

# Titanium reactors for redox-sensitive hydrothermal experiments: An assessment of dissolved salt on $H_2$ activity-concentration relations

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## ABSTRACT

Fixed-volume titanium alloy hydrothermal reactors permit research into fundamental aspects of mineralogy and aqueous geochemistry at the T-P conditions encountered on the frontiers of submarine and terrestrial geothermal system exploration. The impressive mechanical strength of new titanium alloys facilitate studies involving fluids and minerals at conditions up to 500 °C and 50 MPa. The corrosion resistance of titanium is a well-known attribute that also allows experiments to be performed in acidic, NaCl-bearing aqueous fluids. Titanium, however, can suffer irreversible surface reactions in aqueous fluids at high temperatures that may produce or consume appreciable concentrations of dissolved hydrogen ( $H_{2(aq)}$ ), complicating the interpretation of redox processes in homogenous and heterogeneous chemical systems. Here we report results of hydrothermal experiments designed to examine the direction and magnitude of changes in dissolved  $H_{2(aq)}$  in deionized water and NaCl bearing aqueous fluid contained within a newly constructed Ti alloy (Ti-6242) reactor. The redox sensitivity of these and related experiments, however, required testing and assessing surface passivation involving pre-treatment with nitric acid at moderately high temperature. Results indicate that passivation procedures were required to render the Ti surface of the reactor unreactive in both low and high hydrogen-bearing fluid ( $H_2O$  and NaCl- $H_2O$  systems). Once passivated, experiments were then conducted at 400 °C to assess the effect of dissolved NaCl on dissolved  $H_{2(aq)}$  concentrations coexisting with the well-known HM (hematite-magnetite) redox buffer. These data indicate highly non-ideal activity-concentration relations for  $H_{2(aq)}$  in the NaCl bearing fluids. Accordingly, the common assumption of unity for the activity coefficient of dissolved  $H_{2(aq)}$  in hydrothermal fluids is not supported. The implications of this are important for accurate redox reconstruction for compositionally variable natural and experimental hydrothermal systems at elevated temperatures and pressures. The experimental strategy of monitoring the rate and magnitude of  $H_{2(aq)}$  production and consumption *in situ*, during on-going experiments, provides quantitative insight on the effectiveness of the passivation process and the usefulness of redox buffers in hydrothermal geochemical applications.

## 1. Introduction

Mineral oxygen buffers are frequently used in hydrothermal experiments at near critical and supercritical conditions to define oxygen fugacity, hydrogen fugacity, and aqueous hydrogen concentrations (Kishima and Sakai, 1984; Kishima, 1989; Ding and Seyfried Jr., 1992; Seyfried and Ding, 1995; Seyfried Jr. et al., 2007). The oxygen fugacity defined by mineral buffers affects the solubility of mixed valence metals such as iron and copper, data relevant to understanding metal cycling in sub-seafloor and terrestrial hydrothermal systems (Ding and Seyfried Jr., 1992; Seyfried Jr. and Ding, 1993; Seyfried Jr. and Ding, 1995; Stefánsson and Arnórsson, 2002; Foustoukos and Seyfried Jr., 2005; Seyfried Jr. et al., 2007).

Measured  $H_{2(aq)}$  concentrations in natural hydrothermal solutions can provide a powerful indicator of subsurface redox conditions where rock samples are difficult or impossible to acquire, and direct confirmation of the mineralogy is lacking. In using  $H_{2(aq)}$  measurements for this purpose, however, salting out effects on hydrogen concentrations are a necessary consideration. Existing data for  $H_{2(aq)}$  concentrations in equilibrium with HM or PPM assemblages for pure water (Kishima and Sakai, 1984; Kishima, 1989) and NaCl fluid (Ding and Seyfried Jr., 1990; Seyfried Jr. and Ding, 1993; Seyfried Jr. and Ding, 1995) were acquired using unreactive, flexible gold cell hydrothermal apparatus (Seyfried Jr. et al., 1979; Seyfried Jr. et al., 1987). While acquisition of experimental data beyond 400 °C and 40 MPa is possible using this approach, the volume of fluid contained within the cell and durability

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of the cell itself becomes limited at these conditions. At the same time, it is becoming increasingly clear from rock and fluid samples recovered from both subaerial and submarine hydrothermal systems (Von Damm et al., 2003; Friðleifsson et al., 2017; Friðleifsson et al., 2018; McDermott et al., 2018; Scheuermann et al., 2018) that temperature and pressure conditions that intersect the critical curve for the NaCl–H<sub>2</sub>O system are routinely achieved, underscoring the need for more reliable experimental apparatus, if phase equilibria at these conditions are to be investigated.

