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POTENTIAL FUEL PRODUCTION FROM MAGMA

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ABSTRACT

Recent calculations and measurements indicate that basaltic magma is a new, extensive source for fuels (hydrogen, carbon monoxide, and methane). The fuel production processes have been found to occur in nature as well as the laboratory and as a result, our work indicates that current concepts of geothermal energy can be broadened beyond producing only steam and heat. When magma is considered as a geothermal resource, its use for the direct production of fuels should be included. It is possible to generate several mole percent hydrogen when water-rich fluid is equilibrated with the ferrous and ferric iron in magma. This paper describes the basis of the fuel production processes, the fuel yields for injected water and water plus natural organic matter, and the increased geothermal resources that would be made available by these processes.

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POTENTIAL FUEL PRODUCTION FROM MAGMA*

Conventional, high quality energy reserves of the earth are rapidly being depleted. As a result, a reanalysis is now in progress of what energy is, how it affects our lives, how to conserve and extend the present resources, and how to utilize energy alternatives.¹

Recognition of the need for new energy alternatives has led to programs centering on the development of nuclear, solar, wind, and geothermal sources of energy. However, these alternatives characteristically do not emphasize the production of energy in the form of fuel. The depletion of fuel resources is felt by many to be the most urgent part of the energy problem because fuels are a storable as well as portable form of energy and they serve as feedstocks in the production of numerous chemicals. Energy produced by the alternative techniques now under development can be used to produce fuels. For example, proposals to produce hydrogen from nuclear plants include using thermal energy (a) to produce electricity and in turn electrolyze water, (b) to operate thermochemical cycles, and (c) to decompose biomass and water.² Unfortunately, severe economic losses result from the multistage nature of such procedures. To the end user, electricity is a clean and useful form of energy and fills a unique role in the energy system. However, there are appreciable inefficiencies in transmitting electricity over large distances. In addition, the difficulty of storing electrical energy, to allow generating plants to operate at peak capacities, has resulted in a reassessment of the optimum energy carrier. Hydrogen, in fact, is

being considered as an alternative to electricity as a means of distributing energy. It is unclear, however, from proposals such as those outlined above, whether substituting a hydrogen system for electricity would result in an overall increase in efficiency or be cost effective.³

Whether hydrogen is utilized as a primary energy carrier or as a feedstock, the primary stumbling block for implementing hydrogen programs has been obtaining a practical, efficient, long term source. It is our purpose here to call attention to the potential of basaltic magma and hot basaltic rock for the production of hydrogen as well as certain other fuels, such as carbon monoxide and methane.

Natural Volcanic Occurrence of Hydrogen

Recent measurements indicate that such fuel production processes occur naturally. For example, in 1970, Naughton observed flames emanating from vents at the Mauna Ulu volcanic center on the east rift of Kilauea volcano in Hawaii.⁴ Between flaming episodes, he obtained gas samples which subsequent analysis proved to be chiefly water with significant quantities of hydrogen and carbon dioxide. He concluded that the intermittent flames were produced by hydrogen generated from water-lava interactions at high temperatures. Small concentrations of hydrogen and carbon monoxide are commonly found in volcanic gas samples collected from eruptions of basaltic lava under conditions of minimum atmospheric contamination. These collections contain up to 3 percent hydrogen and carbon monoxide.⁵ Spectroscopic evidence has been reported for burning of hydrogen at vents

following an episode of basaltic lava fountaining on the caldera floor of Kilauea volcano. Studies of volatiles released from heated basaltic lava also show as much as 3 percent hydrogen and carbon monoxide.^{5,7} After condensation of water, the remaining active gases may contain from 15 to 60 percent hydrogen. These concentrations are in agreement with thermodynamic investigations of gas systems over a range of compositions, oxidation states, and temperature, displayed by basalts.⁹

