



The occurrence and geoscience of natural hydrogen: A comprehensive review

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ABSTRACT

Using an interdisciplinary approach, this paper reviews current knowledge in the field of natural hydrogen. For the first time, it combines perspectives on hydrogen from the literature of the former Eastern bloc with that of the West, including rare hardcopies and recent studies. Data are summarized and classified in three main sections: hydrogen as a free gas in different environments, as inclusions in various rock types, and as dissolved gas in ground water. This review conclusively demonstrates that molecular hydrogen is much more widespread in nature than was previously thought. Hydrogen has been detected at high concentrations, often as the major gas, in all types of geologic environment. A critical evaluation of all the proposed mechanisms regarding the origin of natural hydrogen shows that a deep-seated origin is potentially the most likely explanation for its abundance in nature. By combining available data, an estimate of 23 Tg/year for the total annual flow of hydrogen from geologic sources is proposed. This value is an order of magnitude greater than previous estimate but most likely still not large enough to account for recently discovered worldwide diffusive seepages. Hydrogen could play a critical role in mechanisms taking place in both the shallow and deep geospheres and it can influence a very wide range of natural phenomena. Hydrogen is an essential energy source for many microorganisms. Sampling for hydrogen can be a useful tool in studying natural environments, geologic mapping, monitoring of earthquakes, plotting fault traces and resource exploration. Hydrogen of geologic origin has the potential to become the renewable energy source of the future, with exploratory projects ongoing at the present time. The topic of natural hydrogen is therefore relevant from many different perspectives.

1. Introduction

“From a geological perspective, hydrogen has been neglected”. This was written by Nigel Smith and colleagues more than a decade ago in a 2005 paper, which appears to be the latest initiative in a review of natural hydrogen (Smith et al., 2005). In 2019 this statement still holds true. I suspect this is because of an existing prejudice that free hydrogen in nature is rare, and descriptions of the few known discoveries are anecdotal and for some reason garner very little notice. Therefore, if no one expects to find free hydrogen, no one samples for it. This prejudice influences the way gas samples are analyzed and sampled, but also the way detection systems are designed. The standard analytical approach for gas chromatography often uses hydrogen as a carrier gas (Angino et al., 1984). Because of this, if there is any hydrogen in a gas sample it will not be detected. It was reported that even in the 1990's, many surveys were not equipped to analyze for hydrogen (Smith, 2002). It still holds true, to this day, that only a few modern portable gas

analyzers used in the natural sciences include a hydrogen sensor in their design. It is difficult to estimate how many times hydrogen has not been identified in H₂-rich samples because of the lack of a suitable detection technique to measure hydrogen concentrations.

For example, hydrogen was not measured (de Boer et al., 2007; Hosgörmmez, 2007) at a location in Turkey, where it is known to occur naturally at concentrations of up to 11.3%. The presence of hydrogen at this location has been confirmed by other studies (Hosgörmmez et al., 2008; Vacquand, 2011). At the location in Turkey, hydrogen-rich natural gas seeps to the surface and burns spontaneously. The flames from this natural gas seep have been known since antiquity and are believed to be the source of the first Olympic flame. Another study reporting on the analysis of gas from Poison bay, New Zealand, did not include hydrogen (Lyon and Giggensbach, 1994) as a constituent, though it had been documented by others (Wood, 1972) to be at concentrations as high as 75.8%.

In view of the above, gas analyses from databases should be

Abbreviations: BTU, British thermal unit; c, concentration; MCFD, Million cubic feet per day; NH, Northern hemisphere; NR, not reported; PSIG, Pounds Per Square Inch Gauge; Tg, Teragram, equal to 10¹² gram or 1 million ton.; SH, Southern hemisphere

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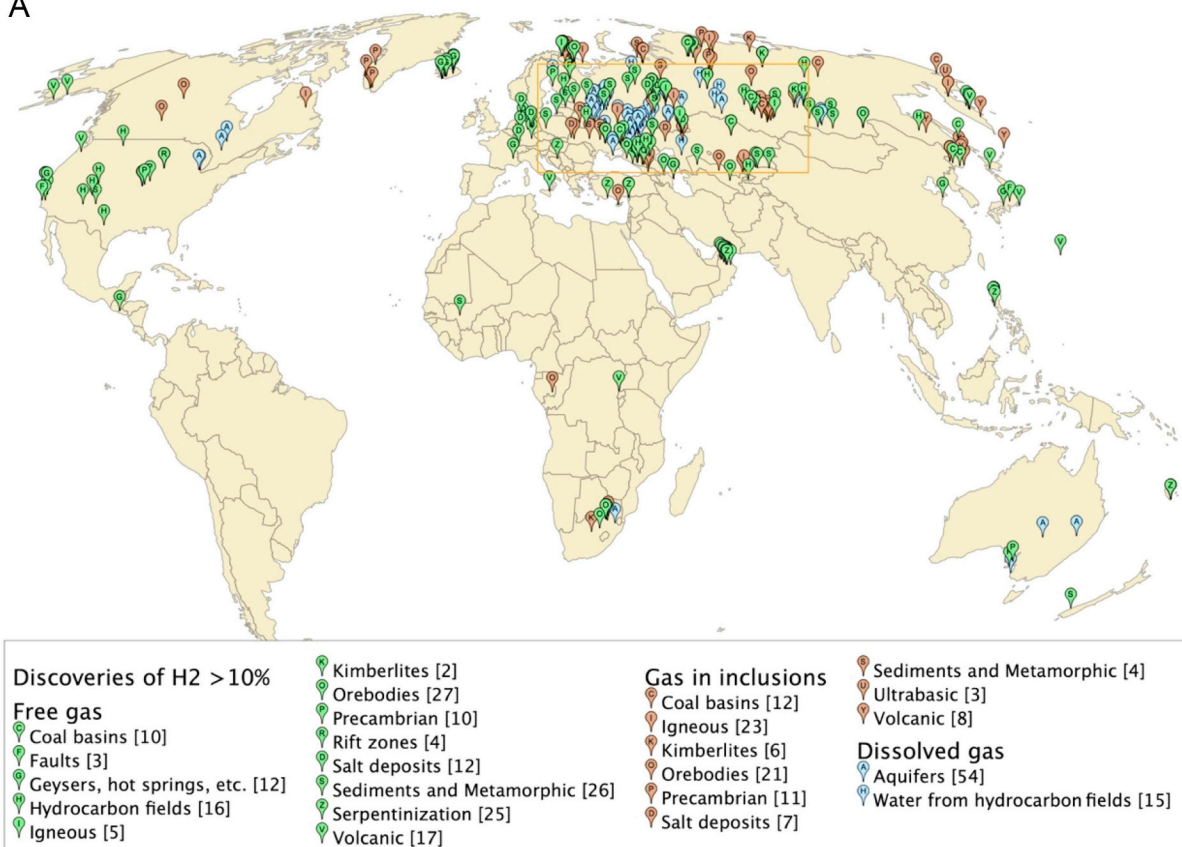
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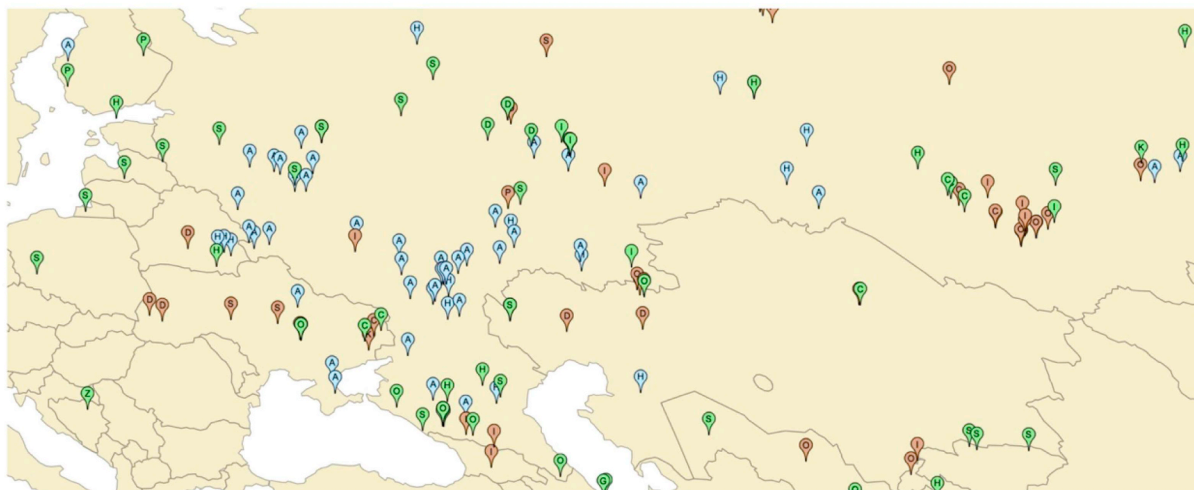


Fig. 1. (a) Map of hydrogen detections in various environments at concentrations > 10% vol. Note: the high density of placemarks across Eastern Europe and Northern Asia is due to the fact that researchers from these regions were looking for hydrogen more frequently, and not because these regions are richer in hydrogen. The area highlighted by the orange rectangle is shown on the (b). Data on each placemark are available in the corresponding tables of this review and in a .kmz file provided in the Supplementary Information. (b) A detail map of the area highlighted by the orange rectangle on the (a).

regarded with caution before any generalized conclusions are made as to the rarity of hydrogen. For example, only 5 out of 14,242 samples of natural gas from wells across the USA reported hydrogen at concentrations greater than 10% (Moore and Sigler, 1987). However, it is very likely that many of these samples were not tested for hydrogen for the aforementioned reasons. The lack of hydrogen testing may be attributed to antiquated analytical techniques and protocols. Indeed, the absence of hydrogen in analyses of natural gases during the 1930's and 1960's can be readily explained by inadequate analytical equipment,

unable to detect hydrogen at concentrations of less than 1 or 2% (Headlee, 1962; Войтов and Осика, 1982). Even when hydrogen was detected, such analyses were considered erroneous (Войтов and Осика, 1982). And even at the time of this writing, recent databases with gas analyses contain only a small number of hydrogen detections. The United States Geological Survey's (USGS) Energy Geochemistry Data Base (EGDB) has 103,000 records of worldwide gas samples with only 8 detections of hydrogen at concentrations > 10%. Another database, the Global Onshore Gas-Oil Seeps Dataset (GLOGOS), does not contain any

hydrogen entries at all. Examples of this kind have led some authors to conclude that the number of known detections of gas with high concentrations of molecular hydrogen is small (Voitov and Rudakov, 2000). However, through this comprehensive literature review it is possible to confirm the original statement cited above, that the importance of naturally occurring hydrogen has largely been overlooked.

An important reason for this situation, besides imperfect analytical techniques, is that most wells drilled worldwide have been drilled in sedimentary basins, which make up half of the Earth's surface, however, these are not the most likely places for hydrogen to be most abundant (Smith, 2002; Truche and Bazarkina, 2019). Another issue preventing hydrogen from being discovered are its diffusive and chemical properties. Being the lightest of all the gases, it diffuses rapidly in air, but also in different materials. Therefore, it quickly leaves the place of its generation and can not be retained in geologic traps for long periods of time (Осика et al., 2002; Johnsgard, 1988). For this reason, samples with hydrogen gas should be handled in a specific way. It is also very reactive and when it combines with oxygen it yields water, leaving no trace of it having been there in the first place as a free gas. Moreover, it is rapidly consumed by microorganisms, representing for them a valuable source of energy.

All these properties of H₂ have puzzled many researchers, some of whom have reported the presence of hydrogen in diverse situations, completely independent of tectonic, stratigraphic or lithological conditions. Hydrogen concentrations appear to be independent of the productivity of the stratum being sampled. No regularities in the hydrogen distribution appear to be apparent, even in a single well (Стадник, 1970). It was reported, that even in the same well, sampling results varied: a second sample from the same hydrogen-rich well during the same day always resulted in a higher hydrogen concentration (Goebel et al., 1984). One could suppose that this result is probably due to replenishment of otherwise consumed or diffused H₂.

Therefore, it is not surprising, that hydrogen gases are sometimes identified later than other gases. For example, H₂-rich combustible gases in Khibiny, Russian Federation, were discovered only after 20 years of research work in the region. Later more detailed studies revealed such gases were present in all types of ore in the mines studied (Онохин, 1959). These same studies showed that hydrogen concentrations varied greatly in space and time: it was reported that even in 50 cm-spaced monitoring holes, H₂ concentrations could be 3 and 7000 ppm simultaneously. Even more surprising, monitoring at several locations situated up to 50 km apart showed H₂ concentrations increasing simultaneously but independently of local meteorological conditions (Satake et al., 1985), suggesting a global-scale process as being the cause of this synchronous behavior.