Fixed-volume titanium alloy reactors are increasingly used for hydrothermal experimentation, and have been tested to temperatures and pressures in excess of 500 °C and 50 MPa, respectively (Shmulovich et al., 1995; Pokrovski et al., 2008; Tagirov and Baranova, 2009; Rempel et al., 2012; Pester et al., 2015; Scheuermann et al., 2018). A potential limitation of using titanium alloys in contact with water at elevated temperatures, however, is that titanium dioxide (Eq. (1)) and titanium sesquioxide (Eq. (2)) form through metal oxidation and can produce significant hydrogen (Lu et al., 2000):



and



Conversely, titanium and its alloys can potentially adsorb hydrogen, particularly at elevated temperatures (Shih et al., 1988; Briant et al., 2002; Tal-Gutelmacher and Eliezer, 2005). Thus, persistent hydrogen production or consumption by titanium reaction in aqueous fluids can interfere with equilibrium between redox dependent aqueous species or mineral oxygen buffers, if appropriate precautions are not taken. In the case of a homogenous chemical system, changes in redox imposed by the reactor can have a highly deleterious effect on time series observations of the distribution of aqueous species. While researchers routinely treat titanium with citric or nitric acid to render it unreactive (Shmulovich et al., 1999; Pokrovski et al., 2008; Tagirov and Baranova, 2009), the effectiveness of the treatment has not been systematically evaluated. Here we show that titanium reactivity leads to H<sub>2(aq)</sub> concentrations that interfere with equilibration in both homogeneous and iron-mineral bearing heterogeneous chemical systems. Treatment with 20% nitric acid at 300 °C for 12 h inhibits or entirely precludes oxidative hydrolysis and hydrogen adsorption effects. Our results also demonstrate the importance of monitoring redox as a method to verify phase equilibria, even at elevated temperatures and pressures. Accordingly, the titanium metal pre-treatment we advocate provides a pathway to perform experiments aimed at exploring redox reactions and metal solubility at P–T conditions for which data are currently unavailable, with implications for better understanding fluid–rock interaction in the roots of submarine hydrothermal and terrestrial geothermal systems.

## 2. Methods

### 2.1. Apparatus

The design of the fixed volume (165 ml) titanium reactors and the experimental approach used in the present study has been described in detail previously (Pester et al., 2015; Scheuermann et al., 2018), and is illustrated in Fig. 1. Briefly, the reactors are constructed from a high-strength titanium alloy Ti-6Al-2Sn-4Zr-2Mo (Ti6242) that has been tested to temperatures and pressures as high as 500 °C and 50 MPa. All capillary lines (1/16" outer diameter) and other wetted parts that contact the fluid are constructed of grade 2 titanium. Capillary lines are connected to titanium fittings using gold-plated stainless-steel ferrules (Valco Instruments Co.) and high-pressure titanium metering valves (Parker Autoclave Engineers), which facilitate fluid sampling at experimental conditions. Temperature is monitored with a Ti-sheathed American National Standards Institute (ANSI) type E thermocouple that

is internal to the reactor, which provides input to three external heating bands through a time and power proportioning control system (988 series; Watlow Electric Manufacturing Co.). The thermocouple is calibrated before each experiment at the anticipated experimental temperatures using a dry block probe calibrator (Omega Hot Point®), which has confirmed accuracy within the theoretical limits of the type E thermocouple. Pressure is controlled up to a maximum of 51.7 MPa using a Teledyne ISCO syringe pump, which is separated from the reaction fluid with a 500 ml in-line titanium piston separator. A nickel-based anti-seize compound was applied to all metal surfaces that did not come in contact with the reactant fluid.

### 2.2. Titanium passivation

The passivation process was initiated at a temperature of 300 °C and pressure of 30 MPa while the reactor was filled with deionized water. The water was evacuated at a rate of 0.1 ml/min by reducing pressure to ~7.5 MPa (below the liquid-vapor saturation pressure of ~8.6 MPa) until 7.5 ml of H<sub>2</sub>O remained inside the reactor. The piston separator was then isolated from the experiment and filled with 20% w/w reagent grade nitric acid (HNO<sub>3</sub>). The separator was then reconnected to the experiment and pressure was increased to 10 MPa, allowing the concentrated HNO<sub>3</sub> to refill the titanium reactor at a flow rate set by the ISCO pump of 0.1 ml/min. Cooling was initiated after 8 h, and after 24 h the reactor was sufficiently cool to dismantle to remove the concentrated HNO<sub>3</sub>.

