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# Hydrogen Produced by Reduction of H<sub>2</sub>O in Rock Reaction: Peridotite vs Basalt

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**Abstract.** The extraction of abiogenic H<sub>2</sub> from the earth as an energy resource[1] is a possibility raised by the recognition that ultramafic rocks yield hydrogen in the course of serpentinization[2-5], through which water is reduced to H<sub>2</sub> as ferrous iron from peridotite minerals oxidizes. Given the straightforward oxidation of iron silicate to magnetite to make H<sub>2</sub>, it would appear that other mafic rocks such as basalt should also yield H<sub>2</sub>, however, H<sub>2</sub> production from basalt-hosted springs and geothermal fluids is small, e.g. Icelandic waters, as compiled by Arnorsson, et al. [6]. To examine whether the apparent difference in H<sub>2</sub> production between peridotite and basalt is rooted in thermodynamically constrained mineral-water equilibria, we compare computed reactions of water with basalt and peridotite. We find that the serpentinization of peridotite yields abundant H<sub>2</sub> as ferrous iron silicates oxidize to form magnetite, but that little H<sub>2</sub> forms in basalt reaction because ferrous silicates alter to ferrous iron chlorite instead of magnetite or other ferric minerals. A principal cause of the difference is that chlorite requires alumina to form, but alumina concentration is minimal in peridotite although substantial in basalt.

**Keywords:** H<sub>2</sub> production, Basalt, Peridotite

**PACS:** 91.67.-y

## INTRODUCTION

The extraction of abiogenic H<sub>2</sub> from the earth as an energy resource[1] is a possibility raised by the recognition that ultramafic rocks yield hydrogen in the course of serpentinization[2-5], through which water is reduced to H<sub>2</sub> as ferrous iron from peridotite minerals oxidizes. Given the straightforward oxidation of iron silicate to magnetite to make H<sub>2</sub>, it would appear that other mafic rocks such as basalt should also yield H<sub>2</sub>, however, H<sub>2</sub> production from basalt-hosted springs and geothermal fluids is small, e.g. Icelandic waters, as compiled by Arnorsson, et al. [6]. To examine whether the apparent difference in H<sub>2</sub> production between peridotite and basalt is rooted in thermodynamically constrained mineral-water equilibria, we compare computed reactions of water with basalt and peridotite. We find that the serpentinization of peridotite yields abundant H<sub>2</sub> as ferrous iron silicates oxidize to form magnetite, but that little H<sub>2</sub> forms in basalt reaction because ferrous silicates alter to ferrous iron chlorite instead of magnetite or other ferric minerals. A principal cause of the difference is that chlorite requires alumina to form, but alumina concentration is minimal in peridotite although substantial in basalt.

## CALCULATIONS

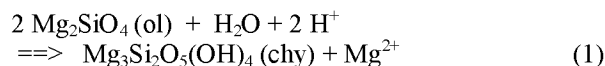
To compare basalt to peridotite in their ability to produce H<sub>2</sub>, we computed reaction of both rock types with seawater at 300°C, and reaction of peridotite with fresh water at 100°C. In every case, we incrementally titrated 5 kg of rock into an initial 1 kg of water. Calculations were carried out with computer program CHILLER[7] using thermochemical data in data base SOLTHERM (see below). In the calculations, we simulate reaction of water with rock by incremental changes of composition with an overall equilibrium calculation at each increment[7]. We compute local chemical equilibria, including metastable equilibria, among minerals and fluid, assuming that thermodynamic equilibrium applies on appropriate scales in time and space; the similarity of computed results to the natural world justifies this assumption. We do know that local chemical equilibrium among fluids and alteration minerals applies in many hydrothermal systems, as argued explicitly by Reed[8], and addressed in other[6,7,9-14], and if fluid flow rates are slow, such equilibrium applies in many sedimentary systems to temperatures as low as 75-80°C[15-17], and in ultramafic systems to temperatures as low as 25°C [18].

The thermodynamic data for the present study are compiled in data base SOLTHERM[19], which contains equilibrium constants for minerals, gases, and aqueous species and serves as an input file for program CHILLER. All data sources are referenced within the data base and most are described by Palandri and Reed[17]. Ultramafic calculations used equilibrium constants computed for pressures and temperatures along the H<sub>2</sub>O liquid/vapor curve; seawater-basalt calculations were executed at 1000 bar.

