MODELING ABIOTIC HYDROGEN GENERATION FROM THE GRANITE BASEMENT IN THE SOULTZ-SOUS-FORÊTS GEOTHERMAL SYSTEM, RHINE GRABEN, FRANCE

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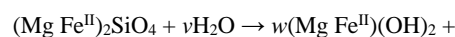
ABSTRACT

Investigations on geochemical processes for H_2 generation in natural reservoirs are important for the present energy transition where alternatives to fossil fuel sources of energy such as H_2 are necessary. Most of the studies related to natural abiotic H_2 generation are focused on the serpentinization of mafic and ultra-mafic rocks, where the source of H_2 is linked to the oxidation of Fe(II) bearing minerals and the so-called reduction of H_2O. In this study, we investigate a route for abiotic H_2 generation from a rich biotite acid rock like granite that constitutes the basement of the Soultz-sous-Forêts Enhanced Geothermal System. Using geochemical and reactive transport modeling and the existing data base of the Soultz-sous-Forêts project, we simulated the hydrothermal alteration of the granite for the in situ temperature of 165 ˚C and the redox potential, of -245 mV. The simulations showed that generation of abiotic H_2 is possible by hydrothermal alteration of biotite as a source of Fe(II), which oxidizes to Fe(III) leading to the precipitation of ferric iron minerals and reduction of protons (H^+) under such low redox conditions. Most likely, optimal conditions for H_2 generation are related to magnetite precipitation, as observed in the serpentinization process. This study has implications for possible coupling of heat extraction with H_2 production.

1. INTRODUCTION

An increased number of investigations on the generation of natural abiotic H_2 (hydrogen-gas) has been developed recently, motivated by the increasing interest in the new CO_2-free energy sources in the world scenario of energetic transition. The H_2 generation by serpentinization of ultramafic rocks (e.g. peridotite) is the most studied natural process for H_2 generation (Shock and Shulte, 1998; McCollom and Batch., 2009; McCollom et al., 2016; Mügler at al., 2016; Miller et al., 2017; Bauchaud et al., 2017; Vacquand et al., 2018). In this process, the source of H_2 is linked to the oxidation of Fe(II) bearing minerals and the so-called reduction of water that can be represented by the general reaction (Klein et al., 2013):

$$(Mg\ Fe^{II})_2SiO_4 + vH_2O \rightarrow w(Mg\ Fe^{II})(OH)_2 +$$

olivine   brucite

$$x(Mg\ Fe^{III})_{3\text{-}}(Si\ Fe^{III})_2)O5(OH)_4 + y\ Fe^{II}\ Fe^{III}_2O_4 + zH_2\ (1)$$

serpentine   magnetite

The Soultz-sous-Forêts project is an Enhanced Geothermal System located in the Upper Rhine Graben (France) with a high local thermal gradient. Three deep wells ($\approx$5000 m depth) were drilled on site penetrating the granite basement, creating a heat exchanger to produce electricity. Previous measurements of gases in the Soultz-sous-Forêts boreholes have reported values in a range of $0.25 - 46.3\%$ vol. of H_2 (Sanjuan et al, 2010; 2016). These values are still not well understood and their natural (granitic reservoir) or anthropogenic origin (reactions between the steel borehole casing and the brine) is not resolved. The basement rock is a massive granite with different petrographic types, very rich in biotite and amphibole, and different grades of fractured and hydrothermal alteration that host a high salinity Na-Cl brine at temperatures up to 200 ˚C.

Using the parallelism with the serpentinization process, where the oxidation of ferrous iron minerals leads to the generation of H_2, in this study we investigate the possibilities of abiotic H_2 generation from the biotite-rich granite cored at the Soultz-sous-Forêts site. For that we applied a geochemical and reactive transport model to simulate the hydrothermal alteration of the granite. The abundant and long-term existing data from the site (since 1987) allowed us to build and calibrate our conceptual model.

2. MODELING APPROACH

2.1 Conceptual model

To test the generation of H_2 by hydrothermal alteration of the granite basement at Soultz-sous-Forêts we simulated the circulation of the hydrothermal brine (Na-Cl) at 165 ˚C through a "fresh" standard porphyritic granite at 3500 m depth. The concentration of ions in the solution, the temperature, and redox conditions are those described by Fritz et al. (2010) (Table 1).