### 2.3. Sampling

Prior to collecting each sample, approximately 0.75 ml of fluid was removed to flush the capillary lines. Approximately 1 g of sample was then removed using a disposable syringe fitted with a gas-tight PTFE Mininert® valve (VICI Precision Sampling). Pressure was monitored during sampling to avoid decompression. Samples were diluted to 5 ml total volume at atmospheric pressure with ultra-high purity nitrogen gas. Hydrogen and carbon dioxide were analyzed using an Agilent Technologies 6890A gas chromatograph (GC) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. Calibration was achieved using commercial gas standards containing a 1% or 2% mixture of H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub> with the balance made of nitrogen. Tests performed by manually diluting the calibration standard yielded a relative standard deviation (% RSD) of 4% for H<sub>2</sub> and 6% for CO<sub>2</sub>. The detection limit was calculated as the concentration equivalent of 2 standard deviations of the peak area for n = 16 measurements of the calibration standard.

### 2.4. Homogenous chemical system

The effect of Ti oxidation on H<sub>2(aq)</sub> production was assessed in a homogenous chemical system, whereby H<sub>2(aq)</sub> produced from the reaction of pure deionized water with the surface of a new and previously unused titanium reactor was monitored for between 16 and 256 h. The experiment was performed isobarically at 30 MPa, while the reaction temperature was increased incrementally to 250, 300, 350 and 400 °C, conditions that fall in the single-phase liquid and supercritical regions of deionized water. The reactor surface was then passivated according to the procedure described previously, and H<sub>2(aq)</sub> was again monitored to test the effectiveness of the passivation procedure.

Following passivation of the titanium reactor, the reactor, piston separator, all capillary lines, fittings, and valves were thoroughly rinsed and flushed with deionized water. The experimental apparatus was then reassembled, the reactor was filled with deionized water, and post-passivation hydrogen production was monitored at 30 MPa and 250, 300, 350, and 400 °C. To verify that the passivation procedure was also effective for mitigating H<sub>2(aq)</sub> consumption, 18 mmol/kg of formic acid (HCOOH) was introduced to the nitric acid-treated reactor through the

