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Water Radiolysis and Chemical Production Rates Near Solid-Water Boundaries

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WATER RADIOLYSIS AND CHEMICAL PRODUCTION
RATES NEAR SOLID-WATER BOUNDARIES

BY

MARY ELIZABETH DZAUGIS

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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IN
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DOCTOR OF PHILOSOPHY DISSERTATION
OF
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ABSTRACT

Water radiolysis is the dissociation of water molecules by ionizing radiation from the decay of radionuclides. Primary products of water radiolysis include reactive chemicals, such as H_2 and H_2O_2 . For this reason, radiolysis is studied in many domains, including nuclear waste, microbiology and planetary evolution. In order to understand the importance of radiolysis in many of these environments, accurate quantification of radiolytic production rates is vital. In this dissertation, I present a new quantitative model calculating radiolytic production rates at solid-water interfaces and apply it to understand the role that radiolysis plays in various environments.

This radiolytic model is the first to explicitly calculate radiolytic production due to α -, β - and γ -radiation near solid-water interfaces. We use this model to investigate the effects of radiolytic compounds on the dissolution rate of spent nuclear fuel. The production of rate of H_2 and H_2O_2 , which control the dissolution rate of the fuel, depends on the amount and type of radiation surrounding breached nuclear spent fuel rods. Understanding the distribution of radiolytic products is important in assessing different hazards associated with spent fuel storage and the potential release of radionuclides into the environment. We find that in old (1000-year-old) spent fuel α -radiation dominates radiolysis, while β - and γ -radiation control the production rates near young (20-year-old) spent fuel.

Radiolysis also is an important process in understanding the extent of life on Earth, as well as possibly providing a means for life on Mars. We investigate the significance of water radiolysis in sustaining microbial communities in Earth's oceanic crust and the potential extent of radiolysis in wet martian environments (such

as the ancient martian surface and the present martian subsurface). These two studies focus specifically on the production of radiolytic H₂ as an electron donor. H₂ is an important source of energy in these two environments where there other resources for microbes are limited. In the oceanic basaltic aquifer of the South Pacific Gyre, we find that radiolytic H₂ production yields depend largely on the width of fractures in basalt and on radionuclide concentrations. We show that in old seafloor (>10 Ma), where there are no other readily available electron donors, radiolytic H₂ may dominate and is able to support up to 10³ cells in the water adjacent to a square cm of basaltic fracture.

The extent of water radiolysis on Mars can be determined for water-saturated martian environments, such as the ancient martian surface or the present martian subsurface. Using the fractured rock radiolytic model as well as a previously developed sediment radiolytic model, we calculate potential H₂ production rates for eleven martian lithologies assuming contact with water. The highest rates on Mars are for water-saturated material with the radionuclide concentrations of Acidalia Planitia, a region with surface materials that are enriched in uranium and thorium. We also calculate production rates for the eight proposed Mars 2020 landing sites, assuming water-saturated porosity. Radiolytic H₂ production rates calculated for wet martian sediment and water-filled microfractured rock are comparable to the range of rates calculated for Earth's South Pacific basement basalt which is known to harbor low concentrations of microbial life.

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PREFACE

The following dissertation examines and quantifies the role that radiolysis plays in various environments. This dissertation is written in manuscript format and is comprised of the following three manuscripts:

The first manuscript, “A quantitative model of water radiolysis and chemical production rates near radionuclide-containing solids”, describes a mathematical model that calculates chemical production rates due to interaction of radiation for a radionuclide-containing solid and water. The model can be applied to various environments and we use it to assess the potential hazards associated with spent fuel storage, including dissolution of spent fuel pellets and the subsequent release of radionuclides into the environment. This manuscript was published in *Radiation physics and chemistry* in October 2015.

The second manuscript, “Radiolytic hydrogen production in the subseafloor basaltic aquifer” was published in *Frontiers in Microbiology* in February of 2016. In this manuscript, we examine the potential importance of radiolytic hydrogen production to microbial communities in subseafloor basalt. We determine that in basalt greater than 10 million years old, radiolytic hydrogen appears likely to be the most important source of energy for microbes in the basalt aquifer.

The third manuscript focuses on the habitability of Mars. This manuscript, “Radiolytic H₂ production in Martian environments” investigates potential radiolytic H₂ rates in wet martian environments (e.g., the ancient martian surface and the present martian subsurface) and compares the rates to previously calculated terrestrial radiolytic rates. We plan to submit this manuscript to *Astrobiology* in Fall 2016.

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MANUSCRIPT I

A quantitative model of water radiolysis and chemical production rates near radionuclide-containing solids

By

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Abstract

We present a mathematical model that quantifies the rate of water radiolysis near radionuclide-containing solids. Our model incorporates the radioactivity of the solid along with the energies and attenuation properties for alpha (α), beta (β), and gamma (γ) radiation to calculate volume normalized dose rate profiles. In the model, these dose rate profiles are then used to calculate radiolytic hydrogen (H_2) and hydrogen peroxide (H_2O_2) production rates as a function of distance from the solid-water interface. It expands on previous water radiolysis models by incorporating planar or cylindrical solid-water interfaces and by explicitly including γ radiation in dose rate calculations. To illustrate our model's utility, we quantify radiolytic H_2 and H_2O_2 production rates surrounding spent nuclear fuel under different conditions (at 20 years and 1000 years of storage, as well as before and after barrier failure). These examples demonstrate the extent to which α , β and γ radiation contributes to total absorbed dose rate and radiolytic production rates. The different cases also illustrate how H_2 and H_2O_2 yields depend on initial composition, shielding and age of the solid. In this way, the examples demonstrate the importance of including all three types of radiation in a general model of total radiolytic production rates.

Keywords: Water radiolysis; Mathematical model; Dose rate; Hydrogen; Hydrogen peroxide; Spent nuclear fuel

1. Introduction

Water radiolysis is the dissociation of water molecules by ionizing radiation. Primary products of water radiolysis include several chemical species: e_{aq}^- , $HO^\bullet$, $H^\bullet$, $HO_2^\bullet$, H_3O^+ , OH^- , H_2O_2 and H_2 (Le Caër, 2011; Spinks and Woods, 1990). Given the potential reactivity of these primary products, water radiolysis is of interest in studies of many domains, including nuclear reactors (Burns et al., 2012), spent nuclear fuel (Jonsson et al., 2007), early Earth history (Draganic et al., 1991), and microbiology (Blair et al., 2007; Lin et al. 2005; Pedersen, 1996). In order to understand the importance of water radiolysis in these and other domains, accurate quantification of chemical production rates by radiolysis is vital. We present a new model to quantify the extent to which radiolysis occurs in water at phase boundaries where radioactive elements are present in a solid phase.

Multiple previous studies have examined product formation by water radiolysis at the interface between solids and water (e.g., Buck et al., 2012; Jonsson et al., 2007; Nielsen and Jonsson, 2006). In general, these studies have examined radiolysis associated with spent nuclear fuel. Experiments and kinetic modeling have focused on the impact of environmental parameters (such as pH, NaCl concentration and groundwater chemistry) on radiolytic production rates (Bruno et al., 2000; Ershov and Gordeev, 2008; Jonsson, 2012). Nielsen and Jonsson (2006) developed a geometric model that provides time extrapolations (100 y to 100 ky) of dose rates due to α and β radiation. Buck et al. (2012) used their model to examine how changing conditions, such as carbonate chemistry, brine concentration, and gas concentrations, affect the redox systems in water repositories.

Our study provides a general quantitative model for calculating radiolytic production rates as a function of distance from the solid-water interface. Our model differs from previous models in several respects. It differs from the models of Nielsen and Jonsson (2006) and Buck et al. (2012) by explicitly accounting for energy attenuation of α , β and γ radiation. It differs from the model of Nielsen and Jonsson (2006) by including γ radiation and by calculating the contribution from all radiation to the total absorbed dose. Our model also differs from previous models by explicitly considering both planar and cylindrical phase boundaries (previous models assumed planar boundaries) and by accounting for the extent of shielding material that surrounds a radioactive solid phase.

Here, we present the model and apply it to an example of spent nuclear fuel to highlight how the distributions of radiation-specific volume normalized dose rates and radiolytic production rates vary as a function of distance. In our example, we focus on radiation dose profiles and radiolytic H_2O_2 and H_2 production profiles around spent fuel before and after barrier failure.

2. Methods

Each type of radiation, α , β and γ , has different radiolytic product yields. In addition, each follows a different attenuation law because α and β radiation behave as charged particles, while γ -rays have no charge or mass. Consequently, we use similar methods to calculate volume normalized dose rates for both α and β radiation, and a somewhat different method for γ radiation. (Throughout the remainder of this paper we refer to “volume normalized dose rate” simply as “dose rate”.) We first present our equations for calculating the dose rate of charged particles and then present the

equations and additional geometric conditions needed to account for γ radiation. We then calculate radiolytic production rates based on the dose rate profiles.

2.1 Radiant flux and dose rate for α and β radiation

Nuclei emit α particles with specific kinetic energies, while β particles have a continuous spectrum of energies. Both α and β particles are emitted isotropically (Spinks and Woods, 1990). To assess the contribution of β particles, we take the average initial energy for each β decay as 1/3 of the maximum energy (L'Annunziata, 2007). Stopping distance (R_{stop}) is the maximum distance traveled by charged particles; it is determined by initial energy and matrix composition (L'Annunziata, 2007). Since the distance traveled by charged particles in solids is relatively small, most solid-water interfaces can be assumed to be planar for α or β particles. For our study, if the stopping distance is less than the radius of curvature, we assume a planar boundary. If a radionuclide within the solid is at a greater depth from the surface than R_{stop} , then the charged particle will not reach the solid-water interface. While 50% of the charged particles emitted by radionuclides located at the solid-water interface are directed into the water.

Determination of the total radiation energy reaching the water per area per time [the radiant flux density (F)] depends on

- power (P),
- irradiance (I), and
- attenuation (a).

Here, power (P) is the initial energy per unit time per solid angle associated with the radiation (kinetic energy for alpha and beta). It is determined by the decay energy

and activity of each radionuclide. We calculate power for individual α and β particles by multiplying the radionuclide activity (A) for each radionuclide (i) by the initial radiation energy (E_0) per decay (j) of the same radionuclide and dividing by 4π steradians (eq. 1),

$$P(i, j) = \frac{A_i * E_{0(i, j)}}{4\pi} \quad (1)$$

The magnitude of F depends on the flux of radiant energy, P , per unit area (the irradiance, I). How much radiation reaches the water depends on the particle's path to the solid-water interface. We assume the path is linear over the projected range along the initial travel direction. The irradiance (eq. 2) for each particle is determined by the angle of incidence (δ) and the inverse square of the distance traveled (R) (Fig. 1).

$$I(i, j) = \frac{\cos \delta}{R_{(i, j)}^2} \quad (2)$$

For both α and β particles, linear energy transfer (LET), energy attenuation per distance traveled, increases toward the end of the particle's path. We derive the energy remaining (E_R) at distance R and the attenuation formula from eq. 3, which is a simplification of an equation developed by Bethe and Ashkin (1953). Bethe's equation describes the relationship between energy and range of charged particles (Friedlander, 1964).

$$\frac{dE}{dR} \cong -\frac{d}{E} \quad (3)$$

The attenuation (a) is

$$a(i, j) = \frac{E_R}{E_0} = \left(1 - \frac{R}{R_{\text{stop}}}\right)^{\frac{1}{b}} \quad (4)$$

where, d and b are constants (eq. 3&4). In the examples we present, the values for b and R_{stop} are both determined using the experimental energy and range data from the ASTAR and ESTAR NIST databases (Berger et al., 2005) as well as the Range and Stopping Power application in Nucleonica (Nucleonica GmbH, 2014a). Although b has a value of 2 from Bethe's equation, experimentally its value varies. At lower initial energies, the dependence on energy is more closely proportional to $E^{3/4}$, whereas at higher energies, it is better approximated by E^2 (Alfassi and Peisach, 1991). To calculate b , we plot the energy versus projected range in log-log coordinates over the range of energies observed from the radioactive elements. The resulting slope is the value we use for b (Table A.2). We also determine R_{stop} values using the energy-range data. The stopping distance depends on the initial energy of the particle and where in the path the charged particle crosses the solid-water interface. Multiple attenuation equations are used in the integration to account for the change of b values in different materials (see appendix for a more detailed discussion).

Combining equations for P , I , and a , and integrating throughout the radionuclide-containing solid, we calculate the total radiant flux density ($F_{\alpha,\beta}$). We sum over each radionuclide for all α and β decays with a unique E_0 for the total radiant energy flux per radionuclide. We then sum the total radiant energy flux of all radionuclides to give the total radiant flux density,

$$F_{\alpha,\beta} = \sum_i \sum_j \int_0^{2\pi} \int_0^{R_{\text{stop}}} \int_0^{z_{\text{max}}} P(i,j) * I(i,j) * a(i,j) * z * dz * dx * d\theta \quad (5)$$

where, z_{max} depends on stopping distance and the distance of the radionuclide from the surface (see eq. A1.9 for expanded form). At any distance in the water from the surface, we calculate the absorbed dose rate ($D_{\alpha,\beta}$), based on F from eq. 5. In our

model, the absorbing volume is the water surrounding the solid. At any distance in the water, the average dose rate is equal to the radiant flux density divergence from solid-water interface divided by the distance in water.

2.2 Radiant flux and dose rate for gamma rays

We use similar methods to calculate the flux and dose rate for γ radiation. Gamma ray absorption, however, obeys an exponential law (the Beer-Lambert law) (eq. 6) characterized by an attenuation coefficient (μ).

$$a_{\gamma}(i, j) = \frac{P_{R_{\gamma}}}{P_0} = e^{-\mu R_{\gamma}} \quad (6)$$

Attenuation coefficients are available for a wide range of elements and composite materials in the NIST X-ray Attenuation database (Hubbell and Seltzer, 2004).

Different attenuation coefficients are used for each material through which γ -rays pass. In the appendix, we describe in detail how this is incorporated into the model. The ability of γ -rays to penetrate a specific matrix can also be described in terms of half-distances. The half-distance, $x_{1/2} = 0.693/\mu$, is the thickness of material required to reduce the initial energy flux by one half (L'Annunziata, 2007). After 10 half-distances, slightly less than 0.1% of the initial radiation energy remains. To make sure that essentially all radiation is accounted for, we use 10 half-distances and operationally call this distance the maximum γ distance, $R_{\text{stop},\gamma}$.

Gamma rays have a smaller LET than charged particles. Consequently, their penetrating distance in a matrix is greater than α and β particles. The greater penetrating distance of γ radiation complicates modeling the radiolytic γ flux because possible curvature of the solid-water interface needs to be considered. Curved interfaces are often relevant for radiolysis studies. For example, spent nuclear fuel is

typically a cylindrical pellet. For this study, we use cylindrical interface geometry when the radius of the cylinder is less than or equal to the maximum penetrating distance of the radiation. At these values, at least 20% of the radiation is not included in the radiant flux density calculations if a planar boundary rather than cylindrical is assumed.