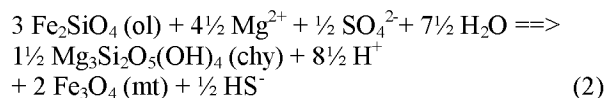
## PERIDOTITE REACTION

Our earlier work on serpentinization of peridotite[17] explored the origin of serpentinite by reaction of water with peridotite, yielding hyperalkaline waters (e.g. pH 11) and producing highly reduced products including H<sub>2</sub> gas, and native Ni and Fe. The seawater-peridotite reaction reported here (Fig. 1) is the same as in the previous study, in which the peridotite is an average harzburgite composition described by Palandri and Reed[17] reacted with a standard seawater composition. For comparison, we also report here on a freshwater peridotite reaction at 100°C, which used the same harzburgite reacted with a US coastal rainwater[20].

The essential reaction in serpentinization is replacement of primary pyroxene and olivine by antigorite (represented below by chrysotile for simplicity; all species are aqueous unless identified otherwise; mineral abbreviations are given in Table 1):



This reaction and its pyroxene analog are accompanied by Mg<sup>2+</sup> and sulfate addition to the Fe-olivine (fayalite) endmember of the reactant olivine (and similarly for pyroxene) as it reacts to serpentine (chy) and magnetite:



Reaction 2 depletes aqueous Mg<sup>2+</sup> in seawater (Fig. 1c) as well as Mg from initial caminite and subsequent brucite (Figs 1a,b) until aqueous Mg<sup>2+</sup> is consumed, whereupon pH increases from 5.3 to 7.8 (Fig.1c) because the brucite buffer ( $\text{Mg}(\text{OH})_2 (\text{bru}) + 2 \text{H}^+ =$

$\text{Mg}^{2+} + 2 \text{H}_2\text{O}$ ) no longer holds pH to 5.3 once Mg<sup>2+</sup> activity becomes small.

Within reaction 2 is the essential redox reaction (3) that converts ferrous iron in olivine to ferric iron in magnetite while reducing sulfate to sulfide:

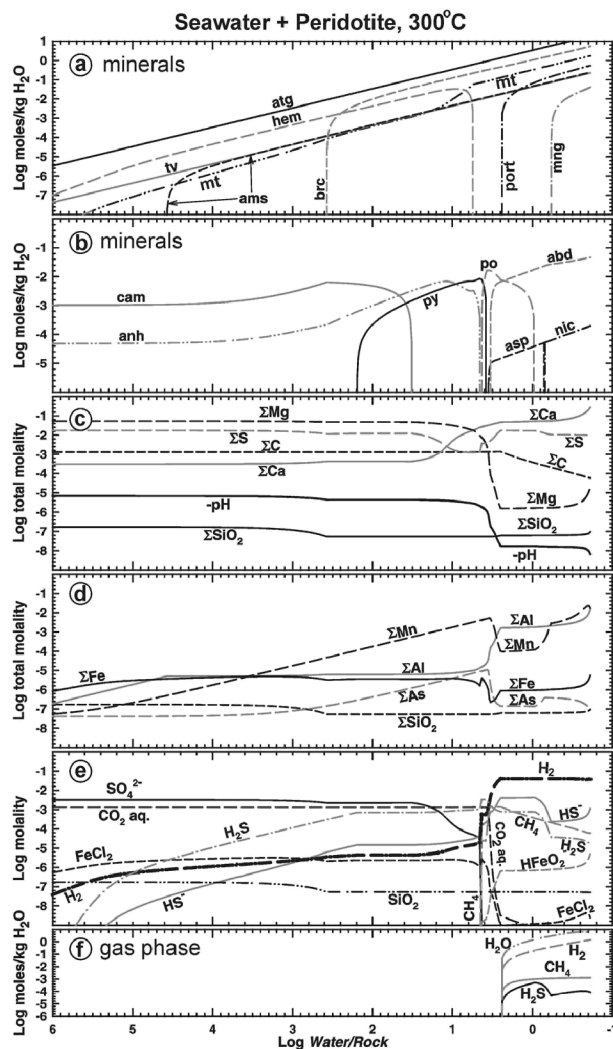
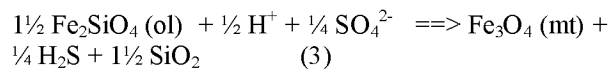
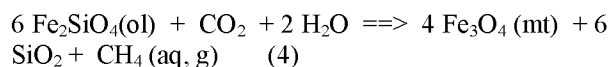


FIGURE 1. Seawater-peridotite reaction. (a,b) minerals in log moles per kg of initial reactant seawater, (c,d) total concentrations of component aqueous species, (e) concentrations of selected individual aqueous species, (f) gas phase composition.