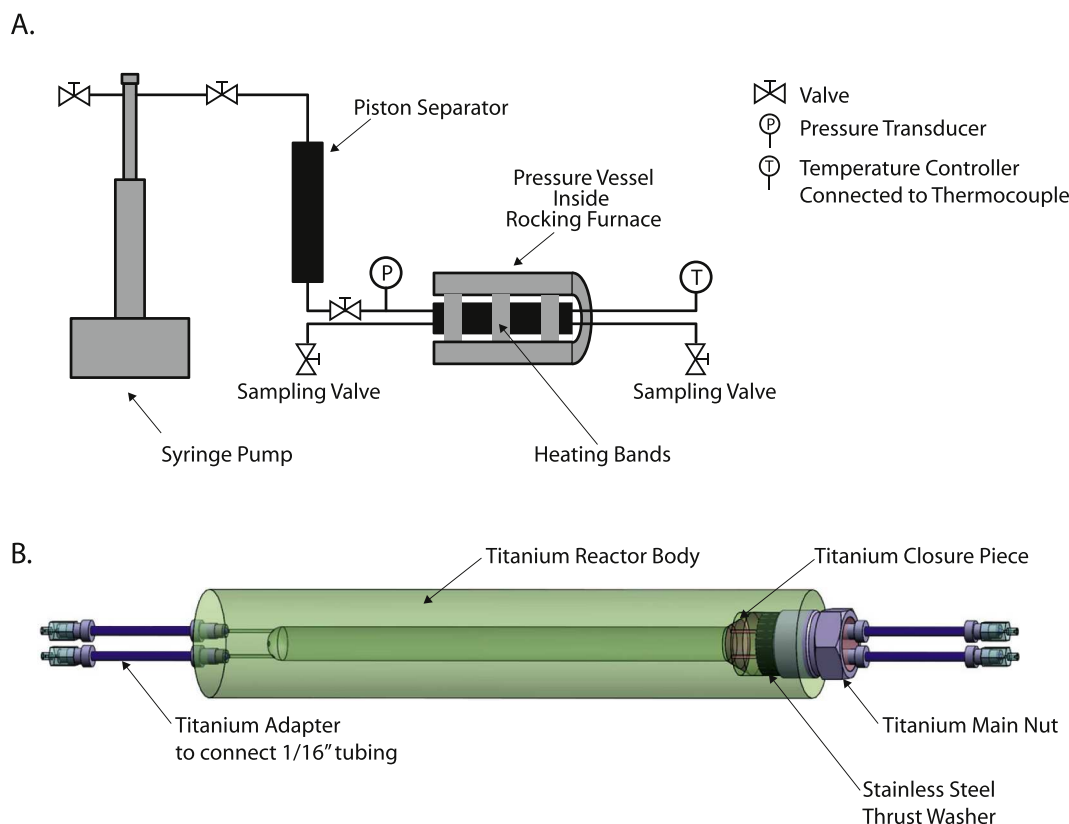


Fig. 1. A) Experimental configuration and B) technical illustration of the titanium reaction vessel, modified after Scheuermann et al. (2018) and Pester et al. (2015).

separator and the resulting carbon dioxide/hydrogen ratio was monitored at 30 MPa and 300 °C for 120 h.

### 2.5. Heterogeneous chemical system

The effect of reactor imposed redox conditions in the presence of a mineral redox buffer was assessed in a heterogeneous equilibria experiment at 400 °C, 45 MPa conducted in a second titanium reactor. In the second and un-passivated reactor, 5 g each of 400-mesh (< 38 μm) hematite and magnetite (Alpha Aesar) were combined under argon with a 640 mmol/kg NaCl solution. Hydrogen production in the experiment was monitored for 480 h. Subsequently, the reactor was disassembled, thoroughly cleaned, and passivated with nitric acid, as previously described, then re-assembled with the same mineral-fluid reactants, while dissolved  $H_{2(aq)}$  was again monitored, in this case for a duration of 336 h.

## 3. Results

### 3.1. Homogenous chemical system

Reaction of the un-passivated reactor with water resulted in a sharp and noteworthy increase in dissolved  $H_{2(aq)}$ , in keeping with oxidation of the unprotected titanium surfaces internal to the reactor. Dissolved  $H_{2(aq)}$  increased with reaction progress and temperature, achieving a value of 4.32 mmol/kg at 400 °C and 30 MPa after a total reaction time of 256 h (Table 1 and Fig. 2).

The high  $H_{2(aq)}$  concentrations achieved, however, motivated the second experiment in the homogenous chemical system in which formic acid was added as a reactant to the now passivated reactor. The decomposition of formic acid to its constituent components ( $H_{2(aq)}$  and  $CO_{2(aq)}$ ), occurs spontaneously and irreversibly at temperatures in excess of 250 °C to stoichiometrically equivalent concentrations of

Table 1

$H_2$  produced from titanium oxidation by pure water.

Cumulative time (hours)	T (°C)	P (bar)	$H_2$ (mmol/kg)
Pre-passivation			
16	250	300	0.14
64	300	300	0.51
112	300	300	0.80
136	350	300	1.28
160	350	300	1.72
184	400	300	3.00
256	400	300	4.32
Post-passivation			
16	250	300	< 0.13
40	250	300	< 0.07
64	300	300	< 0.08
136	300	300	< 0.08
160	350	300	< 0.07
184	350	300	< 0.07
208	400	300	< 0.06
232	400	300	< 0.07
Formic acid addition			$CO_2/H_2$
72	300	300	1.0
96	300	300	1.0
120	300	300	1.0

hydrogen and carbon dioxide (Yu and Savage, 1998; McCollom and Seewald, 2003), providing a source of dissolved  $H_{2(aq)}$ :



Continued  $H_{2(aq)}$  production by the reaction of Ti alloy with water would decrease the  $CO_2/H_2$  ratio, which by virtue of Eq. (3) should be unity if no continued reaction were to occur. Likewise, consumption of hydrogen by metal absorption should increase the  $CO_2/H_2$  ratio. Following introduction of HCOOH to the reactor, the  $CO_2/H_2$  ratio remained at unity, indicating that the reactor surface was rendered inert

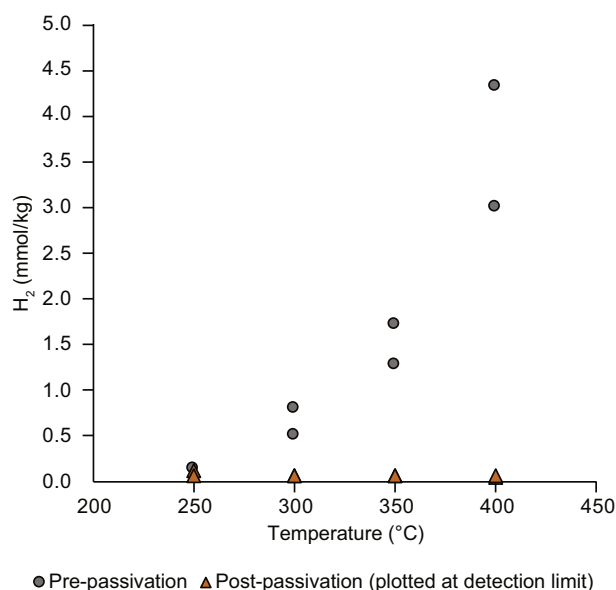


Fig. 2. Analytical results for dissolved hydrogen production from the reaction of titanium alloy with water before and after passivation using 20% nitric acid at 300 °C for 12 h.