Indeed, the presence of hydrogen can be used as a diagnostic tool for geological processes that involve hydrogen in one way or another, because its concentration in the atmosphere is normally very low. As will be shown, it can be used for different monitoring studies. But because of its physicochemical properties it is not an easy compound to work with. Hydrogen has primarily been studied as an atmospheric gas, but geologic hydrogen is so poorly understood, that none of the articles on hydrogen budget accounted for geologically generated hydrogen.

The earliest published analysis of a natural gas sample containing hydrogen it was possible to find while doing this review, is in an 1888 report by D. Mendeleev on the composition of gas seeping from fractures in coal from a mine near the city of Makiivka, in the Donetsk region of Ukraine. Mendeleev documented that the gas contained 5.8–7.5% hydrogen (Менделеев, 1888). It is notable that most of the later discoveries of hydrogen have been made in the same part of the world, mostly in Eastern Europe and Northern Asia (Fig. 1). This is not because this region of the world is richer in hydrogen, but because researchers were looking for hydrogen more frequently. In part this reflects the popularity of an abiogenic theory for the generation of oil and gas in countries which were previously part of the Soviet camp. This theory requires a sustained flux of hydrogen for generation of

hydrocarbons. Many papers and books have been published on natural hydrogen in the Eastern European states, but so far there has been no single review combining all the data from Eastern and Western countries. This current work attempts to cover this gap. Also, it presents the data of hydrogen discoveries in a sorted and easy to use format.

Previous reviews on naturally occurring hydrogen have stated that it is time to take hydrogen more seriously (Smith, 2002) and that this gas is much more widespread than previously thought (Войтов and Осика, 1982; Несмелова and Рогозина, 1963). This review fully supports these statements. The goal in writing this paper has been to show how overlooked natural hydrogen is and how important a role it plays in Earth processes.

2. Summary and classification of hydrogen discoveries

In this section, reported discoveries of hydrogen are separated into three main categories: hydrogen as a free gas, hydrogen as inclusions and hydrogen as dissolved gas in water. Each category is then divided into sub-categories, classifying discoveries by type. In many cases it was very difficult to classify them, therefore these categorizations remain subjective. The main criterion I used to attribute a hydrogen discovery to a specific category was the way the author of the original work was making the attribution, whether advertently or inadvertently. This review does not cover discoveries of hydrogen in samples from mid-ocean ridges and other locations in the ocean because they have already received a lot of attention from the scientific community and have been reviewed elsewhere (see, for example, (Cannat et al., 2010) and references therein).

Everywhere in this article the word hydrogen means naturally occurring H₂, except if otherwise specified, and all concentrations are given by volume. Discoveries of hydrogen are presented and sorted by their concentration. The content of the gas is given when possible. A choice was made to report only discoveries with concentrations greater than 10%, because the number of observations at lower concentrations would be too exhaustive to collect in one work, and also because it is a round number that approximately represents the minimum concentration of hydrogen necessary for ignition in air (assuming that all other gases of a mixture are not also combustible). In some articles, hydrogen content was reported in a way impossible to convert it into a percentage (for example, in cm³/kg of rock, without reference to its' content of other gases). Such results were not included in this review, as it was not possible to know if hydrogen was a significant constituent.

2.1. Hydrogen as a free gas

Free hydrogen has been encountered by humans since ancient time. The continuously burning gas seep at Chimaera (sometimes also called Yanartaş), near Antalya, Turkey, has 7.5–11.3% H₂ and these active vents have been known for more than 2500 years (Fig. 2). They are believed to be the source of the first Olympic flame. It has been reported that they are subject to seasonal variations, being more vigorous in the winter months (Hosgörmez et al., 2008). Another similar occurrence was discovered in the Philippines more than two centuries ago, where flames of burning gas have been continuously active. The place is called "Los Fuegos Eternos" (the eternal flames) with measured hydrogen concentrations ranging from 41.4 to 44.5% depending on the vent (Vacquand, 2011; Abrajano et al., 1990). Continuous monitoring of these vents has shown that the hydrogen content of these gases has been stable over a 25-year period (Abrajano et al., 1990).

Both of the above-mentioned instances are associated with ophiolites, which are regions where oceanic crust has been theorized to have been uplifted by tectonic forces or "obducted" onto the surface of a continental margin. Table 1 summarizes other reported discoveries in equivalent environments. Recent work documented in the literature has compared multiple parameters for gases from ophiolitic complexes and concluded that all such gas samples could be categorized into four



Fig. 2. Picture of the continuously burning gas seep at Chimaera, near Antalya, Turkey. The gas contains 7.5–11.3% H_2 . These active vents have been known for more than 2500 years and are believed to be the source of the first Olympic flame. Picture from Wikimedia by W. Neuheisel distributed under the cc-by-2.0 license.

groups: H_2 -rich, N_2 -rich and mixed N_2 - H_2 - CH_4 or H_2 - CH_4 . These differences have been explained as reflecting different zones of generation (Vacquand et al., 2018).

A map showing all places described in this section is given in Fig. 3.

Ophiolites have received a lot of attention from scientists because hydrogen from these locations is attributed to the process of serpentinization (discussed in the *idem* Section 3.2). Other locations such as rift zones have received attention from researchers for the presence of reduced gases (those which can react with oxygen). A lot of the hydrogen observed and reported in the scientific literature has been sampled from the mid-ocean rift zones, which are not covered in this review (for examples see this publication (Cannat et al., 2010) and references therein). However, onshore hydrogen discoveries attributed by scientists to rift systems remain rare (Table 2).

Many hydrogen discoveries are associated with rocks of Precambrian age (Table 3). One of the highest reported concentrations of hydrogen (84%) detected while drilling a well in South Australia was in free gases sampled from deep Precambrian rocks (Ward, 1933). A similar situation was reported by different authors where the highest hydrogen concentrations were detected in deeper, Precambrian sections of wells (Table 3).

Hydrogen was frequently observed in superdeep wells (drilled to 5 km or deeper). For example, gases from samples of the Kola superdeep drilling project (deepest well in the world, project name SG-3) are mainly nitrogen-hydrogen rich (Войтов, 1990). Hydrogen was detected from 1 to 11 km. Starting at 8.5 km, an increase in hydrogen was observed (Капыс et al., 1984). It is interesting to note, that at depths greater than 8.9 km no zones of free water were detected. This observation puts constraints on the hypothesis that the detected hydrogen is the product of reactions with water (Боревский et al., 1984). Hydrogen was reported to be a major constituent of gas detected during

Table 1

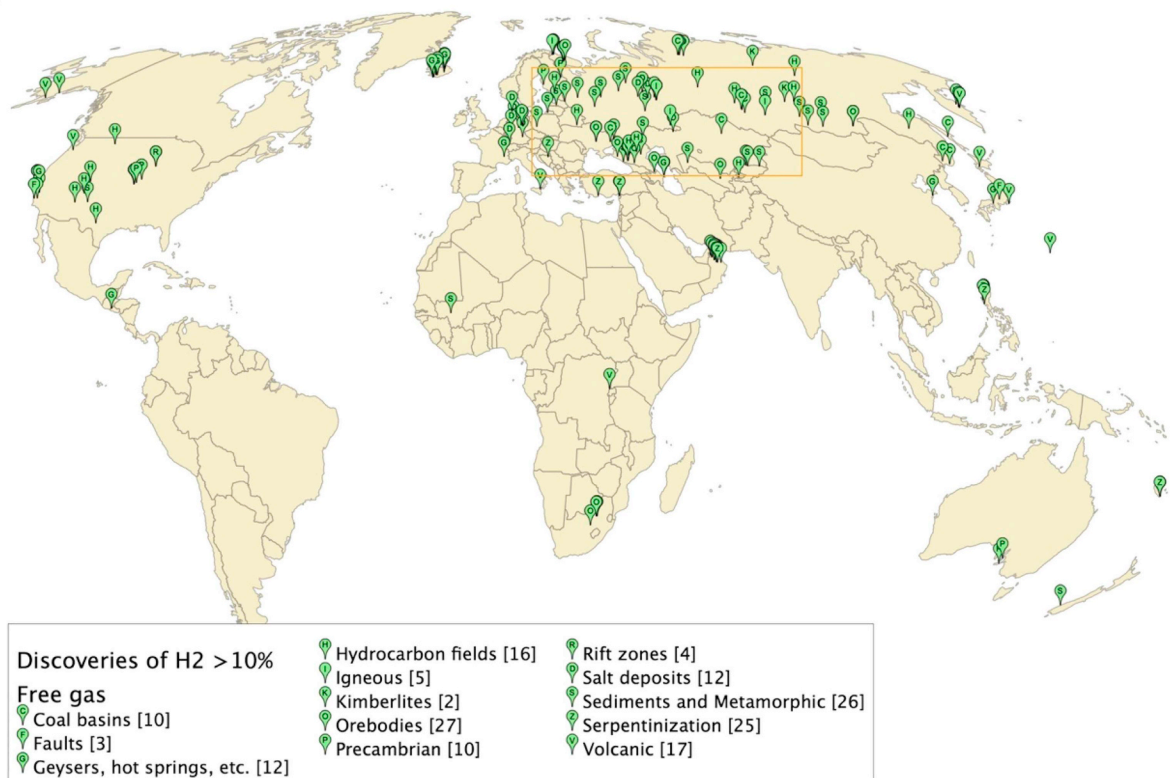
Hydrogen discoveries associated with ophiolites.

H_2 , %	Comments	Country	Name of placemark ^a	Reference
7.5–11.3	Eternal flames of burning natural gases Chimaera. Total H_2 flow about 2 kg/day from the entire site. Proposed origin: mixture of organic thermogenic gas and abiogenic gas	Turkey	Chimaera, 11.3	(Hosgörmez et al., 2008; Vacquand, 2011; Etiope et al., 2011)
15.7	Bubbles from ultra-basic springs. Proposed origin: serpentinization	USA	Austin Creek, 15.7	(Morrill et al., 2013)
35.1	Free gas seeps on the surface. Proposed origin: serpentinization	Philippines	Mangatarem, 35.1	(Vacquand, 2011)
26.8–36.1	Gas-bearing springs in ophiolites of New Caledonia. Proposed origin: serpentinization	New Caledonia	Kaoris, 32.9; Carenage, 36.1	(Vacquand et al., 2018; Deville and Prinzhofer, 2016)
34–39.2	Bubbles from ultra-basic springs. Proposed origin: serpentinization	USA	Barnes Spring, 39.2	(Morrill et al., 2013)
41.4–44.5	Free gas seeps on the surface. Proposed origin: serpentinization	Philippines	Los Fuegos Eternos, 44.5	(Vacquand, 2011; Abrajano et al., 1990)
41.4–45.6	Burning gas in peridotites of the Zambales ophiolite complex. Proposed origin: serpentinization	Philippines	Mt. Lanat, 45.6	(Thayer, 1966; Abrajano et al., 1988)
48.3	Gases in hyperalkaline groundwaters of the serpentinized Dinaride ophiolite belt	Bosnia and Herzegovina	Vaiceva voda, 48.3	(Etiope et al., 2017)
50.9	Bubbles from ultra-basic springs. Proposed origin: serpentinization	USA	Camp Spring, 50.9	(Morrill et al., 2013)
58.5	Free gases seeps on the surface. Proposed origin: serpentinization	Philippines	Nagsasa, 58.5	(Vacquand, 2011; Sherwood Lollar et al., 2014)
37.1–60.5	Gas from bubbling in hyperalkaline spring (Tahtakopru) and free spontaneously igniting gas (Kurtbagi). Proposed origin: serpentinization	Turkey	Kurtbagi, 38.4 Tahtakopru, 60.5	(Yuce et al., 2014)
39–69	Gas seeps on the surface. Proposed origin: serpentinization	Oman	Howqain, 69	(Vacquand, 2011; Sano et al., 1993; Neal and Stanger, 1983)
37.3; 68.1; 73.4; 77; 85.9	Gases from bubbles in different water sources in Oman ophiolite ^b . Proposed origin: serpentinization	Oman	Abyiad, 37.3; Alkar, 68.1; Halhal, 73.4; Haylayn, 77; Hawasina, 85.9	(Vacquand, 2011; Zgonnik et al., 2019)
61; 75.2; 85.4; 87.3	Gases from bubbles in different water sources in Oman ophiolite. Proposed origin: serpentinization	Oman	Lauriers Roses, 61; Kufeis, 85.4; Barrage, 75.2; Magniyat, 87.3	(Vacquand, 2011; Boulart et al., 2013)
81–97	Gas seeps on the surface Ain Al-Waddah. Proposed origin: serpentinization	Oman	Bahla, 97	(Vacquand, 2011; Sano et al., 1993; Neal and Stanger, 1983; Boulart et al., 2013)
22–99	Bubbles in springs. Proposed origin: Fe^{2+} oxidation by water	Oman	Nizwa, 99	(Neal and Stanger, 1983)

^a The .kmz Google Earth file with placemarks is available in Supplementary information.