Using a cylindrical solid-water boundary, the geometry changes the calculation of the γ -ray distance traveled, R_γ (Fig. 2, eq. 7). We give the expansion of eq. 7 in the appendix (eq. A2.4).

$$F_\gamma = \sum_i \sum_j \int_0^{2\pi} \int_0^{R_{stop\gamma}} \int_0^{z_{max\gamma}} P(i,j) * I(i,j) * a_\gamma(i,j) * z * dz * dx * d\theta \quad (7)$$

The equations for P and I are the same as those for α and β particles, however the equation for a_γ is given by eq. 6. Once F_γ is known, we calculate the dose rate (D_γ) due to γ radiation.

2.3 Radiolytic yields

The production rate of radiolytic products is the absorbed dose rate from each type of radiation multiplied by its respective G-value (the number of molecules created per 100 eV of energy) (eq. 8).

$$\text{Production rate} = (G_\alpha D_\alpha + G_\beta D_\beta + G_\gamma D_\gamma) \quad (8)$$

G-values ($G_{\alpha,\beta,\gamma}$) depend on radiation type and differ for each radiolytic product. We list the G-values that we use for this study in Table 1.

2.4 Example

Since much radioactive waste is in the form of spent fuel assemblies, we use our model to calculate the radiolytic production distribution in water surrounding spent

nuclear fuel. We chose this example because it illustrates the applicability of our method to calculate water radiolysis by γ radiation at a curved interface and the result has important implications for safe handling, disposal and storage of spent nuclear fuel. The dissolution rate of UO_2 fuel is directly related to α , β and γ dose rates near the fuel surface. If the integrity of the barrier around a fuel pellet is breached and the barrier is infiltrated by water, radiation from the fuel will dissociate the water. Production of H_2O_2 can increase dissolution of UO_2 in fuel pellets, while H_2 suppresses dissolution by consuming H_2O_2 (Jonsson, 2012; Shoesmith, 2000, 2008).

For our example, we chose to use 20-year-old UO_2 spent fuel with a 55 MWd/kgHM fuel burn-up. At this age, the fuel rod could still be stored in a spent-fuel pool, surrounded by water. The fuel rod contains stacked fuel pellets, which in our example are surrounded by Zircaloy cladding that creates a barrier for much of the radiation. We use nuclides that account for 99% of the radioactivity to calculate H_2O_2 and H_2 production rates (Table A.1). WebKORIGEN was used to determine the activity of the radionuclides in the spent nuclear fuel (Nucleonica GmbH, 2014b). For this study, we assume the distribution of radionuclides within the pellet to be homogenous. In our example, we also assume the interface to be planar for α and β radiation because their maximum R_{stop} in the fuel matrix (20 μm and 500 μm , respectively) is small compared to the curvature of the 1 cm diameter fuel rod. We test this assumption by comparing the area irradiated by α and β radiation using the curvature of the pellet to the area irradiated assuming a planar interface. We find that approximately 99% of the absorbed dose is accounted for when a planar surface is assumed.

We also assume constant G-values in our model and list the values we use in Table 1. For H₂ yields, α radiation chemical yields have been shown to increase with the LET of the particle. However, for the energy range of α particles we are interested in this study (less than 5.8 MeV), LET appears to have a minimal effect on the G(H₂) value. At high LET, G(H₂) appears to plateau around 1.25 molecules/100eV (Crumière et al., 2013). For H₂O₂ yields, Pastina and LaVerne (1999) also show that there is an increase in yield when LET increases. However, they show that an α particle with an LET more than 2 orders of magnitude greater than γ -rays has a H₂O₂ yield only 50% higher. The range of LET that we cover in our study, is much smaller than 2 orders of magnitude and therefore we assume constant G(H₂O₂) values. Pastina and LaVerne conclude that for heavy ions, the same H₂O₂ yields, within $\pm 20\%$, can be used for a wide range of LET. We did not find any work specifically on the effect of β -particle LET, therefore we assume the H₂ and H₂O₂ yields to be constant for G $_{\beta}$ as well.

Table 1. G-values ($\mu\text{mol/J}$) used in model calculation.

	H ₂	H ₂ O ₂
G$_{\alpha}$	0.12 ¹	0.10 ¹
G$_{\beta}$	0.06 ²	0.078 ³
G$_{\gamma}$	0.045 ¹	0.07 ¹

¹Pastina and LaVerne, 2001

²Kohan et al., 2013

³Mustaree et al., 2014

We use our model to quantify the total dose rate and the radiolytic production of H₂O₂ and H₂ as a function of distance from the solid-water boundary. It is important to note that these are production rates, not concentrations. We apply our model to the fuel rod before and after barrier failure, to compare α , β and γ distribution patterns about the fuel rod, and radiolytic production rates, under both conditions. The profiles

also differentiate between the contributions of α , β and γ radiation to the dose and H_2O_2 and H_2 production rates. Below, we describe the results of our model with a spent nuclear fuel example.

3. Results

We show the dose rate profiles from our 20-year-old spent nuclear fuel example in Fig. 3. This figure illustrates the absorbed dose rate for each type of radiation from 1 μm to 1000 μm from the fuel rod's surface. We show dose rate profiles for a fuel rod with intact cladding (Fig. 3A) and a fuel rod after cladding failure (Fig. 3B). The α and β dose rates are zero in Fig. 3A because the cladding stops all of the radiation from reaching the water (the cladding is thicker than the stopping distances for α and β radiation). However, γ radiation travels far enough to reach the water and D_γ decreases away from the cladding-water interface. In Fig. 3B, α , β and γ radiation all are absorbed in the water, as there is no longer a barrier between the fuel surface and water. Dose rates decrease rapidly away from the surface interface. The dose rate due to γ radiation is approximately 5 times higher at the pellet-water interface than when the cladding is intact. For the 20-year-old fuel with barrier failure (Fig. 3B), D_β is higher than the absorbed dose due to α particles. By 1000 μm , α and β particles only contribute about 17% to the average dose rate when barrier failure has occurred. Alpha particles emitted from the solid do not travel further than 50 μm away from the surface of the fuel, while γ radiation from the fuel pellet continues to be absorbed for tens of centimeters.

We also calculated the dose rate profile for 1000-year-old spent fuel with 55 MWd/kg burn-up after cladding failure (Fig. 4). Similar to Figure 3, we show the dose

rate profile for α , β , and γ radiation separately. At the surface of the 1000-year-old fuel, α -dose is responsible for over 99% of the total absorbed dose. The contribution to dose rate by β and γ radiation is non-zero, but very small. After 1000 μm , β - and γ -dose collectively account for 5% of the total dose of the entire volume. The γ -dose contribution is 4 times greater than β -dose at the fuel's surface. The total γ -dose over the whole 1000- μm interval is over an order of magnitude larger than the absorbed dose due to β radiation.

From the dose rates, we calculate radiolytic production rates (Fig. 5). Radiolytic production rates after barrier failure are almost an order of magnitude higher than before failure (Fig. 5). Total radiolytic H_2 production rate is 10 times higher after barrier failure, while radiolytic H_2O_2 production increases 8.5 times. After barrier failure, α and γ radiation together contribute over 80% of radiolytic H_2O_2 and H_2 production near the pellet-water interface. Alpha radiation contributes to water radiolysis only within 50 μm of the pellet. Farther from the interface, radiolytic production due to β and γ radiation dominates.

4. Discussion

Due to the high activity of young fuel assemblies and their close proximity to water in spent-fuel pools, application of our model to a 20-year-old fuel assembly nicely illustrates the model's capabilities. Typically, fuel assemblies are stored underwater in spent-fuel pools for up to 30 years to cool the fuel and provide shielding from radiation (IAEA, 1999). The radioactivity of spent fuel is highest during this time and α , β and γ radiation are emitted.

Hazards associated with spent fuel storage include release of radionuclides into the water or atmosphere and, in some cases, buildup of dangerous levels of H_2 gas (Alvarez, 2011). The dissolution rate of the UO_2 fuel matrix depends on the redox conditions at the fuel surface. Production of radiolytic oxidants (e.g., H_2O_2) and reductants (e.g., H_2) directly influences UO_2 dissolution (Burns, 2012). Previous models focused on the contribution of α and β radiation to radiolysis (i.e. Nielsen and Jonsson, 2006). However, in 20-year-old spent fuel, γ radiation significantly contributes to total dose rate (Fig. 3) and total radiolytic production rates (Fig. 5). Figures 3 and 5 clearly show the importance of including γ radiation for this case. Gamma radiation in the fuel rod is predominantly produced by decay of ^{137m}Ba . ^{137m}Ba is a daughter of ^{137}Cs , which has a 30-year half-life and the highest activity in 20-year-old fuel. Gamma rays from ^{137m}Ba decay account for over 90% of the total gamma radiation emitted from spent fuel of this age. Although γ radiation has a lower G-value than α radiation (Table 1), the high activity of ^{137m}Ba and long half-distances cause γ decay to be the principal cause of radiolytic H_2 and H_2O_2 production in this example (Fig. 5).

We also use our model to examine radiolytic production rates while the Zircaloy cladding of the fuel assembly is intact (Fig. 3A), and after cladding failure (Fig. 3B). While the cladding is intact, only γ radiation can travel far enough to reach the water (Fig. 3A). However, if barrier failure occurs during storage in a spent-fuel pool, penetration of the water by α and β radiation increases total radiolytic production rates by almost an order of magnitude (Fig. 3B). This increase in radiolytic H_2O_2 production may increase the risk of UO_2 dissolution.

These examples illustrate the importance of including γ radiation when quantifying radiolytic production rates, especially with young radioactive material. As radioactive material ages, γ radiation decreases and α -emitting radionuclides become relatively more important for radiolytic production. When spent fuel is older, α radiation dominates radiolytic production near the solid-water interface (Fig. 4). Since α dose is the largest contributor to the total dose, our model produces a similar dose rate, for the 1000-year-old example within the range of α particles, to those calculated by Nielsen and Jonsson (2006). Although the contribution of β and γ radiation to dose rate is relatively small, γ radiation accounts for a larger percent of the total dose rate than β radiation. In short, the importance of γ radiation for radiolytic production rates relative to α and β radiation depends on spent-fuel age. In all cases, its inclusion provides a more complete and accurate understanding of the distribution of radiolytic products.

As stated in our Methods, for this study, we assumed homogenous distribution of radionuclides throughout the solid. This is an ideal case. For example, Burns et al. (2012) showed enrichment in Pu on the rim of fuel pellets. Our model can be adapted to include different zones of activity within the solid, which will produce different radiolytic production profiles.

5. Conclusion

We present a general model for quantifying water radiolysis by α , β and γ radiation near solid-water interfaces. Our model includes explicit consideration of the radiation's energy attenuation. It can be applied to different radionuclide containing materials, such as solid radioactive waste as well as naturally occurring rocks. By

incorporating the activity, irradiance, and attenuation of radiation, our model separately calculates radiolysis due to α , β and γ radiation as a function of distance from the solid surface. As an example, we calculate total dose rates and radiolytic production rates for spent fuel to illustrate the importance of including the contribution from all three types of radiation in a general model of water radiolysis. While α radiation dominates radiolysis near the surface of old (1000-year-old) spent fuel with breached cladding, β and γ radiation contributes greatly to chemical radiolytic production from young (20-year-old) spent fuel with breached cladding. In the young fuel, γ radiation dominates radiolytic chemical production adjacent to spent fuel with intact cladding.

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Figure 1. Schematic illustration for the α and β equations, depicting the path of isotropic radiation. The gray planar surface represents the solid-water interface (water to the right of the plane). R_{stop} is the stopping distance of the travelling α or β particle, x is the distance from the interface where the radionuclide is located, and δ is the angle of incidence (the angle between particle's path and the normal to the planar interface).

Figure 2. Representation of the possible paths of γ -rays emitted from a radionuclide (black dot) within a cylindrical solid. We assume the height, z , of the cylinder (typically a fuel rod) to be greater than the penetrating power of the γ radiation. R is the distance that the γ -ray travels in the solid. For the cylindrical boundary, the angle of incidence is a combination of δ_1 and δ_2 .

Figure 3. Calculated absorbed dose rate as a function of distance from the solid-water interface, with cladding intact (A) and after cladding failure (B) for 20-year-old fuel. Distance from pellet is plotted on a log scale. Dose rate from alpha and beta radiation in (A) are both 0 Gy/s.

Figure 4. Dose rate profile for 1000-year-old fuel after cladding failure.
Distance from interface is plotted on a log scale.

Figure 5. Radiolytic production rates for H_2 before barrier failure (A) and after barrier failure (B). Production rates for H_2O_2 before barrier failure (C) and after barrier failure (D). All radiolytic production rates are for 20-year-old fuel. Distance from pellet is plotted on a log scale. Production rates from alpha and beta radiation in (A and C) are both $0 \mu\text{M/s}$.

Appendix: Derivation of model equations

Definitions of variables used in radiant flux density calculation:

D = Dose rate (Gy s^{-1})

$F_{\alpha,\beta}$ = radiant flux density ($\text{J cm}^{-1}\text{s}^{-1}$)

P = power, energy released per time per solid angle ($\text{MeV s}^{-1} \text{sr}^{-1}$)

A = activity (Bq g^{-1})

E_0 = initial radiation energy (MeV decay^{-1})

I = irradiance, power (P) per unit area (μm^{-2})

δ = angle of incidence on the irradiated surface (rad)

φ = angle integrated for the area irradiated by charged particles on fuel's surface (rad)

θ = angle of rotation about the z-axis of cylindrical solid (rad)

R = distance to the boundary, assumed linear over the projected range along the initial direction of the emitted particle (μm)

R_γ = distance to the cylindrical boundary for γ -rays (μm)

R_{stop} = stopping distance of a charged particle, maximum travel distance determined by the initial energy of the charged particle (μm)

R_0 = diameter of a cylindrical solid (μm)

μ = attenuation coefficient for gamma radiation (μm^{-1})

x = distance from the surface to a radionuclide of interest within the solid (μm)

z = distance irradiated along planar or cylindrical surface, where $z = 0$ is perpendicular to the radionuclide source and $z_{max} = R_{stop}$ (μm)

w = distance in water the from solid-water interface (μm)

A1. Radiant flux for α and β particles

A1.1 Equations used in $F_{\alpha,\beta}$ calculation (as a function of x and z):

- Power

$$P(i, j) = \frac{A_i * E_{0(i, j)}}{4\pi} \quad (\text{A1.1})$$

The initial radiation energy (kinetic energy for α and β and electromagnetic for γ radiation), E_0 , includes the parent-daughter nuclide branching fraction and the α and β branching intensity. The branching intensity values are based on the frequency that particular E_0 values occur per 100 parent decays. We calculate E_0 with values from the Nuclide Datasheets in Nucleonica (Nucleonica GmbH, 2014c). The isotopes used for the example calculations are listed in Table A.1. These isotopes account for 99% of the radioactivity within the pellets. The activity data is from WebKORIGEN (Nucleonica GmbH, 2014b)

Table A.1 List of isotopes.

