Response to reviewer two

Reviewer two has two major objections to our paper.
One, the filling of hydrogen traps under the experimental conditions and, two, the fact that hydrogen dilation near the crack tip can promote fracture rather than enhancing ductility as it has been observed to do in ceramics.

First, we address the “manifest misunderstanding of metal hydrogen interactions” the reviewer cites. The reviewer would be entirely correct in saying anything close to trap saturation is impossible under ordinary atmospheric conditions. We have corrected the paper to avoid giving the misimpression that ordinary atmosphere controlled the hydrogen fugacity, which as the reviewer correctly states, must be very high to cause trap filling. In our experiments hydrogen absorption occurred only when surfaces were actively undergoing the reaction between atmospheric water, chromium, and iron. The atomic hydrogen (enthalpy about 218 kJ/mol) produced in this reaction has been shown to enter the matrix (ref. 17). We observed that dilation only occurred when the surface oxide was forming. We further observed that the dilation slowly diminished when oxidation ceased. We cited none of this in the manuscript reviewer two reviewed and we have corrected the manuscript to reflect his objections. We feel that we are fully in accord with his point of view, that high hydrogen fugacity is indeed required for trap saturation and hope that he will agree that our experimental procedure provided that. Our original manuscript was wrong in our assertion that high hydrogen fugacity was not required for trap saturation. It is. Some of the corrected experimental procedures is shown below.

> “Both the 355 and 440A specimens were baked at 250 °C for two hours before any testing to remove most of the hydrogen. This temperature should remove deformation-produced vacancy clusters, while monovacancies should remain constant at a negligible level. The as-baked, low-hydrogen specimens were lightly sanded for several minutes with 600 grit material to remove the heat tint, whose thickness is less than one μm, thus causing negligible surface cold work. During the repeated surface abrasion, they were then allowed to react with water vapor in ambient air at 25 °C and 60% relative humidity (1.0% water vapor). Hydrogen absorption occurred during the abrasion and continued after abrasion until a full passive film formed. In the undeformed specimens, both 355 and 440A, hydrogen absorption is seen as a length change which continues until saturation. In deformed specimens, 355 only, deflections should be due to the variable absorption of hydrogen in the deformed section’s dislocation gradient. This volume expansion was calculated from the deflection. High binding energy traps such as vacancies, grain boundaries, and incoherent precipitates should show little change in hydrogen content over this temperature range (25–250 °C). Low binding energy traps such as coherent precipitates, though absent, should have negligible hydrogen content in this environment, so we can attribute all expansion to absorption of hydrogen by dislocations. However, we can measure the expansion effect of absorbed hydrogen on deformed material and impute a hydrogen concentration corresponding to an estimated dislocation density.” In the first experiment, undeformed 440A was de-

> hydrogenated by baking at 250 °C for four hours, quenched to room temperature, sanded to remove the heat-tint oxide, and allowed to equilibrate with ambient air as its change in length was monitored. The 440A specimens did not have sufficient surface chromium content to limit ambient corrosion, and red rust on the surface confirmed this.
>
> The same procedures were used on the 355 specimens, but with the added variable of deformation as produced by the special bending described above. Also, the 355 did have a passive film forming surface chromium level so repeated light abrasion was needed to produce saturating levels of hydrogen. The 355 specimens were also equilibrated at intermediate temperatures to observe the effect of lesser amounts of hydrogen removal based on the binding energy of dislocations. The expansion was compared to that which would be expected theoretically from reported experimental partial molar volumes, dislocation density, and trap filling percentage.

> And "In the first experiment, undeformed 440A was de-hydrogenated by baking at 250 °C for four hours, quenched to room temperature, sanded to remove the heat-tint oxide, and allowed to equilibrate with ambient air as its change in length was monitored. The 440A specimens did not have sufficient surface chromium content to limit ambient corrosion, and red rust on the surface confirmed this.
>
> The same procedures were used on the 355 specimens, but with the added variable of deformation as produced by the special bending described above. Also, the 355 did have a passive film forming surface chromium level so repeated light abrasion was needed to produce saturating levels of hydrogen. The 355 specimens were also equilibrated at intermediate temperatures to observe the effect of lesser amounts of hydrogen removal based on the binding energy of dislocations. The expansion was compared to that which would be expected theoretically from reported experimental partial molar volumes, dislocation density, and trap filling percentage."

