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Possible coupling of abiotic hydrogen and heat generation in the EGS Soultz-sous-Forêts site (France): a hydrogeochemical modeling approach

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ABSTRACT

For solving the problem of energy transition for the future, the research for alternatives to fossil fuels sources of energy such as H_2 is necessary. In this general context, investigations on geochemical processes responsible for native H_2 generation in natural reservoirs are of major interest. In most of the recent studies related to natural abiotic H_2 generation the focus is on serpentinization of mafic and ultra-mafic rocks. In these natural systems 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 parallel route of abiotic H_2 generation from a rich biotite granite, an acid rock that constitutes the basement of the Soultz-sous-Forêts EGS site. We used a geochemical and reactive transport modeling, and the existing data base of the Soultz-sous-Forêts project, to simulate the hydrothermal alteration of the granite for the in situ range of temperatures (130 to 200 ˚C), and a Redox potential of around -250 mV. The simulation showed that the generation of abiotic H_2 is possible by hydrothermal alteration of biotite as a source of Fe(II) oxidized into Fe(III) and precipitated as ferric iron minerals, while H^+ is reduced into H_2. The amounts of H_2 that can be produced depend on the type of Fe(II/III) secondary minerals precipitating as a function of temperature and redox conditions of the reservoir. As observed in the serpentinization process, optimal conditions for H_2 generation are related to magnetite precipitation. On the contrary, when Fe(II) secondary minerals (e.g. chamosite) precipitate, the iron oxidation process and H_2 generation is inhibited. This research has implications for possible coupling between heat extraction and H_2 production.

1. INTRODUCTION

In the world scenario of energetic transition recent investigations on the generation of natural abiotic H_2 (hydrogen-gas) have been developed motivated by an increasing interest in the new CO_2-free energy sources. Among these studies, H_2 generation by serpentinization of ultramafic rocks (e.g. peridotite) is the most studied natural process (Shock and Shulte, 1998; McCollom and Batch., 2009; McCollom et al., 2016; Mügler at al., 2016; Miller et al., 2017; Bachaud et al., 2017; Vacquand et al., 2018). On the chemical and mineralogical point of view, the source of H_2 is linked to the oxidation of Fe(II) bearing minerals that can be represented by the general reaction (Klein et al., 2013):

$$(MgFe^{II})_2SiO_4 + vH_2O \rightarrow w(MgFe^{II})(OH)_2 + x(MgFe^{III})_{3\text{-}Fe(III)}(SiFe)_{2\text{-}Fe(III)}O_5(OH)_4 + yFe^{II}\,Fe^{III}{}_2O_4 + zH_2 \quad (R1)$$

$$\text{olivine + water} \rightarrow \text{brucite + serpentine + magnetite + hydrogen}$$

In this mass balance equation H_2 appears as the product of water reduction (as often mentioned by authors), which is in fact the reduction of protons H^+.

However, in continental contexts other sources of Fe(II) exist, as for example - rich biotite granitic basements. In this paper we focus on the case study of the Soultz-sous-Forêts site where the deep Hercynian granite has been hydraulically exploited for a long period of time through an Enhanced Geothermal System (EGS). Soultz-sous-Forêts is located in the Upper Rhine Graben (France) with a high local thermal gradient (more than 100 °C in the first km). Three deep wells (≈5000 m depth) were drilled on site reaching the granite basement, creating a heat exchanger allowing to produce electricity (1.5 MW). Measurements of gases contents in the Soultz-sous-Forêts boreholes have reported values in the range of 0.25 – 46.3% vol. of H_2 (Sanjuan et al., 2010; 2016). The origin of these values is still not well understood. The basement rock is a massive granite with different petrographic types. It is very rich in biotite and amphibole, and is affected by different grades of fractured and hydrothermal alteration. The reservoir contains a high salinity Na-Cl brine (about 100g/l) at temperatures up to 200 °C.

In a previous work, we showed the geochemical mechanism for H_2 generation by hydrothermal alteration of the standard porphyritic granite at a temperature of 165 ˚C and -245 mV, related to the partial dissolution of biotite and the formation of secondary magnetite (Murray et al., 2019). The aim of the present study is to investigate the possibilities of abiotic H_2 generation from the Soultz-sous-Forêts biotite-rich granite at the different range of temperatures observed in the native hydrothermal brine. For that we applied a coupled geochemical and reactive transport model considering three different temperatures measured on site: a minimum of 130 °C, the intermediate of 165 °C, and a maximum of 200 °C.