^b A video from the Haylayn site in Oman is available online: https://www.youtube.com/watch?v=9Qnt_XENDrI

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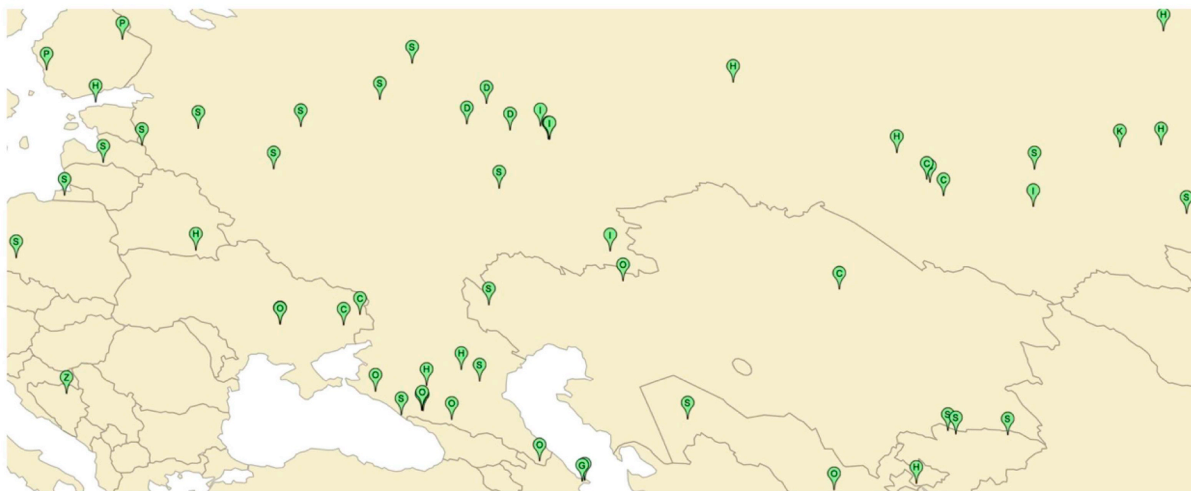


Fig. 3. (a) Map of hydrogen detections in free gases in various environments at concentrations > 10% vol. Note: the high density of placemarks across Eastern Europe and Northern Asia is due to the fact that researchers from these regions were looking for hydrogen more frequently, and not because these regions are richer in hydrogen. The area highlighted by the orange rectangle is shown on the (b). Data on each placemark are available in the corresponding tables of this section and in a .kmz file provided in the Supplementary Information. (b) A detail map of the area highlighted by the orange rectangle on the (a).

the Ural superdeep drilling project (SG-4). The quantity of hydrogen gas was reported to increase with depth (Башта et al., 1991). The amount of hydrogen was also reported to increase with depth during the superdeep drilling program (SG-8) in Kryvyi Rih, Ukraine (Курлов, 2003). High concentrations of hydrogen, 13.8–28.1%, were detected during the drilling of the Aralsor superdeep well in Kazakhstan (Войтов and Осика, 1982; Перевозчиков, 2011; Войтов et al., 1967; Соколов, 1971; Шорохов and Шишенина, 1967). Up to 2% of hydrogen was detected during the drilling of the superdeep Gravberg-1 in the Siljan crater in Sweden. Observed hydrogen increased at depths below 6 km (Smith, 2002; Николаевский, 1988).

Hydrogen discoveries in the Kola and Ural superdeep wells were

associated with igneous rocks. There were a few other reports of hydrogen detections and Table 4 summarizes other reports of hydrogen in such rocks.

Many studies have reported hydrogen in volcanic gases, despite the fact that hydrogen is a reactive gas which is readily oxidized by oxygen either in the air or oxygen bonded to certain minerals. Such reactions produce water vapor, a main component in volcanic gases. The detection of hydrogen (Table 5) implies it can be sufficiently abundant to override the oxidizing capacity of fluids/rocks in volcanic settings.

Hydrogen has been reported in volcanic gases throughout the world. Spectroscopic studies of burning gas from the Hawaiian volcanoes show that the flame is originating from the combustion of H_2 in air

Table 2
Hydrogen discoveries associated with rift zones.

H ₂ , %	Comments	Country	Name of placemark	Reference
33.7	Gas from the Willey #1 well. Proposed origin: associated with mid-continent rift system	USA	Willey #1, 33.7	(Moore and Sigler, 1987; Coveney et al., 1987)
57.3	Gas from a geothermal well in Namafjall. Measured $\delta D = -499$ ‰, δD of water = -97.7 ‰; $c(H_2S) = 16\%$	Iceland	Namafjall, 57.3	(Sano et al., 1985; Кононов, 1983)
64.0	Gas from a borehole. Proposed origin: unknown	Iceland	Namaskard, 64.0	(Sigvaldason, 1966)
96.3	Gas from the Hofmann #3 well. Proposed origin: associated with mid-continent rift system	USA	Hofmann #3, 96.3	(Angino et al., 1984; Moore and Sigler, 1987; Coveney et al., 1987)

Table 3
Hydrogen discoveries associated with Precambrian rocks.

H ₂ , %	Comments	Depth, m	Country	Name of placemark	Reference
12.8	Gas from well Juuka 116, drilled on Fennoscandian shield into Karelian Supracrustals complex, dated 1900–2100 Ma. Proposed origin: serpentinization	Up to 1122	Finland	Juuka, 12.8	(Sherwood Lollar et al., 1993a; Sherwood Lollar et al., 2007)
17.2	Free gas from Wilson #1 well drilled into Precambrian basement rocks. Quantity 28–70 L H ₂ per 1 L of pumped water; $c(He) = 1.5\%$. Proposed origin: serpentinization	1446–1732	USA	Wilson well, 17.2	(Newell et al., 2007)
3.9–27.3	Free gases from the well #1886	1323	Russian Federation	Pechenskaya, 27.3	(Bořtos, 1990)
30.4	Well Pori-D on Fennoscandian shield. Proposed origin: serpentinization	> 300 Total well depth is 7300 m	Finland	Pori, 30.4	(Sherwood Lollar et al., 1993a; Sherwood Lollar et al., 2007; Sherwood Lollar et al., 1993b)
34.9	Gas from a well on the Baltic shield (old craton)	2300	Russian Federation	Pechenegskaya, 34.9	(Bořtos and Ocrka, 1982)
56, up to	Free gas from the Scott well. Maximum H ₂ content associated with Precambrian basement. Proposed origin: mixed (from different sources)	666	USA	Scott well, 56	(Vacquand, 2011; Goebel et al., 1984; Coveney et al., 1987; Newell et al., 2007; Angino et al., 1990; Goebel et al., 1983; Guélaud et al., 2017)
68.6	Well drilled into Precambrian. Located on Kangaroo Island. Proposed origin: reaction of water with ferrous compounds or magmatic (from high-temperature reactions)	290	Australia	Penneshaw, 68.6	(Ward, 1933)
80, up to	Free gas from the Heins well. Maximum H ₂ content associated with Precambrian basement. Proposed origin: mixed	661	USA	Heins well, 80	(Vacquand, 2011; Goebel et al., 1984; Coveney et al., 1987; Newell et al., 2007; Angino et al., 1990)
84	Gas from a well, drilled into Precambrian metamorphic rocks. Yorke Peninsula, Australian shield	508	Australia	Minlaton, 84.0	(Bořtos and Ocrka, 1982; Ward, 1933; Woolnough, 1934)
91.8, up to	Free gas from the Sue Duroche2 well. Maximum H ₂ content associated with Precambrian basement. Proposed origin: mixed	NR	USA	Sue Duroche2 well, 91.8	(Guélaud et al., 2017)

Table 4
Hydrogen discoveries associated with igneous rocks.

kmz	kmz	kmz	kmz	kmz	kmz
20.6	Kola superdeep drilling SG-3. Volume of hydrogen up to 0.3 m ³ per 1 m ³ of drilled rocks; c (He) = 1.5%	1100–1140, and up to 11 km	Russian Federation	Kola superdeep, 20.6	(Войтов, 1990; Карус et al., 1984; Войтов, 1986; Ikorsky et al., 1999)
35.1–38.2	Tubinsk. Gas from well drilled into volcanic pipe	NR	Russian Federation	Tubinsky, 38.2	(Соколов, 1971; Пиковский, 1963)
50, at least	Ural superdeep drilling. Hydrogen is a major gas in the drilling mud when intercepting fracture zones in volcanic tuff and basalt.	2930–3080	Russian Federation	Ural superdeep, > 50	(Багга et al., 1991)
80.4	Irkinksoe canyon, well #14 drilled in extrusive rocks.	3450–3770	Russian Federation	Irkinksoe, 80.4	(Стадник, 1970; Черепеников, 1936)
80.5	In gas, seeping for 2 weeks from the well #1 drilled in dunites. Initial pressure was 60 bar. Proposed origin: mixed, mostly inorganic.	40.6 600	Russian Federation	Nizhny Tagil, 80.5	(Angino et al., 1984; Bogdanowicz, 1934; Заварицкий, 1928; Лидин et al., 1982)

(Cruikshank et al., 1973). Gases sampled from the Icelandic volcano Surtsey were reported to contain 1.7–3.1% H₂ (Smith, 2002). In Japanese volcanoes, hydrogen was detected mainly in gases collected from liquid magma but not from hot sources and fumaroles. To explain this the authors of the published studies proposed that hydrogen was reacting with SO₂ before reaching the surface (Соколов, 1966a). During the eruption of Mount St. Helens, USA continuous soil gas monitoring of hydrogen concentrations at a “non-fumarole” site was performed. Abrupt increases in H₂ concentrations in the surface air were recorded a few days before the eruption. After a few to several hours following seismic and volcanic events, H₂ concentrations were observed to have increased in the soil (Sato and McGee, 1981). Another soil gas survey carried out at the Sabatini volcanoes in Italy, showed generally low levels of hydrogen. In such cases it was hypothesized that these low levels were a function of high permeability at depth (Bertrami et al., 1990). Plots of hydrogen concentration in soil gases in the Canadas caldera, Canary Islands, identified anomalous hydrogen concentrations in places where the most recent eruption of the Tenerife Island occurred. The distribution pattern was shown to be associated with volcanic tectonic lineaments (Hernández et al., 2000).

Table 6 lists examples of hydrogen observed in geysers and hydrothermal systems associated with volcanic activity along with a hydrogen discovery in a standalone gas seep in France and in mud volcanoes in Azerbaijan. In Iceland, it was reported that hydrogen is one of the major constituents of all natural gas samples. When geysers were studied based on δD measurements (ratio of deuterium to protium, two stable isotopes of hydrogen) the calculated equilibrium temperature between H₂ and H₂O (246°C) was reported to be much lower than the observed temperature of the aquifer (465°C) (Sano et al., 1985), which shows that hydrogen was likely not produced in the ground water. The discovery of hydrogen in hot hydrothermal systems is not unique. It was reported that hydrogen-rich hydrothermal systems such as those in Iceland have the highest heat values, up to 10⁸ kcal/s, and very high temperatures, up to 350°C. Similar conditions were observed in hydrothermal systems in California, USA (Sonoma), El Salvador (Ahua-chapan) and Japan (Arima) (Кононов, 1983). High values of the heat flow may be related to the process of hydrogen oxidation.

Hydrogen discoveries in kimberlite pipes have been reported in only a few instances (Table 7), however, one of these holds the record for the highest reported flow of natural hydrogen. Well #42 in the Udachnaya kimberlite pipe blew out during drilling, creating a huge flare of burning gas (Fig. 4). The estimated initial flow from the well was 100,000 m³ H₂/day. The gas burned for 3 days, after which the well started to produce water as a result of an “air-lift effect” (when expanding gas draw fluids to the surface) and was capped. The measured hydrogen concentration on the second day was in the range 27.4–46.6%. After a month, measured H₂ concentrations were around 10% (Фомичев, 2008). Hydrogen measurements were also taken from other kimberlite pipes in the area: Internatsionalnaya and Mir each reported values of H₂ of up to 6% at depths of 550 to 1300 m (Сороченко and Дроздов, 2010).