Fresh basaltic lava contains on the order of 10 weight percent ferrous oxide (FeO) and 1 to 2 weight percent ferric oxide (FeO_{1.5}). These components are present as dissolved constituents within the silicate melt and in minerals (e.g., olivine, pyroxene, magnetite) suspended in the magma. The predominance of ferrous over ferric oxide in basaltic magma is in large part responsible for the reported concentrations of hydrogen and carbon monoxide observed in the above volcanic gas collections. The oxygen fugacity of basaltic lava has been measured as a function of temperature in the field on cooling lava¹⁰ and in the laboratory on basalt samples raised to magmatic temperatures.¹¹ Oxygen fugacities of basaltic lavas have also been inferred from the compositions of coexisting mineral phases.¹² These studies as a whole have revealed that the oxygen fugacity of basaltic lava can be closely simulated by various solid assemblages. That is, mixtures of certain solids, at temperatures and pressures of magmatic environments, develop oxygen fugacities characteristic of those determined for basaltic lavas. The solid assemblages in order of increasing oxygen fugacities

are magnetite-wuestite (MW), quartz-fayalite-magnetite (QFM), nickel-nickel oxide (NNO). Field and laboratory measurements indicate that the oxygen fugacity of basaltic lavas varies within the range established by these assemblages; however, most of the data for relatively unaltered basalts corresponds to oxygen fugacities slightly more reducing than QFM at higher temperatures (>1000°C) to values near NNO at lower temperatures (<800°C). Similar studies of andesites and rhyolites indicate somewhat higher oxygen fugacities usually near those of nickel-nickel oxide. The method of fuel production proposed here depends principally on the reducing action of basaltic magma on injected water; this chemical interaction causes the oxidation of ferrous components in the basalt and the production of hydrogen:

(magma) (fluid) (magma) (fluid)

The results of this process are observed both in the field and in the laboratory. Basalt that has cooled slowly as intrusions, lava lakes, or thick lava flows is often observed to be more oxidized (higher $\text{FeO}_{1.5}:\text{FeO}$) than rapidly quenched lava. This is explained by oxidation of ferrous iron by water with subsequent diffusional loss of hydrogen.¹³ The same process of oxidation and hydrogen escape is observed in hydrothermal experiments on rock plus water mixtures. The concentration of hydrogen obtained from the equilibration of water-rich fluids with basalt can be predicted from the thermochemical properties of the simulant solids mentioned above. This

approach has been followed in the thermodynamic calculations* presented below to evaluate the potential fuel-producing capacity of basaltic magmas and hot basaltic rocks. The thermodynamic calculations have been carried out over the range of oxygen fugacities defined by the above simulant solids and the assemblage hematite-magnetite (HM).

Hydrogen from Water-Basalt Interactions

Figure 1 shows hydrogen concentrations resulting from the equilibration of water with the various solid assemblages for a total pressure of 100.0 MPa (1000 bars), a reasonable value for basalt at shallow depths as, for example, under the ocean ridges. The results are presented in log mole percent hydrogen for the temperature range 600°C to 1300°C, which includes the subsolidus to liquidus region for most magmas at low total pressure. The curve labeled H₂O refers to the percent hydrogen generated by the thermal dissociation of water. Hydrogen concentrations are mainly determined by temperature and oxygen fugacity, although a pressure increase from 0.1 MPa (1 bar) to 100.0 MPa (1000 bars) causes a decrease of about .25 percent in the region of NNO and

*Standard state thermochemical data for gaseous species have been taken from the 1971 JANAF tables and the 1974 supplement to the JANAF tables. Fugacity coefficient data for H₂O¹⁴ and for H₂¹⁵ have been used. Fugacity coefficients for all other species have been calculated from the corresponding state version of the Redlich-Kwong equation.¹⁶ The most current published experimental calibrations for the temperature and pressure dependence of oxygen fugacity have been used in calculations involving these simulant solids.¹⁷ The fluid mixtures have been treated as ideal gaseous solutions.¹⁸ Calculations have been made with a computer routine from steepest descent methods.¹⁹

QFM for most temperatures. Hydrogen concentrations for systems with oxygen fugacities near NNO and QFM range from 0.5 to 2.5 percent; hydrogen fugacities in this region range from 2.1 MPa (21 bars) to .3 MPa (3 bars). Before eruption and post-eruption oxidation, most basaltic magmas probably have oxygen fugacities equal to or somewhat less than QFM. Hence, hydrogen concentrations of up to 3 percent are potentially possible from water-basalt interactions.