2. METHODOLOGY

2.1 Conceptual Model

For our simulations we considered the circulation of the hydrothermal brine (Na-Cl) at 130 ˚C, 165 ˚C, and 200 ˚C through a “fresh” standard porphyritic granite at 3500 m depth (Fig. 1). The concentration of ions in the solution, pH, and redox conditions (-245 mV) are those described by Fritz et al. (2010) (Table 1).

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 H_2O)
Si	1.8
pH	4.8
Eh	-245 (mV)

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.

The standard porphyritic granite is the most abundant type of granite described on the Soultz-sous-Forêts site. It extends from 1400 to 3900 m depth (Hooijkaas et al., 2006). For this study we considered that the standard porphyritic granite is initially “fresh” or without any propylitic or vein hydrothermal alteration (Fig. 1). We developed the simulation using the set of primary and secondary minerals described in previous studies (Traineau et al., 1991; Ledésert et al., 2010) (Table 2). The type and amount of primary minerals selected for the model are the following: plagioclase (35% vol. albite; 4% vol. anorthite), quartz (27 % vol.), K-feldspar (24% vol.), biotite (8% vol.), and amphibole (2% vol.) (Table 2). In these simulations the porosity of the so called “fresh” standard porphyritic granite is saturated with the brine. We considered a connected porosity of 1% as described by previous studies (Kohl et al., 1995; Surma and Géraud, 2003; Rosener and Géraud, 2007; Magnenet et al., 2014). The simulations were carried out considering an open system with respect to the solution and the gas phases: the gas produced is not accumulated in the reactive cells.

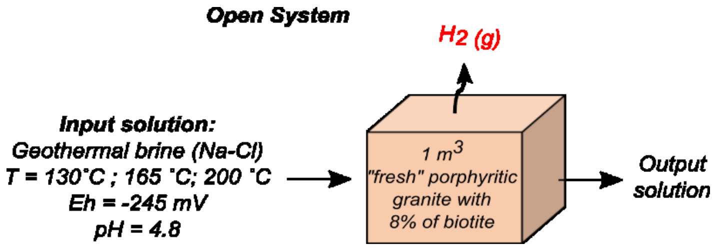

Figure 1. Conceptual model for the circulation of hydrothermal fluids in the “fresh” standard porphyritic granite and the production of H_2 in an open system.

Primary minerals	***Stoichiometry***
Quartz	SiO_2
K-Feldspar	$K(AlSi_3)O_8$
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	$K_{0.34}Al_{2.34}Si_{3.66}O_{10}(OH)_2$

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

2.2. Numerical code

The simulations were made using the numerical code KIRMAT (KInetics of Reaction and MAss Transfer). KIRMAT is a coupled reactive and transport hydro-chemical code (Gérard et al., 1998). The porosity is supposed to be connected and totally water-saturated. The mass transport phenomena are solved over one spatial dimension (1D). We considered a reactive cell of 1m^3 of "fresh" standard porphyritic granite and the circulation of the fluid was regulated by a Darcy's rate of 6 cm/yr (Vallier et al., 2019) (Fig. 1). With our "open system' assumption the produced gas is exported outside from the reactive cell and the partial pressure of hydrogen P_{H_2} is assumed to be constant. In other terms, if H_2 is produced, the gas is connected to an infinite reservoir so that 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:

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

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

$$r_d = k_d S^{eff}_m\, a^n_{H+} [\ 1- (Q_m/K_m)^{na})^{nb}] \quad \text{[Eq. 2]}$$

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_2O), a^n_{H+} is the activity of proton, and n, na, and nb 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 minerals was considered using the thermodynamic equilibrium condition. The solubility products for the minerals selected in this study were obtained from the Thermoddem database which is updated by the French Geological Survey (BRGM) (Blanc, 2017). However, the kinetic precipitation approach was used for quartz at temperatures lower than 150 °C in which the initial oversaturation of the mineral was detected by calculating the chemical speciation.