Many instances of naturally occurring hydrogen have been reported from various mining sites, exploring for iron, gold, uranium, mercury, nickel, copper and polymetallic ores such as niobium-tantalum and tungsten-molybdenum. Table 8 lists instances of hydrogen detected in association with many different types of ore. Several estimates are available for the quantity of gas: in the Khibiny massif, Russian Federation, the flow rates of gas are in the range of 0.05–5 L/min per individual borehole or gryphon (seep) (Nivin, 2009) and 0.5 ml/min/m² in the Lovozero loparite deposit mine or 0.2–1.6 m³ of total gas per 1 m³ of undisturbed rock (Nivin, 2016). The duration of gas seepage ranges from several days to up to 20+ years (Nivin, 2009; Nivin, 2016). A systematic study of these gases has divided them into three types: free (seeping from the fractures), occluded (stored in closed pores), and diffusively-dispersed (intermediate between the two previous types (diffusively dispersed gases refer to gas stored in micropores, mostly in

Table 5
Hydrogen in volcanic gases.

H ₂ , %	Comments	Country	Name of placemark	Reference
10.8	Gas from small low-temperature fumarole. Proposed origin: H ₂ S reaction with water; c (H ₂ S) = 2.16%	Washington, USA	Mount St. Helens, 10.8	(Evans et al., 1981)
14	Volcanic gases in Askja volcano	Iceland	Askja, 14	(Кононов, 1983)
14.9	Volcanic gases from the rift-zone-related to the Nyiragongo volcano; c (SO ₂) = 18.3%	Democratic Republic of Kongo	Nyiragongo, 14.9	(Canfield et al., 2006)
6–16	Fumarole gases from Shiveluch volcano	Russian Federation	Shiveluch, 16	(Соколов, 1966a)
16.6	Gas from fumarole from Kverkfjöll volcano	Iceland	Kverkfjöll, 16.6	(Sigvaldason, 1966)
18	Gases from fumaroles in Iwo Jima volcano	Japan	Iwo Jima, 18	(Соколов, 1971)
25	Volcanic gases in Showashinzan volcano; c (NH ₃) = 0.06%	Japan	Showashinzan, 25	(Кононов, 1983)
0.002–25.5	Composition of dry gases separated from water vapor (~90 % of the gas volume) by condensation, taken from the hot (1000°C ± 65°C) liquid lavas during the 1975–1976 Tolbachik volcano fissure eruption	Russian Federation	Tolbachik, 25.5	(Gilat and Vol, 2005)
14.4–29.2	Fumarole gases, South-East vent, Trident volcano; c (He) = 1.8–2.8%	USA	Trident, 29.2	(Symonds et al., 2003)
34.4	Volcanic gases in Surtsey volcano	Iceland	Surtsey, 34.4	(Кононов, 1983)
51.5	Fumarole gases, Spine vent, Augustine volcano; c (He) = 4.5%	USA	Augustine, 51.5	(Symonds et al., 2003)
Up to 54	High-temperature volcanic gases in Eldfell volcano	Iceland	Eldfell, 54	(Кононов, 1983)
Up to 57.8	Hot gases from fumaroles and during the eruptions of the volcano Etna. c (O ₂) = 34.5%	Italy	Etna, 57.8	(Войтов and Осика, 1982; Соколов, 1971; Соколов, 1966a; Соколов, 1966b; Huntingdon, 1973)
Up to 67	Gases from Hekla volcano	Iceland	Hekla, 67	(Соколов, 1971; Соколов, 1966a)
15.3–69.5	Klyuchevskaya Sopka volcano, gases from various volcanic craters and fumaroles. In total 672 analyses of gases from 15 side craters; c (CO) up to 34%	Russian Federation	Kliuchevskoi, 82.2	(Пиковский, 1963; Соколов, 1966a; Куликова, 1966; Фроловская, 1964)
72–90.2	Gases from Mihara volcano	Japan	Mihara, 90.2	(Войтов and Осика, 1982; Соколов, 1966a; Соколов, 1966b)
63–93	Volcanic gases from Plosky Tolbachik volcano	Russian Federation	Plosky Tolbachik, 93	(Щека and Гребенников, 2009)

Table 6
Hydrogen in gases of geysers, hot springs, mud volcanoes and standalone seeps.

H ₂ , %	Comments	Country	Name of placemark	Reference
2.4–12.5	Gas from hot springs and geothermal wells	China	Jimo hot spring, 12.5	(Hao et al., 2020)
14.1	Gas from mofetta (gas seep)	France	Les Tiogaux, 14.1	(Blavoux and Dazy, 1990)
14.7	Gas from the hot geyser “Old Faithful”; c (H ₂ S) = 1.7%	California, USA	Sonoma, 14.7	(Кононов, 1983; Соколов, 1971)
15.4	Gases from mud volcano	Azerbaijan	Baladzhar, 15.4	(Фроловская, 1964)
22.2	Free gases from hydrothermal spring in vapour/hydrothermal system; c (H ₂ S) = 1.7%	Iceland	Torfajokull, 22.2	(Кононов, 1983)
24.1	Gases of Namafjall geysers. Estimated daily flow 1000 m ³ /day of H ₂ ; c (H ₂ S) = 32.8%	Iceland	Namafjall, 24.1	(Войтов and Осика, 1982; Кононов, 1983; Shcherbakov and Kozlova, 1986)
9–36	Gases from hydrogenous hot springs of Icelandic type	Iceland	Landmannlaugar, 36	(Smith et al., 2005)
10–40	Free gases from the well #1 in vapor/hydrothermal system	El Salvador	Ahuachapan, 40	(Кононов, 1983)
46.4	Free gases from hydrothermal site in vapor/hydrothermal system; c (H ₂ S) = 7.6%	Iceland	Nesjavellir, 46.4	(Кононов, 1983)
51.4	Free gases from hot spring in hydrothermal system	Japan	Arima, 51.4	(Кононов, 1983; Nakamura and Meda, 1961)

an adsorbed state and which can be degassed from a sample shortly after sample collection). By analysing these three types of gas in more than 10,000 samples it was shown that the average concentrations for each type were very similar. However, the volume of gases sampled varied by up to 6 orders of magnitude (Нивин, 2013). Another study reported that during the drilling of a well in the Tyrynauz mine, in the Caucasus mountains of the Russian Federation, at a depth of 763 m a flow of hydrogen gas with up to 87.3% H₂ was encountered. It continued to flow for several months, and hydrogen concentrations progressively declined to 0.5%, being totally replaced by CO₂. The calculated volume of total degassed hydrogen was 3237 m³. The authors suggested that it was a local accumulation of natural hydrogen (Гуревич et al., 1960).

Another important instance of naturally occurring hydrogen is that associated with the exploration for oil and natural gas (Table 9). In some cases, it has been shown that hydrogen is one of the main components of gases associated with hydrocarbon deposits. It has been reported that almost all of the combustible gases derived from the Cambrian of Eastern Siberia contain hydrogen, at concentrations as high as 10% and higher (Войтов and Осика, 1982). Another study complements this observation, reporting that hydrogen and helium

concentrations in Eastern Siberia wells systematically increase with depth (Levshounova, 1991). Recent studies from the Volga-Ural oil and gas province have shown that hydrogen has been systematically logged during drilling and that it is present across the entire sedimentary section with peak-values correlating to hydrocarbon peak values (Шевченко and Силкин, 2015). A probable causal link between hydrocarbons and hydrogen is discussed in the Section 5.5 Oil, gas and minerals.

Besides association with oil & gas fields, coal basins are another common locale where significant quantities of hydrogen have been observed (see Table 10). As already mentioned above, the first discovery of natural hydrogen was made in gas from a coal mine in Ukraine (Менделеев, 1888). Sometimes, hydrogen can be the main component of gas sampled from coal mines: it was detected at different concentrations in 60% of gas samples from coal mines in the Russian Far East (Гресов et al., 2010).

Multiple discoveries of hydrogen have been reported in sedimentary rocks (Table 11). This is not surprising, because sedimentary basins make-up about half the world's surface area, and have been thoroughly drilled (Smith, 2002) in the search for hydrocarbons. It been suggested that hydrogen is present in any sample of gas from sediments, however,

Table 7
Hydrogen discovered in kimberlite pipes.

H ₂ , %	Comments	Depth, m	Country	Name of placemark	Reference
48.8	In gas-water released from a well drilled into kimberlite or volcanic pipe Zheldon III		Russian Federation	Zheldon, 48.8	(Соколов, 1971; Фридман, 1970)
51 in well #42	Gas from wells #42 and 217 in kimberlite pipe Udachnaya. Estimated initial flow	365–367 (well #42);	Russian Federation	Udachnaya, 58.9	(Войтов and Осика, 1982; Соколов, 1971; Войтов, 1986; Фоминчев, 2008; Дроздов, 2011)
58.9 in well #217	from well #42: 100,000 m ³ H ₂ /day	370 (well #217)			



Fig. 4. Burning gas from well #42 in the Udachnaya kimberlite pipe. Picture from (Фридман, 1970).

special conditions are required for it to accumulate and reach high concentrations (Молчанов, 1981).

Salt deposit hydrogen discoveries are presented in a separate Table 12, because the origins of hydrogen discovered in salt is debated (see Section 3.4 Water radiolysis). It has been proposed that high concentrations of hydrogen in salt deposits can be explained by the fact that hydrogen can be effectively trapped by alternating layers of clays and salt (Суббота and Сардонников, 1968).

2.2. Diffusive flow

Hydrogen is the most diffusive of all gases and for this reason one would expect it to exist mainly in a diffused state in the natural environment and not concentrated as has been presented in the examples above. Indeed, many studies have shown that hydrogen diffuses through the Earth's crust to reach the surface. Soil gas measurements carried out at the surface over an area of more than 7000 km² show a zone of anomalously high hydrogen concentrations extending as much as 85 km west of certain hydrogen-rich wells in Kansas, USA (described in the Table 3). Abnormally high, up to 6000 ppm (0.6%) hydrogen concentrations were observed in soils sampled in Kansas. The area with anomalously high hydrogen soil gas concentrations appears to correlate with gravity and magnetic anomalies defining the North American Mid-Continent Rift System (Angino et al., 1990; Angino et al., 1988). A very recent study reports that hydrogen along with other gases has been mapped over a variety of sites in Ukraine (165 in total), mostly in oil and gas fields, but also coal mines, astroblemes and offshore continental shelf areas. The authors conclude that hydrogen is a useful tool for geoecological research and prospecting (Барпій et al., 2019).

Indeed, hydrogen plotting appears to be a useful technique in geological analysis and the locating of deep structures. For instance, it was used to identify zones of high fluid conductivity on the East-European

Table 8
Hydrogen discoveries associated with orebodies.