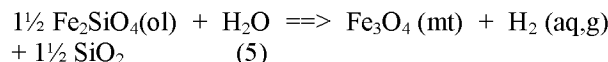
**Table 1. Mineral Abbreviations and Formulae**

abbr	name	formula	abbr	name	formula
ab	albite	$\text{NaAlSi}_3\text{O}_8$	grs	grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$
abd	alabandite	$\text{MnS}$	gt	garnet	solid solution of grs, andr
ams	amesite	$\text{Mg}_4\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_8$	hem	hematite	$\text{Fe}_2\text{O}_3$
ams	amesite	$\text{Mg}_4\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_8$	mfg	magnesioferrite	$\text{MgFe}_2\text{O}_4$
an	anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	mic	microcline	$\text{KAlSi}_3\text{O}_8$
andr	andradite	$\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$	mng	manganosite	$\text{MnO}$
anh	anhydrite	$\text{CaSO}_4$	mt	magnetite	$\text{Fe}_3\text{O}_4$
asp	arsenopyrite	$\text{FeAsS}$	nic	niccolite	$\text{NiAs}$
atg	antigorite	$\text{Mg}_{48}\text{Si}_{34}\text{O}_{85}(\text{OH})_{62}$	ol	olivine	solid solution of fo, fay
brc	brucite	$\text{Mg}(\text{OH})_2$	par	paragonite	$\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
cam	caminite	$\text{Mg}_{1.5}\text{SO}_4 \cdot (\text{OH})$	port	portlandite	$\text{Ca}(\text{OH})_2$
chl	chlorite	solid soln. of Fe & Mg chlorite	py	pyrite	$\text{FeS}_2$
chl-Fe	Fe-chlorite	$\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	pyro	pyrophyllite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
chl-Mg	Mg-chlorite	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	po	pyrrhotite	$\text{FeS}$
chy	chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	qz	quartz	$\text{SiO}_2$
ep	epidote	$\text{Ca}_2(\text{FeAl}_2)_3(\text{SiO}_4)_3(\text{OH})$	sulf	sulfide minerals	
fay	fayalite	$\text{Fe}_2\text{SiO}_4$	tc	talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
fo	forsterite	$\text{Mg}_2\text{SiO}_4$	tv	trevorite	$\text{NiFe}_2\text{O}_4$
			wrk	wairakite	$\text{CaAl}_2\text{Si}_4\text{O}_{10} \cdot (\text{OH})_4$

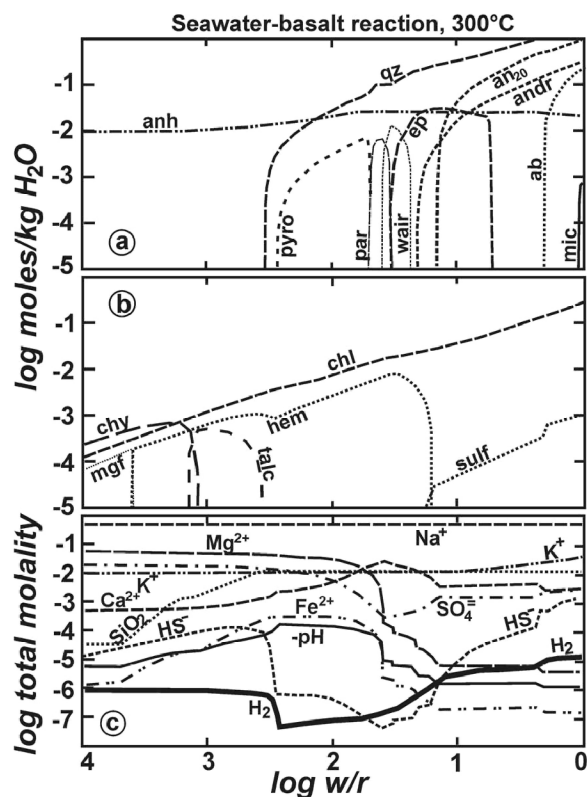
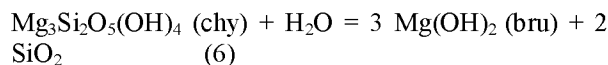
The  $\text{H}_2\text{S}$  dissolves in the aqueous phase (Fig. 1e) and forms sulfide minerals such as pyrite and pyrrhotite (Fig. 1b). Once the sulfate is reduced, aqueous  $\text{CO}_2$  is reduced to methane:



and  $\text{H}_2\text{O}$  is reduced to hydrogen (Fig. 1e) as ferrous iron in silicates oxidizes to form magnetite (Fig. 1a):