For the kinetic precipitation of minerals, KIRMAT code considers the following expression:

$$r_p = k_p S^{eff}_m\ [(Q_m/K_m)^p - 1]^q \quad \text{[Eq. 3]}$$

where kp is the kinetic rate constant of precipitation (mol m^{-1} year^{-1}), and p and q are experimental values describing the dependence of the reaction on the saturation state (Murray et al., 2020).

The extended Debye-Hückel law was used to calculate the activity coefficients of ions. One may argue that this could be a weakness of the model when applied to a geothermal brine. However aqueous trace elements activities calculation for Al^{3+}, Fe^{2+}, Fe^{3+}, are needed in our model (particularly for testing clay minerals formation) and cannot be calculated by Pitzer's type models for brines. In our simulations the ionic strength values are almost constant (≈ 1.5), which limits the errors due to the extended Debye-Hückel model.

Concerning other gases than H_2, P_{O_2} is extremely low because our simulations are deep in the reservoir (>3000m) with anoxic conditions and with very low Eh values. P_{CO_2} is fixed in the calculation and equal to 0.1 MPa. 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 to dissolve is considered unlimited.

2. RESULTS AND DISCUSSION

In previous studies we showed that the alteration process induced by the circulation of the geothermal brine with the "fresh" standard porphyritic granite at the temperature of 165 ˚C and -245 mV generates the production of H_2 (Murray et al., 2019; Murray et al., 2020). The generation of H_2 is clearly related to the partial dissolution of biotite and the formation of secondary magnetite. In the simulation biotite is totally dissolved in around 180 years while magnetite precipitates and H_2 is produced (Fig. 2 a, b, and c). This simulated evolution of primary and secondary minerals is in good agreement with the mineralogical composition of the granitic rock in the hydrothermal system, particularly in the vein alteration, where partial dissolution of biotite, plagioclase, and feldspar are observed, 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).

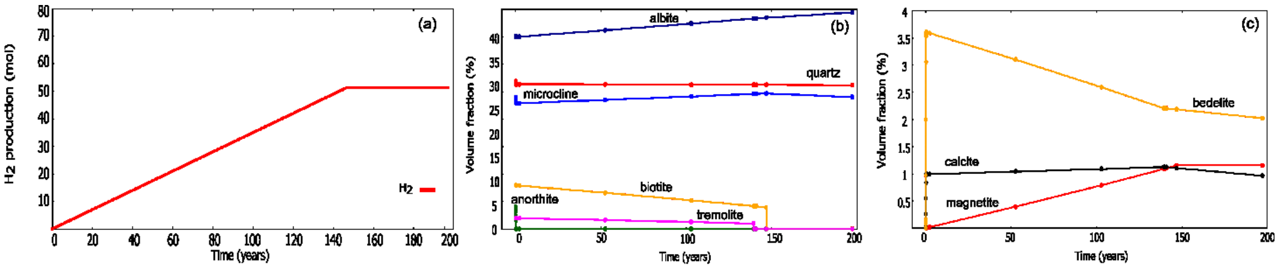

Figure 2. a)- Production of hydrogen. b)- Evolution of primary minerals during the circulation of the brine at 165 °C and -245 mV through the "fresh" standard porphyritic granite. c)- Evolution of secondary minerals. Modified after Murray et al. (2020).

The alteration of biotite releases Fe^{2+} to the solution. These ferrous ions are partially oxidized into ferric ions which co-precipitated with ferrous ions in magnetite (Murray et al., 2019). The mineralogical and chemical balances of this reaction can be written as follows for the total reactive cell:

$$51.3\ KFe_3^{2+}(AlSi_3)O_{10}(OH)_2 + 102.4H_2O \rightarrow 51.2\ Fe_2^{3+}Fe^{2+}O_4 + 51.2\ H_2 + 102.4\ (OH)^- \quad (R2)$$

biotite + water → magnetite + hydrogen

In this process the oxidation of Fe^{2+} from the biotite provides electrons (reaction R3) that will reduce protons (H^+) to produce H_2 (reaction R4). In the serpentinization process, the H_2 generation is addressed by authors 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 (reaction R5).