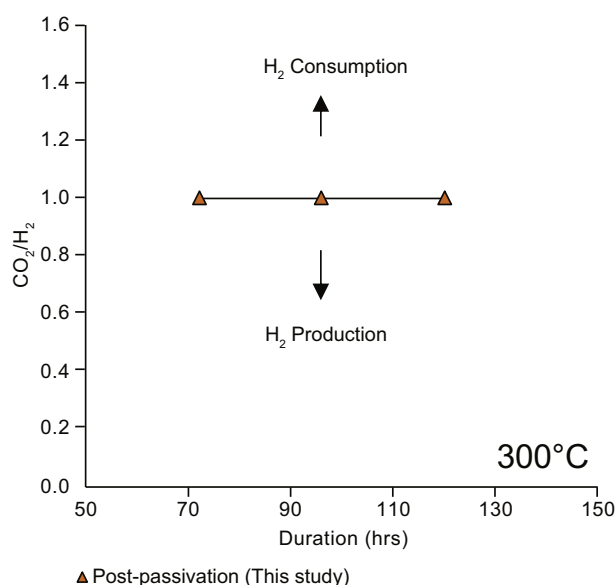


Fig. 3. Analytical results for the carbon dioxide/hydrogen mole ratio following passivation of a titanium reactor using nitric acid and the addition of formic acid. Hydrogen production by oxidation of titanium metal would result in a  $\text{CO}_2/\text{H}_2$  ratio less than unity, while hydrogen consumption by metal embrittlement would result in a  $\text{CO}_2/\text{H}_2$  ratio greater than unity. Following treatment of the reactor with nitric acid, the  $\text{CO}_2/\text{H}_2$  ratio resulting from addition of formic acid remained stable at unity (e.g. McCollom and Seewald, 2003).

(Table 1 and Fig. 3). This result shows that Ti alloy in the hydrothermal reactor was effectively passivated, and that neither a sink nor source of  $\text{H}_{2(\text{aq})}$  existed subsequent to the treatment process (Table 1 and Fig. 2).

### 3.2. Heterogeneous chemical system

In the HM buffered experiment at 400 °C and 45 MPa using an untreated Ti reactor and a 640 mmol/kg NaCl solution,  $\text{H}_{2(\text{aq})}$  concentrations remained low and did not achieve a steady state, even after 480 h