Table 1: Composition of the hydrothermal fluid at 3500 m depth (Fritz et al., 2010). The concentration of Fe and Al as trace elements were reduced to avoid the initial oversaturation of some secondary minerals.

Parameter	Molality (mMol/Kg H_2O)
Na	1190
K	65.5
Ca	166
Mg	4.17
Cl	1580
S	3.22
Fe	0.0116
Al	7.44 E-05
Alkalinity	15 (meq/Kg)
Si	1.8
Temperature	165 (˚C)
pH	4.8
Eh	-245 (mV)

The standard porphyritic granite is the most abundant type of granite described on site that extends from 1400 to 3900 m depth (Hooijkaas et al., 2006). In this work we considered that the standard porphyritic granite is initially "fresh" or without any propylitic or vein hydrothermal alteration. The type and distribution of primary minerals selected for the model is the following: plagioclase (35% vol. albite; 4% vol. anorthite), quartz (27 % vol.), K-feldspar (24% vol.), biotite (8% vol.), and amphibole (2% vol.). In this simulations the so called "fresh" standard porphyritic granite is saturated with the brine and secondary minerals and H_2 gas can be formed (Fig.1).
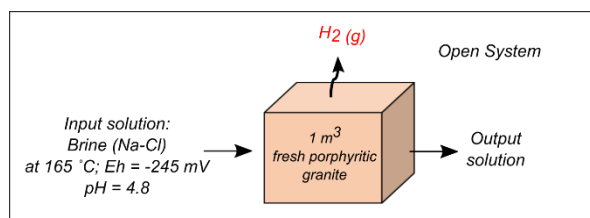

Figure 1: Conceptual model for the circulation of hydrothermal fluids in the "fresh" standard porphyritic granite and the production of H_2 in an open system.

The set of secondary minerals selected for this model are those described in the two types of hydrothermal alteration of the granite: the propylitic and the vein alteration (Traineau et al., 1991; Ledésert et al., 2010) (Table 2). The simulations were carried out considering an open system with respect to the solution and the gas phases.

Table 2: Primary and secondary minerals considered in this study. The ideal stoichiometry is based on the Thermoddem (BRGM) data base (June-2017).

Mineral	
Primary minerals	**Stoichiometry**
Quartz	SiO_2
Feldespar- K	$K(AlSi_3)O_8$
Anorthite	$Ca(Al_2Si_2)O_8$
Albite	$Na(AlSi_3)O_8$
Biotite (annite)	$KFe^{II}_3(AlSi_3)O_{10}(OH)_2$
Amphibole (tremolite)	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Secondary minerals	
Illite-Al	$K_{0.85}Al_{2.85}Si_{3.15}O_{10}(OH)_2$
Montmorrillonite (MgCa)	$Ca_{0.17}Mg_{0.34}Al_{1.66}Si_4O_{10}(OH)_2$
Montmorrillonite (MgNa)	$Na_{0.34}Mg_{0.34}Al_{1.66}Si_4O_{10}(OH)_2$
Nontronite (K)	$K_{0.34}Fe_{1.67}Al_{0.67}Si_{3.66}O_{10}(OH)_2$
Magnetite-III	$Fe^{III}_2 Fe^{II}O_4$
Hematite-III	$Fe^{III}_2O_3$
Goethite-III	$Fe^{III}O(OH)$
Epidote	$Ca_2Fe^{III}Al_2Si_3O_{12}(OH)$
Chamosite (Chlorite group)	$Fe^{II}_5Al(AlSi_3)O_{10}(OH)_8$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Beidellite-K	$K_{0.34}Al_{2.34}Si_{3.66}O_{10}(OH)_2$

2.2. KIRMAT code

The simulations were made with the numerical code KIRMAT (KInetics of Reaction and MAss Transfer). It is a reactive transport or hydro chemical code (Gérard et al., 1998). The mass transport phenomena through the total connected porosity of a water-saturated porous medium are solved over one spatial dimension (1D). In this study we considered our porous media made up of $1m^3$ of "fresh" standard porphyritic granite. We considered a porosity of 1% (Kohl et al., 1995; Surma and Geraud, 2003; Rosener and Geraud, 2007; Magnenet et al., 2014), and a Darcy's rate of 6 cm/yr (Vallier et al., 2019). In this work we considered the system as an open system (Fig. 1). Therefore, in our simulations, the gas produced is exported outside from the reactive cell (Fig. 1). In this context, P_{H_2} (partial pressure of H_2) is assumed to be constant. A constant P_{H_2} assumption indicates that when H_2 is produced, the gas is connected to an infinite reservoir with an infinite volume so that the P_{H_2} remains constant.