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad (R3)$$
$$H^+ + e^- \leftrightarrow 0.5H_2 \qquad (R4)$$
$$H_2O \leftrightarrow H^+ + OH^- \qquad (R5)$$

The new simulations performed at different temperatures, but maintaining the same initial Eh (-245 mV) show different amount of H_2 generated according to the temperature. In the case of 130 °C, the lower temperature measured for the native brine in the granitic reservoir, the H_2 generation is very low (0.003 mol) (Fig. 3 a). This is related to the precipitation of chamosite ($Fe^{2+}_5Al(AlSi_3)O_{10}(OH)_8$), a secondary mineral composed of Fe^{2+} formed after the alteration of biotite (Fig. 3 b). The formation of this chloritoid inhibits the oxidation of Fe^{2+} to Fe^{3+} (R3), therefore the generation of H_2 (R4) is inhibited as well.

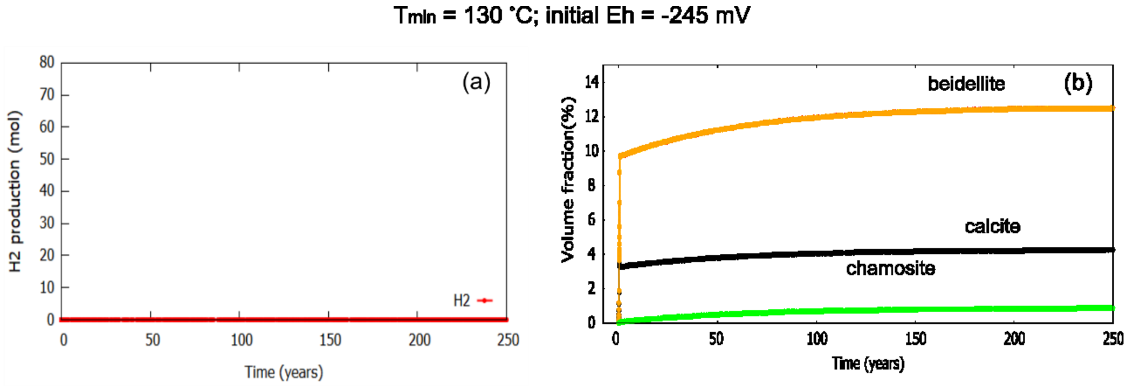

Figure 3. a)- Amount of H_2 gas generated at 130 °C and -245 mV. b)- Precipitation of secondary minerals at 130 °C and -245 mV. Modified after Murray et al. (2020).

In the case of the simulation at 200 °C, the higher temperature measured for the native brine in the granitic reservoir, the H_2 produced is of 51.2 mol (Fig. 4 a). This amount of H_2 is similar to the one produced at 165 °C and is related to the precipitation of magnetite ($Fe_2^{3+}Fe^{2+}O_4$) as well (Fig. 4 b), linked to the reactions R2 to R5. The main difference between these two simulations is that at 200 °C, epidote ($Ca_2Fe^{III}Al_2Si_3O_{12}(OH)$) precipitates as a consequence of the higher temperatures. However, with the progression of the simulation, the precipitation of this Fe^{3+} secondary phase stops and magnetite is the dominant phase.

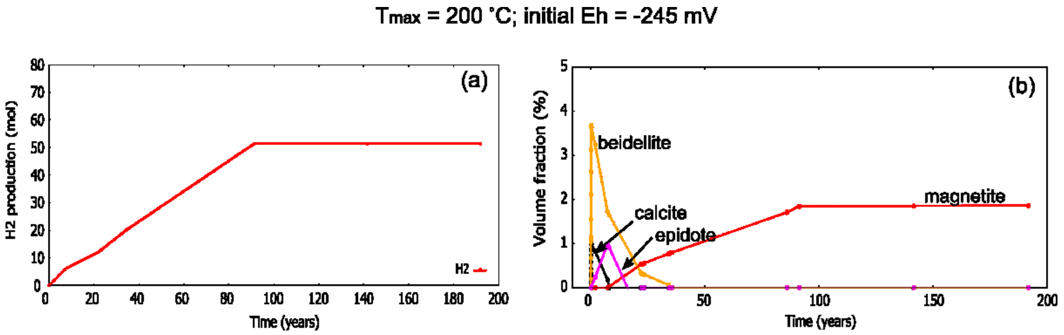

Figure 4 a)- Amount of H_2 gas generated at 200 °C and -245 mV. b)- Precipitation of secondary minerals at 200 °C and -245mV. Modified after Murray et al. (2020).

