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Hydrogen generation from mantle source rocks in Oman

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Hydrogen gas, associated with Ca^{2+} OH-rich alkaline groundwaters (pH = 10–12), is at present emanating from ultramafic rocks of the Oman ophiolite. Isotopic and chemical evidence indicates that hydrogen is formed by low-temperature redox reactions in a closed groundwater environment. This is normally a cryptic process in the hydrosphere but is fortuitously revealed by the unusual hydrogeological conditions in Oman where atmospheric oxygen is totally assimilated. It is suggested that hydrogen generation in mantle source rocks at depth and in the early Archaean surface environment may be more widespread than has hitherto been realised.

1. Introduction

Many diverse sources have recorded hydrogen-rich gas from a variety of deep crustal and upper mantle rocks, notably from peridotite/serpentine inclusions, and from some major deep-rooted faults [1–18]. Such gas formation is commonly assumed to be magmatic or hydrothermal in origin. Here, evidence from the Semail nappe of Oman is presented to show that hydrogen may also form inorganically within the relatively low temperatures of the hydrosphere during both shearing of ultramafic rocks and by post-serpentinisation chemical degradation.

2. Gas occurrence

During a water resources survey and subsequent NERC-funded and independent groundwater surveys of Oman (1974–1981), natural gases were found in association with spring waters emerging from ultramafic rocks [19]. These rocks form the lower and most massive part of the

TABLE 1

Typical chemical compositions of highly alkaline spring waters from Oman [a] (all ion concentrations are expressed as meq l^{-1})

	1	2	3	4	5	6	7
Na	16.2	11.5	7.26	5.28	7.55	12.1	9.57
K	0.23	0.27	0.14	0.20	0.12	0.29	0.269
Mg	0.06	0.02	0.003	0.007	0.162	0.005	0.008
Ca	3.21	3.78	3.64	3.10	9.11	2.94	4.69
OH	7.49	6.00	4.46	3.18	1.80	5.74	4.79
Cl	11.8	9.66	6.40	5.36	5.99	9.94	9.03
SO_4	0.09	0.10	1.43	0.05	0.84	0.21	0.13
$CO_3^2 + HCO_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
pH	12.1	11.6	11.4	11.4	11.3	11.3	11.1

[a] Spring sites: 1 = Jill D; 2 = Karku, 3 = East Izki, 4 = Rustaq, 5 = Sayma, 6 = Jalah, 7 = Wihi al Murr.

"Semail nappe"; an exceptionally large area of ophiolites comprising oceanic crust (basic) and upper mantle (ultramafic) lithologies, totalling up to 7 km in thickness [20].

The springs, which are of a calcium hydroxide type well documented from several ultramafic environments [21], provide some of the most highly alkaline waters found in nature in which the pH sometimes exceeds 12. Some typical chemical analyses of these waters are given in Table 1.

Gases emerge along fault and shear discontinuities in partly to wholly serpentinised ultramafic rocks and are observed at the same exit points as the spring waters. Measurable gas flows vary from barely detectable to about 10 ml s^{-1}, but more substantial flows (> 10 l s^{-1}) occur from an inaccessible rock crevice at B'lad and from an 80-m borehole in mantle sequence rocks at Nizwa (Fig. 1). Occasional bubbles to irregular streams of gas were observed in only a dozen of the alkaline springs, but the presence of soft white carbonate mud in the bottom of most spring chambers led to the fortuitous widespread preservation of conical

depressions caused by gas flow, and the conclusion that persistent gas release has occurred at some stage in all the alkaline springs (> 60) investigated.

3. Methods

Eighteen gas samples were collected in glass gas bottles (sample locations given in Fig. 1) with teflon seals by water displacement from 7 spring sites. These samples were subsequently analysed using a VG-Micromass 16-B mass spectrometer and a Perkin-Elmer F11 flame ionisation gas chromatograph to give their chemical compositions. Stable hydrogen isotope analyses, determined by isotope ratio mass spectrometry on a VG 602E instrument, were obtained for four of the hydrogen-rich gases.