The P_{H_2} value is determined at the beginning of the simulation with the initial Eh and pH according to the thermodynamic equilibrium condition represented in Equation 1, where [H$^+$] is the activity of protons, [e$^-$] is the activity of electrons, and K_{H_2} is the solubility constant of hydrogen.

$$[P_{H_2}] = [H^+]^2 [e^-]^2 / K_{H_2} \quad [eq. 1]$$

The dissolution of primary minerals was simulated using the kinetic approach [eq. 2]:

$$r_d = k_d S^{eff}_m a^n_{H+} [1 - (Q_m/K_m)^{n1})^{n2}] \quad [eq. 2]$$

where k_d is the dissolution rate constant of a mineral m (mol m^{-2} year^{-1}), S^{eff}_m is the reactive surface area of the mineral (m^2 kg^{-1} H$_2$O), aH$^+$ is the activity of proton, n, n1, and n2 are experimental exponents depending on the pH of the solution. Q_m is the ion activity product of the mineral and K_m is the equilibrium constant for the hydrolysis reaction at a given temperature and pressure.

The precipitation of primary and secondary minerals were considered in thermodynamic equilibrium. The values of reference for the minerals selected in this study were obtained from the Thermoddem database which is updated by the French Geological Survey (BRGM) (Blanc, 2017).
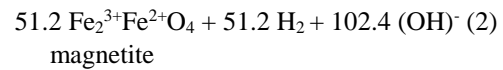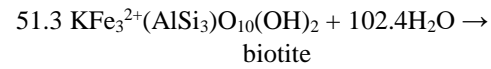
The extended Debye-Hückel law was used to calculate the activity coefficients of ions. That is because aqueous trace elements activities (Al^{3+}, Fe^{2+}, Fe^{3+}) are needed in our model (particularly for clay minerals) and cannot be calculated by Pitzer's type models for brines. In our simulations the ionic strength values are almost constant ($\approx$ 1.5), which limits the errors.

In this study the concentration of O$_2$ is considered to be extremely low because we simulate conditions at more than 3000 m depth from the surface with very low Eh values. The P_{CO_2} is fixed and since CO$_2$ is the main gas phase in the system (14.2 – 89.7% vol.) (Sanjuan et al, 2010; 2016), the amount of CO$_2$ available in the model is considered unlimited.

3. RESULTS AND DISCUSSION

The generation of H$_2$ is observed during the circulation of the brine (Na-Cl) through the "fresh" standard porphyritic granite at 165 ˚C and -245 mV. The mineral phases involved in the generation of H$_2$ are biotite and magnetite. During the simulation, biotite dissolves in around 180 years while magnetite precipitates and H$_2$ is produced (Fig. 2 a, b, and c).

During this process, biotite releases Fe^{2+} to the solution which is partially oxidized and precipitated in magnetite leading to the production of H$_2$. A simplification of this reaction can be written as follows:

51.3 KFe$_3^{2+}$(AlSi$_3$)O$_{10}$(OH)$_2$ + 102.4H$_2$O $\rightarrow$
biotite

51.2 Fe$_2^{3+}$Fe^{2+}O$_4$ + 51.2 H$_2$ + 102.4 (OH)$^-$ (2)
magnetite

In detail, the oxidation of Fe^{2+} released form biotite will provide electrons (3) that will reduce protons (H$^+$) to produce H$_2$ (4). In the serpentinization process, the H$_2$ generation is addressed as the oxidation of iron and the reduction of water into molecular hydrogen. Indeed, H$_2$ is produced by the reduction of H$^+$ where the protons are provided by the dissociation of water (5).