H ₂ , %	Comments	Depth, m	Country	Name of placemark	Reference
8.3–11.8	Seeping of gas and water from the well during 5 days in an apatite-nepheline ore mine; $c(\text{NH}_3) = 0.05\%$	53	Russian Federation	Kuksivumchorr, 11.8	(Фридман, 1970; Nivin et al., 2005)
13.7	Free gas in production zone of iron ore mine Lenina. Estimated flow into two ventilation galleries $734.4 \text{ m}^3/\text{day}$; $c(\text{He}) = 1.1\%$	825	Ukraine	Kryvyi Rih, 13.7	(Войтов and Осика, 1982; Войтов, 1986; Войтов, 1971)
13.9	Gas seep from the ijolite-urtites (igneous rocks consisting essentially of nepheline) in apatite-nepheline ore mine of Yuksporsk orebody		Russian Federation	Yuksporsk, 13.9	(Онохин, 1959; Nivin et al., 2005; Войтов, 1962)
15.2	Gas, which exploded and then continued to burn. Horizontal tunnel in quartzites of gold mine	1621	South Africa	Robinson Deep, 15.2	(Фридман, 1970)
16.3, up to	During drilling, when encountering crushed and hydrothermally modified ore in mercury orebody mine		Russian Federation	Belokamennoe, 16.3	(Фридман, 1970)
17.6	Gas-air mixtures from boreholes in Khibiny alkaline igneous complex		Russian Federation	Eveslogchorr, 17.6	(Nivin et al., 2005)
17.9	Gas-air mixtures from boreholes in Khibiny alkaline igneous complex		Russian Federation	Apatitovyi Tsirk, 17.9	(Nivin et al., 2005)
19	Free gas in production zone of iron ore mine "Hvardiiska". Estimated flow in two ventilation galleries $5438 \text{ m}^3/\text{day}$	680	Ukraine	Kryvyi Rih, 19	(Войтов, 1971)
19.0, up to, in free gases in mine; 2.6–14.0 in drilling mud	Free gas in the mine #8 orebody goldfield. Hydrogen in drilling mud: $36.6\text{--}68.9 \text{ cm}^3/\text{per kg of drilled rock}$	316	Russian Federation	Taseevskoe, 19.0	(Куликова, 1972)
1.4–19.5 in gryphons; 20.1, up to, in drilled holes in mine	Free gas seeps in the railway tunnel blast-hole #28 in Mount Rasvumchorr. Linearly distributed seeps, several tens per 100 m^2 in late Devonian-early Carboniferous urtites. Estimated flow of H_2 $0.1\text{--}0.2 \text{ L}/\text{min}$ per seep; $c(\text{He})$ up to 3.67% ; $c(\text{Ar})$ up to 6%		Russian Federation	Rasvumchorr, 20.1	(Войтов and Осика, 1982; Войтов, 1986; Крицков et al., 1967; Хитгаров et al., 1979; Петерсилье, 1964)
7.1–20.3	Gas from drilling mud in a well in gold ore. Volume of hydrogen $37\text{--}69 \text{ cm}^3/\text{L}$ of drilling mud. Maximum content in Cretaceous-Jurassic sandstones		Russian Federation	Baleysky graben, 20.3	(Куликова, 1966)
21.5	Gas seeping from a well drilled in nickel mine. Flow rate up to $6 \text{ L H}_2/\text{min}$. Proposed origin: magmatic		Russian Federation	Zapolyarny, 21.5	(Фридман, 1970)
24	Gas seep in tunnel of gold mine #4. The seep was located near a fault	2192	South Africa	City-Dan, 24.0	(Фридман, 1970)
24.6	In chalcocopyrite orebody copper mine		Russian Federation	Kizil-Dere, 24.6	(Войтов and Осика, 1982)
25.1	Gas seeping from well drilled into nickel ore intrusion. Flow rate $32 \text{ cm}^3/\text{L}$ of drilling mud. Proposed origin: magmatic		Russian Federation	Imangda Rudnaya, 25.1	(Фридман, 1970)
34.8	Gospodskaya shakhta mine, situated in dunite massif Nizhne-Tagilsky	183	Russian Federation	Gospodskaya shakhta, 34.8	(Черепеников, 1936; Заварицкий, 1928; Лидин et al., 1982)
50	St. Helena Gold Mine, African shield		South Africa	St. Helena Gold Mine, 50	(Войтов and Осика, 1982)
40–70 in free gas; 26, up to, from fractures in mine	Urupsky chalcocopyrite orebody mine: Hydrogen content in drilling mud up to $157 \text{ cm}^3/\text{L}$		Russian Federation	Urupsky, 70	(Соколов, 1966a; Соколов, 1966b; Фридман, 1970; Войтов, 1962)
43.3 in drilling mud	Gas from fractures depleted in hydrogen after 2 days. Proposed origin: action of hydrogen flow on shales		South Africa	Crown mine, 77.5	(Фридман, 1970)
77.5	Gas, which exploded and was burning 4 days after drilling in quartzites in gold mine. Later, gas was seeping for a long time without burning.	1426	South Africa	Vlasenchinskoe, 80	(Фридман, 1970)
80, up to	In drilling mud of a well drilled in copper mine. Flow rate up to $120 \text{ cm}^3 \text{ H}_2/\text{L}$ of drilling mud. Proposed origin: magmatic	350–460	Russian Federation	Krasny Ural, 81.8	(Войтов and Осика, 1982; Стадник, 1970)
79.4–81.8	Gas from #1 well drilled in dunite massif of mine Krasny Ural	600	Russian Federation	Hudesskoe, 82.6	(Войтов and Осика, 1982; Фридман, 1970; Войтов, 1962; Фридман, 1961)
63.2–82.6	Strong degassing for 3–4 years in wells #2 and #27 of Kyzylkolskoe mine. Well #7 in chalcocopyrite orebody copper mine. Hydrogen concentration decreased progressively by 2.5–5%. Proposed origin: magmatic		Russian Federation	Tymuauz, 87.4	(Войтов and Осика, 1982; Войтов, 1986; Соколов, 1966b; Гуревич et al., 1960; Гуревич, 1967)
87.4, up to	Gas from well #104 in tungsten-molybdenum mine Tymuauz. Total volume of degassed hydrogen estimated 3237 m^3	763	Russian Federation	Lovozero, 57.8	(Nivin, 2016)
90.6, up to	Free gases in Lovozero loparite mine. Mean concentration 35.6%		Russian Federation	Norilsk, 96.8	(Соколов, 1966a)
37.8–96.8	Gas from drilling mud for a well drilled in porphyry and diabase of nickel orebody mine		Russian Federation	Rudnoe, 98	(Перевозчиков, 2011)
98		100	Uzbekistan		

(continued on next page)

Table 8 (continued)

H ₂ , %	Comments	Depth, m	Country	Name of placemark	Reference
93.5–98.5	Hydrogen seeped for several weeks from a well drilled into metamorphic Ordovician-Silurian uranium ore deposit Gas from chromites and serpentinitized dunites in chromite mine Molodezhnaya in Kempirsae massif. Gas was identified as the fuel for a flame which was stable for 12 h. Also, in several places in the shaft with bubbling. Estimated flow 0.1–20 m ³ /day. Measured $\delta D = -766\text{‰}$, δD of water = -122‰ . Proposed origin: deep-seated	300–513	Kazakhstan	Khromtau, 98.5	(Лидин et al., 1982; Уханов et al., 1987; Уханов et al., 1984)

Table 9
Hydrogen discoveries associated with oil & gas fields.

H ₂ , %	Comments	Depth, m	Country	Name of placemark	Reference
6–10	In oilfield gases		Russian Federation	Lenno-Viluisik, 10	(Гресов et al., 2010)
11.0	Moiseevskaya oil field, well #2	2576–2589	Russian Federation	Moiseevskaya, 11	(Молчанов, 1981)
11.5	Gas from the Navajo No1A well drilled into Pennsylvanian age Hermosa Formation, Paradox Basin USA, near Rattlesnake and Hogback oil pools. BTU value = 238. Proposed origin: igneous or coal.	2365	USA	Navajo, 11.5	(Headlee, 1962; Boone, 1958; USGS, 2009)
12.7	Gas from well #17 in ozokerite, oil and sulfur field Shor-Su		Uzbekistan	Shor-Su, 12.7	(Черепеников, 1936)
14.7	Hydrocarbon well #1, parcel 573		Azerbaijan	Absheron, 14.7	(Молчанов, 1981)
17.9	Kama field. BTU value 1778, open flow 7000 mcf/d	2262	USA	Jeffers, 17.9	(USGS, 2009)
19.5	Gas from the well drilled into Devonian strata. Vaughn field, Cascade County, MT. Reported wellhead pressure 50 psig. open flow rate 10 mcf/d	965	USA	Cascade, 19.5	(Moore and Sigler, 1987; Headlee, 1962; Anderson and Hinson, 1951)
20.4	Pinta Dome hydrocarbon field. Late Triassic, Chinle formation in. BTU value = 60; c (He) = 4%	325	USA	Hortenstein, 20.4	(USGS, 2009)
20.8	Gas in well drilled in Glacial deposits. Gas may be related to Baltic Cambrian reservoirs in offshore Swedish gas field	27	Estonia	Koksher, 20.8	(Smith et al., 2005; Bogdanowicz, 1934)
26.3	Gas from Horse point 1-X well drilled into Cretaceous rocks. BTU value = 744, wellhead pressure 999 psig, open flow 2169 mcf/d	2472	USA	Horse point, 26.3	(Moore and Sigler, 1987; USGS, 2009)
27.3	Upper Miocene gas well. Max pressure 0.15 atm, flow rate 2–3 m ³ /s. Proposed origin: mixed, mostly inorganic		Russian Federation	Stavropol, 27.3	(Angino et al., 1984; Bogdanowicz, 1934)
27.3, up to 30, up to 40, up to 47.3	Free gases #1-PR well. In the drilling mud of well #16 drilled into Cambrian sediments Gas from hydrocarbon field Well #101 in Severnaya oil field	2530	Russian Federation	Verhne-Bureinsk, 27.3	(Гресов et al., 2010)
52.5–95.2	Drilling mud #2-R well drilled into Carboniferous sediments	2261–2263	Russian Federation	Iki-Burul, 30	(Левшунов, 1972)
		1105	Belarus	Markovskoe, 40	(Молчанов, 1981; Левшунов, 1972)
				Severnaya, 47.3	(Молчанов, 1981)
				Yelskaya, 95.2	(Шорохов, 1960)

Table 10
Hydrogen discoveries associated with coal basins.

H ₂ , %	Comments	Country	Name of placemark	Reference
10	In gases from drilling muds. Karagandinsky coal basin	Kazakhstan	Karagandinsky, 10	(Зингер, 1962)
18.4	In gases from drilling muds. Kuznetsk coal basin	Russian Federation	Kuznetsky, 18.4	(Зингер, 1962)
20	Gas seep in mine Kirova, horizon 35. Kuznetsk coal basin	Russian Federation	Leninsk-Kuznetsky, 20	(Молчанов, 1981; Гуревич, 1946)
10.9–21 in the mine	In coal mine and gas samples from the Luhanska well 1500. Donbas coal basin	Ukraine	Luhanska, 23.1	(Молчанов, 1981)
23.1 in the well				
21.2–27	Gas from reservoirs in coal basins Uglovsky, Partizansky and Sakhalinsky. Estimated volumes 100–1,000,000 m ³	Russian Federation	Uglovsky, 27 Partizansky, 27 Sakhalinsky, 21.2	(Гресов et al., 2010)
40, up to	In gases from drilling muds. Donbas coal basin	Ukraine	Donetskyy, 40	(Зингер, 1962)
87.2	In gas from well #110. Berzassk region of Kuznetsk coal basin	Russian Federation	Berzassk, 87.2	(Стадник, 1970)
95.4, up to	Drilling mud gas, coal mine well #V-335. 539 out of 820 samples contained > 10% of hydrogen	Russian Federation	Kayerkan, 95.4	(Молчанов, 1981; Сивак, 1962)

platform (Козлова, 2004). It has been shown that the source of H₂ is natural and that hydrogen anomalies related to anthropogenic factors are localized to small areas of only a few square meters (Гусев, 1997). The plotting of hydrogen concentrations in subsurface soil has proved to be useful in identifying geological structures over large areas of Uzbekistan in the Gazli gas field area. Regions where no detect values were measured were interpreted to be areas where the upward migration of hydrogen was obstructed by ground water (Перевозчиков, 2012). Indeed, studies have shown that hydrogen flux through water-saturated porous media is reduced by a factor of ten compared to hydrogen flow through pure water. This retardation of hydrogen diffusion by water-saturated sediments may be related to the Van der Waals radii (the distance at which Van der Waals forces become effective). The study's authors note that molecular hydrogen and certain noble gases have similar radii, and as a result the migration properties of these gases in porous media are similar. In this case, the migration of hydrogen could possibly be retarded by traps and aquifers (Vacquand, 2011). However, the Van der Waals radius of the hydrogen molecule varies depending on pressure and the presence of other molecules and other factors (Batsanov, 1999). In the gas phase the Van der Waals radius of H₂ is equal to 152 pm, which is closer to that of Neon atom (155 pm), rather than that of Argon (188 pm). Therefore, it seems that depending on the geology, hydrogen can diffuse more or less efficiently as a function of multiplicity of factors.

It should be noted that plots of hydrogen concentration in soil-gas have limitations. This is because soils have been proven to efficiently decompose hydrogen (Conrad and Seiler, 1981). These reactions are discussed in more detail the Section 3.5 Biological activity. The implications are that in soil covered areas subsurface hydrogen seepage will be taken up by soil and microorganisms. Therefore, for hydrogen to be observed in soil, the influx of hydrogen must be greater than the hydrogen consumption rate. For hydrogen flux to be accurately evaluated it should be sampled in strata below any zones of biologic and/or soil activity.

Recent studies have identified thousands of sites in the Eastern Russian Federation (Larin et al., 2015; Sukhanova et al., 2013), along the Atlantic Coastal Plain of the USA (Zgonnik et al., 2015), and more recently in Mali (Prinzhofer et al., 2018) and Brazil (Prinzhofer et al., 2019), where hydrogen has been measured seeping from "pockmarked shaped" surface depressions referred in the literature as "Zapadyny", "Carolina Bays" and other local terms for a characteristic circular topographic feature. These shallow sub-circular depressions range from a hundred meters to several kilometers in diameter. There are thousands of them in certain areas worldwide. It has been postulated that hydrogen originates from deep below the sedimentary section and migrating upwards the Earth's surface. The observed circular depressions are interpreted by the authors of two of the above cited papers as being the result of localized collapse caused by the alteration of rock along hydrogen migration pathways. Estimated flow rates at some locations

in the Russian Federation and USA give volumes of up to 27,000 m³ H₂ per day. It is possible that the hydrogen flow at such locations has been continuous for thousands of years.