The calculated hydrogen percentages based on the simulant solids have been tested and verified experimentally for water vapor reacting with a single crushed basalt sample. Water vapor at low pressures was passed through a bed of porous, vesicular, degassed basaltic lava at 950°C, about 100°C below its solidus temperature. Tholeiitic basalt from the September 1971 pahoehoe flow in Kilauea caldera, Hawaii, was used. This lava contains about 10.5 weight percent FeO and 1.5 weight percent Fe_2O_3 .²⁰ Seventy-seven grams of the lava was placed in a fused-silica tube, open at both ends and enclosed in a larger fused-silica tube placed in a furnace and connected via stainless steel flanges and tubing to a mechanical vacuum pump. The lava was first degassed at 400°C for 7 hours, then heated to 950°C and the experiment begun when total pressure had fallen to 6 Pa (45 microns). Gases being evolved at the end of the degassing period contained approximately 0.6 volume percent hydrogen at a total pressure of 6 Pa. Water vapor from a flask of deaerated water at room temperature was allowed to flow over the bed of lava (Figure 2). Gases were analyzed with a UTI quadrupole mass

spectrometer; samples were first withdrawn into a liquid-nitrogen-cooled cold trap to condense water vapor and then admitted to the mass spectrometer. The analyses were calibrated both by the use of a calibrated hydrogen leak cylinder and by the introduction of a measured pressure of hydrogen into the system.

Measured mole fractions of hydrogen are recorded in Table 1 as a function of total pressure and contact time. The contact time of 0.6 and 3.0 seconds are the calculated times for the gas to flow through the length (30.5 cm) of the lava-filled tube in a continuously flowing situation. The flow speed and total pressure were controlled by regulating the inflow rate of water vapor and the outflow of gas to the vacuum pump. The contact time of 360 seconds was obtained by holding a fixed sample of water vapor in contact with the lava for that period of time without any flow of gas. All of these measurements were performed using the identical sample of basalt sealed within the fused-silica tube. Since the oxygen fugacity of this basaltic lava should lie somewhere within or near the range defined by the QFM and NNO assemblages, the hydrogen production is anticipated to be within the range of 0.65 to 2.1 mole percent. The observed production, upon attaining apparent equilibrium, of between 1.1 and 2.7 mole percent hydrogen is in good agreement with the prediction. The time required for attainment of equilibrium in our experiments appears to be quite short, in contrast, for example to the experiments of Kennedy²¹ and Fudali¹¹. Their experiments, however, required the bulk molten rock sample

to achieve equilibrium with the gas phase, while we were concerned only with driving the gas phase toward equilibrium with the surfaces of the rock.

The hydrogen concentrations obtained in the above calculations and experiments apply to initial conditions in which the ratio of water to basalt is small and the basalt effectively buffers the fluid. In a water-rich system the basalt could become progressively oxidized as it interacted with water by the conversion of FeO to $\text{FeO}_{1.5}$. Continual addition of water could ultimately impose the oxygen fugacity of water (Figure 1) on the system, converting most of the iron in the basalt to $\text{FeO}_{1.5}$. This would correspond to production of the maximum possible amount of hydrogen. However, as the reaction progressed, the hydrogen concentration could drop to levels

TABLE 1
BASALT + H_2O 950°C

Total Pressure, MPa	Mole Percent H_2 Produced			Mole Percent H_2 Calculated	
	0.6 seconds	3.0 seconds	360 seconds	NNO	QFM
1.3×10^{-3}	0.16	1.1	1.3	0.65	2.1
2.6×10^{-4}	0.28	2.3	1.1	0.65	2.1
1.3×10^{-4}	--	2.7	--	0.65	2.1

which would probably make recovery impractical long before oxidation was complete. The quantity of hydrogen potentially recoverable up to some practical oxidation limit can be estimated from Fudali's¹¹ experimental data on the FeO:FeO ratios of basalts and andesites as a function of oxygen fugacity at 1200°C. The average for this relationship of Fudali's experiments on basaltic lavas is shown by the lower line in Figure 3. Fudali found that a straight-line relationship for mole fraction ratio, $X_{\text{FeO}}:X_{\text{FeO}_{1.5}}$ such as shown in figure 3 was obtained for the reaction relation between these components even under conditions so oxidizing as to cause precipitation of magnetite.

Figure 3 can be used to trace the drop in hydrogen concentration with oxidation of the ferrous oxide in a basalt at 1200°C. Fresh basalt containing on the order of 10 weight percent FeO at a temperature near 1200°C with an oxygen fugacity one half order of magnitude less than QFM, gives a corresponding $X_{\text{FeO}}:X_{\text{FeO}_{1.5}}$ ratio of 7.4 and a weight percent FeO_{1.5} of 1.5. As the reaction proceeds, new values for the weight ratio of FeO to FeO_{1.5} and the mass of FeO progressively oxidized can be calculated from Figure 3. Table 2 summarizes reaction progress from the initial condition to a point where only .01 percent hydrogen is compatible with the oxidation state of the basalt. The cumulative hydrogen production from the oxidation of a given volume of basalt can be calculated from the above oxidation reaction, progressive values for the mass of FeO oxidized, and an average basalt density (3g/cm³). Table 2 shows the results of such calculations in units of moles of hydrogen per km³ basalt oxidized.