20-year-old Pellets	1000-year-old Pellets
¹³⁷ Cs	²⁴¹ Am
^{137m} Ba	²⁴⁰ Pu
²⁴¹ Pu	²³⁹ Pu
⁹⁰ Y	^{235m} U
⁹⁰ Sr	²⁴³ Am
²³⁸ Pu	²³⁹ Np
⁸⁵ Kr	⁹⁹ Tc
²⁴⁴ Cm	
²⁴¹ Am	
¹⁵⁴ Eu	

- Irradiance

Irradiance (eq. A1.2) determines how P changes as a function of the angle of incidence and the distance radiation has traveled.

$$I = \frac{\cos \delta}{R^2} \quad (\text{A1.2})$$

Substituting $\cos \delta = \frac{x}{R}$ and $R = \sqrt{(x+w)^2 + z^2}$ gives irradiance at a specific distance from the interface, w , in terms of x and z (eq. A1.3);

$$I = \frac{x}{((x+w)^2 + z^2)^{3/2}} \quad (\text{A1.3})$$

As a test case, we calculate the flux, F , for a non-attenuated radioactive source at any depth, x . The total power flux through an infinite planar boundary is described by:

$$F = \int_0^{2\pi} \int_0^\infty P * I * z * dz * d\varphi = \frac{P}{2}$$

Half of the power reaches the solid-water boundary regardless of the location of the radioactive source. This is what we expect with no attenuation of the particles. However α and β particles lose energy as they travel, which reduces the total flux.

- Attenuation

Theoretically, energy loss is inversely proportional to the particle's energy (Bethe and Ashkin, 1953). We base derivation of the attenuation equation (eq. A1.5) on a simplification of Bethe's formula, which describes the energy loss of a particle traveling through matter,

$$\frac{dE}{dr} \cong -\frac{d}{E} \quad (\text{A1.4})$$

where d is constant for a constant travel matrix. However, experimentally this value depends on E_0 of the charged particle. For the derivation of the attenuation equation, we integrate E^{b-1} to assign more correct values to the attenuation equation by using E_0 and range relationships to determine a value for b . We calculate the fraction of initial energy remaining at distance R (E_R) by integrating eq. A1.4.

$$\int_0^R dr = \int_{E_0}^{E_R} \frac{-E^{b-1}}{d} dE$$

$$R = \frac{E_0^b}{d * b} - \frac{E_R^b}{d * b}$$

$$R_{\text{stop}} = \frac{E_0^b}{d * b}$$

Therefore, the fraction of the total stopping distance a particle travels at some distance R is

$$\frac{R}{R_{\text{stop}}} = 1 - \frac{E_R^b}{E_0^b}$$

The attenuation, or fraction of initial energy that reaches some distance w into the water, is described by eq. A1.5 or in terms of x and z as eq. A1.6,

$$a = \frac{E_R}{E_0} = \left(1 - \frac{R}{R_{\text{stop}}}\right)^{\frac{1}{b}} \quad (\text{A1.5})$$

Substituting $R = \sqrt{(x + w)^2 + z^2}$,

$$a = \left(1 - \frac{\sqrt{(x + w)^2 + z^2}}{R_{\text{stop}}}\right)^{\frac{1}{b}} \quad (\text{A1.6})$$

The attenuation equation (eq. A1.6) depends on the particle energy and material. Using the energy-range data, we determine b and R_{stop} by fitting an equation to the data over the energy ranges emitted by the radioisotopes. Table A.2 summarizes the values we use in this study. We calculate the particle's travel range (μm) for the energy ranges indicated in Table A.2 with the formula $R = h * E_0^b$. The values of b used in this study are comparable to those used in other studies. For example, the travel range we calculate for the α particles emitted in our UO_2 examples are within 7% of those calculated using the equation presented in Nielsen and Jonsson (2006).

Table A.2. Energy-Range equations and b-values used in calculations.

Radiation Type	Material	Energy Range (MeV)	h	b value
Alpha	UO_2^1	3.00 – 9.00	1.275	1.39
	Water ²	2.00 – 9.00	3.627	1.47
		< 2.00	5.490	0.81
Beta	UO_2^2	1.00E-02 – 4.50E-01	1.00E03	1.58
		4.50E-01 – 4.50E00	6.63E02	1.07
	Water ²	1.00E-02 – 4.50E-01	6.69E03	1.70
		4.50E-01 – 4.50E00	4.19E03	1.17

¹Data from Nucleonica Range & Stopping Power application using a user defined compound of UO_2 (Nucleonica GmbH, 2014a).

²Data from NIST ASTAR and ESTAR databases (Berger et al., 2005).

R_{stop} is calculated by determining the distance radiation travels through the pellet matrix (or cladding) before reaching the water. If R_{stop} is greater than the distance to the interface then the energy remaining, E_R , is calculated (eq. A1.5) and used as the initial energy for calculating how far the particle will penetrate the water. We then use this distance to calculate the new attenuation equation of the particle through water. Two different attenuation equations are included in the final integration, in our case one for the pellet and one for the water.

A1.2 $F_{\alpha,\beta}$ calculation

To calculate the total radiant flux density that reaches the solid-water boundary, we integrate the equations presented above over the depth of the radionuclide-containing solid, x_{max} , and over the irradiated area of the planar boundary (eq. A1.7). We can calculate the flux for any distance from the solid-water interface.

$$F_{\alpha,\beta} = \int_0^{\theta_{\text{max}}} \int_0^{x_{\text{max}}} \int_0^{z_{\text{max}}} P(i,j) * I(i,j) * a(i,j) * z * dz * dx * d\theta \quad (\text{A1.7})$$

where z_{max} depends on stopping distance of the particle through water, R_{water} , the depth of the radionuclide, and the distance in water from the solid-water interface (w) (eq. A1.8). x_{max} is the depth at which only the most energetic α or β particle reaches the solid-water boundary (the greatest depth within the solid where particles can reach the water) and φ varies from 0 to 2π . We calculate the total radiant flux density by integrating and summing over all α and β particles and radionuclides (eq. A1.9).

$$x_{\text{max}} = \sqrt{R_{\text{water}}^2 - (x + w)^2} \quad (\text{A1.8})$$

$$F_{\alpha,\beta} = \sum_i \sum_j \int_0^{2\pi} \int_0^{x_{\text{max}}} \int_0^{\sqrt{R_{\text{water}}^2 - (x+w)^2}} P(i,j) * I(i,j) * a(i,j) * z * dz * dx * d\varphi \quad (\text{A1.9})$$

A2. Radiant flux density for gamma radiation

Due to the greater penetrating power of gamma rays, the cylindrical shape of the fuel rod needs to be considered. While this does not affect the overall structure of the flux equation, it does change the expression for R_γ in terms of x and z . In the following equations, θ is the angle of rotation about the z -axis.

A2.1 Equations used in F_γ calculation (in terms of x , θ and z):

- Power, same calculation used for α and β particles (eq. A1.1)
- Irradiance for γ -rays and cylindrical pellet (eq. A2.2, Fig. 2 for illustration of angles δ_1 and δ_2)

$$I_\gamma = \frac{\cos \delta_1 * \cos \delta_2}{R_\gamma^2} \quad (\text{A2.1})$$

Where,

$$\delta_1 = \tan^{-1} \left(\frac{R_0 * \sin \theta}{R_0 * \cos \theta - x} \right) - \theta \quad \text{for } 0 \leq \theta \leq \cos^{-1} \left(\frac{x}{R_0} \right),$$

$$\delta_1 = \pi - \tan^{-1} \left(\frac{R_0 * \sin \theta}{R_0 * \cos \theta - x} \right) - \theta \quad \text{for } \cos^{-1} \left(\frac{x}{R_0} \right) \leq \theta \leq \pi,$$

$$\cos \delta_2 = \frac{r'}{R_\gamma},$$

$$r' = \sqrt{(R_0 + w)^2 - 2(R_0 + w)x \cos \theta + x^2}, \text{ and}$$

$$R_\gamma = \sqrt{r'^2 + z^2},$$

$$I_\gamma = \frac{\cos \delta_1 * r'}{R_\gamma^{3/2}} \quad (\text{A2.2})$$

- Attenuation of γ -rays (eq. A2.3)

$$a_\gamma = \frac{P_R}{P_0} = e^{-\mu R_\gamma} \quad (\text{A2.3})$$

We use specific μ values to calculate the attenuation through the solid and water, to get the total attenuation of the γ -rays at some distance, w . The attenuation coefficients are from the X-ray attenuation database (Hubbell and Seltzer, 2004). To account for different materials γ -rays encounter, each material has its own attenuation equation. For example, if a γ -ray was to pass through the pellet and then water, the total attenuation equation would be $a_\gamma = e^{-\mu_{\text{pellet}} R_{\text{pellet}}} * e^{-\mu_{\text{water}} R_{\text{water}}}$. Where μ_{pellet} and μ_{water} are the attenuation coefficients for γ radiation in the pellet and water, respectively and R_{pellet} and R_{water} is the distance the γ -ray travelled through the pellet and water, respectively. These distances are calculated in a similar way to the R_γ however the distance is divided into the pellet and water components.

A2.2 F_γ calculation

F_γ calculation is very similar to charged particles. However, we divide the integral into two parts to account for the geometric effects on δ_1 and δ_2 .

$$\begin{aligned} F_\gamma = & \sum_i \sum_j 2 \int_0^{z_{\max}} \int_0^{x_{\max}} \int_0^{\cos^{-1}(\frac{x}{R_0})} P(i, j) * I_\gamma(i, j) * a_\gamma(i, j) * z * d\theta * dx * dz \\ & + 2 \int_0^{z_{\max}} \int_0^{x_{\max}} \int_{\cos^{-1}(\frac{x}{R_0})}^{\pi} P(i, j) * I_\gamma(i, j) * a_\gamma(i, j) * z * d\theta * dx * dz \end{aligned} \quad (\text{A2.4})$$

where $x_{\max}$ is equal to radius of the cylinder, R_0 , and $z_{\max}$ is equal to 10 times the half-distance of the γ -ray.

A3. Volume normalized dose rate calculation

The volume normalized dose rate calculation is described by eq. A3.1. The dose rate is calculated per volume of water surrounding the pellet, as thick as the w of interest.

$F_{\alpha, \beta, \gamma}$ is in units of $\text{J } \mu\text{m}^{-1} \text{s}^{-1}$. By multiplying by the density of water, ρ_{water} , the dose rate can be converted into Gy s^{-1} .

$$D_{\alpha, \beta, \gamma} = \frac{F_w - F_{\text{interface}}}{w} * \rho_{\text{water}} \quad (\text{A3.1})$$

MANUSCRIPT II

Radiolytic hydrogen production in the seafloor basaltic aquifer

By

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Abstract

Hydrogen (H_2) is produced in geological settings by dissociation of water due to radiation from radioactive decay of naturally occurring uranium (^{238}U , ^{235}U), thorium (^{232}Th) and potassium (^{40}K). To quantify the potential significance of radiolytic H_2 as an electron donor for microbes within the South Pacific subseafloor basaltic aquifer, we use radionuclide concentrations of 43 basalt samples from IODP Expedition 329 to calculate radiolytic H_2 production rates in basement fractures. The samples are from three sites with very different basement ages and a wide range of alteration types. U, Th and K concentrations vary by up to an order of magnitude from sample to sample at each site. Comparison of our samples to each other and to the results of previous studies of unaltered East Pacific Rise basalt suggests that significant variations in radionuclide concentrations are due to differences in initial (unaltered basalt) concentrations (which can vary between eruptive events) and post-emplacement alteration. However, there is no clear relationship between alteration type and calculated radiolytic yields. Local maxima in U, Th, and K produce hotspots of H_2 production, causing calculated radiolytic rates to differ by up to a factor of 80 from sample to sample. Fracture width also greatly influences H_2 production, where microfractures are hotspots for radiolytic H_2 production. For example, H_2 production rates normalized to water volume are 190 times higher in 1 μm wide fractures than in fractures that are 10 cm wide. To assess the importance of water radiolysis for microbial communities in subseafloor basaltic aquifers, we compare electron transfer rates from radiolysis to rates from iron oxidation in subseafloor basalt. Radiolysis appears likely to be a more important electron donor source than iron oxidation in old

(>10 Ma) basement basalt. Radiolytic H₂ production in the volume of water adjacent to a square cm of the most radioactive SPG basalt may support as many as 1500 cells.

Keywords: Radiolysis; Hydrogen; Basalt; Ocean crust; Geochemistry; Deep biosphere

1. Introduction

The oceanic basement contains the largest aquifer on Earth. Its fractured rock contains nearly 2% of Earth's total volume of seawater (Johnson and Pruis, 2003). Although the extent of life and microbial activity in oceanic basement is not well known, a variety of evidence suggests that microbes reside within the aquifer (Cowen et al., 2003; Edwards et al., 2012; Lever et al., 2013; Orcutt et al., 2013; Jungbluth et al., 2013). Fisk et al. (1998) and Staudigel et al. (2008) report weathering textures suggestive of microbial alteration in subseafloor basaltic glass. Microorganisms have been found in fluid flowing through 3.5 million year old basalt on the Juan de Fuca ridge flank (Cowen et al., 2003). DNA and isotopic signatures of mineral alteration provide evidence of microbes and microbial activity in ridge-flank basalt (Lever et al., 2013).

Physical and chemical properties limit microbial habitability of the oceanic basement. For example, habitability within subseafloor basalt is constrained by availability of electron donors [e.g., organic carbon, ferrous iron (Fe²⁺), and hydrogen (H₂)] and electron acceptors [e.g., oxygen (O₂), nitrate (NO₃⁻), and sulfate (SO₄²⁻)] (Madigan et al., 2000; Bach and Edwards, 2003; D'Hondt et al., 2004). A number of studies have suggested that microbial life in igneous-rock aquifers may be supported

by oxidation of electron donors native to the rock or produced by water-rock interactions (Pedersen, 1993; Stevens and McKinley 1995; Kelley et al., 2001; Chapelle et al., 2002; Bach and Edwards, 2003; Edwards et al., 2005). For example, basement basalt has high concentrations of reduced elements, specifically iron (Fe) and sulfur (S) (Bach and Edwards, 2003). Oxidation of these elements with O_2 or NO_3^- in the seawater provides energy that microorganisms might utilize. Water-rock interactions that can produce electron donors in the form of molecular hydrogen (H_2) include serpentinization (Kelley et al., 2001) and radiolysis of water due to radioactive decay of radionuclides within the rock (Pedersen, 1993; Lin et al., 2005a/b; Blair et al., 2007; D'Hondt et al., 2009, 2015; Edwards et al., 2011; Lollar et al., 2014). Water radiolysis within subseafloor basalt is the focus of this study.

Water radiolysis is the decomposition of water molecules by ionizing radiation produced during the decay of radioactive elements (Debierne, 1914; Le Caër, 2011). The principal radioactive elements that produce ionizing radiation in basalt are uranium (^{238}U and ^{235}U), thorium (^{232}Th) and potassium (^{40}K), which collectively emit alpha (α), beta (β) and gamma (γ) radiation as they and their daughter nuclides decay. Transfer of energy from this radiation excites and ionizes water molecules, producing several chemical species: e_{aq}^- , $HO\bullet$, $H\bullet$, $HO_2\bullet$, H_3O^+ , OH^- , H_2O_2 and H_2 (Spinks and Woods, 1990; Le Caër, 2011). The distribution and rate of formation of these products depends on the linear energy transfer (LET) of the radiation (the amount of energy deposited by the radiation along its path). Low-LET radiation (γ -rays and β particles) ionizes water discretely along the radiation path. High-LET radiation (e.g., α particles) deposits energy densely along the particles' track. The radiolytic yields of the radicals

decline with LET. The radicals are short-lived and highly reactive; they recombine in the radiation track to produce stable decomposition products (H_2 and H_2O_2).