Some evaluations are available for diffusive flow of hydrogen at other locations. The volume of hydrogen degassing from the entire region of Kryvyi Rih, Ukraine, was estimated to be 120,000 m³/day (Войтов, 1971). Another study estimated the flow of hydrogen from the Ukrainian shield to be 10–12 cm³ of H₂ per year per square meter. On the alkaline massifs of the Ukrainian shield, this number is estimated to be 100–120 cm³ of H₂ per year per m² (Войтов, 1975). Indeed, when estimated hydrogen releases from the alkaline rocks of Khibiny and Lovozero massifs in the Russian Federation were compared with releases from alkaline rocks from the eight massifs of the Ukrainian shield, the latter were shown to be less rich in hydrogen. At the same time, alkaline rocks of Khibiny and Lovozero massifs are characterized by a high oxidized iron content (Kryvdik et al., 2007), contrary to what would be expected, if the rate of hydrogen production was related to iron oxidation.

In a recent study of hydrogen in Oman, a general diffused flow of molecular hydrogen was observed to emanate from the Western Hajar mountains (Zgonnik et al., 2019). Notably, the most significant flows were observed to emanate from the deeper underlying structural units and not the ophiolites which suggests a probable deep source for the hydrogen. Minimum estimated H₂ flows from the Oman study range from 73 to 147 m³/km² per day from the Oman peridotites and up to 1300 m³/km² per day in the shales and marbles of the Oman Upper Proterozoic. Another study recently done in the French and Italian Western Alps also detected hydrogen seepage (Dugamin et al., 2019).

2.3. Relationship of hydrogen with faults and with some noble gases

Numerous studies show an association of hydrogen with faults because they represent a natural pathway for fluids. It was in Japan that the first experiments were carried out showing that hydrogen concentrations are strongly correlated with the faults and their activity (Wakita et al., 1980). Later, H₂ concentrations of up to 9.36% were recorded from some Japanese faults (Sugisaki et al., 1983). As a result, hydrogen was confirmed as a useful tool for mapping faults (Ware et al., 1985). Table 13 summarizes a few examples from the literature.

Studies of hydrogen in soil gas were carried out in the USA over the San Andreas (California) and Duchesne (Utah) fault systems. Hydrogen and helium soil gas concentrations show a clear association with deep-seated fault zones. Concentrations of helium in soil gas at some locations were as high as 1243 ppm, which indirectly proves that when it is associated with helium, hydrogen is of geologic provenance (Jones and Pirkle, 1981). Geochemical sampling for hydrogen in USA has been used to map faulting associated with mineral deposits in the Trans-Challis fault systems of Idaho and the Carlin trend in Nevada. It was suggested that based on anomalous concentrations useful fault zone

Table 11
Hydrogen discoveries associated with sedimentary rocks.

H ₂ , %	Comments	Depth, m	Country	Name of placemark	Reference
4.2–10.7	Gas discovered in 1906		Russian Federation	Novo-Usensk, 10.7	(Rogers, 1921)
13.6	Well #1-P drilled in Lower Carboniferous. Proposed origin: deep-seated	4140–4155	Russian Federation	Sukhoi Hrebet, 13.6	(Суббота and Сардонников, 1968)
16.6	Well #2-T drilled in Paleocene, sandstone and gravel; c (CO) = 35.4%. Proposed hydrogen origin: deep-seated	1135–1170	Kyrgyzstan	Frunzenskaya, 16.6	(Суббота and Сардонников, 1968)
18.6	Gas discovered during construction of tunnel #5, Black Sea railroad		Russian Federation	Мамайка, 18.6	(Молчанов, 1981)
18.9	Gas from a water well		USA	Bernalillo, 18.9	(Moore and Sigler, 1987)
20	Gas from well #2, Paleocene-Eocene epoch; c (CO) = 20%	2954–2980	Kyrgyzstan	Serafimovskaya, 20	(Войтов and Осика, 1982; Суббота and Сардонников, 1968)
7.3–21.2	Gas seeping for 1 month from a well drilled into Middle Jurassic. Pressure at the wellhead 2 bar. Proposed origin: deep hydrogen rising in a fault	2849–2888	Uzbekistan	Alambek, 21.2	(Войтов and Осика, 1982; Бегелев, 1965)
26.7	Drilling mud gas, R-1 well drilled into Silurian sediments	910	Latvia	Bauska, 26.7	(Шорохов, 1960)
13.8–28.1	Gas from Triassic sediments during the Superdeep drilling SG-2	5475–5500	Kazakhstan	Aralsor superdeep, 28.1	(Войтов and Осика, 1982; Первозчиков, 2011; Войтов et al., 1967; Соколов, 1971; Шорохов and Шпеннина, 1967)
37.5	In the drilling mud of the well 1-R drilled into Permian sediments	1185	Russian Federation	Kaliningradskaya, 37.5	(Шорохов, 1960)
42.3; 11.3	Drilling mudgas two wells: #1-RA and #2-RA. Proposed origin: biological	908; 1076	Russian Federation	Ivanovka, 42.3	(Несмелова and Рогозина, 1963)
42.3	Drilling mud gas, well #68 drilled into Devonian sediments	330	Latvia	Loknovskaya, 42.3	(Шорохов, 1960)
31.7–43.5	Free gas from well #1-R drilled into Cambrian sandstones in Nukuty	2503–2520	Russian Federation	Nukuty, 43.5	(Несмелова and Рогозина, 1963; Пиковский, 1963; Фроловская, 1964)
20–50	During testing of wells drilled into Mesozoic sediments. Gas pressure 20–64 atm		Russian Federation	Prikumskoe, 50	(Осика et al., 2002)
56.9	In the drilling mud, well R-1 drilled into Devonian sediments	846	Russian Federation	Lubinskaya, 56.9	(Шорохов, 1960)
57.6	Drilling mud gas, well 3-R drilled into Permian sediments	365	Russian Federation	Anybskaya, 57.6	(Шорохов, 1960)
57.7	Gas from the well Slope Indicator hole #6 drilled into Cretaceous	40	USA	O'Neil pumping plant, 57.7	(Moore and Sigler, 1987)
73.1	Gas associated with sediments. Proposed origin: mixed, mostly inorganic		Poland	Lubina, 73.1	(Angino et al., 1984; Coveney et al., 1987)
75.8	Bubbling on the surface and seabed offshore, associated with Metamorphic rocks. Estimated flow 0.7–1.4 m ³ /day per bubbling. Proposed origin: serpentinization		New Zealand	Poison bay, 75.8	(Wood, 1972)
76.9, up to	In the drilling mud of a well drilled into Permian sediments	860–867	Russian Federation	Oparsinskaya, 76.9	(Шорохов, 1960)
80, in average	Gas from Tertiary sediments		Russian Federation	Barguzin, 80	(Пиковский, 1963; Бодунов-Скворцов, 1958)
80, in average	Gas from Tertiary sediments		Russian Federation	Tunka, 80	(Пиковский, 1963; Shcherbakov and Kozlova, 1986; Бодунов-Скворцов, 1958)
86.6	In the drilling mud, Structural well drilled into Cambrian sediments	1475	Russian Federation	Povarovskaya, 86.6	(Шорохов, 1960)
90.5	In the drilling mud of the well 2-R drilled into Cambrian sediments	760	Russian Federation	Krestetskaya, 90.5	(Шорохов, 1960)
78–95	Gas from Tertiary sediments		Russian Federation	Selenga, 95	(Пиковский, 1963; Shcherbakov and Kozlova, 1986; Бодунов-Скворцов, 1958; Сывороткин, 2002)
98	First producing hydrogen well. Opened in 2012 and as of 2018 has produced hydrogen without a decrease in pressure	109	Mali	Bourakebougou, 98	(Guélad, 2016; Prinzhofer and Deville, 2015; Briere and Jerzykiewicz, 2016; Prinzhofer et al., 2018)

Table 12
Hydrogen discoveries associated with salt deposits.

H ₂ , %	Comments	Country	Name of placemark	Reference
11.3	Gas from potash mine in Salzmunde	Germany	Salzmunde, 11.3	(Черепенников, 1936)
12–12.9	Gas from potash mine in Rossleben	Germany	Rossleben, 12.9	(Черепенников, 1936)
8.4–13.3	Gas from potash mine in Siegfried-Giesen	Germany	Siegfried-Giesen, 13.3	(Черепенников, 1936)
16	Gas in association with potash deposit	Denmark	Tonder, 16	(Smith, 2002)
17.4	Gases from well drilled into carnallite zone	Russian Federation	Chusovskie Gorodki, 17.4	(Bogdanowicz, 1934)
22.1	Gas from potash mine in Eristgal	Germany	Eristgal, 22.1	(Черепенников, 1936)
24.6	Gas from potash mine in Burbach	Germany	Burbach, 24.6	(Черепенников, 1936)
32.9, up to	Gas from wells and mines in Solikamsk potassium field. 5.3–18.5 in carnallite zones; 32.9 in bubbles on the border of the lake	Russian Federation	Solikamsk, 32.9	(Черепенников, 1936; Молчанов, 1981; Savchenko, 1958)
> 50	Main component of the gas in a potash deposit	France	Wittelsheim, > 50	(Молчанов, 1981)
54.3, up to	Gas in carnallite and sylvinite layers. Proposed origin: from organic matter	Russian Federation	Verhnekamsk, 54.3	(Войтов and Осика, 1982; Молчанов, 1981; Морачевский et al., 1937)
61.5	Gas from a well (probably) in a salt deposit. Proposed gas origin: mixed, mostly inorganic	Germany	Muhlhausen, 61.5	(Angino et al., 1984)
82.3–93	Gas from potash mine in Leopoldshall potassium field near Stassfurt. Was seeping for at least for 4.5 years with flow 3.6 m ³ /day	Germany	Stassfurt, 93	(Черепенников, 1936; Rogers, 1921)

maps could be prepared (McCarthy and Kiilsgaard, 2001; McCarthy and McGuire, 1998). Based on an assumption for annual hydrogen flow of $2.7 \cdot 10^4$ t/year (Giardini and Melton, 1983) a flow rate for H₂ migrating along the faults was estimated at $3.6 \cdot 10^{-7}$ cm³/cm²·s (Su et al., 1992), which is a very conservative number when compared to other estimates (see Table 25).

Data on hydrogen from hundreds of soil gas measurements in North-Central Kansas, USA suggests that fractures act as preferential conduits for the vertical migration of free hydrogen (Johnsgard, 1988). Another study of soil gas sampled near hydrogen-rich wells in Kansas suggests a relationship between anomalous hydrogen concentrations and faulting (McCarthy et al., 1986). In an extensive review of the occurrence of hydrogen in Ukraine and Belarus the highest concentrations of hydrogen were found in subsurface fluids from the North Prypyat fault zone (Shcherbakov and Kozlova, 1986). Another study analyzed more than two thousand detections of hydrogen in ground water and concluded that the hydrogen content of ground water associated with deep faults is two orders of magnitude greater than that of ground water sampled from background areas (Щербakov, 1985).

A geophysical study of deep faults in the Moscow region of the Russian Federation with the simultaneous plotting of subsurface hydrogen concentrations showed a correlation between the highest observed concentrations and deep faults (Rogozhin et al., 2010). In another study, the concentrations of hydrogen-rich gases in kimberlitic pipes were shown to be related to the presence of fractures which were the likely conduits for the migration of these gases in the subsurface (Сороченко and Дроздов, 2010).

Hydrogen subsurface concentrations were monitored over large areas of south-western Belarus. It was shown that areas of abnormally high hydrogen concentration were associated with deep faults. In such cases hydrogen concentrations were 10–50 times higher than background concentrations, which were also close to hydrogen concentrations in air. A correlation coefficient of 0.7 between H₂ and helium concentrations suggests an association of high hydrogen and helium concentrations with deep faults (Гусев, 1997; Гумен and Гусев, 1997).

It is commonly accepted that faults control the flow of the mantle fluids into a sedimentary basin. A well-studied example from North Sea oil fields, where analyses using multiple isotope systems (Os, C, He, Ar, Ne, O and D isotopes) to identify fluid sources elucidated a mantle component in the origination of fluids trapped in the field (Ballentine et al., 1996; Fallick, 1993; Finlay et al., 2010). Apparently, hydrogen flux was not directly addressed, but helium flux may serve as a proxy for hydrogen, what has been demonstrated in the other works discussed above.