The hydrogen production estimates with reaction progress presented in Table 2 apply only at 1200°C. The addition of water to magma will cool it to temperatures lower than 1200°C depending on flow rates, heats of reaction in the basalt, and heat transfer rates from the surrounding reservoir of magma. Lower temperatures may permit a greater amount of FeO to be oxidized and, therefore, greater hydrogen production, because experimentally it has been found that at fixed oxygen fugacities, decreased temperature tends to give lower FeO:FeO_{1.5} ratios in basalts for a given oxygen fugacity.²¹ On the other hand, shift of the fluid equilibria with decrease in temperature will tend to decrease hydrogen concentrations by increasing the association of hydrogen and oxygen to form water within the fluid phase. Also, lower temperatures may lead to less favorable kinetics for the oxidation process. At the present time there are not adequate data with which to predict the consequences of these opposing tendencies, and future research should address these questions.

It appears from the data presented in Table 2 that on the order of 10^{12} moles of hydrogen are potentially recoverable from water interaction with a km³ of basalt for temperatures greater than 800 C. This quantity of hydrogen is equal to $20 \times 10^9 \text{ m}^3$ (S.T.P) or 2×10^{12} grams hydrogen per km³ of basalt. Approximately 7×10^{14} moles of water as a working fluid would be required to produce this quantity of hydrogen (this value could be considerably reduced if fluid were recycled). Of this amount, 10^{12} moles (2×10^{13} grams)

Table 2

Log fO ₂	X FeO	% H ₂	Moles H ₂
	X FeO 1.5		Km ³ basalt
-9.	7.4	3.	0.
-8.	4.8	1.2	1.3 x 10 ¹¹
-7.	3.2	.45	3 x 10 ¹¹
-6.	2.	.17	5.5 x 10 ¹¹
-5.	1.3	.07	8 x 10 ¹²
-4.	.9	.025	1 x 10 ¹²
-3.	.58	.01	1.3 x 10 ¹²

would be consumed in oxidation. Some unknown amount will probably also be consumed in hydration reactions. Therefore, approximately 10^{13} moles is probably a reasonable upper limit for water consumption in the production of 10^{12} grams of hydrogen from a km³ of basalt.* Thermal equilibration between cold water and hot magma in this ratio (10^{13} moles of 25°C to 1 Km of 1200°C magma) would result in only about a 50°C cooling of this quantity of magma.

*For comparison, the oceans contain approximately 10^{23} moles of water. The average discharge of the Wairakei, N.Z., geothermal field is 3×10^{12} moles/yr.²²

Enhancement of Fuel Production

The capacity for fuel production by water injection into magma is large by any currently available estimate, but for any given magma body, the reducing capacity is finite as shown in Table 2. The addition of biomass to the injected water is a way of extending the reducing capabilities of a magma body and of utilizing a second primary energy source, solar energy, to enhance the geochemical fuel production capability of the magma. Mixtures of water with small percentages of biomass material are themselves reducing in nature and therefore decrease the consumption of FeO and H₂O per unit of fuel generated. Thus, small percentage additions of these components to the working fluid may allow fuel production from less FeO rich, lower temperature, andesitic and rhyolitic magmas. The possibility also exists of producing fuels directly from mixtures of water and biomass matter using magma or hot rock as a source only of thermal energy.²²

Biomass may generally be regarded as a fuel itself; however, many forms of biomass are not being utilized today and are in such a form or location as to make them unattractive for most uses. A relevant example is the seaweed, sargassum, which occurs at sea in fields close to attractive magma sources along the mid-Atlantic ridge. Thus, there is a possibility that new forms of biomass can be refined to higher quality fuel in this way and that other more conventional forms can be utilized as well.²²

Calculated results are presented below for the addition of cellulose

($C_6H_{10}O_5$) to the injection fluid. Cellulose is one of the principal constituents of plant material, and it is abundantly available in a variety of substances: bagasse, municipal sewage, forest slash, seaweed, etc. We have used this cellulose molecule because it best characterizes the results obtained for a variety of substances (nitrogen-containing cellulose, lignin, coal, etc.) which make reducing mixtures when added to water at magmatic temperatures and pressures.

