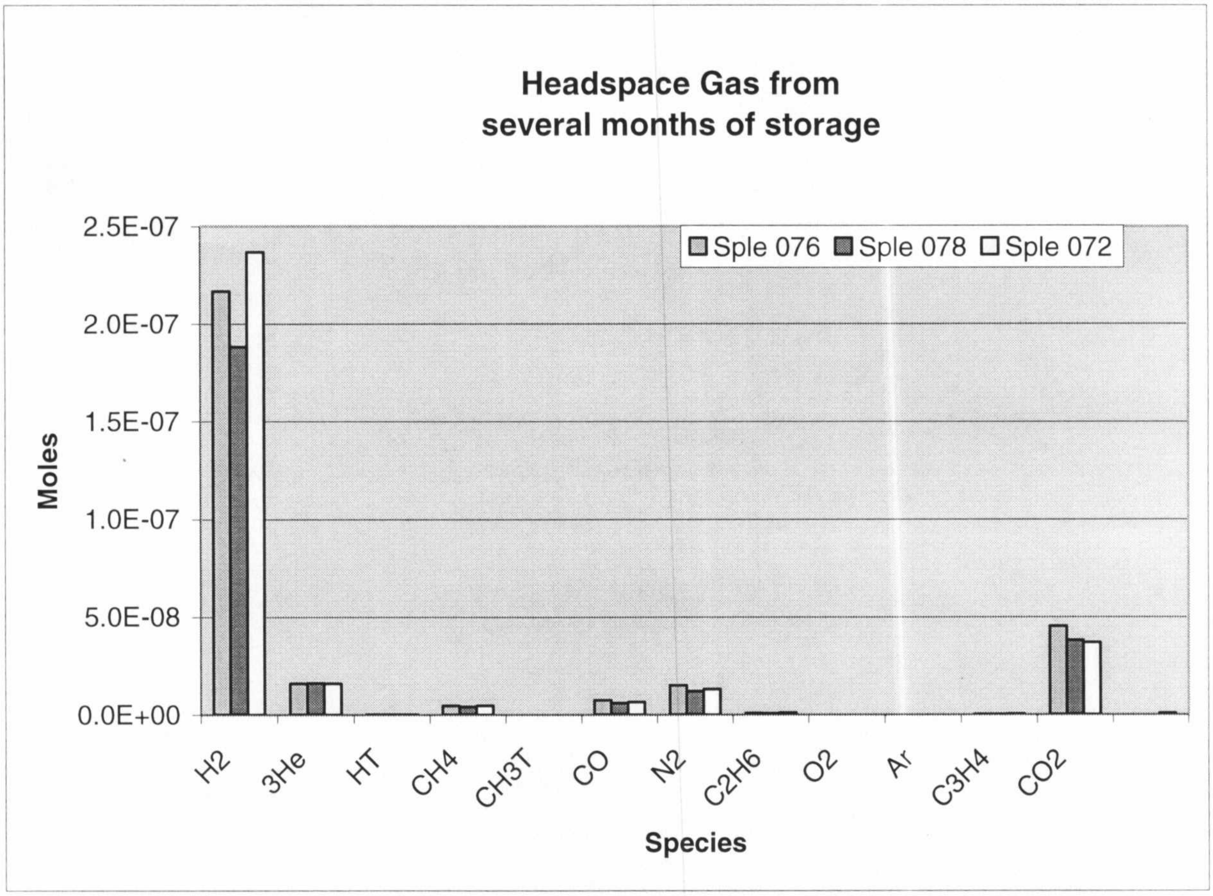

Figure 7. Composition of headspace gas accumulated in 3 storage vessels from Fig. 4, courtesy of Sandia National Laboratories. Note that these measurements yield an independent ^{3}He release rate in close agreement with our results.

One caveat to our results is that ^{3}He release may be influenced by this accumulation of gas in the storage vessels. Hydrogen could exchange with tritium and water/CO2 could contribute (slightly, Ref 12) to further oxidation of the surfaces. We do observe that there is tritium released into our analysis system -- the blank for ^{3}He went from undetectable to easily detectable with the very first sample. The amount of ^{3}He accumulated during a system blank suggests that at least a few parts per million of the tritium on the film was transferred to our analysis system. This amount cannot be explained by the estimated vapor pressure of ErH_2 (10^{-24} Torr, Ref 16). Blanks of ErD_2 films and a Mo substrate that was exposed to the (tritium) hydriding process had negligible amounts of ^{3}He. Thus, the release characteristics we measure are directly related to the ErT_2 films, plus their associated oxide and hydroxide surface layers.