Production of H_2 and H_2O_2 increases with increasing LET (Pastina and LaVerne, 2001; Le Caër, 2011).

For seafloor environments, we are particularly interested in the production of the reductant H_2 . Many organisms catabolically utilize H_2 , including methanogens, sulfate-reducers, iron reducers, and nitrate reducers (Fang and Zhang, 2011). There is evidence that some of these organisms, specifically sulfate reducers and methanogens, are active in seafloor basalt (Lever et al., 2013). Radiolysis undoubtedly occurs in seafloor basalt, as both water and radiation are present. Edwards et al. (2012) suggested that in the old and relatively weathered basaltic basement of the South Pacific Gyre (SPG), radiolytic H_2 may be the dominant electron donor.

The potential of radiolytic H_2 as an electron donor has been studied for other environments, such as continental crust (Pedersen, 1993; Lin et al., 2005a/b) and deep-sea sediment (Blair et al., 2007). In these environments, water radiolysis supplies H_2 that may support microbial communities. In deep-sea sediment, H_2 may be especially important to microbial communities where organic carbon availability is very low (Blair et al., 2007; D'Hondt et al., 2009).

Here, we focus on calculating the rate of radiolytic H_2 production in oceanic basement. More specifically, we use our recently published water radiolysis model to calculate H_2 production rates in fractures of South Pacific seafloor basalt (Dzaugis et al., 2015). Our model more accurately quantifies radiolytic H_2 production in fractured hard rock than previous models, which are more appropriate for physically

homogenous environments where solid particles are small compared to the distance that the ionizing radiation travels, such as deep-sea sediment.

To determine variations in radionuclide concentrations of relatively old SPG basalt, we analyzed basalt samples from three SPG sites with basement ages of circa 13 to 100 Ma. Our samples include a wide variety of alteration types. To identify effects of basement age, initial composition, and alteration on radiolysis rates, we compare our H₂ production calculations for these samples to calculations for which we use previously published U, Th and K data from young basalt samples on the East Pacific Rise (EPR) (Gale et al., 2013). In addition, we quantify the effect of fracture width on the H₂ production rates. We assess the possible significance of radiolytic H₂ production for microbial communities in subseafloor basaltic aquifers by comparing the electron transfer flux from radiolytic H₂ to the electron transfer flux from iron oxidation in the basalt. Finally, we estimate the number of cells that might be supported by radiolysis in the basement.

2. Materials and Methods

2.1 Materials

Integrated Ocean Drilling Program (IODP) Expedition 329 collected subseafloor basalt samples at three sites (Sites U1365, U1367, U1368) (Fig. 1). We analyzed 43 samples from these sites to determine the range of U, Th and K concentrations in SPG basalt.

Site U1365 is located in the western part of the SPG, where the seafloor is approximately 5695 meters below sea level (Expedition 329 Scientists, 2011a). At this location, basement is mainly composed of massive lava flows that are approximately

100 Ma (Dunlea et al., 2015a). Recovery of cored basalt was 74.6% at this site. Throughout the cored sequence, alteration extent of the recovered basalt varies between 2% and 95%, with alteration mainly associated with veins and vesicles near flow margins and breccias (Expedition 329 Scientists, 2011a). We analyzed 17 samples from Site U1365 for this study.

The second site, U1367, is east of Site U1365, with seafloor approximately 4288 meters below sea level (Expedition 329 Scientists, 2011b). The basement is younger at this site, with an approximate age of 33.5 Ma. The uppermost basement is mostly composed of fractured pillow fragments with a small thin flow at the base of the recovered basalt. Due to the fractured nature of the basalt cored at this site, core recovery was low (11.2%). The extent of alteration in recovered basalt from this site varies between 2% and 25%. Most basalt alteration at Site U1367 occurs around vein-filled fractures of chilled margins (Expedition 329 Scientists, 2011b). We analyzed 5 samples from Site U1367.

Site U1368 is the eastern-most site of Expedition 329. Seafloor here is 3740 meters below sea level (Expedition 329 Scientists, 2011c). Basement at Site U1368 is approximately 13.5 Ma. Core recovery was 27.6%. The recovered portion of the basement is dominantly composed of pillow basalt. Basalt alteration at this site is mainly in veins, vesicles, along chilled margins, and within volcanoclastic breccias. The recovered basalt varies in alteration extent from 2% to 60% (Expedition 329 Scientists, 2011c). There are 21 samples from Site U1368 used in this study.

2.2 Alteration Categories

Our 43 samples are characterized by wide ranges of alteration extent and alteration type. We assign samples to the following rock types based on macroscopic visual appearance; brown halos, dark gray halos, carbonate veins, iron oxyhydroxide (Fe) stained, breccia, mixed alteration, and minimally altered. The term brown halo refers to all halos that vary from red to brown in color. Similarly, dark gray halo refers to halos ranging from very dark gray to dark green in color. Fe staining includes samples with iron oxyhydroxide staining of secondary minerals or filling of veins and vesicles. Iron oxyhydroxides leave behind a bright red-orange color. We define samples as mixed-alteration when they are visibly altered but without a dominant single alteration type, such as samples with veins and vesicles filled with carbonate, clays and iron oxyhydroxides and have secondary mineral emplacement. Finally, we classify all aphyric samples without visibly altered regions as minimally altered.

Where possible, we analyzed samples of different visibly altered regions within the same basaltic rock to compare the radioactive element concentrations of the different alteration zones. For example, we took two samples from a piece of light gray basalt with a brown halo. For all analyses of alteration halos and carbonate veins, we separated each alteration type from the rest of the rock. Other alteration categories included a mixture of altered rock and background basalt, as they could not be fully separated. We analyzed the 43 samples for their U, Th and K concentrations.

2.3 U, Th and K measurements

We used well-established protocols to measure concentrations of U, Th, and K in the 43 samples by inductively coupled plasma-emission spectrometry (ICP-ES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Dunlea et al., 2015b). We

analyzed these samples at Boston University with a VG PlasmaQuad Excell ICP-MS for U and Th concentrations, and a Jobin-Yvon (JY) Ultima-C ICP-ES for K concentrations. Based on replicate analysis, U and Th precision was 2% and 1%, respectively, of their measured values. The K measurements were within 1% of the measured value. To assess analytical accuracy, we analyzed BHVO-2 Standard Reference Material independently from our calibrations. The measured values agree with the reported accepted values within the analytical precision (Jochum et al., 2005). We list all U, Th and K data in Supplemental Table S1.

2.4 Radiolytic H₂ production model

Our radiolysis model calculates production rates in water near a radionuclide-containing solid (Dzaugis et al., 2015). Previous models, such as those used in sediment (Blair et al., 2007), are not applicable to basalt, because studies of basalt cannot assume homogenous porosity or grain/crystal size smaller than the stopping distance of the radiation. Dzaugis et al. (2015) gives a detailed description of the model that we apply to our samples. In this section, we describe the inputs and assumptions that we used to calculate radiolytic H₂ production rates in fractures.

There are four dominant parent radionuclides in basalt: ²³⁸U, ²³⁵U, ²³²Th, and ⁴⁰K. When these nuclides decay, α , β and/or γ radiation is emitted. Each type of radiation has different properties that affect radiolytic yield. For example, α particles travel short distances (tens of μm) but have high initial energies and produce the most H₂ molecules per unit of energy absorbed. Our calculations assume that the entire decay series of ²³⁸U, ²³⁵U, and ²³²Th are in secular equilibrium. This assumption is valid for basalt older than 377,000 years (five half-lives of ²³⁰Th) (LaTourrette et al., 1993).

However, younger basalt is characterized by isotopic disequilibrium within the ^{238}U -decay series, because fractionation during partial melting leads to excess ^{230}Th relative to ^{238}U (LaTourrette et al., 1993). Due to this ^{230}Th enrichment, we slightly underestimate radiolytic H_2 production rates when we assume secular equilibrium for young basalt.

The distance that α or β radiation travels before losing all of its kinetic energy is called its stopping distance (Spinks and Woods, 1990). Gamma radiation loses energy exponentially with distance and therefore is not assigned a specific stopping distance. Instead, we use the maximum distance traveled by γ -rays to be 10 half-distances, at which point less than 0.1% of their initial energy remains. Stopping distance and γ travel distance depend on the matrix; for example, a 5 MeV α particle will travel about 20 μm in basalt but 40 μm in water. If radiation is emitted from a radionuclide farther from the water interface than the stopping distance, it does not contribute to water radiolysis. Once radiation reaches the basalt-water interface, it continuously ionizes water along its path until it reaches its stopping distance (Le Caër, 2011) or re-enters basalt from the water. Our model incorporates radioactivity, decay energy of each radionuclide, and how each type of radiation attenuates energy along its path. It sums all of the radiation that is absorbed in a fracture. Consequently, the inputs to our model are U, Th and K concentration, initial energy for all radiation emitted from the isotopes, energy-range relationships for α , β and γ radiation in basalt and water, H_2 yield per unit energy for each type of radiation, and distance the radiation travels through water. For the calculations in this paper, we assume there is one centimeter of basalt on either side of the fracture, unless noted otherwise.

We used the data in Supplemental Table S1 to calculate the radioactivity of our SPG basalt samples for ^{238}U , ^{235}U , ^{232}Th and ^{40}K . We used published radionuclide data (Gale et al., 2013) to calculate the radioactivity of EPR basalt at its time of formation. We used the program RadDecay (Hacker, 1997) to find the initial energy for all radiation emitted from radionuclides in basalt. We calculated stopping distances of α and β particles and half-distances of γ -rays for basalt and water using the energy-range data from the ASTAR, ESTAR (Berger et al., 2005) and X-ray Attenuation (Hubbell and Seltzer, 2004) programs in the NIST database. To determine stopping distances in basalt, we used energy-range data for borosilicate glass (in the NIST database, borosilicate glass is the material with electron density most similar to oceanic basalt). Using these relationships, we developed equations to calculate travel distance given an initial energy. Supplemental Table S2 summarizes the equations we use in this study.

Using radioactivity, energy and range data, and how many H_2 molecules are produced per 100 eV (G-values), we calculated volume-normalized H_2 production rates for basalt fractures of widths between 1 μm and 1 m. These rates assume (i) basalt of the same composition on both sides of a fracture and (ii) homogeneous distribution of the radionuclides throughout the basalt.

3. Results

3.1 Radiolytic H_2 production model

We calculated radiolytic H_2 production rates as a function of fracture width for all 43 samples. We show the results of these calculations separately for each site in Figure 2. Volume-normalized H_2 production decreases greatly as fracture width increases (from 1 μm to 1 m in width) (Fig. 2). For each width, the differences in H_2 yields

between samples are due to variations in radioactive element concentrations. Site U1365 contains the oldest and generally most altered basalt of the three sites (Expedition 329 Scientists, 2011a). It exhibits the lowest H₂ production rates (Fig. 2A), while Site U1368, with the youngest basalt age, generally has the highest rates (Fig. 2C). The SPG sample with the lowest H₂ production rate (approximately 3X lower than other samples) is from Site U1365 with a Th concentration below the detection limit (0.01ppm). We calculated the radiolytic H₂ production rate for this sample using the below detection limit value.

3.2 Radionuclide compositional variance

U and K variance in basalt is due to geochemical composition at the time of basalt formation (initial composition) and post-emplacement alteration. In contrast, Th is not significantly modified during post-emplacement alteration (Kelley et al., 2005). We use Th to constrain abundance variations due to initial composition and U/Th ratios to constrain the magnitude of U alteration.

In our samples, Th ranges from below the detection limit (0.01 ppm) to 1.17 ppm. This range is comparable to the entire range of values observed in unaltered basalt glass from the EPR (compositional data from Gale et al., 2013). The U/Th ratios of our samples range from 0.32 to 4.1 (excluding samples with Th below detection limit). This is much greater than ratios observed in unaltered EPR basaltic glass (Gale et al., 2013). However, it is similar to the range in altered material from other studies (e.g., Kelley et al., 2003). About 1/3 of our samples have U/Th ratios that fall within two standard deviations of the mean U/Th ratio in unaltered EPR glass samples. Most of the SPG samples that fall into this category are from the site with youngest basement

age, U1368 (11 samples). Only one and two samples at Site U1367 and U1365, respectively, have U/Th ratios indicative of unaltered composition.

3.3 H_2 yields and alteration

We separately describe the calculated radiolytic rates of the three SPG sites because they have different geographic origins, different eruptive histories, and different degrees of deviation from the mean U/Th ratio of unaltered EPR glass. Site U1365 exhibits a 21-fold range in rates, whereas Sites U1367 and U1368 show 7- to 8-fold ranges. Overall, Site U1365 has the lowest rates, while Site U1368 has the highest (Fig. 2).

Our samples show no clear relationship between alteration type and H_2 production rates. The H_2 production rates calculated for all alteration categories, including minimally altered samples, seem to span the entire range; no alteration type exhibits a significantly different range of H_2 production rates than the others (Fig. 3). There is some separation of alteration types within the individual sites. At Site U1365, iron stained samples tend to have higher rates, while at Site U1368 the mixed alteration samples and the breccia are highest (Fig. 3). Two of the three mixed alteration samples at U1368 have U/Th ratios within the unaltered range indicating that the high range may not completely be due to alteration. Many of the H_2 production rates for the different samples overlap; the rates calculated for each sample at the basalt-water interface are given in Supplemental Figure S1. To further investigate the impact of alteration, we calculate the U due to alteration (U_{alt}) as

$$U_{alt} = U_{meas} - \left(\frac{U}{Th} \right)_{unalt} * Th_{meas}$$

where the subscript *meas* refers to measured values and $\left(\frac{U}{Th}\right)_{unalt}$ is the average ratio in unaltered EPR basalt (0.37 ± 0.08). We then calculate H_2 yield due to U_{alt} and determine its fractional contribution to the total yield. There are 27 samples that have excess U that is significantly (more than two standard deviations) different than zero. For these samples, the H_2 yield based on U_{alt} ranges from 0 to $4.9 \times 10^{-1} \pm 1.5 \times 10^{-2}$ nM H_2 yr⁻¹, and can contribute up to $85 \pm 3\%$ of the radiolytic H_2 produced (average of $31 \pm 7\%$ for all samples with altered U/Th ratios).

3.4 Influence of fracture width and basalt width on H_2 production

While compositional variation leads to a large range of radiolytic H_2 production rates (almost two orders of magnitude within the SPG samples), fracture width has an even greater effect on volume-normalized H_2 production (moles per vol. of water per time). The production rate per volume of water decreases as fracture width increases. This decline in volume-normalized rates is most pronounced after α and β particles run out of energy. To illustrate this effect, we calculated volume-normalized production rates for a range of fracture widths that occur in basement basalt (1 μ m to 1 m). Volume-normalized H_2 production rates are highest in microfractures (<10 μ m), regardless of radionuclide concentration, and strongly decrease as fracture width increases (Fig. 2). Production rates in 1 μ m wide fractures differ by more than three orders of magnitude from rates in 1 m wide fractures. Volume-normalized H_2 production rates are highest at the rock-water interface, due to high dose rates. However, if production rate is normalized to the surface area of fractures, it increases with fracture width as more radiation, especially from γ -rays, is absorbed in wider fractures than narrower fractures.