Figure 4 illustrates compositional relationships of interest for fluid mixtures of water and carbonaceous materials at 600°C. The line joining H_2O and $C_6H_{10}O_5$ represents the locus of atomic compositions ranging from 100 percent water to 100 percent cellulose. A large proportion of cellulose brings the mixture composition near lines G_{1000} and G_1 which are the 600°C phase boundaries for graphite precipitation at 100.0 MPa (1000 bars) and 0.1 MPa (1 bar) respectively. These lines limit the equilibrium concentration of cellulose component that a homogeneous working fluid could contain in the pressure range of interest. At higher temperatures the graphite phase boundaries shift to more carbonrich compositions, thus allowing larger maximum cellulose concentrations in the mixture. Except for lines G_1 and G_{1000} atomic compositions having an oxygen fugacity equivalent to QFM at 600°C and 100.0 MPa (1000 bars) shown in Figure 4 change very little for temperatures between 600°C and 1300°C. Isobars for other oxygen fugacities are roughly parallel to this QFM-line; those more oxidizing than QFM plot above the line, and those more reducing than QFM occur below the line.

Figure 4 shows that except for extremely water-rich mixtures, water-cellulose fluid compositions will have oxygen fugacities lower than QFM and will therefore be more reducing than most magmas or hot rocks. Figures 5 and 6 summarize the concentrations of principal fluid species in mole percent for fluids along the $\text{H}_2\text{O}-\text{C}_6\text{H}_{10}\text{O}_5$ mixing line in Figure 4 at 100.0 MPa (1000 bars) over the temperature range 600°C to 1300°C. Graphite is not a stable phase over this range of conditions unless greater than 30 weight percent cellulose component is added to the fluid mixture. At 600°C hydrogen concentrations level out at 2 percent after the addition of at least 3 weight percent cellulose. With the addition of larger proportions of cellulose, methane concentration becomes significant and predominates over hydrogen. At temperatures greater than 800°C, fluid equilibria shift toward larger hydrogen and carbon monoxide concentrations for low cellulose contents (Figure 6). Thus, mixtures of water with a few weight percent cellulose in a closed system loop heated by magma or hot rock could produce fuels of hydrogen and methane at lower temperatures and of hydrogen and carbon monoxide at higher temperatures.

If mixtures of water and cellulose are interacted directly with magma (or hot rock), the fuels produced will depend primarily on temperature and the composition and oxidation state of the fluid relative to that of the magma. Initially, the magma would alter the fluid composition imposing on it a magmatic oxygen fugacity. For example, a basalt magma would react with the fluid giving rise to hydrogen concentrations similar to those obtained for water-basalt interactions; some carbon monoxide and methane could

also be produced depending on the concentration of cellulose component in the fluid mixture. After sufficient circulation the system could develop an oxygen fugacity similar to that of the fluid mixture, and fuel production could stabilize at the values indicated by Figures 5 and 6 for appropriate temperature and cellulose content. Perhaps the most significant aspect of the addition of small amounts of cellulose to water is its effect on oxygen fugacity. One weight percent cellulose lowers the oxygen fugacity of the fluid to that of QFM at 1200°C and to values below QFM for all temperatures less than 800°C. Consequently, small cellulose additions to the working fluid could be used to prolong and increase the potential fuel recoverable from magma or hot rock of any composition over that obtained using water alone as a reactant fluid.

Site Location

A site for fuel production from magma requires both a large source of available water and a magma body of significant proportions. Molten rock exists sporadically in place and time within the earth's crust, but it is most abundant in two plate tectonic environments. Along the 75,000 km, oceanic ridge system, partial melting in rising diapirs of hot, plastic mantle peridotite is believed to produce basaltic magma which cools to form the oceanic crust. Volcanic belts located above subduction zones at convergent plate boundaries are the loci of basaltic to rhyolitic magmatism. The former existence of large bodies of magma is attested to²⁴ by gabbroic ($10^2 - 10^4 \text{ km}^3$) and granitic

$(10^4 - 10^5 \text{ km}^3)$ plutons; prehistoric eruptions of great volumes of pyroclastic deposits $(10^1 - 10^2 \text{ km}^3)$ and ash-flow tuffs $(10^2 - 10^3 \text{ km}^3)$; and by voluminous historic lava flows $(10^{-1} - 10^1 \text{ km}^3)$ in Iceland and Hawaii. Data on the actual location and size of probable magma bodies in the crust is just beginning to come into existence, and recent geophysical studies tentatively located bodies of magma in Kamchatka, Yellowstone, Alaska, the Azores, and New Mexico. Smith and Shaw²⁶ have recently estimated that about $2 \times 10^4 \text{ km}^3$ of molten magma presently exist within 10 km of the surface in the coterminus U.S.