The newly formed  $\text{H}_2$ , together with steam,  $\text{CH}_4$  and  $\text{H}_2\text{S}$ , form a gas phase (Fig. 1f) at the imposed pressure of this calculation, 100 bar. The iron oxidation reaction (5) is the key hydrogen-producing reaction at play in ultramafic systems in general; it prevails because magnetite is a stable iron phase in the system, forming in preference to iron silicates, which are substantially precluded by the very small concentration of aqueous  $\text{SiO}_2$  (Figs 1c,d), which concentration is buffered by the serpentine-brucite mineral pair (Fig. 1a):



**FIGURE 2.** Seawater-basalt reaction. (a, b) minerals precipitated per kg of initial seawater, (c) total concentration of selected component species plus pH and concentration of dissolved hydrogen.

**Table 2 Hydrogen production in relation to Fe oxidation at w/r=0.2 (5kg rock into 1kg water)**

Rock reaction*	Moles Fe from reactant rock		Moles Fe in alteration min		Moles new Fe(3)	Moles H <sub>2</sub>	Principal Iron alteration minerals (wt%)
	Fe(3)	Fe(2)	Fe(3)	Fe(2)			
harz-freshwater	0.8	4.5	3.6	1.8	2.8	1.2	magnetite (6.7), andradite (1.5)
harz-seawater	0.8	4.5	3.7	1.7	2.9	1.4	magnetite (6.7), trevorite (0.9)
basalt-seawater	3.1	4.9	3.3	4.7	0.2	.00001	Fe-chlorite (13.6), andradite (1.7)

\* Freshwater reaction at 100°C; Seawater reactions at 300°C

## BASALT REACTION

A seawater-basalt reaction was computed at 300°C and 1kb using an Icelandic basalt composition. The dominant Mg and Fe alteration mineral is chlorite (Fig.2b) which holds nearly all of the iron (Table 2) in its iron end member, the mole fraction of which ranges from 0.18 at w/r=100 to 0.37 at w/r = 0.2 (treated here as an ideal multi-site mixture). Although ferric iron minerals form, including hematite, epidote and andradite (Figs 2a, b), the quantity of ferric iron in them is nearly equal to that in the original reactant rock, thus little of the original ferrous iron is oxidized in the course of reaction so only a small amount of H<sub>2</sub> is produced (Fig. 2c).

## DISCUSSION

The seawater reaction with peridotite produces far more H<sub>2</sub> than does reaction with basalt because newly oxidized ferric iron in alteration minerals is minimal in the basalt reaction, i.e. little iron is oxidized, so little H<sub>2</sub>O is reduced to H<sub>2</sub>. Essentially, peridotite iron forms magnetite, but basalt iron forms Fe-chlorite, wherein the iron remains in the ferrous state. This effect is illustrated in Table 2 at a water/rock ratio of 0.2 (5kg rock in 1 kg water). Table 2 shows that although both rocks contain significant ferrous iron at the start, newly formed ferric iron is far more abundant in the peridotite alteration products (magnetite) than it is in the altered basalt, thus the H<sub>2</sub> production by Reaction 5 does not proceed in the basalt reaction. Fundamentally, the difference results from the relatively large concentration of Al<sub>2</sub>O<sub>3</sub> in basalt in contrast to the minimal Al<sub>2</sub>O<sub>3</sub> in peridotite; thus aluminous mineral chlorite is able to form in basalt, and the chlorite takes up ferrous iron.

Another conclusion shown by Table 2 is that peridotite reaction with both freshwater and seawater yields about the same amount of magnetite and thus

about the same amount of H<sub>2</sub>; i.e. there is no difference in H<sub>2</sub> production depending on whether the reactant is seawater or freshwater.

Hydrogen-rich fluids derived from ultramafic rocks are known from sea floor vents[21] subaerial springs and seeps[2,4] and gas fields in sediments[5]. On the other hand, fluids from basaltic sources have relatively small hydrogen concentrations (e.g. [6,22]). These differences can be ascribed to the basic thermodynamic constraints on reaction of water with the rock, such that magnetite and consequent hydrogen are produced by peridotite reaction but not by basalt reaction.

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