Radiolytic H₂ production rates also vary with the thickness of basalt that abuts a fracture (Fig. 4). To illustrate this effect, we calculated production rates based on a single SPG sample and three different thicknesses: 1 m, 1 cm and 100 μ m. Thickness affects the amount of radiation emitted to water. One meter of basalt is approximately equivalent to an infinite basalt thickness because less than 0.1% of the radiation travels beyond a meter (10 half-distances of γ -rays); the amount of energy that reaches the water approaches its maximum at about a meter of basalt.

This dependence on basalt thickness is clearly illustrated by comparing H₂ production by β and γ radiation with 100 μ m thick basalt (Fig. 4C) to H₂ production by β and γ radiation with 1 cm thick or 1 m thick basalt (Fig. 4A,B). The decrease in thickness from 1 m to 100 μ m of basalt causes a 20% decrease in β -produced H₂ and a 98.9% decrease in γ -produced H₂. Because the stopping distance for β and γ radiation is much greater than 100 μ m in basalt, the change in thickness greatly impacts the number of β particles and γ -rays emitted from the basalt. Despite these effects of basalt thickness on H₂ production by β and γ radiation, total radiolytic H₂ production rate is not greatly affected by basalt thickness, because α radiation is responsible for most radiolytic H₂ production in our examples (Fig. 4). Total H₂ production rate is only 4% less with 1 cm of basalt and 10% less with 100 μ m than 1 m of basalt. In all three cases, α -dose rate is the same, because α particles penetrate no more than 50 μ m of basalt (25 μ m on average). Therefore, in all three scenarios, all the α radiation that can reach fracture water does.

4. Discussion

In this section, we discuss (i) factors that impact radiolytic H_2 production rates, (ii) their potential importance to electron donor fluxes in subseafloor basalt, and (iii) the number of cells that might be supported by rates of radiolytic H_2 production in representative fractures. We first consider the fractured nature of oceanic basement and how both fracture width and basalt thickness affect radiolysis rates. We address how source-melt composition and subsequent low-temperature alteration play a role in determining the distribution of radionuclides in our sample set and rates of radiolytic H_2 production. We then compare electron donor fluxes from radiolytic H_2 production and from iron oxidation. Finally, we estimate numbers of cells that might be supported by radiolysis in SPG basaltic fractures, based on comparison to per-cell O_2 consumption rates in SPG sediment.

4.1 Factors that influence H_2 production

We focused this study on radiolysis in fractures because most of the water in oceanic basement resides in, and travels through, fractures (Fisher, 1998). The three primary categories of porosity in oceanic crust are (i) macroscopic features, such as lithological boundaries (e.g., surfaces of lava flows), voids associated with pillow basalts, and collapse structures; (ii) microcracks which have narrow widths and limited lateral extent, and (iii) vesicles and other primary porosity, which we do not consider since they are typically disconnected and isolated. Of these three categories, the first is most closely related to formation-scale permeability (Fisher, 1998). Fluid flow in the igneous basement is mostly through interconnected fractures in the oceanic basement (Wang, 2004), e.g., through fractures between pillow basalts and along the margins of lava flows. This relationship between fluid flow and interconnected

fractures is apparent in the distribution of alteration halos, which are mainly associated with veins in the basalt, indicating that chemical transport is very limited in the low porosity, impermeable basalt matrix (Bach and Edwards, 2003).

Our focus on quantifying radiolytic rates in fractures differs from previous studies of radiolysis in continental crust (e.g., Lin et al., 2005a), which assume porosity to be homogeneously distributed throughout the rock. Such an assumption is very problematic for estimating radiolytic H₂ production in hard-rock aquifers, where most porosity is in heterogeneously distributed fractures and much of the radiation emitted from radionuclides in the rock will never reach water. As we discussed in Results, properties that most affect H₂ production rates in hard-rock aquifers include fracture width, rock thickness and rock composition. Of these properties, fracture width and rock composition are the most important.

Fracture width greatly influences radiolytic H₂ production rates (Figs. 2-4) because volume-normalized H₂ production rapidly decreases with distance from the rock-water interface. This decrease in H₂ production is due to the limited ranges of α and β radiation and increased volume of water. Of the three types of radiation, α radiation has the highest initial energy and highest G-value at 1.2 molecules H₂ per 100 eV (Pastina and LaVerne, 2001). However it also has the shortest range. Consequently, H₂ production by α radiation extends only several tens of microns into fracture water. Beta and gamma radiation have lower G-values (0.6 and 0.45 molecules H₂ 100 eV⁻¹, respectively) than α particles (Kohan et al., 2013; Mustaree et al., 2014), but β particles can travel thousands of μ m in water and γ -rays travel for tens of cm. Consequently, α radiation dominates total radiolytic H₂ production near the

rock-water interface, while γ -produced H_2 is highest in fractures greater than 1 cm (Fig. 4). Due to the very high rate of H_2 production from α radiation, volume-normalized H_2 production rates in 1 μm fractures are on average 190 times higher than fractures 10 cm in width and 1.6×10^3 times higher than in 1 m fractures. In short, microfractures are hotspots of radiolytic H_2 production.

To a much lesser extent, total radiolytic H_2 production varies with the thickness of the abutting rock (Fig. 4). Over a four-order magnitude of change in basalt thickness (from 100 μm to 1 meter of basalt), H_2 production rates change by only 10% at the rock-water interface. This change is due to differences in the absorbed doses of β and γ radiation. This change is small because α radiation from deeper in the rock does not penetrate to the surface. If the thickness of basalt facing a fracture is less than 50 μm , the rates will drop more dramatically due to a lower absorbed α -dose rate.

Along with microfractures, high concentrations of U, Th and K create hotspots of radiolytic H_2 production. Uranium, Th and K concentrations differ widely from sample to sample within and between the three sites. To illustrate the range of H_2 yields due to initial composition variance, we show a H_2 production range for unaltered basaltic EPR glass samples (Gale et al., 2013). The range of calculated H_2 production at the basalt-water interface is approximately 10-fold for the group of EPR samples with Th composition within two standard deviations of the mean (~90% of the samples) (black lines, Fig. 2). The range is much greater (93-fold) if we consider all EPR glass measurements reported by Gale et al. (2013), which include measurements of enriched mid-ocean ridge basalt (E-MORB) that have much higher U

and Th concentrations. Basement comprised of E-MORB will have higher radiolytic yields than normal ocean basalt.

The 10-fold difference in H₂ yields from EPR data suggests that basaltic source-melt composition has a significant effect on radiolytic rates. Given the wide range of compositions exhibited by the EPR samples, we expect variation in radiolytic H₂ production rates from one SPG site to another, as they all have different geographic locations and ages of origin (Fig. 1). In addition, the basalt at Site U1365 has a very different eruption history than the basalt at Sites U1367 and U1368. The basalt drilled at Site U1365 was accreted during medium to fast spreading and is comprised mostly of large sheet flows. In contrast, the basalts drilled at Sites U1367 and U1368 are predominantly pillow basalt, and were likely produced during slower spreading than at Site U1365 (Zhang et al., 2013; Zhang and Smith-Duque, 2014).

Site U1365 has lower radiolytic H₂ production rates than Sites U1367 and U1368, despite having the oldest and most altered basalt (Fig. 2). This can be attributed to low initial concentrations, as indicated by Th values. Thorium concentrations of U1365 samples are all below 0.2 ppm. These concentrations are lower than those in the samples from the other localities and fall into the bottom half of EPR Th data from Gale et al. (2013). Even with enrichment of U during alteration (indicated by high U/Th ratios) at Site U1365, the radiolytic rates are low compared to the other localities indicating that they are greatly affected by initial radioisotope concentrations. This variation in source-melt composition is consistent with the results of Zhang and Smith-Duque (2014), who used differences in initial composition to explain geochemical variance between Sites U1365 and U1368. In addition, there is also likely

vertical variation at each site due to changes in source composition between eruptive events (e.g., Bergmanis et al., 2007). Zhang et al. (2013) reported some vertical variation at Site U1368. Using U, Th and K from Zhang et al. (2013) results in a 6X difference in radiolytic rates between their lowest normal-MORB sample and the sample they suggest was influenced by an enriched-MORB source. This difference is similar to the 7-fold range in rates calculated from our radioisotope concentration data for this site.

Concentrations of U and K often increase with alteration (e.g., Staudigel et al., 1996; Teagle et al., 1996; Kelley et al., 2003). We use U/Th ratios to constrain how much excess U a sample contains. We don't calculate excess values for K, because K/Th ratios in fresh basalt are not consistent enough to calculate excess K in this manner. Potassium is typically concentrated in such alteration minerals as smectite and zeolite, as well as K-feldspar (Alt and Teagle, 2003; Baretzko, 2005). Shipboard logs of natural gamma radiation (NGR) show clear evidence of such K concentration at alteration fronts in Site U1365 basalt (D'Hondt et al., 2011, 2013). However of the three radionuclides, K contributes the least to total H₂ production because it only produces β and γ radiation when it decays. Using an average concentration for the SPG samples, K contributes 13% to total production at the basalt-water interface. Uranium and Th decay series account for 65% and 22% of the H₂ produced, respectively. Of our SPG basalt samples, K decay dominates H₂ production in only one sample (U1365E-3R-4W 25/30), where it accounts for 48% of the total H₂ yield.

The U decay series is overwhelmingly the largest contributor to H₂ production. Uranium enrichment often occurs in carbonate veins and at oxidation/reduction fronts

during basalt alteration (Alt et al., 1992; Farr et al., 2001; Kelley et al., 2003). Twenty-seven of our SPG samples exhibit U/Th ratios that indicate U enrichment, excluding the sample with Th below the detection limit. In these twenty-seven samples, U enrichment ranges up to a 10X increase, with an average U/Th ratio indicating a 2X increase in U. Our samples bracket the typical enrichment value of 5X for altered basalt when compared to unaltered glass (Kelley et al., 2003). The samples with excess U increase H₂ yields on average by $29\pm6\%$, $60\pm3\%$, and $23\pm10\%$ at Sites U1365, U1367 and U1368, respectively. Therefore, the variation in radiolytic H₂ production rates that we calculate for bulk basalt likely accounts for much of the variation that would be seen in the oceanic crust.

As shown by the variety of visual alteration categories and the wide range of U/Th ratios exhibited by our SPG samples, the kind and extent of alteration vary greatly on a variety of spatial scales. The most intensely altered samples are likely those with most U enrichment, however that does not mean that they have the highest radionuclide concentrations. This can make links between alteration extent and radiolytic yields difficult to clearly identify. Separation of samples by alteration category or by U/Th ratios does not result in obvious patterns, suggesting that there is no simple relationship between radiolytic rates and alteration. Visual inspection of the samples is not enough to fully assess the impact of alteration on radiolytic rates. For example, some of the SPG samples with brown and dark gray alteration halos have U/Th ratios that indicate no U enrichment. Other studies, such as the SPG study of Zhang and Smith-Duque (2014) and the western Pacific study of Kelley et al. (2003) have shown U enrichment especially within these zones. Much closer analysis of

mineral and chemical composition would be needed to fully assess effects of alteration on radionuclide concentrations and radiolytic H₂ production rates of SPG basalt.

The rates we calculate are based on bulk-rock analyses and may underestimate radiolytic H₂ production associated with specific alteration phases. For localized mineral phases with high U, Th or K concentrations rates will be much higher. Staudigel et al. (2008) suggest that weathering of basaltic glass is the dominant process of chemical exchange between basalt and seawater. Alteration of basaltic glass produces palagonite (Staudigel et al., 2008; Türke et al., 2015), a very porous mineral (~14-38 wt% H₂O; Pauly et al., 2011) with high concentrations of radioactive elements (Türke et al., 2015).

Palagonite is of special interest for studies of radiolytic H₂ production in subseafloor basalt because its porous nature and its enriched radionuclide concentrations must result in high radiolytic rates (Türke et al., 2015). Türke et al. (2015) calculated H₂ production rates within palagonite rims and show that H₂ can accumulate to minimum concentrations needed for hydrogentrophy at North Pond (on the western flank of the Mid-Atlantic Ridge). For their calculations, Türke et al. (2015) used a porosity model based on protocols from Lin et al. (2005a) and Blair et al. (2007). Because palagonite is so porous, these models' assumptions of fine grain size and homogeneously distributed porosity are broadly relevant for palagonite calculations. However, these models' assumption that all of the radiation interacts with water is not appropriate for relatively thin palagonite occurrences. Türke et al. note this issue and calculate yields assuming 1% efficiency. However, there is no explicit way to calculate the actual efficiency using their model. The average H₂ production

rates calculated by Türke et al. (2015) are about four times higher than average SPG rates in microfractures. Consequently, palagonite and other similarly porous alteration minerals may significantly increase radiolytic H₂ production relative to neighboring basalt.

Calculating the global rate of radiolytic H₂ production in oceanic basement requires firm constraints on the distribution of fracture widths in the basement, mean concentrations of U, Th and K in the basalt, and porosity and abundance of alteration minerals in the basement. Mapping the horizontal and vertical distribution of radiolytic H₂ production rates in subseafloor basalt requires information beyond the mean, including knowledge of horizontal and vertical variation in fracture width and number, radionuclide (U, Th and K) concentrations, and porosity of alteration phases. Spatial variation in radionuclide concentrations is especially difficult to constrain, because it in turn depends on both (i) initial composition [which can vary from region to region, and even between successive eruptive events at the same location (Bergmanis et al., 2007)] and (ii) alteration history (including the extent and kinds of secondary mineralization) (Alt, 2004).

4.2 Comparison of electron donor fluxes from radiolytic H₂ production and iron oxidation

To assess the potential importance of radiolytic H₂ production for microbial communities in subseafloor basalt, we compare our calculated radiolytic H₂ production rates to iron oxidation rates calculated from Fe(III)/ΣFe ratios compiled by Bach and Edwards (2003) (Fig. 5).

To compare these rates, we convert them to electron transfer rates per unit volume. For Fe oxidation, 1 electron is transferred during oxidation of Fe(II) to Fe(III); for H₂, 2 electrons are transferred for each H₂ molecule produced. For direct comparison, we assume a cubic meter of basalt with 10% porosity, density of 2950 kg/m³ and 8 wt.% Fe (Bach and Edwards, 2003). We use an initial Fe(III)/ΣFe ratio of 0.15±0.05 for fresh basalt and a final ratio of 0.45±0.15 for basalt greater than 10 Ma (Bach and Edwards, 2003). These values include the variation associated with the average Fe(III)/ΣFe ratios at their respective basalt ages. Given these ratios, we calculate a mean oxidation rate of 0.19±0.1 mol Fe oxidized kg basalt⁻¹ Myr⁻¹ for the first 10 Myr of the basalt's existence. Considerable variability in the Fe(III)/ΣFe ratios given by Bach and Edwards (2003) indicates that different regions within the basement have higher, or lower, Fe oxidation rates. For H₂ calculations, we assume that each unique fracture width makes up the 10% porosity in the basalt. For example, there are one thousand 100 μm fractures or one 10 cm fracture in our calculations to account for the correct water-rock ratio.