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad (3)$$
$$H^+ + e^- \leftrightarrow 0.5H_2 \qquad (4)$$
$$H_2O \leftrightarrow H^+ + OH^- \qquad (5)$$
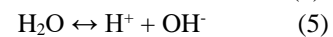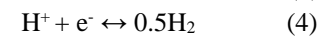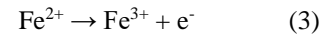
The total amount of H$_2$ produced during this simulation at 165 ˚C and -245 mV is of 51.2 mol/m^3 of "fresh" standard porphyritic granite in 180 years. This amount of H$_2$ is generated by the complete dissolution of the total amount of biotite (51.2 mol) and the precipitation of 51.2 mol of magnetite in 1 m^3 of "fresh" standard porphyritic granite. This quantity of H$_2$ (51.2 mol) is considered as the total potential of 1m^3 of "fresh" standard porphyritic granite at 165 ˚C and -245 mV.

There is a parallelism between the H$_2$ production from hydrothermal alteration of the granite and the serpentinization process. In both cases the source of H$_2$ is related to the oxidation of ferrous iron bearing minerals (e.g. biotite in the granite case and olivine/ pyroxene in peridotites) and the precipitation of ferric iron in secondary minerals. Laboratory experiments and simulations show that magnetite is a common secondary mineral associated to H$_2$ generation during serpentinization (McCollom and Bach 2009; MacCollom et al., 2016; Bauchaud et al., 2017; Miller at al., 2017). However, changes in temperature and oxidation state of iron (Fe(II)/Fe(III)) in secondary minerals (brucite and serpentinite), can limit or favor the production of H$_2$ accordingly (Klein et al., 2013). In this sense, a wider range of temperatures contemplating the whole range of temperature of the granite reservoir at Soultz-sous-Forêts (130 – 200 ˚C) should be considered in the simulations. In this way the stability of magnetite and/or the precipitation of other iron rich secondary minerals (such as chamosite, hematite, goethite, nontronite) already mentioned in the hydrothermal alteration of the granite would be tested. Another important mineral to consider in future simulations is pyrite. Pyrite precipitation can also lead to the generation of H$_2$ from an existing sulfide precursor reacting with sulfuric acid below 300 °C. This is known as the Berzelius reaction (Rickard and Luther 2007). Since pyrite is one of the sulfide minerals associated to the hydrothermal alteration at Soultz-sous-Forêts, the precipitation of pyrite should also be tested.
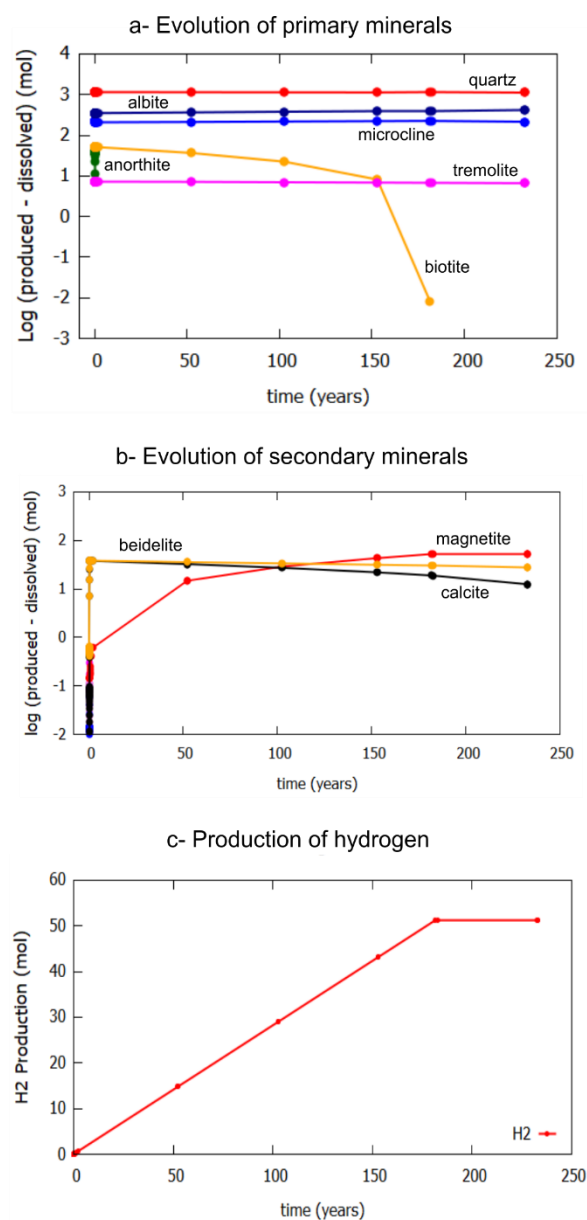
a- Evolution of primary minerals

b- Evolution of secondary minerals

c- Production of hydrogen

Figure 2: a)- Evolution of primary minerals during the circulation of the brine at 165 C and -245 mV through the "fresh" standard porphyritic granite. b)- Evolution of secondary minerals. c)- Production of hydrogen.