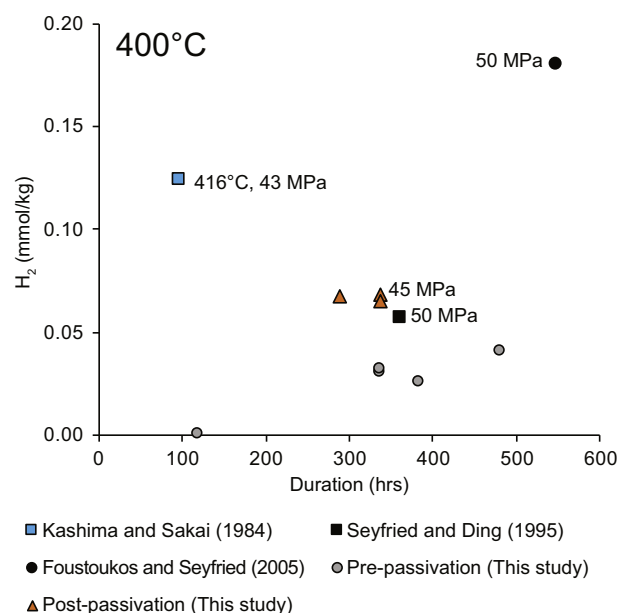
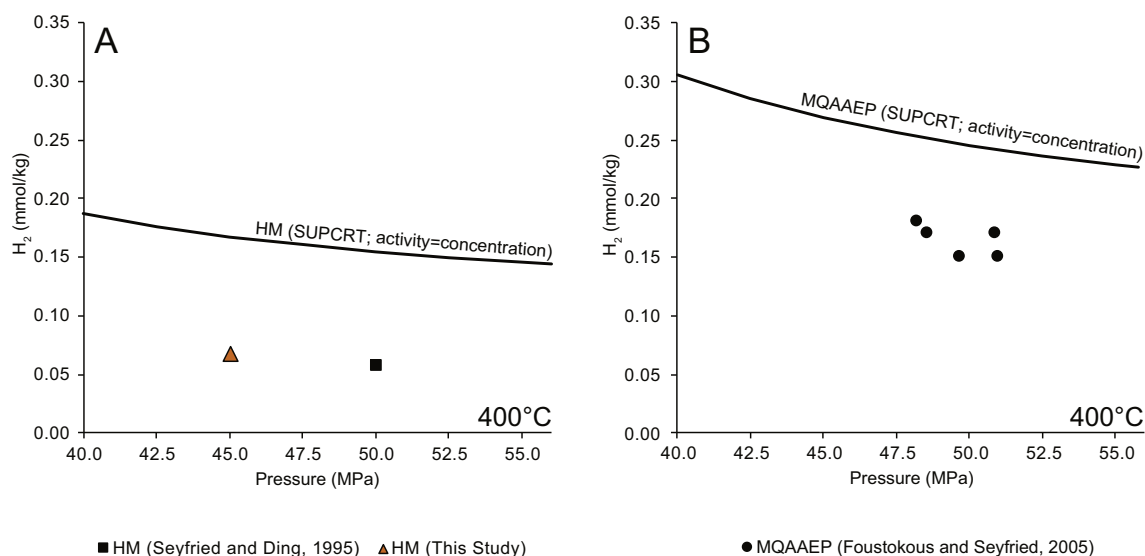


Fig. 4. Coexisting aqueous hydrogen concentrations in hematite-magnetite (HM) buffered experiments at various pressures and at 400 °C (unless otherwise specified). Shown on the figure are results for pure water in a flexible gold cell reactor (Kishima and Sakai, 1984), for a 550 mmol/kg NaCl brine in a flexible gold cell reactor (Seyfried Jr. and Ding, 1995), and 640 mmol/kg NaCl brine before and after nitric acid passivation of a titanium reactor (present study). For reference, results from a more reducing magnetite-bornite-anhydrite buffered experiment using a 640 mmol/kg NaCl brine are given (Foustoukos and Seyfried Jr., 2005). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2  
Hematite-Magnetite analytical results (640 mM/kg NaCl solution).

Cumulative time (hours)	T (°C)	P (bar)	H <sub>2</sub> (mmol/kg)
Pre-passivation			
120	400	450	< 0.06
336	400	450	0.030
336	400	450	0.032
480	400	450	0.040
384	400	450	0.025
Post-passivation			
288	400	450	0.067
336	400	450	0.068
336	400	450	0.065

of reaction time (Fig. 4 and Table 2). Following passivation, however,  $\text{H}_{2(\text{aq})}$  concentrations remained stable and achieved comparable concentrations to those obtained using the flexible gold cell reactor at similar P-T-X conditions (Seyfried Jr. and Ding, 1995) (Fig. 4 and Table 2). Dissolved  $\text{H}_{2(\text{aq})}$  concentrations, however, are notably lower than indicated for HM-pure water equilibria, when compared with experimental (Kishima and Sakai, 1984) and theoretical (SUPCRT92) data (Johnson et al., 1992) at similar temperature and pressure conditions (Fig. 4). Thus, we interpret these results to not only indicate effective passivation of the Ti reactor, but also to confirm the existence of non-ideal activity-concentration relations for dissolved  $\text{H}_{2(\text{aq})}$  imposed by high dissolved NaCl in equilibrium with the HM redox buffer (Fig. 5a). Importantly, this result demonstrates the passivated titanium apparatus is suitable for reproducing previous HM redox equilibria in NaCl solutions, and provides a pathway for expanding experimental calibrations of heterogeneous redox equilibria in NaCl solutions at more extreme P-T conditions.



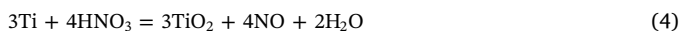
**Fig. 5.** Aqueous hydrogen ( $H_{2aq}$ ) concentrations in mineral buffered experiments conducted at 400 °C (unless otherwise specified) using A) hematite-magnetite (HM) and B) magnetite-quartz-anorthite-anhydrite-epidote-pyrite (MQAAP). Theoretical predictions for HM and MQAAP buffered  $H_{2aq}$  concentrations at various pressures, that assume activity = concentration, based on the SUPCRT database (Johnson et al., 1992) are shown for reference. Data for HM buffered experiments from Kishima and Sakai (1984) and Seyfried and Ding (1995b); data for MQAAP buffered experiments from Foustoukos and Seyfried Jr. (2005).