Given these assumptions, for oceanic crust younger than 10 Ma, calculated electron transfer rates (mol e⁻ per m³ rock per year) due to Fe oxidation are about three orders of magnitude higher than electron transfer rates associated with radiolytic H₂ production (Fig. 5). However, after circa 10 Ma, mean Fe(III)/ΣFe ratios appear to plateau, suggesting that all available Fe has been oxidized (Bach and Edwards, 2003). This means that Fe oxidation rates in basalt older than circa 10 Ma are near zero. In this older basalt, radiolytic H₂ may be more important than Fe(II) as an electron donor for microbial communities.

This change from Fe(II) to radiolytic H₂ as the predominant electron donor is consistent with the palagonite-based conclusion of Türke et al. (2015). In young ridge flanks, Fe oxidation is a main source of energy for microorganisms due to interaction of seawater with fresh basalt in fractures. However in older crust, after permeability decreases and access to fresh basalt is prevented by alteration phases, the availability of Fe decreases and the dominant electron donor may be radiolytic H₂ (Türke et al., 2015).

4.3 Number of cells that might be supported by radiolytic H₂ production in fractures

To estimate how many cells might be supported by oxidation of radiolytic H₂, we divide the radiolytic H₂ flux for different fracture widths by the net per-cell oxygen reduction rates in SPG sediment (Table 1). As with our comparison to Fe(II) oxidation, we convert both radiolytic H₂ production rates and oxygen reduction rates to electron transfer rates. Net per-cell oxygen reduction rates in subseafloor SPG sediment range between $4.2 \times 10^{-17} \pm 2.6 \times 10^{-17} \text{ mol e}^- \text{ cell}^{-1} \text{ yr}^{-1}$ and $6.8 \times 10^{-15} \pm 1.3 \times 10^{-15} \text{ mol e}^- \text{ cell}^{-1} \text{ yr}^{-1}$ (D'Hondt et al., 2015). Using these maximum and minimum oxygen reduction rates and the radiolytic electron fluxes ($\text{mol e}^- \text{ cm}^{-2} \text{ yr}^{-1}$) for discrete fracture widths in our least and most radioactive basalt samples, we can estimate the number of cells that might be supported by H₂ production. If the cells respire at the same rate as the aerobic communities in subseafloor SPG sediment, radiolytic H₂ production in the volume of water adjacent to a square cm of the least radioactive SPG basalt might support up to 30 cells. H₂ production in the same volume of water adjacent to a square cm of the most radioactive SPG basalt might support up to 1500 cells.

5. Conclusions

The extent of life in oceanic crust must depend in large part on the availability of electron donors and acceptors. Water radiolysis produces H_2 , which can be metabolized by microorganisms. Microfractures and local maxima in radionuclide concentrations serve as hotspots for radiolytic H_2 production and may also act as hotspots for microbial life. Differences in initial melt composition and low-temperature alteration by seawater affect concentrations and distributions of U, Th and K within the basement, and consequently also change radiolytic H_2 production rates. Our calculations suggest that in young (less than 10 Ma) basalt, oxidizable Fe(II) is a far more abundant electron donor than radiolytic H_2 . However, in older seafloor, where little Fe is accessible to oxidants in the formation water, radiolytic H_2 may be the dominant electron donor. Radiolytic H_2 in the water adjacent to a square cm of SPG basaltic fracture may support up to 10^3 cells if the cells respire at the same rate as net per-cell oxygen reduction in subseafloor SPG sediment.

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Figure 1. Site locations. Colored dots mark site locations: Site U1365 (yellow), Site U1367 (orange), Site U1368 (red). The site localities are superimposed on a bathymetry map with the East Pacific Rise in light gray. Black lines indicate basement age (20 Myr contours).

Figure 2. Radiolytic H_2 production rates calculated from radionuclide concentrations of our SPG samples. Volume-normalized rates are shown as a function of fracture width for (A) Site U1365, (B) Site U1367 and (C) Site U1368. Black lines mark maximum and minimum rates calculated from EPR glass samples (Gale et al., 2013). Note that both axes are log scale.

Figure 3. Relation of rock alteration to radiolytic H_2 production rates. Volume-normalized rates are given for Sites (A) U1365, (B) U1367, (C) U1368. Colors show the alteration type to which we assigned each sample. Note that both axes are log scale. As in Fig. 2, rates are given as a function of fracture width.

Figure 4. Effect of basalt thickness on radiolytic H₂ production rates. (A) Volume-normalized radiolytic H₂ production for 1-m thick basalt using an average SPG composition of our samples, (B) 1-cm thick basalt and (C) 100- μ m thick basalt. Total production rates are shown as black lines. Rates due to α radiation are shown in blue, β radiation in green and γ radiation in red (x-axis is log scale).

Figure 5. Comparison of electron transfer rates supportable by Fe oxidation and radiolytic H₂ production. Ranges of electron (e^-) transfer rates due to Fe oxidation are shown for basalt of two different ages, 1 Ma and 10 Ma shown by the gray and orange shading, respectively. The blue-hatched region indicates the range of electron transfer supportable by radiolytic H₂ production.

Table 1. Numbers of cells that might be supported by radiolytic H₂ production in SPG basalt. Electron fluxes are calculated from radiolytic H₂ production rates for one square cm of basalt for the least radioactive and most radioactive SPG basalt samples. The ranges of cell numbers that might be supported are calculated from minimum and maximum O₂ consumption rates that are distinguishable from zero within subseafloor SPG sediment (D'Hondt et al., 2015).

Fracture Width (μm)	Least Radioactive SPG Basalt Sample		Most Radioactive SPG Basalt Sample	
	e ⁻ flux per area of fracture surface (mol e ⁻ /cm ² /yr)	Number of cells that might be supported by this flux	e ⁻ flux per area of fracture surface (mol e ⁻ /cm ² /yr)	Number of cells that might be supported by this flux
10 ⁰	7.65E-19	1.1E-04 ± 2E-05 to 1.8E-02 ± 1E-02	6.25E-17	9.2E-03 ± 2E-03 to 1.5E+00 ± 9E-01
10 ¹	6.50E-18	9.6E-04 ± 2E-04 to 1.6E-01 ± 1E-01	4.72E-16	7.0E-02 ± 1E-02 to 1.1E+01 ± 7E+00
10 ²	3.82E-17	5.6E-03 ± 1E-03 to 9.2E-01 ± 6E-01	1.86E-15	2.8E-01 ± 5E-02 to 4.5E+01 ± 3E+01
10 ³	1.08E-16	1.6E-02 ± 3E-03 to 2.6E+00 ± 2E+00	6.80E-15	1.0E+00 ± 2E-01 to 1.6E+02 ± 1E+02
10 ⁴	3.53E-16	5.2E-02 ± 1E-02 to 8.5E+00 ± 5E+00	1.99E-14	2.9E+00 ± 5E-01 to 4.8E+02 ± 3E+02
10 ⁵	9.90E-16	1.5E-01 ± 3E-02 to 2.4E+01 ± 1E+01	5.45E-14	8.1E+00 ± 1E+00 to 1.3E+03 ± 8E+02
10 ⁶	1.16E-15	1.7E-01 ± 3E-02 to 2.8E+01 ± 2E+01	6.35E-14	9.4E+00 ± 2E+00 to 1.5E+03 ± 1E+03

Supplemental Materials

Figure S1. Comparison of volume-normalized radiolytic H₂ production rates for different alteration types at the water-rock interface. The rates are separated by alteration type for Site (A) U1365, (B) U1367, and (C) U1368.

Table S1. Radionuclide concentration of SPG basalt from IODP Expedition 329.
This list includes the U, Th and K concentrations for the 43 samples as well as their alteration type. Sample naming scheme Site-Hole-Core-Section.

Sample Name	Interval Top	Interval Bot	Description	K₂O (wt.%)	Th (ppm)	U (ppm)
U1365-E-3R-1	51	54	Minimally Altered	0.079	0.103	0.052
U1365-E-3R-3	40	44	Carbonate Vein	0.110	0.006*	0.005
U1365-E-3R-3	40	44	Minimally Altered	0.080	0.069	0.030
U1365-E-3R-4	25	30	Mixed	1.550	0.191	0.098
U1365-E-5R-1	50	54	Minimally Altered	0.099	0.100	0.067
U1365-E-5R-3	13	17	Mixed	0.526	0.106	0.073
U1365-E-6R-2	14	16	Minimally Altered	0.044	0.143	0.142
U1365-E-6R-1	40	45	Minimally Altered	0.055	0.094	0.051
U1365-E-6R-2	108	111	Minimally Altered	0.033	0.057	0.024
U1365-E-8R-1	58	63	Carbonate Vein	0.024	0.001*	0.096
U1365-E-8R-1	58	63	Minimally Altered	0.089	0.041	0.029
U1365-E-9R-3	130	133	Minimally Altered	0.061	0.128	0.088
U1365-E-11R-1	80	86	Dark Gray Halo	0.321	0.178	0.143
U1365-E-12R-2	39	45	Fe Staining	0.738	0.170	0.131
U1365-E-12R-2	39	45	Fe Staining	0.753	0.163	0.145
U1365-E-12R-2	117	122	Fe Staining	0.639	0.163	0.223
U1365-E-12R-4	31	34	Dark Gray Halo	0.093	0.174	0.080
U1367-F-2R-3	35	39	Dark Gray Halo	0.224	0.220	0.092
U1367-F-2R-3	69	74	Dark Gray Halo	0.582	0.203	0.204
U1367-F-2R-3	69	74	Minimally Altered	0.241	0.238	0.982
U1367-F-5R-1	40	43	Dark Gray Halo	0.392	0.231	0.250
U1367-F-6R-1	80	85	Minimally Altered	0.175	0.209	0.089
U1368-F-2R-1	33	36	Mixed	0.397	0.800	0.347
U1368-F-2R-1	72	76	Fe Staining	0.434	0.557	0.182
U1368-F-2R-2	88	92	Mixed	0.644	1.173	0.541
U1368-F-2R-3	57	62	Mixed	0.665	0.857	0.327
U1368-F-2R-4	102	107	Minimally Altered	0.496	0.769	0.254
U1368-F-4R-1	71	75	Dark Gray Halo	0.531	0.292	0.216
U1368-F-5R-2	43	48	Minimally Altered	0.116	0.293	0.140
U1368-F-7R-2	24	28	Minimally Altered	0.361	0.304	0.168
U1368-F-7R-2	24	28	Dark Gray Halo	0.415	0.285	0.166
U1368-F-9R-1	42	47	Fe Staining	0.183	0.242	0.086
U1368-F-10R-2	117	120	Minimally Altered	0.317	0.301	0.141
U1368-F-10R-2	117	120	Dark Gray Halo	0.589	0.264	0.113
U1368-F-12R-2	87	91	Dark Gray Halo	0.157	0.270	0.116
U1368-F-12R-4	21	24	Fe Staining	0.161	0.260	0.142
U1368-F-13R-2	0	5	Minimally Altered	0.136	0.252	0.109
U1368-F-13R-2	0	5	Brown Halo	0.317	0.240	0.111
U1368-F-13R-2	31	34	Minimally Altered	0.151	0.241	0.101
U1368-F-13R-2	31	34	Brown Halo	0.355	0.245	0.106
U1368-F-13R-2	57	59	Minimally Altered	0.146	0.242	0.101
U1368-F-13R-2	57	59	Brown Halo	0.424	0.230	0.115
U1368-F-14R-1	111	114	Breccia	3.720	0.243	0.822

*Samples measurement below detection limit of 0.01 ppm

MANUSCRIPT III

Radiolytic H₂ production in Martian environments

By

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Abstract

Identifying habitable environments on Mars is one of the key drivers in the Mars exploration program. To be habitable, an environment must have a source of bioavailable energy. Hydrogen from water radiolysis has been suggested to support microbial communities on Mars. To assess the extent to which H_2 may be produced by water radiolysis in wet martian environments (such as the ancient martian surface and the present martian subsurface), we use satellite radionuclide measurements, an assumption of water saturation, and previously published protocols to calculate radiolytic H_2 production rates ($nM\ H_2\ yr^{-1}$) for the radionuclide compositions of (i) eight proposed Mars 2020 landing sites and (ii) three sites that individually yield the highest or lowest calculated radiolytic H_2 production rates. Production rates for the compositions of the proposed landing sites differ by a factor of two. Production rates for the three comparison sites differ by a factor of six. H_2 production rates calculated for low porosity, fine-grained martian sediment generally exceed rates previously calculated for South Pacific basaltic basement. Rates for water-saturated high-porosity martian sediment ($> 35\%$) and water-filled martian microfractures ($1\ \mu m$) match South Pacific basalt rates. Rates for larger water-filled martian fractures ($1\ cm$ and $10\ cm$) are generally one to two orders of magnitude lower than South Pacific basalt rates. Radiolytic H_2 production rates in wet martian sediment and microfractured rock are comparable to rates in terrestrial regions known to harbor low concentrations of microbial life. If a mineral (such as zeolite) or brine that amplifies radiolytic H_2 production rates is present, potential H_2 production may be even higher.

Keywords: Mars; Water Radiolysis; Habitability; Geochemistry; Hydrogen

1. Introduction

The search for extraterrestrial life has prompted over twenty surface and orbital missions to Mars. Many of these missions focus on identifying past and present aqueous environments, as water is a fundamental requirement for life as we know it. However, it is not the only requirement for life. For an environment to be habitable, it must also provide biologically harvestable energy. A variety of geochemical processes produce chemical species that can be metabolized by microorganisms for energy. Several studies have proposed that some subsurface microbial communities on Earth rely on molecular hydrogen (H_2) as their primary electron donor. In terrestrial subsurface environments H_2 can be produced through water radiolysis (i.e. Pedersen, 2000; Lin et al., 2005a; Blair et al., 2007; Dzaugis et al., 2016), rock weathering (i.e. Stevens and McKinley, 1995; Pedersen, 2000) or serpentinization (i.e. Kelley *et al.*, 2001; 2005). These chemosynthetic communities serve as models for life on other planets, such as Mars (McCollom and Seewald, 2013). Here we quantify the potential of water radiolysis' production of H_2 as an electron donor source on Mars. Our radiolysis calculations are relevant for water-saturated martian environments, such as the ancient martian surface or the present martian subsurface.

Previous studies have suggested that radiolytic processes might support life on Mars (i.e. Lollar et al., 2007; Lin et al., 2005b; Lefticariu et al., 2010; Türke et al., 2015). However, few studies have quantified radiolysis rates. In order to better understand the origin of the subsurface methane flux on Mars, Onstott et al. (2006) investigated the diffusion of He, H_2 , and CH_4 through the martian crust. Onstott et al (2006) calculated a general H_2 production rate for the deep subsurface martian crust

and coupled that rate to microbial CH_4 production. In contrast, we calculate specific rates for a broad range of martian lithologies, based on compositional data from the martian surface.