By performing simulations at different temperatures (but maintaining the same Eh) it is possible to obtain different amounts of H_2 related to the amount of Fe^{2+} oxidized to Fe^{3+} and precipitated in a secondary phase. In our modelling we found that magnetite is a potential mineral related to H_2 generation while chamosite indicates conditions of non Fe^{2+} oxidation and non H_2 generation. Magnetite precipitation related to H_2 generation was also observed in laboratory experiments and simulations of serpentinization (McCollom and Bach 2009; MacCollom et al., 2016; Bachaud et al., 2017; Miller at al., 2017).

Therefore, the final redox status of iron appears to be crucial: if iron is precipitated in secondary minerals as ferrous iron (e.g. chamosite) the process will not produce hydrogen (no iron oxidation, no proton reduction). If iron is precipitated as ferric ion (e.g. magnetite), the production of hydrogen can be possible (oxidation of ferrous ion). Klein et al., (2013) also showed that 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 during serpentinization. To test the relative stabilities of magnetite and other iron rich secondary minerals (such as hematite, goethite, nontronite) at different Eh values seems necessary in future simulations.

Another question to be addressed for the production of H_2, is the accessibility to the oxidation of Fe^{2+} or the alteration of biotite in the granite. While looking at the actual granite in the Soultz-sous-Forêts geothermal reservoir, the massive granite is still very rich in fresh or non-altered biotite (Hooijkaas et al., 2006). The transformation of biotite into secondary minerals such as iron-oxides or chloritoids is only observed in the fractured zones of the granite and in the propylitic alteration areas. This point out a problem related to rock-water interaction conditions: the iron bearing minerals (i.e. biotite) have to be exposed to circulating fluid creating conditions of disequilibrium. If the fractures are not open enough to the circulation of the fluid, biotite may remain in equilibrium reducing the possibilities for H_2 production (e.g. reaction 2). This is what obviously occurred over geological time:

- Either fluids circulating with a potential of disequilibrium for ferrous iron did not reach all the concerned minerals.
- Or the production of hydrogen in a quasi-closed system did stop the reaction (Reaction R2).

Regarding to the implications of assuming an open system and constant P_{H_2} during the simulation, it implies that the H_2 gas produced has to be exported out of the system. Considering reaction R2, this condition favours 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 and increase its concentration (i. e. a finite reservoir or a system with very slow brine circulation) and R2 will tend to the left, stabilizing the biotite and limiting the production of H_2.

Future studies should focus on i) the problem of the redox control by the circulating fluid, ii) the problem of access of the fluid to the iron-bearing minerals in the micro-fractures of the granite, and iii) the question of open-system for the water-rock interaction cells in the granite. In our simulations the fluid was supposed to be in contact with the ferrous iron bearing minerals in open system.

3. CONCLUSIONS

We have tested the generation of abiotic H_2 from the granitic rock in the Enhanced Geothermal System at Soultz-sous-Forêts. Biotite is the mineral phase providing the ferrous iron which can provide the necessary electrons for the so called "water reduction" by hydrothermal alteration. If the conditions are favorable to oxidation of ferrous to ferric iron and if secondary minerals (e.g. magnetite) precipitate, the oxidation process of iron will be balanced by a reduction process of protons into H_2 gas. We show that this is possible in conditions comparable to those from the deep geothermal reservoir at temperatures of 165 ˚C and 200 °C and redox potential around -245 mV in an open system. However, at temperatures of 130 °C the precipitation of chamosite inhibits the oxidation of iron and the production of H_2. Despite the fact that our 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. The total potential for hydrogen production has not been used up over geological time in the reservoir. Iron oxides or chlorite have been observed only in fractured zones of the granite or in the propilytic alteration. The zones not affected by fractures were probably not concerned by the geochemical disequilibrium for redox process and H_2 production, either because the fluids did not reach all the iron bearing mineral phases, or because the reacting cells were in quasi-closed system. 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 at 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.

AKNOLEDGMENTS

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