During the hydrothermal alteration of the granite, the initial condition of dissolution of primary minerals has been imposed. Therefore, it is observed that all the minerals are initially dissolved. However, quartz, and albite reach rapidly equilibrium and start to precipitate in a very small amount (Fig. 2 a). In the case of biotite, tremolite, microcline, and anorthite, their dissolution continue progressively over time (Fig. 2 a). Anorthite is completely removed from the system at the very beginning of the simulation, while tremolite and microcline dissolve very slowly.

Regarding to the secondary minerals, beidellite and calcite reach equilibrium and start to precipitate (Fig. 2

b). With the progress of the simulation beidellite and calcite are re-dissolved while magnetite precipitation increases continuously until around 180 years.

The evolution of primary and secondary minerals in the simulations are in agreement with the mineralogical composition of the hydrothermal system in the granitic rock. Especially with the vein alteration, where there is a dissolution of biotite, plagioclase, and feldspar, associated with precipitation of quartz, clay minerals (mainly illites, smectites), carbonates (calcite and dolomite), and iron oxides (Traineau et al., 1991; Ledésert et al., 2010).

Despite the simulations provide insights of the hydrogen generation process, while looking at the actual granite system of Soultz-sous-Forêts, the massive granite is still very rich in fresh or non-altered biotite (Hooijkaas et al., 2006). Only in the fractured zones of the granite and in the propylitic alteration areas biotite shows transformation to secondary minerals such as iron-oxides or chlorite respectively. Thus indicating that unless the granite is exposed to a disequilibrium condition (by fractures, changes in temperature, changes in the chemistry of the fluids, etc.) biotite can remain in equilibrium reducing the possibilities for H_2 production (e.g. reaction 2).

In addition, our assumption of open system implies an imposed constant P_{H_2}, and the H_2 gas produced has to be exported out of the system. Looking at reaction 2, this condition will favour the reaction to the right where magnetite and H_2 will be formed with the consequent destabilization of biotite. If a closed system condition would be imposed, then H_2 would remain in the system (i. e. a finite reservoir or a system with very slow brine circulation) reaction 2 will tend to the left and so to the stability of biotite limiting the production of H_2.

Therefore, it seems necessary to better understand the conditions that may lead to the destabilization of biotite, and in what extent the supposed value of P_{H_2} used in the modelling influences the H_2 production at Soultz-sous-Forêts by a feed-back effect on the oxidation of ferrous iron.

3. CONCLUSIONS

Geochemical and reactive transport simulations indicates that the generation of abiotic H_2 at Soultz-sous-Forêts at 165 ˚C and -245 mV is possible by hydrothermal alteration of the biotite as a source of Fe^{2+}, which oxidizes to Fe^{3+} leading to the precipitation of magnetite and reduction of protons (H^+).

The total amount of H_2 produced at 165 ˚C and -245 mV is of 51.2 mol/m³ of "fresh" standard porphyritic granite which is the total potential of 1 m³ of "fresh" standard porphyritic granite after the complete dissolution of the total amount of biotite and the precipitation of magnetite in around 180 years.

A wider range of temperatures covering the whole temperature range of the granite reservoir (130 – 200

˚C) and the possible precipitation of other Fe(II)/Fe(III) secondary minerals should be tested in further simulations.

Despite the simulations provide insights of the hydrogen generation process, while looking at the actual granite system of Soultz-sous-Forêts, the massive granite is still very rich in fresh or non-altered biotite. Only in the fractured zones of the granite and in the propylitic alteration areas biotite shows transformation to secondary minerals such as iron-oxides or chlorite respectively. Thus indicating that unless the granite is exposed to a disequilibrium condition (by fractures, changes in temperature, changes in the chemistry of the fluids, etc.) biotite can remain in equilibrium reducing the possibilities for H_2 production.

Understanding the processes or the conditions that may lead to the destabilization of biotite, and in what extent P_{H_2} influences the H_2 production at Soultz-sous-Forêts by a feed-back effect on the oxidation of ferrous iron, are future needs of this research.

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