4. Results

4.1. Gas composition

The gases vary in chemical composition (Table 2, Fig. 2) from that of almost pure hydrogen (99% at Huwayl Qufays) to almost pure nitrogen (96% at Murayrat) and an approximation to air (atmospheric composition [22] in italics: 76.9, *78.1* % N$_2$, 20.5, *20.9* % O$_2$ and 0.9, *0.93* % Ar at Wadi Zabin). In addition small amounts of methane (< 4.5%) together with trace amounts of the higher-saturated hydrocarbons (< 120 vpm) occur with the hydrogen-rich gas and trace amounts of CO (< 0.1%) occur with the most nitrogen-rich gas. The largest
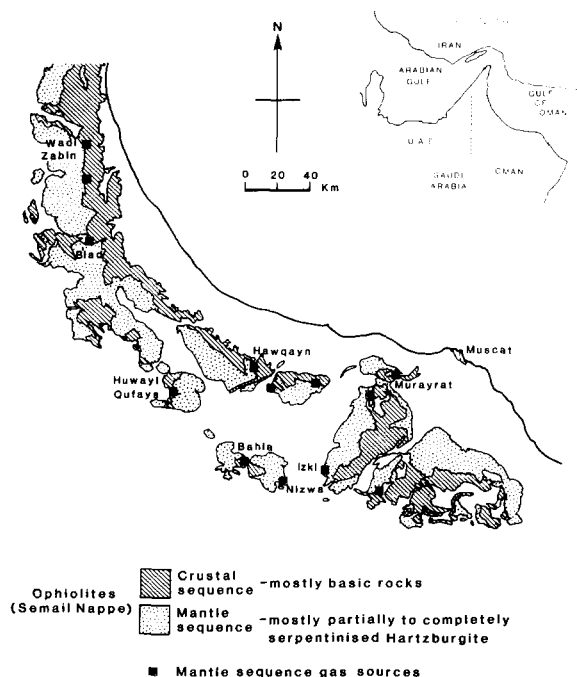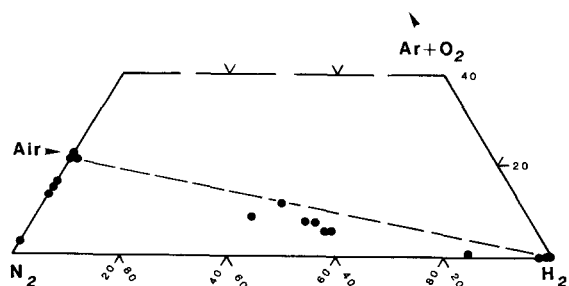

Fig. 1. Location of gas sources in the Semail Nappe.

Fig. 2. Gas compositions from sites in Oman.

gas flow emanated from a borehole in serpentinised lherzolite at Nizwa (Fig. 1). Although contaminated by entrained air at the wellhead, "Draeger" chromatography tests of this source indicated hydrogen > 5% and hydrocarbons (probably methane) at about 0.5%.

4.2. Isotope geothermometry

The Oman hydrogen-rich gases provide some of the most deuterium-depleted hydrogen gases found in nature (Table 3) and correspond to low temperatures of formation [23–25]. Assuming isotopic equilibrium between hydrogen and water at the time of hydrogen formation, and insignificant subsequent isotopic exchange, the temperature-frac-

tionation relationship for H_2-H_2O vapour indicates a formation temperature range from about 20–50°C [26,27], i.e. bracketing the mean groundwater temperature in Oman of 32°C. This estimate is based upon a range of δ^2H values of + 10 to − 10‰ (with respect to SMOW) observed for 30 alkaline spring waters. The narrow range of hydrogen isotope composition from samples collected over a wide region of the Oman mantle sequence implies both a remarkably uniform fractionation throughout the groundwater system, and that the physical release of pre-existing hydrogen inclusions, of higher-temperature origin, known to be present in partly serpentinized mantle rocks [3–8], is volumetrically unimportant.