Because hydrogen and helium have similar diffusive properties,

they show a close relationship in their behavior and distribution. Geochemical maps of hydrogen and helium concentrations in ground water and soil gas were made for a study of a large area of Uzbekistan in the Gazli gas field area. Anomalous helium and hydrogen concentrations were well correlated and related to zones of high fluid conductivity. Hydrogen concentrations were usually two orders of magnitude greater than those of helium. At locations where helium was not detected hydrogen was also not detected (Перевозчиков, 2012). Helium and hydrogen anomalies were studied in Uzbekistan over an area of 100,000 km². Anomalous concentrations of both gases appeared to be associated with fault zones. The bivariate correlation coefficient of hydrogen and helium is 60%, which suggests a linkage between them. No indicators were detected for an anthropogenic origin of these gases (Перевозчиков, 2011).

Radon levels are commonly monitored for environmental safety reasons. Since the properties of hydrogen and radon are diametrically opposed, monitoring of these two gases might be useful in obtaining complimentary information about the properties of the environment. One attempt to simultaneously monitor both gases was done in a 1-month study near the city Essentuki in the Stavropol region of the Russian Federation. No obvious correlations were reported (Рудаков and Уточкин, 1993). However, later studies of hydrogen/radon monitoring in Belarus demonstrated that temporary variations in concentration of these gases correlated in time (Гусев, 1997). More recently, hydrogen was simultaneously measured with radon concentrations and the electrical conductivity of the air at the surface. It was shown, that peaks of hydrogen correlate with peaks of Rn and the electrical conductivity of the air over fault zones. It was suggested, that hydrogen plays a role as a carrier for radon gas (Козлова et al., 1999; Войтов et al., 2000). In later studies, hydrogen and radon were continuously monitored for 1.5 years at two locations in the Russian Federation, one in a seismically active area and the other over a seismically more stable area. It was concluded that the variations observed were a response to planetary scale geodynamic events and could be used for the monitoring of such events (Рудаков and Цыплаков, 2011).

2.4. Periodic variations in concentration

Variations in hydrogen concentration are not stable with time when measured in natural environments. For example, hydrogen monitoring over active faults in Japan on a regular basis shows that H₂ concentrations fluctuate spatially and temporally (Sugisaki et al., 1983). Continuous monitoring of hydrogen concentration along the San Andreas and Calaveras faults in California, USA, from 1980 to 1984 revealed diurnal changes in H₂ concentration with abrupt increases

Table 13
Hydrogen discoveries associated with faults.

H ₂ , %	Comments	Country	Name of placemark	Reference
9.4	Measurements at 1 m depth in active faults. Proposed origin of gas: rock-water reactions	Japan	Atera, 9.4	(Sugisaki et al., 1983)
13.3, up to	Mud logging samples from the drilling of 3433 m borehole for the San Andreas Fault Observatory at Depth (SAFOD) project. Proposed origin of gas: water reactions with fresh fractures	USA	SAFOD, 13.3	(Wiersberg and Erzinger, 2008)
70	Burro mountain, bubbles of gas in strike-slip fault in dunites. Proposed origin of gas: decomposition of Fe(OH) ₂	USA	Burro, 70	(Ware et al., 1985)

correlating with tectonic events (Sato et al., 1986). It has been proposed that these variations are the result of hydrogen being a very mobile gas, the measured concentrations of which are sensitive to weak forces such as tides (Хитаров and Войтов, 1982). Multiple studies have shown periodic changes in H₂ concentration over time. Indeed, it is well known that gas seeps from the Earth have a periodic character. A possible mechanism to explain such phenomena could be tide-induced sorption-desorption (Хитаров and Войтов, 1982).

A large amount of data on variations in hydrogen concentration with time was collected in the Khibiny massif on the Kola peninsula in the Russian Federation. The first measurements were started in the 1960s and showed a relationship between hydrogen and hydrocarbons in the Khibiny gas seeps. These variations demonstrated a 14 days periodic trend corresponding to lunar tides with a correlation coefficient of 0.65. This trend was stable and only interrupted by seismic events, which changed the chemical composition of the seeping gases (Хитаров and Войтов, 1985). Later studies showed that the ratio of hydrogen to hydrocarbons changes periodically with time and pronounced peaks at 2 weeks and 6 months were observed (Кривцов et al., 1967). Another study of periodic trends in gas concentration in the Khibiny massif showed evidence of tidal effects (Хитаров et al., 1979). Later, the intensity of hydrogen-rich gas seeps was monitored in the Khibiny and Lovozero massifs continuously for 5 years, with measurements being taken at 5-min intervals. These data showed the intensity varying with time in a complex way, including periodic and non-periodic trends and that major factors influencing gas seeps are probably tectonic and cosmic in nature. Hydrogen concentrations increased during the summer months, and became very unstable during the syzygy of Moon, Earth and Sun. Other regular trends include monthly, daily, half- and quarter-daily cycles (Нивин, 2013; Nivin et al., 2016). More recent interpretations of the same data lead the authors to conclude that the most important factors controlling the dynamics of H₂ concentration are changes in atmospheric pressure and mining activity (Nivin et al., 2018; Nivin, 2019).

It has been shown that hydrogen concentrations respond to ongoing tectonic activity. In one study, subsurface hydrogen concentration were monitored in Belarus at 1-min intervals. A cyclicity of 12- and 24-h changes in hydrogen concentration was observed, which was attributed to tidal influences. A correlation coefficient of 0.6–0.75 confirmed attribution to theoretical tidal deformations, while taking into account that peaks were appearing with a delay of 2–4 h (Гусев, 1997). The study also showed a perfect correlation with measured deformations of the Earth's crust (Гумен and Гусев, 1997). Longer cycles of 10–18 and 22–32 days were attributed to lunar tides of 14 and 28 days (Гусев, 1997). A later study, which compared tidal effects in wells to predicted effects showed a perfect correlation (Гумен, 2000).

During several months, hydrogen soil gas concentrations were monitored constantly at several points in a tectonically stable region of Belarus. Some locations were situated over known faults, and others on what were believed to be un-faulted areas. The results unambiguously demonstrated that hydrogen concentrations varied periodically according to 12 and 24-h cycles that were not related to changes in temperature or biological activity, but according to the diurnal solid tides of the Earth. The highest amplitudes in concentration variations were observed at locations situated on faults. These variations were attributed to the higher sensitivity of such zones to the Earth's tidal deformations. Hydrogen concentrations also showed a weak correlation with changes in atmospheric pressure. Moreover, in winter months, concentrations were lower, which the authors attributed to the sealing of soil porosity by frost. A single instance of a sharp increase in H₂ concentration was observed, which was attributed to the activation of a deep fault zone (Гумен et al., 1998).

Another study, which monitored hydrogen concentrations in soil gas from surface and subsurface deposits at several locations in the city of Obninsk in the Russian Federation, pointed to higher H₂ content during summer months and a decrease during autumn (Войтов et al.,

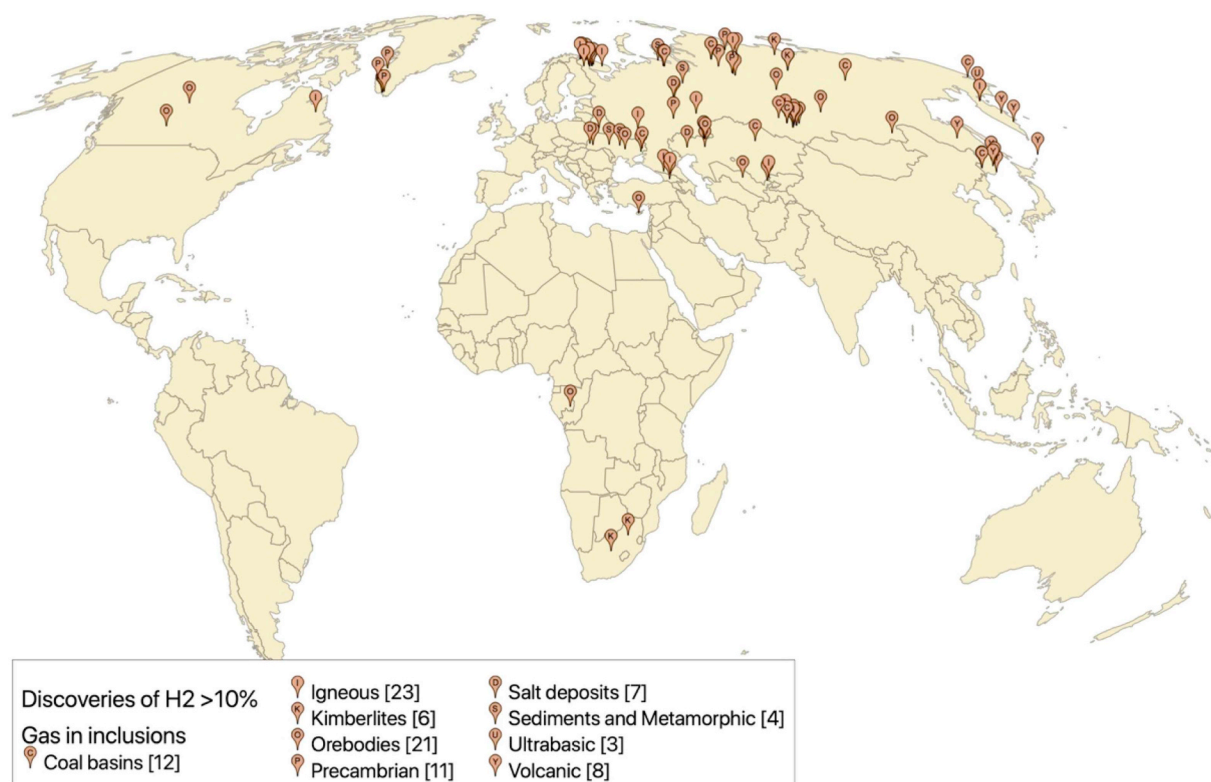


Fig. 5. Map of hydrogen detections in inclusions in various environments at concentrations > 10% vol. Note: high density of placemarks across Eastern Europe and Northern Asia is due to the fact that researchers from these regions were looking for hydrogen more frequently, and not because these regions are richer in hydrogen. Data on each placemark are available in the corresponding tables of this section and in a .kmz file provided in the Supplementary Information.

1995). In the Gomel region of Belarus and in the town Essentuki, Stavropol Krai, Russian Federation, H_2 concentrations showed monthly peaks of 12–75% above background concentrations (Войтов *et al.*, 1995). Hydrogen monitoring on the South Coast of Crimea, Ukraine, showed high background concentrations with frequent and non-regular changes in peak amplitude probably related to tectonic processes (Войтов *et al.*, 1995).

When hydrogen concentrations are monitored in soil, many factors may affect the measurements. For instance, the effect of soil humidity was studied showing that with an increase in soil humidity concentrations of hydrogen also increase, which is attributed to a decrease in soil permeability. Also, the highest hydrogen concentrations were detected during winter months, when soil freezes (Гусев, 1997). Another study indicated that concentrations of hydrogen increase several times at the contact between permafrost and talik (an area of unfrozen ground surrounded by permafrost) (Гресов *et al.*, 2010). A recent study of the causes of formation of Yamal crater, formed in 2014 in Yamal peninsula by an explosion of permafrost, demonstrated that concentrations of hydrogen in the permafrost could be very high, from 13 to 63% (Vorobyev *et al.*, 2019). This is probably due to low permeability of permafrost for gases.

Correlations between atmospheric pressure, air temperature and hydrogen concentration in soil gas were studied in the two fields in Belarus. The maximum observed correlation coefficient was 0.45 with less than a 1 day delay. There appeared to be zero correlation with air temperature (Гусев, 1997). In a recent monitoring study of hydrogen seepage at a circular surface depression in Brazil it has been demonstrated that concentrations vary greatly between day and night (Prinzhofer *et al.*, 2019). The authors proposed that daily increases correlated with the solar radiation, but the mechanisms of causation are not fully understood and may be related to increases in temperature affecting soil evaporation effects, microbiological activity, H_2 detectors' efficiency depending on temperature etc.

Hydrogen concentrations were also monitored as a function of depth, where atmospheric conditions would be supposed to have less effect. Measurements were made on an hourly basis in two wells in Moscow (at depths of 399 m and 1013 m respectively) for 455 days. Periodic cycles of 0.5, 1, 1.74, 21.33 and 85 days were observed. After analyzing the results, it was determined that variations in hydrogen concentration could be attributed to geodynamic processes (Козлова, 2004). In the same study, the authors monitored hydrogen concentrations in the Moscow metro network. The study revealed a high degree of heterogeneity in hydrogen concentration from station to station. At certain times, concentration differences ranged up to 100 ppm. It was concluded that the variations in hydrogen concentration were not connected to anthropogenic sources but rather to be natural (Козлова, 2004).