One of the key questions for the Mars 2020 rover mission is directed at the potential for life on Mars. The mission is focused on searching for habitable conditions on ancient Mars, as well as searching for biosignatures of past microbial life (Mustard et al., 2013). To determine if radiolytic H_2 was a potential source of energy for ancient life, we calculate radiolysis rates for the eight potential Mars 2020 Rover landing sites. We also determine what lithology on Mars is associated with the highest and lowest H_2 production, giving a range of H_2 that may be produced in present day martian subsurface groundwater.

The physical structure of Martian material ranges from loose, fine-grained regolith to large pieces of fractured rock. To account for this heterogeneity, we calculate H_2 production rates using two different radiolysis models. One is for a fractured hard-rock aquifer (Dzaugis et al., 2015), while the other is for water-saturated fine-grained sediment (Blair et al., 2007). We use these models to quantitatively estimate radiolytic H_2 production in water-saturated martian environments. We then discuss the relevance of these results for eight locations that have been proposed as future landing sites.

2. Methods

In this section, we describe the radiolysis models and discuss the variables that underlie our calculations. These variables include the composition of the fractured rock, sediment porosity, radioactivity, density, and the number of H_2 molecules

produced per energy absorbed (G-value). We also briefly describe the landing sites we consider in our study.

2.1 Fractured hard-rock model

We have previously used this model (Dzaugis et al., 2015) to calculate production rates in oceanic basaltic aquifers on Earth (Dzaugis et al. 2016). While we use the same overall method for Mars as we used for the oceanic basalt aquifer, we have modified some parameters, such as density, for application to Mars.

In fractured rock, radionuclides not located on the rock-water interface emit radiation that first travels through the rock matrix before interacting with water. Geochemical analysis of martian surface rock and martian meteorites suggests that rock on Mars is dominantly basaltic in composition (McSween et al., 2015). The composition of igneous rocks from Gusev and Gale craters and SNC meteorites, as well as measurements from the gamma ray spectrometer on Mars Odyssey, all indicate ~40-55 wt% SiO₂ (McSween et al., 2003). To understand how α -, β -, and γ -radiation energy attenuates as it travels through rock, we use stopping power and range data from the NIST database (Berger et al., 2005; Hubbell and Seltzer, 2004). The NIST database does not have energy-range data specifically for basalt; therefore we use data from SiO₂ as it is the closest material in the database to martian rock. The density of the rock is also an important parameter, which we discuss further in Section 2.4.

We calculate H₂ production rates normalized to water volume (nM H₂ yr⁻¹) for a wide range of fracture apertures. Fracture width greatly affects the production rate of H₂. Since we do not know the distribution of fracture widths on Mars, we present three cases to illustrate how H₂ yields change as a function of width (1 μ m, 1cm and 10cm).

In our calculation, we take into account the radiation emitted from both sides of the fracture. We use dose rates (radiation absorbed per time) produced by 1 meter of rock abutting both sides of the fracture. Using 1m allows us to calculate the maximum H₂ production. Radiation generated in the ²³⁸U, ²³⁵U and ²³²Th decay series or by ⁴⁰K decay cannot travel through more than 1m of rock. However, since α -particles generate the most H₂ per energy absorbed and travel in rock on average $\sim 30\mu\text{m}$, rates do not greatly decrease until there is less than $50\mu\text{m}$ of rock. For example, calculations using 1cm and $100\mu\text{m}$ of rock decrease the H₂ production rate by less than 4% and 10% respectively, relative to 1m of rock.

2.2 Sediment Model

We also calculate radiolysis rates for fine-grained water-saturated sediment. This model assumes a homogenous mixture of water and particles less than $30\mu\text{m}$ in diameter (the stopping distance of α -particles) (Blair et al., 2007).

We convert the sediment results from $\text{molH}_2 \text{ yr}^{-1} \text{ cm}^{-3}_{\text{sed}}$ to a concentration per volume of water over time (nM yr^{-1}) to compare sediment results to fractured-rock results. We include results for three different porosities (1%, 35%, and 80%) to parallel the fractured rock model. We include calculations at 1% porosity since it produces the highest H₂ production rate per volume of water. A porosity value of 35% is used in various studies that calculate formation timescales for martian depositional fans and deltas, such as in channelized fans located in Holden crater and Melas Chasma (Jerolmack et al., 2004; Kleinhans, 2005; Metz et al., 2009). Lastly we give results for 80% porosity, a porosity value estimated for pelagic oceanic clay on Earth's seafloor (Hamilton, 1976; Spinelli et al., 2004). We compare to pelagic clay since the

sediment model is restricted to sediment clay to medium-silt grain size (30 μ m). Grain density is also an important variable in the calculation; for the value we use for martian lithologies see Section 2.4

We also updated values given in Blair et al. (2007) for the total energy emitted from ^{238}U , ^{235}U and ^{232}Th decay series, assuming secular equilibrium, and ^{40}K decay. For each radionuclide the energy of each α -, β -, and/or γ -radiation emitted is summed separately (MeV/decay series). Note the β -energy sums differ greatly because we calculate an average initial energy for each β -particle. Beta particles are emitted with a continuous spectrum of energy ranging from near zero to a maximum value specific to each radionuclide. To account for this continuous energy distribution, we use the average initial energy, or 1/3 of the maximum energy, when calculating β -decay energy sums (L'Annunziata, 2007). These updated values match those used in fractured rock calculations (Supplemental Table S3).

2.3 Radionuclide concentrations

Water radiolysis is the dissociation of water molecules by ionizing radiation from decay of radioisotopes. The principle radioisotopes on Mars are in the uranium (^{238}U and ^{235}U) decay series, thorium (^{232}Th) decay series and potassium (^{40}K). The uranium and thorium series emit α -, β - and/or γ -radiation as they and their daughter nuclides decay, while ^{40}K decay emits β - and γ -radiation. The radiolysis rate is directly related to radionuclide activities. For martian ^{40}K and ^{232}Th concentrations, we used data collected by the Gamma Ray Spectrometer (GRS) on the Mars Odyssey (Boynton et al., 2007). Gamma ray spectrometers calculate the abundance and distribution of K and Th by measuring characteristic gamma rays that are emitted from the top ten

centimeters of the planet's surface (Boynton et al., 2004). Landers and rovers have also collected information on K concentrations (McLennan, 2001). These lander and rover measurements, however, are spatially restricted and trace element concentrations are not always reported. When available, abundance based on satellite GRS show good correlation to in situ data collected at landing sites by surface instruments (Boynton et al. 2007; Karunatillake et al. 2007).

Radiogenic Th and K concentrations are measured for the globe, while other elements in the GRS dataset are constrained to the mid-latitudes because high H abundance (a neutron moderator) affects the neutron flux at high latitudes where there is subsurface ice. Independent of the moderation of neutrons, ice cover near the poles can bias K and Th concentrations toward lower values because some of the top ten centimeters is composed of ice (Taylor et al., 2006; Boynton et al., 2007). Boynton et al. (2007) summed elemental spectra and binned them in 5 x 5 degree bins to improve signal to noise ratios and stated instrumental spatial resolution for K and Th at approximately 215 km and 240 km arc radius, respectively. We include the reported uncertainty associated with smoothed radionuclide concentration measurements in our final radiolysis error calculations (Supplemental Table S1 and S2). Uranium abundance has not been calculated from GRS data, due to its weak signal to noise ratio (Boynton et al. 2007; Karunatillake et al. 2007). In this study, we calculate U concentrations by using Th concentrations from GRS data, and assuming a constant U/Th ratio of 0.28, a value representative of most SNC meteorites (McLennan, 2003; Baratoux et al., 2011). We show global maps of U, Th and K distributions in Figure 1.

Radiogenic element concentrations vary with lithology on the martian surface. There is some evidence on Mars for a uniform global dust unit with relatively constant basaltic mineralogy (Yen et al., 2005). If present, however, it is less than ten centimeters thick, since otherwise the martian surface would exhibit a constant radionuclide distribution. We calculate the activity of each radionuclide and use this value to generate radiolytic H₂ production rates.

2.4 Density

As stated previously, radiolytic H₂ production rates depend on rock density. The density values for our calculations are based on the range suggested by Baratoux et al. (2014) for martian crust (3100 to 3300 kg/m³). Previous studies suggested a lower range of 2700 to 3100 kg/m³ (i.e., Zuber, 2001; McGovern et al., 2002; Wieczorek and Zuber, 2004; Neumann et al., 2004). Baratoux et al. (2014) based their conclusions on new and updated density calculations from GRS measurements, chemical analysis of Martian meteorites and analysis of material in the Gusev crater. Their results indicate that the crust is thicker than previously thought and suggest that the most plausible densities range from 3100 to 3200 kg/m³ (Baratoux et al., 2014; Zharkov and Gudkova, 2016). For our study, we use a minimum density of 3000 kg/m³ (to account for some decrease in bulk density due to surface porosity) and a maximum of 3300 kg/m³ (the upper bound of martian basalt density). Because radiolysis rates scale linearly with density, the calculated rates change by less than 10% due to uncertainty in density. We include this effect in our uncertainty calculations reported in Supplemental Tables S1 and S2.

2.5 G-values

We calculate H₂ production rates using pure-water G-values (the number of H₂ molecules produced per 100 eV) (Table 1). Pure water G-values are well constrained for each type of radiation, however, they provide a minimum estimate of H₂ production because the presence of catalytic minerals (Sauvage et al., 2016) and/or radiolysis of brine (Kelm and Bohnert, 2004) can increase H₂ production. We include a short discussion in Section 3.3 on the effects of minerals and brine on G-values and radiolytic H₂ production rates.

2.6 Localities

We discuss in detail radiolytic H₂ production rates derived from the radioisotope composition of eleven locations on Mars (Fig. 2). Eight of these locations are proposed landing sites for the Mars 2020 rover. These include Columbia Hills (Gusev Crater), Eberswalde Crater, Holden Crater, Jezero Crater, Mawrth Vallis, Nili Fossae, NE Syrtis Major and SW Melas Chasma. The radioisotope composition of the three additional locations yields our minimum and maximum radiolytic H₂ production rates for Mars. These three locations are in Acidalia Planitia (maximum rates), the northern pole (minimum rates) and Promethei Terra (minimum rates for a region without ice cover). We list the locations and lithologies of these eleven localities in Table 2 and our calculated H₂ production rates in Table 3.

3. Results and Discussion

In the following sections, we discuss H₂ production rates given the radioisotope compositions of proposed Mars landing sites and comparison sites. Because our calculated rates assume water saturation, they correspond to ancient (wet Mars) rates at these sites, and to rates for present-day wet subsurface environments with the same

radioisotope compositions. Finally, to assess whether radiolysis can sustain life on Mars, we compare martian rates to terrestrial rates.

As we mentioned previously, fracture width and porosity affect the H_2 production rate in a given volume of water ($nM\ yr^{-1}$). Volcanic rocks are characterized by a range of fracture widths. In fractured rock of constant radioisotope composition, microfractures have the highest H_2 production rate per volume of water (Table 3) (Dzaugis et al., 2016). Production rates in a $1\mu m$ wide fracture are more than two orders of magnitude higher than production rates in a 10cm wide fracture (Table 3). Sediment porosity also affects H_2 production rates per volume water. Production rate ($nM\ yr^{-1}$) in sediment at 1% porosity is over an order of magnitude higher than at 80% porosity (Table 3). Production rates in fine-grained sediment are overall higher than those produced in fractured rock. At any given site, the H_2 production rate in sediment with ~60% porosity is similar to the production rate in microfractured rock.

3.1 H_2 production rates at potential Mars 2020 landing sites

Identifying past and present habitable environments is one of the main objectives of Mars Exploration missions (Mustard et al., 2013). Many of the locations have similar geological and topological features in part due to the criteria for selecting safe sites for rovers to land and travel. Most of the selected regions are rich in clay-like mineral deposits. In addition, each site must integrate science objectives, such as having an ancient environment likely to have been habitable, accessibility to rocks with biosignature preservation potential, and presence of geologic materials to help answer questions about planetary evolution (Mustard et al., 2013). Since oxidation of H_2 is a known source of chemical energy for microbial life, estimates of H_2 production

rates in water-saturated lithologies that match the radioisotope compositions of proposed Mars 2020 sites are important for understanding the ancient habitability of those sites.

Deltaic, fluvial, lacustrine and hydrothermal sites are among those flagged as ideal due to evidence of flowing aqueous fluids and the presence of clays which have the potential for recording signs of ancient life (Ehlmann et al., 2008). Deltas are amongst the best environments to support organic matter formation and preservation (Summons et al., 2011). Deltaic environments include Eberswalde Crater and Jezero Crater. Eberswalde Crater contains extensive, layered deltaic sediments believed to recently been exposed (Rice et al., 2013). Jezero crater has both deltaic and lacustrine deposits. Its stratigraphy is well defined, including volcanic, alteration mineral-bearing and fluvio-lacustrine units (Schon et al., 2012).

Ancient lacustrine sites are similarly favored for their biotic production, concentration and preservation of organic materials. Paleolake deposits occur in Holden Crater and in the SW Melas basin. There is evidence of layered flood deposits and bedrock outcrops at Holden Crater (Irwin et al., 2015). SW Melas basin is home to many ancient aqueous landforms and canyons that cut through layered lake deposits with well-defined stratigraphic units (Williams and Weitz, 2014). Mawrth Vallis is an ancient channel that is rich in clay-like sediment (containing phyllosilicate minerals) (Bishop et al., 2008). It may also contain a paleosol sequence, which has high potential for preserving biosignatures and preserving diverse geochemical environments (Loizeau et al., 2015).

Hydrothermal sites are also of interest in the search for ancient life. Evidence of ancient hydrothermal activity and/or hot springs was discovered at Columbia hills by the Mars Exploration rover, Spirit (Squyres et al., 2008). NE Syrtis Major was volcanically active, with widespread liquid water activity and a variety of distinct environments of interest (Hiesinger and Head, 2004). There are large methane plumes, as well as carbonate and altered clay minerals near Nili Fossae, located north of Syrtis Major. The carbonates likely formed in subsurface hydrothermal environments, while surface sedimentary systems deposited the clays (Ehlmann et al., 2009).

Calculated radiolytic H₂ production rates for water-saturated lithologies with radioisotope compositions of the eight landing sites are all within a factor of two. The eight sites have similar relative errors, ~8% of the production rate (Supplemental Table S1 & S2). These errors include the reported uncertainty of GRS radionuclide measurements as well as uncertainty in martian crustal density values. The radioisotope composition of Mawrth Vallis yields the highest H₂ production rate of the lander sites, while the composition of the SW Melas basin yields the lowest rate (Table 3). For fine-grained sediment with 1% porosity, calculated H₂ production rates approach 1 nM yr⁻¹ at Mawrth Vallis. The highest rates produced using the fractured rock model are 3-4 times lower. If radiolytic H₂ supported life on Mars in the past and the physical properties of the sites were the same, water-saturated sediment or rock with the radioisotope content of Mawrth Vallis could have support 1.6 ± 0.2 times more cells than water-saturated sediment or rock with the radioisotope composition of Melas basin. Larger variations may have occurred if the dominant sediment and rock at the sites respectively differed in porosity and fracture width.