TABLE 2

Compositions of natural gases from Oman

Location	H_2 (%)	N_2 (%)	O_2 + Ar (%)	CH_4 (%)	CO (%)
Bahla (1)	82	15	2	2	0
(2)	55	38	7	2	0
(3)	43	43	13	0.9	0
(4)	97	2	< 0.1	1	0
(5)	53	38		2.2	0
Hawqayn (1)	39	50	10	1.1	0
(2)	48	40	8	4.3	0
(3)	47	39	8	4.3	0
Wadi Zabin (1)	2	76	21	0.2	0
(2)	1	77	21	0.2	0
Murayrat (1)	< 0.1	96	4	0	0.1
(2)	0	78	22	0	0
Nizwa	95	1	0	4.0	0
Huwayl Qufays	99	1	0	0	0
B'lad	22	76	1	0	0
Air	0	78.1	21.8	0	0

	Ethane	Propane	iso-Butane (vpm)	n-Butane (vpm)	Total hydrocarbons (vpm)
Bahla (2)	63	17	2	.11	114
(3)	70	15	2	10	112
(4)	78	18	2	12	110
Hawqayn (2)	5	1	1	1	8
(3)	5	1	1	1	8

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TABLE 3

Deuterium content and temperature of outgased hydrogen

Location	δ^2H (‰ vs. SMOW)	Isotope formation temperature (°C)
Nizwa, Oman	−697	
Bahla, Oman	−699	20–50
Huwayl Qufays, Oman	−699	
B'lad, Oman	−714 [a]	
Geothermal areas, Iceland [25]	−358 to −632	~170–290
Surtsey volcanic gas, Iceland [24]	−110 to 157	~1150
Yellowstone, U.S.A. [23]	−661	150
Broadland, New Zealand [23]	−457	265

[a] This deviant value might be attributable to the presence of N_2 in the gas which gives rise to mass spectrographic interference.
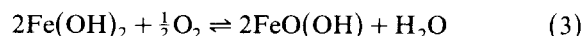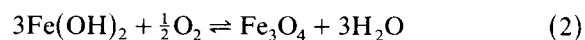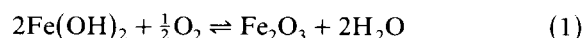
4.3. Iron phases in the aquifer

The generation of hydrogen and assimilation of atmospheric oxygen depend upon the availability of reduced iron phases in the aquifer matrix. These originate as the primary minerals olivine and pyroxene, of typical Fe^{II}/Mg^{II} molar ratio 1:10, which hydrate to form serpentine and ferrous oxide/hydroxide. Positive identification of these brown amorphous iron alteration products is difficult, but the microscopic characteristics are closer to goethite (α-FeO·OH) than to haematite (α-Fe_2O_3), whereas the lack of any relationship between degree of serpentinisation and magnetic susceptibility excludes magnetite (Fe_3O_4) as the dominant iron-rich phase.

5. Discussion

The hydrogeological aspects of the Semail nappe are unusual in that large areas of partly serpentinised and deeply fractured peridotites, set in an arid soil-free environment, are subjected to infrequent rainfall [19]. Since significant recharge occurs at irregular and infrequent intervals of typically 2–4 years [19], groundwater with a high rock to water ratio is able to react with the aquifer matrix under closed quiescent conditions, i.e. in cycles during which both water and gas compositions evolve as by products of low-temperature serpentinisation [21].

Such cycles are initiated by recharge, in which both dissolved and entrained air from the atmo-

sphere and phreatic zone is isolated within the ultramafic rock. Separation of the individual gas components from this water, by physical (solubility) processes is minimised by uniform chemical conditions and only slightly elevated temperature of the aquifer (relative to air temperature), thus leaving aerated conditions in the upper saturated zone. Reduction in the groundwater system occurs as a two-stage process. Initially the dissolved and free oxygen is removed, to leave an apparent excess of gaseous nitrogen, by such reactions as [28–30]:

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 \rightleftharpoons Fe_2O_3 + 2H_2O \quad (1)$$

$$3Fe(OH)_2 + \tfrac{1}{2}O_2 \rightleftharpoons Fe_3O_4 + 3H_2O \quad (2)$$

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 \rightleftharpoons 2FeO(OH) + H_2O \quad (3)$$

