

Hydrogen Produced by Reduction of H₂O in Rock Reaction: Peridotite vs Basalt

M. H. Reed and J. Palandri

Citation: *AIP Conf. Proc.* **987**, 100 (2008); doi: 10.1063/1.2896951

View online: <http://dx.doi.org/10.1063/1.2896951>

View Table of Contents: <http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=987&Issue=1>

Published by the *AIP Publishing LLC*.

Additional information on AIP Conf. Proc.

Journal Homepage: <http://proceedings.aip.org/>

Journal Information: http://proceedings.aip.org/about/about_the_proceedings

Top downloads: http://proceedings.aip.org/dbt/most_downloaded.jsp?KEY=APCPCS

Information for Authors: http://proceedings.aip.org/authors/information_for_authors

ADVERTISEMENT



AIPAdvances

Submit Now

**Explore AIP's new
open-access journal**

- **Article-level metrics
now available**
- **Join the conversation!
Rate & comment on articles**

Hydrogen Produced by Reduction of H₂O in Rock Reaction: Peridotite vs Basalt

M. H. Reed and J. Palandri

Department of Geological Sciences, University of Oregon, Eugene, Oregon, USA

Abstract. The extraction of abiogenic H₂ 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 H₂ as ferrous iron from peridotite minerals oxidizes. Given the straightforward oxidation of iron silicate to magnetite to make H₂, it would appear that other mafic rocks such as basalt should also yield H₂, however, H₂ production from basalt-hosted springs and geothermal fluids is small, e.g. Icelandic waters, as compiled by Amorrsson, et al. [6]. To examine whether the apparent difference in H₂ 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 H₂ as ferrous iron silicates oxidize to form magnetite, but that little H₂ 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: H₂ production, Basalt, Peridotite

PACS: 91.67.-y

INTRODUCTION

The extraction of abiogenic H₂ 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 H₂ as ferrous iron from peridotite minerals oxidizes. Given the straightforward oxidation of iron silicate to magnetite to make H₂, it would appear that other mafic rocks such as basalt should also yield H₂, however, H₂ production from basalt-hosted springs and geothermal fluids is small, e.g. Icelandic waters, as compiled by Amorrsson, et al. [6]. To examine whether the apparent difference in H₂ 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 H₂ as ferrous iron silicates oxidize to form magnetite, but that little H₂ 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

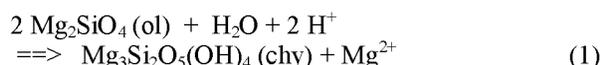
To compare basalt to peridotite in their ability to produce H₂, we computed reaction of both rock types with seawater at 300°C, and reaction of peridotite with fresh water at 100°C. In every case, we incrementally titrated 5 kg of rock into an initial 1 kg of water. Calculations were carried out with 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 H₂O liquid/vapor curve; seawater-basalt calculations were executed at 1000 bar.

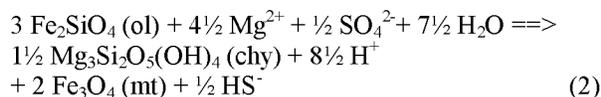
PERIDOTITE REACTION

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 H₂ 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 Mg²⁺ 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 Mg²⁺ in seawater (Fig. 1c) as well as Mg from initial caminite and subsequent brucite (Figs 1a,b) until aqueous Mg²⁺ is consumed, whereupon pH increases from 5.3 to 7.8 (Fig.1c) because the brucite buffer (Mg(OH)₂ (bru) + 2 H⁺ =

Mg²⁺ + 2 H₂O) no longer holds pH to 5.3 once Mg²⁺ 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:

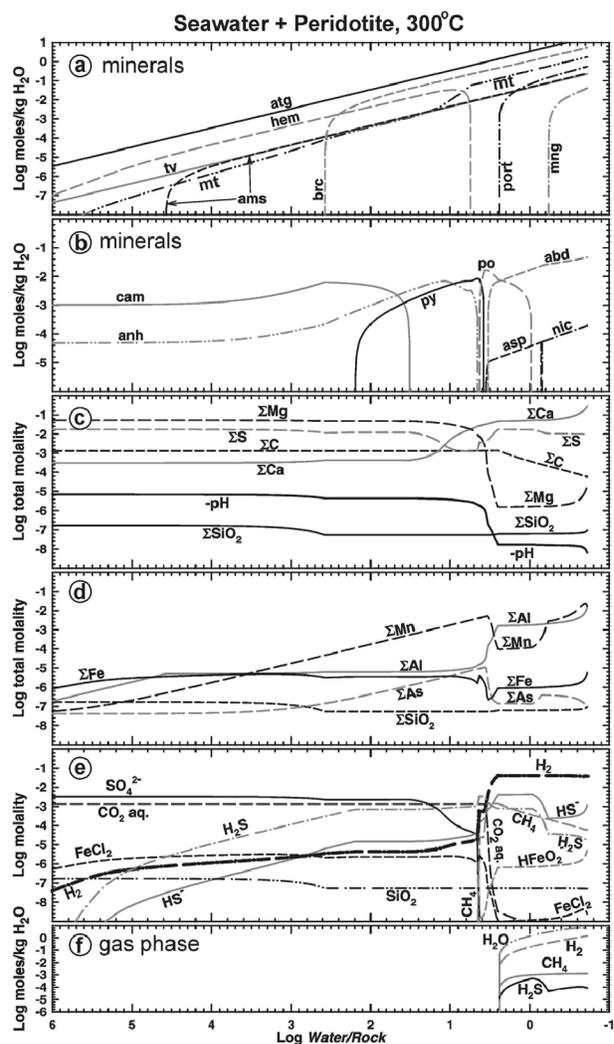
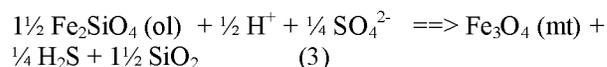
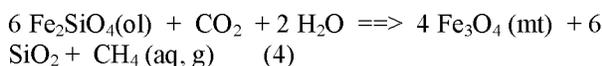


FIGURE 1. Seawater-peridotite reaction. (a,b) minerals in log moles per kg of initial reactant seawater, (c,d) total concentrations of component aqueous species, (e) concentrations of selected individual aqueous species, (f) gas phase composition.

Table 1. Mineral Abbreviations and Formulae

abbr	name	formula	abbr	name	formula
ab	albite	NaAlSi ₃ O ₈	grs	grossular	Ca ₃ Al ₂ (SiO ₄) ₃
abd	alabandite	MnS	gt	garnet solid solution of grs, andr	
ams	amesite	Mg ₄ Al ₄ Si ₂ O ₁₀ (OH) ₈	hem	hematite	Fe ₂ O ₃
ams	amesite	Mg ₄ Al ₄ Si ₂ O ₁₀ (OH) ₈	mfg	magnesioferrite	MgFe ₂ O ₄
an	anorthite	CaAl ₂ Si ₂ O ₈	mic	microcline	KAlSi ₃ O ₈
andr	andradite	Ca ₃ Fe ₂ (SiO ₄) ₃	mng	manganosite	MnO
anh	anhydrite	CaSO ₄	mt	magnetite	Fe ₃ O ₄
asp	arsenopyrite	FeAsS	nic	niccolite	NiAs
atg	antigorite	Mg ₄₈ Si ₃₄ O ₈₅ (OH) ₆₂	ol	olivine	solid solution of fo, fay
brc	brucite	Mg(OH) ₂	par	paragonite	NaAl ₃ Si ₃ O ₁₀ (OH) ₂
cam	caminite	Mg _{1.5} SO ₄ •(OH)	port	portlandite	Ca(OH) ₂
chl	chlorite solid soln. of Fe & Mg chlorite		py	pyrite	FeS ₂
chl-Fe	Fe-chlorite	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	pyro	pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂
chl-Mg	Mg-chlorite	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	po	pyrrhotite	FeS
chy	chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	qz	quartz	SiO ₂
ep	epidote	Ca ₂ (FeAl ₂) ₃ (SiO ₄) ₃ (OH)	sulf	sulfide minerals	
fay	fayalite	Fe ₂ SiO ₄	tc	talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂
fo	forsterite	Mg ₂ SiO ₄	tv	trevorite	NiFe ₂ O ₄
			wrk	wairakite	CaAl ₂ Si ₄ O ₁₀ •(OH) ₄

The H₂S dissolves in the aqueous phase (Fig. 1e) and forms sulfide minerals such as pyrite and pyrrhotite (Fig. 1b). Once the sulfate is reduced, aqueous CO₂ is reduced to methane:



and H₂O is reduced to hydrogen (Fig. 1e) as ferrous iron in silicates oxidizes to form magnetite (Fig. 1a):



The newly formed H₂, together with steam, CH₄ and H₂S, 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 SiO₂ (Figs 1c,d), which concentration is buffered by the serpentine-brucite mineral pair (Fig. 1a):