#### 4. Discussion

Use of a Ti-alloy hydrothermal reactor with improved process controls provides the necessary temperature and pressure stability to perform hydrothermal experiments in the low-density and supercritical regions of water. The lack of experimental data for these conditions effectively precludes prediction of the geochemical evolution of hydrothermal fluids issuing from vent sites on the seafloor, where evidence exists suggesting high temperatures and correspondingly elevated concentrations of hydrogen and redox-sensitive dissolved metals (i.e., Mid Cayman Rise (McDermott et al., 2018) and 9° 50' N on the East Pacific Rise (Pester et al., 2014)).

While the physical properties of Ti-alloys are suitable for experimentation at sufficiently high pressure-temperature conditions to provide the requisite experimental data, a critical drawback is the persistent production of dissolved hydrogen, obfuscating results of experiments sensitive to oxygen fugacity. Such oxidation of Ti by water at temperatures above 175 °C continues to produce a surface layer of  $TiO_2$  and  $Ti_2O_3$  even after several reaction cycles (Lu et al., 2000). The levels of hydrogen produced by titanium oxidation in the course of the present study would have a profound effect on the aqueous speciation of redox sensitive elements. Furthermore, the competing effects of what are essentially two redox buffers would produce a dynamic state, facilitating formation of metastable minerals, while inhibiting an overall approach to equilibrium.

Titanium oxidation and  $H_2$  production can be effectively eliminated by “passivating” the Ti-alloy reactor, a chemical process used to remove surface impurities from the surface of metals and accelerate the formation of an inert oxide layer to improve chemical resistance (e.g. ASTM Standard F86-13, 2018). Rather than a mixture of  $TiO_2/Ti_2O_3$  that forms in less oxidizing conditions (Schutz and Covington, 1981), nitric acid-based passivation of Ti alloys forms a thick rutile surface along with oxides of the alloying elements: (Sittig et al., 1999):



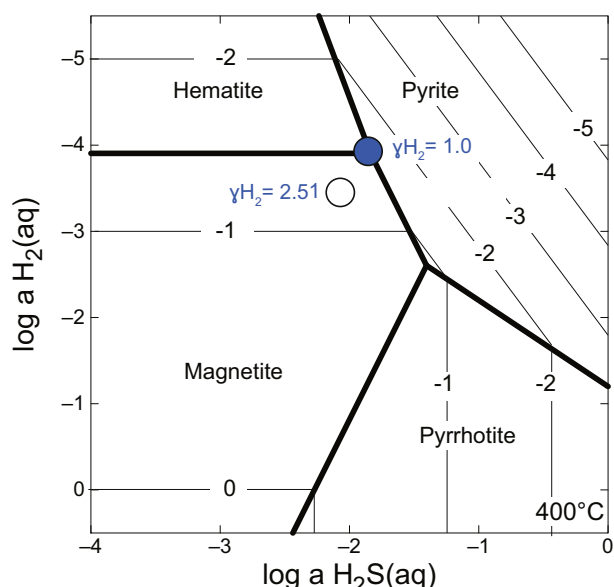
The resulting crystalline  $TiO_2$  (rutile) surface is essentially inert and significantly reduces hydrogen absorption by titanium (Schutz and Covington, 1981; Shankar et al., 2013). The results of the present study show that the oxide coating produced by nitric acid passivation provides a protective layer on titanium that significantly, if not completely,

reduces hydrogen production, a requisite condition if the titanium reactor is to be used for redox studies at elevated temperatures and pressures.

We further demonstrate the importance of titanium passivation from the apparent lack of equilibrium of the 640 mmol/kg NaCl with the HM redox buffer at 400 °C and 45 MPa (Fig. 4). Once passivated, however, reproducible results were obtained that were largely in keeping with analogous data using gold cell technology at a similar temperature and pressure. That the passivated Ti-reactor and gold cell data yield similar results at similar chemical and physical conditions, effectively serves as a calibration, justifying application at still higher temperatures and pressures, where the gold cell system is less suitable and where the need for experimental data is great.