Generation of Fe_2O_3 was observed at one ophiolite spring (Wadi Bani Kharus) where perennial "upstream" surface water recharge occurs, and a relatively high groundwater oxygen content may be maintained. Elsewhere, groundwaters are depleted of available oxygen and evolve under more anoxic conditions (reaction (2)). Reducing conditions are characterised by partial reduction of sulphate to sulphide and nitrate to nitrite whereas Eh values are typically about −165 mV (mean of 18 field measurements) but exceptionally reach as low as −630 mV (Izki). This may be judged against the water stability limits of about −650 and −715 mV for pH values of 11 and 12, respectively [31]. Given this combination of decreasing redox potential and increasing pH, the water and ferrous hydroxide would be in equi-

librium but would progressively approach the limit of water stability. Ultimately, total oxygen depletion would result in the second stage; that of water decomposition by further ferrous iron oxidation reactions such as [14,17,29,30]:

$$2Fe(OH)_2 \rightleftharpoons Fe_2O_3 + H_2O + H_2 \qquad (4)$$

$$3Fe(OH)_2 \rightleftharpoons Fe_3O_4 + 2H_2O + H_2 \qquad (5)$$
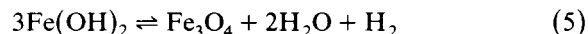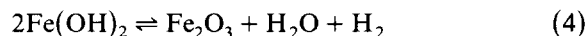
Whilst this second-stage mechanism might at first seem implausible at low temperatures, there is convincing laboratory and theoretical evidence to show that it can take place, albeit erratically, in the presence of a catalyst such as some transition metal hydroxides [29–33]. The presence of strongly reducing conditions, and catalytic agents, necessary for hydrogen formation are verified by the coexistence of highly alkaline groundwater and nickel-iron alloys within serpentinised mantle sequence rocks [9,14,21,34–38].

The non-equilibrium coexistence of the three main component gases suggests that different stages of the cycle may be degassing simultaneously at any spring site, as would be expected from variations in residence time, differential rates of fluid flow and varying groundwater pathways. The full extent of this redox reaction is normally concealed in the oxygen-rich surface environment. It is only the chance conditions of relatively unweathered mantle-derived rocks, an arid groundwater regime, coincident gas and groundwater emergence, and lack of any CO_2- and O_2-rich soil cover that has led to the elucidation of the process in Oman. There is evidence that hydrogen could be generated throughout the temperature range encountered from the earth's surface to the upper mantle, though in practice the limiting factor is probably the availability of Fe^{II} hydroxide. With decreasing temperature, this phase becomes available between about 500 and 450°C as a by-product of serpentinisation [17]. With increasing temperature it is uncertain how and at what temperature dehydration would occur.

6. Geochemical implications

Hydrogen generation by oxidation of Fe^{II} could occur in other subsurface environments and, al-though the extent of this process is unknown, the conditions required for hydrogen generation, i.e. the generation of water flow pathways in ultra-mafic rocks under anoxic conditions, are potentially widespread along the margins of oceanic spreading centres, oceanic transform faults and possible subduction zones. If the process is volumetrically significant, a plausible basis for the deep generation of abiological gaseous hydro-carbons has been found. This is a controversial hypothesis, but evidence such as the lack of any depth/gas volume relationship from deep bore-holes suggests that not all natural gas is generated from organic sediments. Furthermore hydrogenation of crustal carbon, facilitated by relatively high temperatures at depth, could easily occur in deep fracture systems and regions of deeply circulating chemically active groundwaters, especially in aquifers rich in Fe^{II}.

Under anoxic conditions hydrogen generation by the process described could have arisen from surface weathering of Fe^{II}-rich rocks. Such conditions prevailed in the early Precambrian era when the earth's atmosphere was still evolving [39–42]. Therefore, it seems that the reducing groundwater system in northern Oman may be a small-scale analogue of major processes relating to the early evolution of the earth's atmosphere.

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