A crucial consideration for the availability of magmatic heat is the form taken by magmatic intrusions. If magma rises rapidly from great depth along narrow fractures to erupt as submarine or surface flows or to form dike swarms, very little will exist at any given time in the molten state. The most favorable situation is large-scale "ponding" of magma in a "reservoir" without eruption. Conductive cooling rates for intrusions can be estimated from the equations of Jaeger.²⁷ Both the rate and mode of magma emplacement will determine the amount in existence at a given time. Menard²⁸ made an estimate of the rate of lava extrusion along the mid-oceanic rift system based on crustal spreading rates $(0.7 \text{ to } 4.5 \text{ cm yr.}^{-1})$ and the thickness of layer 2 $(1.0 \text{ to } 3.5 \text{ km})$ of the oceanic crust. He derived a total present production rate of $5 - 6 \text{ km}^3 \text{ yr.}^{-1}$ for the entire planetary rift system, corresponding to $50 - 90 \times 10 \text{ km}^6/\text{yr.}^{-1}$ per km of rift length. If we include magma intruded

to form the gabbroic layer 3, assuming a 5 km thickness for this layer,²⁹ the total estimated rate of magma emplacement is increased by 250 percent. The areal variation in compositions of basalt in the medial valley of the Mid-Atlantic ridge in the FAMOUS area (37°N) suggests the existence of a magma chamber about 3 km across.³⁰ Sleep's thermal modelling of ridge axes³¹ suggest that steady-state magma accumulations should not exist at ridges with low spreading rates (less than 1.0 cm yr^{-1} per flank), but that magma chambers with dimensions of the order of a few km should exist at faster-spreading ridges. Sleep's model predicts a magma chamber a km or so in width with a top lying about 3 km below the sea floor for the Mid-Atlantic ridge at 37°N (1.1 cm yr^{-1} average half-spreading rate). Magmatism accompanying spreading at the rifts is likely to be temporally discontinuous in many areas, proceeding by dike injection at intervals. This would produce local concentrations of magma, like the thermal anomaly in the Gulf of California, which has been inferred to be a 1.3 km wide intrusive dike produced by spreading along a segment of the East Pacific Rise.³²

The Mid-Ocean ridges appear to be particularly favorable for fuel production processes because magma of the ridge environment is characterized by high FeO content, high temperature, and low oxygen fugacity. Silicic magma bodies on continents or island arcs have lower temperature and iron content: they would be useful mainly as heat sources for fuel production by heating mixtures of water and carbonaceous material.

Toward Practicality

Much information is still required to evaluate the feasibility of magma-hot rock fuel production, especially for systems in which injected fluids and host silicates interact. Needed studies include methods for developing and maintaining porosity-permeability in hot rock, glass, and foam, and for predicting temperature distributions in fluid-rock systems. The kinetics of fluid and silicate reactions must be investigated to determine reaction times and minimum operating temperatures. Fluid loss by solubility of injected fluids in magma may be an important problem although chilling or partial crystallization of the magma may obviate this difficulty. Also, the ubiquitous occurrence of vesicles in ridge lavas suggests the source magma under the ridges is at or near saturation with respect to a volatile phase.³³ Of equal concern is the solubility of magma and rock components in the aqueous fluid and their redistribution and reprecipitation. Studies by Helgeson³⁴ show that extensive mass transfer results from water-rock interactions at temperatures below 300°C. Volatization and leaching at higher temperatures by water-rich fluids is poorly understood but may be substantial in magmatic environments. The redeposition of transferred materials must be understood particularly as it affects porosity-permeability of the host material. Investigations of the C-O-H-S-N-Cl-F system over a range of temperatures and pressures are currently in progress to evaluate the scavenging of hydrogen by other volatile components at higher pressures. So far these studies indicate that hydrogen concentrations are substantial as long as total pressure is less than 2000

bars and $H_2O:CO_2$ ratios are greater than unity. The use of seawater as a working fluid needs to be studied to determine the nature of its interaction with magma, the possibility of salt precipitation, and corrosive effects on equipment.