Gold coating of two storage vessels before use was an attempt to reduce the hydrogen in growth in the vessels. The coating apparentdid not change the ^{3}He release characteristics of the films -- the results fall in the trend with the rest of the samples (Fig. 5). Providing gettering for reactive gases and/or passivating the walls of the storage vessels are two techniques being considered to rule out the influence of storage atmosphere on ^{3}He release characteristics of ErT2 films.

Conclusions:

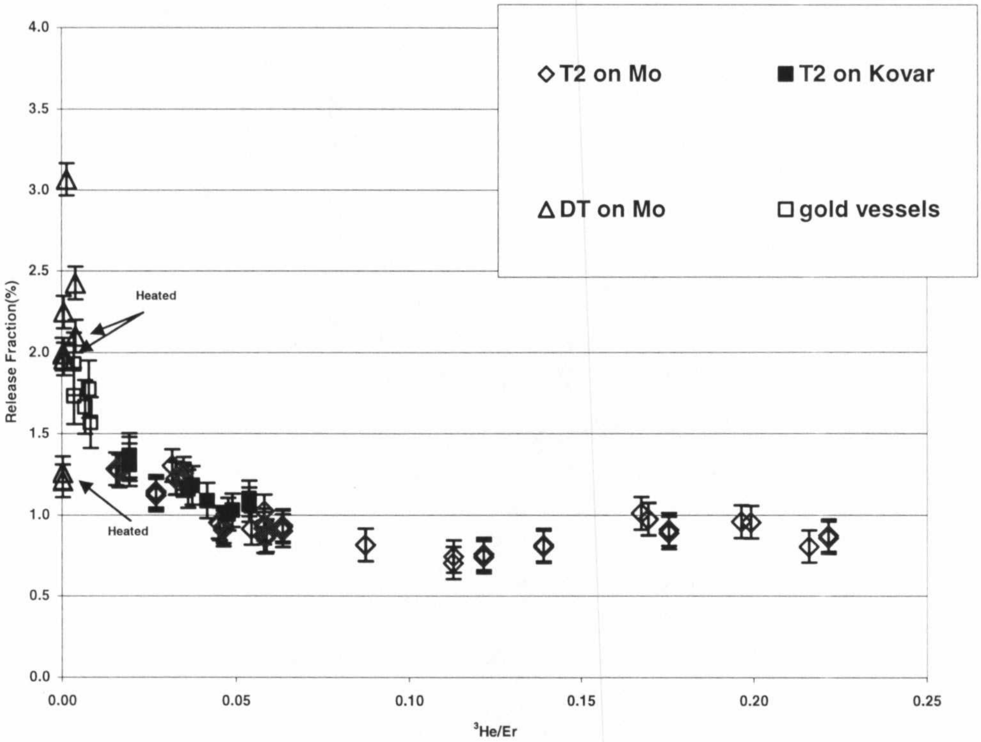

Figure 8: Summary, with all ^{3}He release data for all samples. The data generally show a single, consistent trend.

At ^{3}He/Er < 0.22, release of ^{3}He from ErT_2 samples is very reproducible between sister samples and is similar between samples of different types, and for different storage times. This finding implies that helium is rapidly either trapped or released upon tritium decay, and previous stores of helium have little influence on trapping or release for ^{3}He/Er between 0.05 and 0.22.

ErDT samples at very early time (^{3}He/Er ratios < 0.007) shows elevated ^{3}He release rates as high as 2.5 to 3.0%, compared to fairly constant release rates of about 0.8% at ^{3}He/Er between 0.07 and 0.22 for ErT_2. All samples that we analyzed seem to follow a single trend. The increased release at ^{3}He/Er < 0.01 supports the models where trapping of ^{3}He is enhanced only after the early formation of bubbles within the lattice.

Two observations suggest that surface conditions do not strongly influence ^{3}He release rates. First, despite a rougher surface for Mo vs. Kovar, the ^{3}He release rates from ErT_2 on these two substrates is similar. Second, despite an apparently thicker oxide layer on heated films, their ^{3}He release rates very rapidly approach those from unheated samples.

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