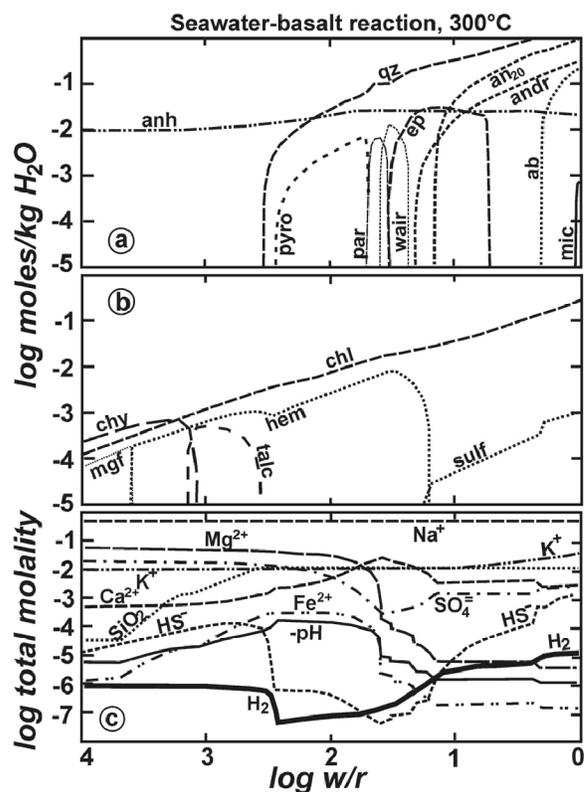
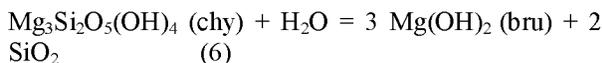


FIGURE 2. Seawater-basalt reaction. (a, b) minerals precipitated per kg of initial seawater, (c) total concentration of selected component species plus pH and concentration of dissolved hydrogen.

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 ₂	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 H₂ is produced (Fig. 2c).

DISCUSSION

The seawater reaction with peridotite produces far more H₂ 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 H₂O is reduced to H₂. 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 H₂ production by Reaction 5 does not proceed in the basalt reaction. Fundamentally, the difference results from the relatively large concentration of Al₂O₃ in basalt in contrast to the minimal Al₂O₃ 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 H₂; i.e. there is no difference in H₂ 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.

REFERENCES

1. Apps, J.A. and Kamp, P.C. van de, United States Geological Survey, Professional Paper 1570, 81-132 (1993).
2. Neal C. and Stanger G., Earth Planet Sci. Lett. 66, 315-320 (1983).
3. Abrajano T. A., Sturchio N. C., Bohlke J. K., Poreda R. J., and Stevens C. M., Chem. Geol. 71, 211-222 (1988).
4. Abrajano T. A., Sturchio N. C., Kennedy B. M., Lyon G. L., Muehlenbachs K., and Bohlke J. K., Appl. Geochem. 5, 625-630 (1990).
5. Coveney R. M., Goebel E. B., Jr., Zeller E. J., Dreschhoff G. A. M., and Angino E. E., AAPG Bull. 71, 39-48 (1987).
6. Amórsson S., Gunnlaugsson E., and Hördur S., Geochim. Cosmochim. Acta 47, 547-566 (1983).
7. Reed, M.H. (1998) Calculation of simultaneous chemical equilibria in aqueous-mineral-gas systems and its application to modeling hydrothermal processes, Chapter 5, in J. Richards, and P. Larson, eds., Techniques in Hydrothermal Ore Deposits Geology, Reviews in Economic Geology, Volume 10, p. 109-124.
8. Reed, M., (1997) Hydrothermal Alteration and Its Relationship to Ore Fluid Composition, in H.L. Barnes, ed., Geochemistry of Hydrothermal Ore Deposits, Third Edition, p. 303-366, Wiley, 972 p.
9. Amórsson S., Geothermics 12, 119-128 (1983).
10. Giggenbach W. F., Geochim. Cosmochim. Acta 44, 2021-2032 (1980).
11. Giggenbach W. F., Geochim. Cosmochim. Acta 45, 393-410 (1981).

12. Pang Z. and Reed M. H., *Geochim. Cosmochim. Acta* **62**, 1082-1091 (1998).
13. Reed M. H., *Geochim. Cosmochim. Acta* **46**, 513-528 (1982).
15. Bazin B., Brosse E., and Sommer F., *Bulletin de la Société géologique de France* **168**, 231-242 (1997).
16. Bazin B., Brosse É., and Sommer F., *Marine and Petroleum Geology* **14**, 481-495 (1997).
17. Palandri, J., and Reed, M.H., *Geochimica et Cosmochimica Acta* **65**, 1741-1767 (2001).
18. Palandri, J., and Reed, M., *Geochimica et Cosmochimica Acta* **68**, 1115-1133 (2004).
19. Reed, M. and Palandri, J (2006) **SOLTHERM.H06**, a data base of equilibrium constants for minerals and aqueous species. Available from the authors, University of Oregon.
20. Berner E. K. and Berner R. A. (1996) *Global Environment: Water, Air, and Geochemical Cycles*. Prentice Hall, Upper Saddle River, N.J.
21. Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P., Holm, N., *Chemical Geology* **191**, 345– 359 (2002).
22. Wetzel L. R. and Shock E. L., *J. Geophys. Res.* **105**, 8319-8340 (2000).