Conclusions and Summary

Most geothermal power installations are located in regions of contemporary or recent lithospheric plate convergence within or on the margins of continental masses. In these areas intrusions of magma into thick, permeable reservoir rocks with intervening capping strata have produced deposits of thermal water which conventionally have been exploited for heat and electricity. Our investigations suggest that serious consideration should also be given to the large potential of magma and hot rocks for producing fuels such as hydrogen, carbon monoxide, and methane. This concept also offers the interesting possibility of utilizing the basalt magmas and hot rocks of the mid-ocean ridge system for energy extraction. With few exceptions (e.g., Iceland), the ridge zone of magmatism has been unexploited for energy because it is largely removed from major markets for electricity and thermal energy. The direct production of hydrogen from the abundantly available water and basalt in these regions could significantly increase the contribution of geothermal sources to the overall energy resources of the earth. When magma or hot rocks are coupled with a second energy source by using carbonaceous additives obtained from renewable solar energy sources, the fuel yields can be increased significantly. For example, the United States consumed approximately 6×10^{12} grams of hydrogen in 1975.² This value of hydrogen consumption includes all

petrochemical processes, ammonia production, methanol production, and specialty gas uses (fabrication of steels, etc.). We estimate that 1×10^{12} grams of hydrogen could be obtained per km^3 of basaltic magma by reacting the basalt with water alone. Adding organic matter to the injection stream could increase the hydrogen production to values exceeding the 1975 U. S. consumption rate.

The principal sources of hydrogen are now fossil fuels (petroleum and natural gas). As these sources become more scarce, the value of hydrogen will continue to increase. Whether hydrogen is used as a consumable fuel, a feedstock to a chemical process or as a storage medium for primary energy, alternative processes for producing hydrogen must be sought because of the limitation of currently available sources. Many questions must be answered before these fuel production processes could be utilized on a large scale; however, it is clear that existing magma is a large untapped source of fuels.

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FIGURE 1. Hydrogen concentrations in log₁₀ mole percent as a function of temperature for equilibration of water with the assemblages hermatite-magnetite (HM), nickel-nickel oxide (NNO), quartz-fayalite-magnetite (QFM), and magnetite-wuestite (MW) at 100.0 MPa total pressure. The curve labeled H₂O refers to the percent of hydrogen generated by thermal dissociation of water at 100.0 MPa.

FIGURE 2. Experimental system for verifying the production of hydrogen from water-basalt reactions. When water vapor contacts fresh, heated basalt, hydrogen is generated in amounts equal to the theoretically predicted values which were based on the approximate oxygen fugacities of the rock.

FIGURE 3. Mole percent hydrogen ($\% \text{H}_2$) from water-basalt interactions and the mole fraction ratio of FeO to FeO_{1.5} for an average basalt $\% \text{H}_2$ and $\frac{X_{\text{FeO}}}{X_{\text{FeO}_{1.5}}}$ shown as a function of oxygen fugacity at 1200°C and 100.0 MPa. The oxygen fugacities for the buffers quartz-fayalite-magnetite (QFM), nickel-nickel oxide (NNO), and hematite-magnetite (HM), are indicated by the dashed lines. The iron oxide mole fraction ratio curve was obtained from experimental data.¹¹

PHASE DIAGRAM FOR C-H-O SYSTEM

FIGURE 4. Compositional characteristics of the C-O-H system at 600°C. Solid lines G_{100} and $G_{0.1}$ are the phase boundaries for graphite at 100 MPa and 0.1 MPa respectively. The dashed line QFM is the lows of atomic compositions in the system with oxygen fugacities equivalent to that of the quartz-fayalite-magnetite buffer. The mixing line for H_2O - $C_6H_{10}O_5$ is also shown. Note that small additions of cellulose to water gives an oxygen fugacity equal to QFM and that larger additions result in mixtures with oxygen fugacities less than QFM.

FIGURE 5. Concentrations of principal species in mole percent for mixtures of water and cellulose ($C_6H_{10}O_5$) at 600°C and 100.0 MPa. The concentrations are shown as a function of the weight percent $C_6H_{10}O_5$ in the mixture.

FIGURE 6. Concentrations of principal species in mole percent for mixtures of water and cellulose (C₆H₁₀O₅) at 1300°C and 100.0 MPa. The concentrations are shown as a function of the weight percent C₆H₁₀O₅ in the mixture.

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