3.2 Total range of radiolytic H_2 production rates

H_2 production rates ($nM\ yr^{-1}$) calculated from surface martian radioisotope concentrations vary by a factor of 5 to 7 when ice-covered regions are included (Table 3). As stated previously, although GRS reports radionuclide concentrations at latitudes greater than $75^\circ N$, they are likely biased toward low values due to the presence of ice. If ice-covered regions are excluded, the range is 2.5-fold to 4.5-fold.

If water content, sediment porosity and fracture width are held constant, the distribution of H_2 production is principally dictated by U and Th series nuclide concentrations (Fig. 1). Alpha radiation generates the most H_2 . Both Th and U decay series produce α -, β - and γ - radiation, while K decay only produces β - and γ - radiation. Therefore, per decay, the U and Th series are most effective in generating H_2 . Uranium ($^{238}U + ^{235}U$) and ^{232}Th decay series activity explains 49-53% and 39-42% of the H_2 production for each site, respectively, while ^{40}K decay contributes only 4-11%.

The highest production rate is associated with the radioisotope content of Acidalia Planitia in the northern highlands (Table 3). If this composition is present at depth where water is present or was in the past in contact with water, fine-grained sediment with 1% porosity yields rates of $1.18 \pm 0.081\ nM\ yr^{-1}$, while microfractured rock produces a H_2 production rate of $0.350 \pm 0.024\ nM\ yr^{-1}$. The high H_2 production associated with Acidalia Planitia is due to local enrichment in radionuclides. Acidalia Planitia contains plains of eolian deposits as well as cone and dome structures possibly formed by mud volcanism, hot spring/geysers or lava flows (Farrand et al., 2005). If mud volcanism is responsible for the cones, sediment from depth has been transported to the surface. Sediment from a fluid-rich environment may be of importance when

searching for past or present life on Mars (Farrand et al., 2005; Oehler and Allen, 2010). In general, the northern highlands are enriched in K and Th (Fig. 1). This region contains andesite, basaltic andesite, or weathered basalt (Bandfield, 2000; Wyatt and McSween, 2002). Basaltic lava flows at Tharsis Montes and Olympus Mons shield volcanoes have less than average K and Th concentrations.

Just as the maximum H₂ production rate occurs in a region enriched in radionuclides, the minimum H₂ production rate occurs where the sediment or rock is depleted in radionuclides (Fig. 1). Within the bounds of 75°N and 75°S, the radioisotope composition of Promethei Terra yields the lowest calculated rates: $0.331 \pm 0.051 \text{ nM yr}^{-1}$ for 1% porosity sediment and $9.87\text{E-}02 \pm 1.5\text{E-}02 \text{ nM yr}^{-1}$ in 1 μm fractures (Table 3). Promethei Terra consists of interbedded volcanic rock and impact breccia. There is evidence that both fluvial and glacial processes shaped the terrain. The landscape of Promethei Terra was also shaped by the impact that formed the Hellas basin (Ivanov et al., 2010). The radioisotope composition of the large impact basin, Hellas Planitia, also yields a very low calculated H₂ production rate: $0.434 \pm 0.115 \text{ nM yr}^{-1}$ for 1% porosity sediment (the large percent error is due to high uncertainty in GRS measurements). The basin floor of Hellas Planitia contains mesas and ridges covered by dust and eroded mantle materials. The older ridged plains material is covered by a combination of breccia, interbedded volcanic materials, as well as eolian and fluvial deposits (Leonard and Tanaka, 2001).

The lithology of Promethei Terra may not produce the lowest H₂ production rate. The lowest calculated rates result from GRS-measured radioisotope concentrations in the northernmost latitudes, where the measured concentrations are likely decreased by

the permanent ice cap (Table 3). Despite this effect, in this region covered by water ice and dust (Bibring et al., 2004), calculated H_2 production can reach rates higher than those found in ice-free regions of Mars; maximum rate in the ice-capped area calculated for sediment is 0.602 nM yr^{-1} . This comparison suggests that there may be locally high H_2 generation rates within or under the polar ice caps.

3.3 Comparison to terrestrial H_2 production rates

Calculated rates for microfractured rock and sediment in this study overlap with calculated H_2 production rates in Earth's oceanic basement basalt. In the upper 100m of South Pacific basement basalt, radiolytic H_2 rates range from ~ 0.02 to 0.6 nM yr^{-1} (Dzaugis et al., 2016). Calculated martian H_2 production rates for water-saturated low-porosity sediment with the radioisotope composition of the eight Mars 2020 sites generally exceed those of South Pacific basement basalt. Rates for water-saturated, high-porosity martian sediment ($\geq 35\%$) and water-filled martian microfractures ($1\mu\text{m}$) are comparable to South Pacific basalt rates. Rates for larger water-filled martian fractures (1cm and 10cm) are generally one to two orders of magnitude lower than South Pacific basalt rates (compare to Dzaugis et al., 2016).

Some material properties might lead radiolytic H_2 production rates in water-saturated martian materials to be significantly higher than the values that we have calculated. For example, some minerals catalyze H_2 production from water radiolysis (e.g., Laverne and Tandon, 2003). Sauvage et al. (2016) recently showed that zeolitic deep-sea clay increases $G_{\alpha,\gamma}(H_2)$ values by a factor of 5-33. There is spectral evidence of zeolite minerals on Mars' surface (Ruff, 2004). If and where zeolite is present on

Mars, radiolytic H₂ production rates on Mars may approach rates that are thought to support life in ocean sediment (Sauvage et al., 2016).

The amount of salt in the water may also affect the amount of H₂ generated. In this study we use pure water G(H₂) values in our calculations, however Kelm and Bohnert (2004) suggest radiolysis of 5M NaCl brine can produce more H₂ molecules per energy absorbed than pure water. There is physical evidence of brine on the surface of Mars (Martínez and Renno, 2013). Where liquid brine is present, H₂ production rates may be higher than the values we calculate.

4. Conclusions

We calculated radiolytic H₂ production rates (nM yr⁻¹) for a range of martian lithologies assuming water-saturated porosity. These rates vary by up to a factor of two from one proposed Mars 2020 site to another. The highest rates on Mars are for water-saturated material with the radioisotope concentrations of Acidalia Planitia (where surface materials are enriched in U and Th).

If the levels of radioactivity of the surface lithologies extend into the martian subsurface, where water is likely to exist, the subsurface could prove to be a prime target for the search for extant life on Mars. Rates calculated for wet low-porosity martian sediment consistently match or exceed rates previously calculated for South Pacific basement basalt. Rates calculated for microfractured rock (1μm) and sediment with >35% porosity at the Mars 2020 sites match the low-end rates calculated for South Pacific basement basalt. In short, radiolytic H₂ production rates in wet martian sediment and microfractured rock are comparable to rates in terrestrial regions known to harbor low concentrations of microbial life.

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Figure 1. Radionuclide concentrations. (A) Uranium (ppm); (B) Thorium (ppm); and (C) Potassium (wt %). Th and K concentrations are based on results from the Mars Odyssey Gamma Ray Spectrometer (Boynton et al., 2007). As described in the text, we calculated U concentrations using a constant U/Th ratio of 0.28.

Figure 2. Topographic map of Mars. Site names and significant features identified. Topology map from MOLA.

Table 1. G-values in $\mu\text{mol J}^{-1}$ for pure water. $G(\text{H}_2)$ values are given for α -, β -, and γ -radiation and used in both models.

	Alpha	Beta	Gamma
$G(\text{H}_2)$	0.135 ¹	0.06 ²	0.025 ¹

¹Essehli et al., 2011

²Kohan et al., 2013

Table 2. Locations, radioisotope concentrations, and lithologic descriptions of sites used to calculate potential martian radiolytic H_2 production rates. Radionuclide concentrations are determined from the interpolated distribution maps in Figure 1.

Site	Location (lat °N, long °E)	Uranium (ppm)	Thorium (ppm)	Potassium (wt %)	Main Lithology/ Geologic feature
Acidalia Planitia	48, -32	0.262	0.942	0.436	Mottled lava plains
Mawrth Vallis	24.0, -18.9	0.205	0.738	0.351	Channel deposits, phyllosilicate minerals
Columbia Hills	-14.4, 175.6	0.174	0.629	0.323	Hydrothermal, hot springs
NE Syrtis Major	17.8, 77.1	0.165	0.595	0.313	Volcanic and hot spring activity
Jezero Crater	18.5, 77.4	0.164	0.593	0.313	Ancient delta rich in clay minerals
Nili Fossae	21.0, 74.5	0.158	0.569	0.292	Methane plumes, carbonate and altered clay minerals
Holden Crater	-26.4, -34.9	0.146	0.527	0.278	Ancient lake and flood deposits, alluvial fans
Eberswalde Crater	-23.0, -33.0	0.141	0.508	0.299	Ancient delta, possible lake deposits
SW Melas Basin	-12.2, -70.0	0.125	0.450	0.310	Canyon, cuts through lake deposits
Promethei Terra	-67, 97	7.01E-02	0.252	0.216	Interbedded volcanic rock and impact breccia
Northern pole	87,5	4.58E-02	0.166	7.71E-02	Dust and ice

Table 3. Radiolytic H₂ production rates given the radionuclide concentrations of 11 localities on Mars' surface. We show production rates for both fractured rock and sediment models. Volume-normalized rates are given for three fractured-rock scenarios (varying fracture width) and three sediment scenarios (varying porosity).

Site	Main Lithology/ Geologic feature	H ₂ production rates for water-filled rock fractures (nMH ₂ yr ⁻¹)			H ₂ production rates for water-saturated sediment (nMH ₂ yr ⁻¹)		
		Width: 1μm	Width: 1cm	Width: 10cm	Porosity: 1%	Porosity: 35%	Porosity: 80%
Acidalia Planitia	Mottled lava plains	0.350	8.68E-03	3.43E-03	1.18	0.667	0.174
Mawrth Vallis	Channel deposits, phyllosilicate minerals	0.276	6.87E-03	2.73E-03	0.926	0.524	0.136
Columbia Hills	Hydrothermal, hot springs	0.236	6.05E-03	2.42E-03	0.793	0.449	0.117
NE Syrtis Major	Ancient delta rich in clay minerals	0.222	5.77E-03	2.28E-03	0.748	0.424	0.110
Jezero Crater	Volcanic and hot spring activity	0.222	5.76E-03	2.28E-03	0.747	0.422	0.110
Nili Fossae	Methane plumes, carbonate and altered clay minerals	0.213	5.46E-03	2.16E-03	0.716	0.404	0.105
Holden Crater	Ancient lake and flood deposits, alluvial fans	0.197	5.12E-03	2.02E-03	0.664	0.376	9.78E-02
Eberswalde Crater	Ancient delta, possible lake deposits	0.192	5.19E-03	2.04E-03	0.645	0.365	9.50E-02
SW Melas Basin	Canyon, cuts through lake deposits	0.173	4.96E-03	1.96E-03	0.578	0.327	8.55E-02
Promethei Terra	Interbedded volcanic rock and impact breccia	9.87E-02	3.11E-03	1.22E-03	0.331	0.187	0.049
Northern pole	Dust and ice	6.14E-02	1.52E-03	6.05E-04	0.207	0.117	0.030

Supplemental Material

Table S1. Fractured-rock rates with uncertainty values (SE). Sites identify where radionuclide concentrations are used to calculate H₂ production rates. Results are given for three different fracture widths.

Site	H ₂ production rates with SE for water-filled rock fractures (nMH ₂ yr ⁻¹)		
	Width: 1μm	Width: 1cm	Width: 10cm
Acidalia Planitia	0.350 ± 0.024	8.68E-03 ± 4.7E-04	3.43E-03 ± 1.9E-04
Mawrth Vallis	0.276 ± 0.021	6.87E-03 ± 4.0E-04	2.73E-03 ± 1.6E-04
Columbia Hills	0.236 ± 0.018	6.05E-03 ± 3.4E-04	2.42E-03 ± 1.4E-04
NE Syrtis Major	0.222 ± 0.018	5.77E-03 ± 3.4E-04	2.28E-03 ± 1.4E-04
Jezero Crater	0.222 ± 0.018	5.76E-03 ± 3.4E-04	2.28E-03 ± 1.4E-04
Nili Fossae	0.213 ± 0.017	5.46E-03 ± 3.2E-04	2.16E-03 ± 1.3E-04
Holden Crater	0.197 ± 0.016	5.12E-03 ± 3.0E-04	2.02E-03 ± 1.2E-04
Eberswalde Crater	0.192 ± 0.016	5.19E-03 ± 3.0E-04	2.04E-03 ± 1.2E-04
SW Melas Basin	0.173 ± 0.014	4.96E-03 ± 2.8E-04	1.96E-03 ± 1.1E-04
Promethei Terra	9.87E-02 ± 1.5E-02	3.11E-03 ± 2.3E-04	1.22E-03 ± 1.0E-04
Northern pole	6.14E-02 ± 8.7E-03	1.52E-03 ± 1.3E-04	6.05E-04 ± 5.5E-05

Table S2. Sediment rates with uncertainty values (SE). Sites identify where radionuclide concentrations are used to calculate H₂ production rates. Results are given for three sediment porosity values.

Site	H ₂ production rates with SE for water-saturated sediment (nMH ₂ yr ⁻¹)		
	Porosity: 1%	Porosity: 35%	Porosity: 80%
Acidalia Planitia	1.18 ± 0.081	0.667 ± 0.045	0.174 ± 0.012
Mawrth Vallis	0.926 ± 0.072	0.524 ± 0.040	0.136 ± 0.010
Columbia Hills	0.793 ± 0.060	0.449 ± 0.034	0.117 ± 8.8E-03
NE Syrtis Major	0.748 ± 0.062	0.424 ± 0.035	0.110 ± 9.0E-03
Jezero Crater	0.747 ± 0.062	0.422 ± 0.035	0.110 ± 9.0E-03
Nili Fossae	0.716 ± 0.059	0.404 ± 0.033	0.105 ± 8.6E-03
Holden Crater	0.664 ± 0.054	0.376 ± 0.031	9.78E-02 ± 7.9E-03
Eberswalde Crater	0.645 ± 0.055	0.365 ± 0.031	9.50E-02 ± 8.1E-03
SW Melas Basin	0.578 ± 0.048	0.327 ± 0.027	8.55E-02 ± 7.0E-03
Promethei Terra	0.331 ± 0.051	0.187 ± 0.029	4.90E-02 ± 7.4E-03
Northern pole	0.207 ± 0.030	0.117 ± 0.017	3.05E-02 ± 4.3E-03

Table S3. Energy sum for α -, β -, and γ -decay. Calculation of these parameters is based on values from nuclear data tables^{1,2}.

	α -decay energy sum (MeV/decay)	β -decay energy sum (MeV/decay)	γ -decay energy sum (MeV/decay)
²³⁸ U	56.68	2.307	5.834
²³⁵ U	55.01	1.353	1.427
²³² Th	39.10	1.290	4.276
⁴⁰ K	--	0.3502	0.1606

¹Nucleonica GmbH, Nuclide Datasheets, Nucleonica Nuclear Science Portal (www.nucleonica.com), Version 3.0.49, Karlsruhe (2014c).

²Hacker, C. (1997). Radiation Decay (RadDecay) Code, Version 4. Engineering and Applied Science, Griffith University, Australia.