Assuming equilibrium in the NaCl fluid-HM experiment, results confirm the strong effect of dissolved salt on mineral buffered  $H_{2(aq)}$  concentrations. Theoretical predictions assuming  $\gamma = 1$  for an HM buffered system at 400 °C and a relevant pressure range using the SUPCRT database (Johnson et al., 1992), yield an  $H_{2(aq)}$  concentration of 0.167 mmol/kg at 50 MPa (Fig. 5a). The predicted  $H_{2(aq)}$  concentration is notably higher than experimentally determined  $H_{2(aq)}$  concentrations buffered by HM in the NaCl- $H_2O$  system. Indeed, by comparing the  $H_{2(aq)}$  concentration calculated from SUPCRT data (assuming  $\gamma = 1$ ) for the HM system to our experimental results, and assuming the algorithm used to extrapolate the SUPCRT thermodynamic data to the experimental conditions is valid, an activity coefficient of  $\gamma = 2.51$  is indicated. Non ideal activity-concentration relations for dissolved  $H_2(aq)$  in NaCl bearing fluids are also apparent for the more reducing magnetite-quartz-anorthite-anhydrite-epidote-pyrite (MQAAP) redox buffer (Foustoukos and Seyfried Jr., 2005), in keeping with data from the present study (Fig. 5b). Thus, assuming an activity coefficient of unity for dissolved  $H_{2(aq)}$  in natural or experimental systems at elevated temperatures, pressures and total dissolved chloride, can result in misleading interpretation of phase equilibria controls (Fig. 6), especially at temperatures in excess of 400 °C, where experimental data are presently lacking. The high dissolved  $H_{2(aq)}$  concentrations (~19.9 mmol/kg) recently reported for hydrothermal fluids issuing from Beebe vent at Mid-Cayman Rise, for example, have been interpreted to indicate control by a relatively oxidizing alteration mineral assemblage at a temperature in excess of 500 °C (McDermott et al., 2018). This inference, however, assumes ideality ( $m_{H_2} = a_{H_2}$ ),





**Fig. 6.** Fe solubility contours in mol/kg (thin solid lines) superimposed on a hematite, pyrite, magnetite, pyrrhotite mineral stability diagram, plotted as a function of log activity  $H_2(aq)$  and log activity  $H_2S(aq)$  at 400 °C, 50 MPa, pH 4.5, 1.0 mol/kg NaCl; solid lines indicate mineral stability boundaries. Data was extrapolated to the specified conditions using the SUPCRT database modified using the DB Create software (Kong et al., 2013) and processed using Geochemists' Workbench. The blue circle indicates the  $H_2(aq)$  and  $H_2S(aq)$  concentration buffered by a hematite-magnetite-pyrite (HMP) assemblage and assuming ideality (activity = molality). The white circle shows how the effect on the previous point when an activity coefficient for  $H_2$  of 2.51 is considered. A similar  $\gamma$  for  $H_2S$  is assumed for simplicity, although in reality the magnitude of the salting out effect is less for  $H_2S$  (Ding and Seyfried Jr., 1990). This example serves to illustrate that ignoring an activity coefficient correction of this magnitude at the modeled conditions would underestimate the Fe concentration by > 35% and lead to misinterpretation of the buffering mineral assemblage. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which is almost certainly not the case, underscoring the need to consider the role of more reducing assemblages on the composition of the vent fluids.

## 5. Conclusions

Experimental calibration of activity coefficients for  $H_{2(aq)}$  is required to accurately predict mineral-fluid buffering assemblages in natural systems based on dissolved gas concentration data. Existing experimental apparatus, however, is limited by its durability at requisite physical and chemical conditions. Titanium hydrothermal reactors provide a means to accomplish this, although deleterious redox reactions between titanium and coexisting fluid and minerals can represent a serious impediment to the full range of applications possible. Nitric acid treatment of Ti-alloy renders the surface of titanium inert, facilitating performance of redox sensitive experiments involving both homogeneous and heterogeneous chemical systems. Once passivated, dissolved  $H_{2(aq)}$  monitored during equilibria involving hematite-magnetite-NaCl (0.64 m/kg) coexistence at 400 °C (45–50 MPa) is shown to be in excellent agreement with analogous data acquired from experiments using gold reaction cell technology, where internal redox reactions can be ruled out. These data lend confidence to the use of passivated Ti reactors for experiments at even more challenging conditions. Moreover, data from these experiments indicate highly non-ideal activity-concentration relations for  $H_{2(aq)}$  in the NaCl bearing fluids. Accordingly, the common assumption of unity for the activity coefficient of dissolved  $H_{2(aq)}$  in natural hydrothermal fluids is not supported.

The implications of this are important for accurate redox reconstruction for compositionally variable natural systems, such as the Mid Cayman Rise, where some of the most extreme hydrothermal conditions have been encountered thus far.

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