Second, we address the second objection that hydrogen dilation at a crack tip in ferrous martensite should behave similarly to that seen in ceramics. The strain-induced diffusion of hydrogen to the triaxial zone of a ceramic, with assumed negligible ability to form dislocations, should by the logic we have used in our manuscript, cause the triaxial stress to be diminished. We agree fully with the reviewer. In the martensitic steels we studied the same effect would occur. The enthalpy of solution of hydrogen is decreased by the production of the partial molar volume of hydrogen multiplied by the hydrostatic stress. However, at a hydrostatic stress of three times the yield strength, the amount of hydrogen brought into solution in a 1000 MPa yield strength steel crack tip is still negligible. What is not negligible is the amount of hydrogen trapped by the dense array of dislocations which have been created in the fracture process zone, which is not centered on the point of maximum triaxial stress (PMT), but adjacent to it between the crack opening and the PMT. Lattice expansion in this location asymmetrically affects the stress state at the PMT. The dilation increases the shear stress at the PMT, a very different effect than the beneficial effect seen in ceramics. We have made abundant changes in the manuscript to better describe this phenomenon. We did not feel it desirable to lengthen the manuscript by citing analogous behavior, even after it was pointed out to us by reviewer two, although we are grateful for his insight. The section which describes this asymmetric stress created by hydrogen dilation is below:

### *4.2. Effect of hydrogen-induced dilation*

The experimental results are hardly a discovery; and although they are not generally mentioned in discussion of hydrogen embrittlement, they are elementary. We can apply what was learned from simple expansion of sheet samples and sheet samples deformed in plane strain to plane strain fracture toughness specimens where expansion effects can be quantified. The implications of the dilation on crack mechanics are nearly as straightforward, as we will now discuss. In terms of classical mechanics, the radius of the FPZ for a martensitic steel can be determined by Eq. 6, and can be represented schematically by Fig. 3A:

$$\delta = \frac{K^2}{E\,\sigma_{ys}} \tag{6}$$

where δ is the FPZ diameter, $K$ is the applied stress intensity, $E$ is the elastic modulus, and $\sigma_{ys}$ is yield strength.

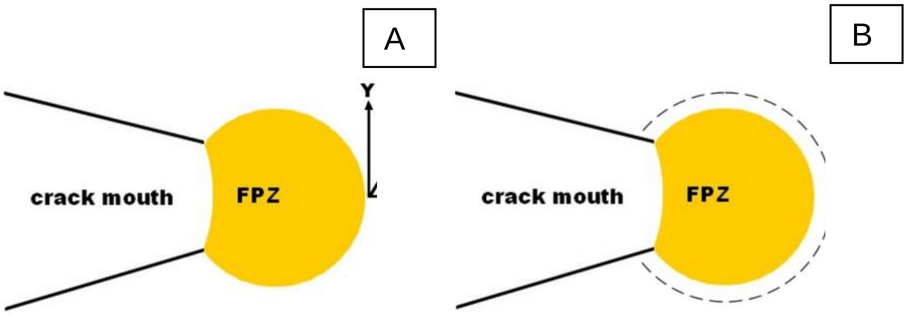

**Fig. 3. A)** Depictions of the fracture process zone (FPZ) region. All points in the FPZ except the free surface are in triaxial tension and the maximum is reached at the PMT where the coordinates are drawn. Deformation has ceased and stresses are in balance. B) Hydrogen has caused the FPZ to enlarge, as shown by a dashed line, thereby altering the stress state at the PMT.

The coordinates shown in Fig. 3A are located at the point of maximum triaxial stress (PMT) and serve as our reference system. As Eq. 5 indicates, increasing the crack mouth opening by increasing the load increases the size of the FPZ. However, the stress state at the PMT remains constant with ($\sigma_y - \sigma_x$) slightly above the yield strength. The value of $\sigma_y$, the y-direction stress at the point of maximum triaxial stress, is commonly approximated as three times the yield strength in steels [20]. Except for the surface of the blunted crack opening, the entire FPZ is in triaxial tension after load application and arrest. The formation of a triaxial stress resisting crack opening is characteristic of elastic/plastic materials and is seen when the z dimension is adequate to provide plane strain. The level of deformation is approximated to vary linearly in the x direction, so it is close to the base level of the surrounding matrix at the PMT and increases linearly from the PMT to the crack opening.

In an actual rising-stress fracture toughness test in the absence of hydrogen, a rising stress intensity increases the FPZ size until fracture begins at the crack tip by the same failure mode seen under plane stress conditions. The FPZ triaxial zone itself is a fundamental characteristic of elastic/plastic behavior. In thick specimen plane strain, resistance of the FPZ to volume expansion confines the deformation to a small zone, in contrast to a thin sheet where there is no constraint to lateral contraction and the deformation zone is much larger in extent for a given load per unit width. In the absence of hydrogen, in either the thin or thick specimen, failure occurs at the crack tip opening when the elongation limit of the material is reached at the crack tip surface. The triaxial stress state in the FPZ is mechanically precarious. It cannot tolerate a volume change in the FPZ without crack destabilization. The three orthogonal stresses are above the yield strength but are balanced so that plastic flow has stopped at crack arrest, leaving ($\sigma_y - \sigma_x$) everywhere in the FPZ above the yield strength. But by the Tresca flow criterion we know that if the algebraic sum of the maximum and minimum principal stresses ($\sigma_y - \sigma_x$) increases, plastic flow will resume. Now, it becomes obvious why we concern ourselves with hydrogen-induced expansion. The balance of stresses is established instantly with deformation, but after deformation hydrogen enters the FPZ to bind with the defects which the deformation has created. Expansion occurs, and the stress balance is lost. Our model characterizes how the crack responds to this destabilization.

Our focus is on the FPZ. If it expands relative to the volume around it, as depicted in Fig. 3B, stress states are altered. In a crack under stress any increase in the difference between $\sigma_y$ and either $\sigma_x$ or $\sigma_z$ will cause further deformation. Hydrogen expansion would provide that change in stress because the expansion occurs almost entirely between the crack tip surface and the PMT. This asymmetry of the hydrogen lattice expansion is key. How can we quantify the destabilization which would occur when the stress balance is altered? The FPZ itself can be considered an Eschelby zone [21]: a deformed zone nearly surrounded by a less-deformed matrix. This assumption simply allows us to approximate the interfacial stress component acting normal to the PMT in the x direction ($\sigma_H$), caused by the expansion of the FPZ lattice to be one half of the expansion volume strain times the bulk modulus, 160 GPa, according to [20]. The FPZ "pressurizes" with absorbed hydrogen and expands. The surrounding matrix recoils until the stress at the interface between the two is equal. So, at the PMT, which only borders the expanding FPZ Eshelby zone, the crack opening stress ($\sigma_y$) increase marginally because of the expansion of the FPZ, and some crack opening load is shifted beyond the PMT. The effect on $\sigma_z$. at the PMT is also negligible. The critical effect is on $\sigma_x$ because the addition of the compressive hydrogen expansion stress to the existing tensile $\sigma_x$ results in a net decrease in $\sigma_x$, increasing the difference between $\sigma_y$ and $\sigma_x$. Eq. 7 below expresses the relationship between hydrogen expansion stress and $\sigma_x$:

$$\sigma_x = \sigma_{xi} + \sigma_H \tag{7}$$

where $\sigma_x$ is the post-expansion stress acting on the PMT, $\sigma_{xi}$ is the pre-expansion stress, and $\sigma_H$ is the stress induced by the hydrogen expansion after the Eshelby factor has been considered. $\sigma_{xi}$ is tensile and approximately twice the yield strength while $\sigma_H$ is compressive and therefore causes a decrease in $\sigma_x$.

A small change means additional plastic flow and incremental crack mouth opening. A sufficiently large change will cause the difference between $\sigma_y$ and $\sigma_x$ to exceed the material's tensile strength. In this way it is possible for hydrogen to cause "embrittlement" with altering the inherent mechanical properties of the material. The recognition of the importance of the radial component of the expansion stress is the main factor of the hydrogen lattice dilation model, HLD.

Hydrogen does not need to cause huge stresses to cause plastic flow or even decohesion; it simply must marginally lower $\sigma_x$. The stress decrement required to cause decohesion is the difference between the yield strength and the tensile strength, since the PMT and the rest of the FPZ is on the verge of further yielding. Lesser reductions in $\sigma_x$ will not cause brittle failure but can cause enhanced plastic flow sufficient for failure.

The effects of hydrogen on the stress state define the proposed model, which we call the hydrogen lattice dilation model (HLD). It is nothing more than the dilation of the lattice due to hydrogen being absorbed after deformation by the defects formed during deformation. The stresses created by the hydrogen absorption can thus be superimposed on those of classical stress analysis without hydrogen present.