Periodic changes in global hydrogen degassing were deduced by studying changes in the thickness of the ozone layer (see Section 5.3 Atmosphere) (Сывороткин, 2013).

The above cited examples demonstrate that hydrogen, being the most mobile component of geologic fluids, responds to tides more than other gases. Even though tidal effects are several orders of magnitude weaker than the stresses associated with an earthquake or other seismic event, they are nevertheless sufficient to dynamically influence unstable processes (Довбнич and Солдатенко, 2008) such as the release of H_2 molecules (which are very light) from within the geosphere. The relationship of hydrogen to strong seismic events is described in the Section 5.4 Earthquakes.

2.5. Hydrogen in inclusions

Analyses of gases extracted from inclusions in rock samples has long been considered useful by investigators. However, attention should be paid to the methodology used to extract gases from rock samples. When rock samples are heated to high temperatures or melted, or dissolved in

acid, it is not possible to determine whether or not hydrogen was in the sample. For example, it was reported that gases from samples of the Kola superdeep drilling were mainly nitrogen-hydrogen rich. To determine their composition, two types of degassing were used: mechanical, by crushing in argon atmosphere and chemical, by dissolution in hydrochloric acid. Chemical degassing produces gas enriched in hydrogen, compared to gas from crushed samples (Войтов, 1990), which indicates that some hydrogen may have been a by-product of chemical reactions between the sample and acid. On the other hand, when samples are heated or melted, any hydrogen in the original sample will be destroyed by such analytical procedure. Therefore, analyses of samples subjected to excessive heat or chemical agents were excluded from this review.

Hydrogen has been detected as a major occluded gas (trapped inside of rock in form of inclusions or in adsorbed form) in a variety of different rock types. Each type of rock releases gas with a characteristic composition (Giardini et al., 1976; Fong-liang and Gui-ru, 1981). However, the number of instances where hydrogen has been extracted from inclusions in rocks derived from the same environment of deposition has yielded results that are not always consistent. Fig. 5 shows all placemarks from the tables of this section.

While there are many studies describing instances of the detection of hydrogen as a free gas in an ophiolitic context (Table 1), only one very recent study was found with analyses of hydrogen gas in inclusions in such rocks. It was shown that in inclusions in olivine samples from Zambales in Philippines hydrogen is the dominant component (Grozeva et al., 2020). Such small number of articles on this topic begs the question: was hydrogen not detected within rock inclusions in other places, or was hydrogen overlooked because researchers were not looking for it? I'm convinced that it is the last one, because the recent analyses of samples taken during by our group the field trip in Oman (Zgonnik et al., 2019) demonstrated that inclusions in rocks are hydrogen-rich (results were not published yet).

Only two instances of hydrogen from inclusions in ultrabasic rocks have been referenced. (Table 14). The source of the hydrogen is believed to be related to water-rock reactions (see Section 3.2 Serpentinization).

It has been reported that minerals from rift zones have gas inclusions high in hydrogen. In oceanic rifts the average hydrogen concentration found in inclusions is 21.4% (Моисеенко and Сахно, 1982). However, no studies with analyses of hydrogen inclusions in rocks from cratonic rift zones were found by this review.

More hydrogen detections were reported for inclusions in rocks of Precambrian age (Table 15). As in the free gas data, increases in hydrogen concentration with depth with the highest values observed in Precambrian basement from inclusions sampled (Зорькин et al., 1984). A recent study of Precambrian samples from around the globe demonstrated that hydrogen is consistent component and its mean concentration is 0.14%, while in younger basement samples concentrations are lower by one order of magnitude (Parnell and Blamey, 2017a).

A large number of detections of hydrogen in gas inclusions was reported for rocks of igneous origin (Table 16). The examples from this table do not support the idea proposed in one paper that “under crustal conditions, typical water-saturated granitic rocks could contain only minor quantities of hydrogen” (Apps and Van De Kamp, 1993). Indeed, it was reported in another study that the concentration of hydrogen in inclusions in granites is very high, up to 99% (Петерсилье and Припачкин, 1979).

Samples of volcanic rocks often contain hydrogen in gas inclusions (Table 17). Reported average concentrations of hydrogen degassed from fresh volcanic rocks is 45% (Соколов, 1966b).

Samples from kimberlite pipes were reported to have a high percentage of hydrogen in gas inclusions (Table 18). Fluid inclusions in xenoliths from the Kimberlite pipe Obnazhonnaya in the Russian Federation demonstrate that fluids at a depth of more than 70 km consists mainly of hydrogen (Петерсилье and Припачкин, 1979). Also,

Table 14
Hydrogen discoveries in inclusions in samples from ultrabasic rocks.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
15		In serpentinites of Koriaksko-Kamchatskaya orogen region	Russian Federation	Koriaksko-Kamchatskaya orogen, 15	(Велинский, 1978)
39.8–61	2.4–3.9	Inclusions in dunite and peridotite	Russian Federation	Gornaya Shoria, 61	(Андреева and Молчанов, 1978)
100, up to	6.3, up to	Gas inclusions in basic and ultrabasic rocks. Highest concentration detected in serpentinites.	Russian Federation	Anadyrsko-Kamchatskaya, 100	(Андреева and Молчанов, 1978)

Table 15
Hydrogen discoveries in inclusions in samples from Precambrian rocks.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
12.6 (av.)		Inclusions in augite and syenite; inclusions in sodalite and fayalite from igneous intrusions	Greenland	Kangerdluarssuk, 12.6; Tunugdliarfik, 12.6	(Petersilye and Sørensen, 1970)
18.8 (av.)		Inclusions in rocks from Precambrian igneous intrusions. Maximum in arvedsonite	Greenland	Ilimaussaq, 18.8	(Konnerup-Madsen and Rose-Hansen, 1982)
17.5–26.1	15.5–20.78	In siliceous rocks	Russian Federation	Miroediba, 26.1	(Молчанов, 1981; Андреева and Молчанов, 1978)
68.4 in average		Inclusions in arvedsonite and lujuvrite from igneous intrusions	Greenland	Igdlunguaq, 68.4	(Petersilye and Sørensen, 1970)
13.1–69.5; 8–87.7	7.48–43.2; 3.65–30.64	In siliceous rocks: precipitates from thermal fluids	Russian Federation	Sukhaya Tunguska, 69.5 Nijnaya Tunguska, 87.7	(Молчанов, 1981; Андреева and Молчанов, 1978)
14–89.5	6.88–25.8 cm ³ /kg	In precipitates from thermal fluids	Russian Federation	Igarka, 89.5	(Молчанов, 1981; Андреева and Молчанов, 1978)
93.1 in average		Inclusions in olivine and gabbro from igneous intrusions	Greenland	Narsaq, 93.1	(Petersilye and Sørensen, 1970)
95.5	10.9	Gas in siliceous concretions in gypsum	Russian Federation	Kotuy, 95.5	(Молчанов, 1981; Андреева and Молчанов, 1978)
61.1–97.8		Gases from crushed basement rocks from the well #20000	Russian Federation	Mimbibaevskaya, 97.8	(Boifrov, 1990)

hydrogen appears to be always present in inclusions in diamonds, often as a major gas (Федоров, 2001; Smith et al., 2016; Melton and Giardini, 1974). Another study confirms that hydrogen content increases with depth by measuring hydrogen to water ratios in gases from diamond inclusions. These studies showed that hydrogen is 140 times higher for diamonds estimated to have been generated at a depth of 400 km versus those deemed to have been generated at depths of 120 km (Перчук, 2000).

Hydrogen was discovered in inclusions in minerals from different mines and orebodies, such as: iron, uranium, gold, nickel, chrome and polymetallic ores (Table 19). It was shown that the concentration of H₂ in quartz inclusions in gold and tungsten ore deposits increased with depth (Letnikov and Narseev, 1991). Other studies report that hydrogen is often present in gold mines. Its concentration in gold-bearing veins can be extremely high, from 200 to 460 cm³/kg of rock, which is hundreds of times higher than the adjacent rocks (Фридман, 1970). The same study indicates that hydrogen is present as inclusions in rock samples from mercury orebodies with contents as high as 144 cm³/kg of rock. In some inclusions hydrogen concentrations attained values of 19% (Фридман, 1970). Analyses of gas inclusions in silver and polymetallic hydrothermal minerals in the Kurusaik mining district in Uzbekistan show concentrations of up to 42.6% H₂ with a content of 102 cm³/kg in a sample of quartz. Other minerals contain (percent/(cm³/kg)): 23/36 in garnet, 12/15 in sphalerite, 4/1.9 in calcite, 11.6/2.6 in galena, 7.1/6.8 in barite (Соколов, 1971; Hawkes, 1980). It was reported that hydrogen in high concentrations is present as an occluded gas in most samples of rock from the Tyrnauz tungsten-molybdenum mine in the Caucasus mountains of the Russian Federation (Гуревич et al., 1960). A borehole drilled in Tyrnauz mine produced hydrogen-rich gas for several months (see Table 8).

Many papers report on the results of studies of gas in Khibiny and Lovozero massifs, on the Kola peninsula in the Russian Federation. The highest hydrogen gas content in the ore-rich region of the massifs was found in rocks surrounding apatite-nepheline ores. Gas is concentrated in water-free blocks with a well-developed network of microfractures surrounded by low permeability blocks (Нивин, 2013). A study of the difference between open and closed pores, showed that most of the gas in Khibiny massif is present in closed pores, and the gas content of open pores is limited (Онохин, 1959). A study and analysis of diffusively disseminated hydrogen–hydrocarbon gases in the rocks of both massifs, which compared their distribution with gases occluded in fluid inclusions and free gases in fractures showed that hydrogen is the predominant diffusively disseminated gas in the undisturbed massif (Nivin, 2009). The mean hydrogen content of the gas phase in the Khibiny massif was measured at 4% in occluded gases, and 20% in gases from fractures (Nivin et al., 2005). Hydrogen concentration in occluded gases was seen to decrease with depth (Нивин, 2013). No correlations were found between methane-hydrogen ratios (CH₄/H₂) in free and occluded gases (Нивин, 2013) and between hydrogen and hydrocarbon concentrations (Нивин, 2007). A very recent review summarized the data for this region (Nivin, 2019).

Hydrogen was measured in gas inclusions of samples from different coal basins (Table 20).

Only a few instances of hydrogen in sedimentary or metamorphic rocks have been reported in the literature (Table 21). Probably, because sedimentary rocks have for the most part high porosity and permeability, allowing hydrogen to readily diffuse out of the rock. However, laboratory experiments on the hydrogen saturation in clastic and carbonate rocks show that the rock can adsorb very large quantities of hydrogen (24–57 times) compared to their initial content and not to release it for several days. The most absorptive rocks were found to be limestones (Levshounova, 1991). Laboratory analyses of hydrogen content in different types of sedimentary rock showed that most samples have occluded hydrogen. The highest hydrogen contents were observed in carbonates with up to 77.2 cm³/kg with an average of 14.8 cm³/kg. It has been suggested that carbonates are prone to absorb and

Table 16
Hydrogen discoveries in inclusions in samples of igneous origin.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
11.8	2.1	Gas occluded in granites of Elbrusskoe orebody mine	Russian Federation	Elbrusskoe, 11.8	(Фроловская, 1964; Гуревич et al., 1960)
13–21		In crushed diabases from Borjomi	Georgia	Borjomi, 21	(Соколов, 1971)
35.0, up to 5.1–35.2	1.1–7.8	Inclusions in pegmatites from a plutonic body	Canada	Strange Lake, 35.0	(Salvi and Williams-Jones, 1997)
		Gases in rocks of the Kola basic massifs. Highest concentrations in lujaivrite.	Russian Federation	Lovozero, 35.2	(Соколов, 1971; Potter et al., 2004)
8.8–40.8	71–84	In crushed quartz from the Mayndayntal igneous massif.	Kazakhstan	Mayndayntal, 40.8	(Соколов, 1971; Соколов, 1966a; Соколов, 1966b; Элинсон and Йолыковский, 1961; Элинсон and Полюковский, 1961)
56.5	2.1	Proposed origin: deep-seated			
25.8–71	0.6–2	In crushed conglomerate of Sadonsky igneous formation	Russian Federation	Sadonsky, 56.5	(Соколов, 1966b; Гуревич et al., 1960)
76.4	0.94	Inclusions in syenites and syenito-diorites of a granite massif	Russian Federation	Uibatsky, 71	(Андреева and Молчанов, 1978)
79		Inclusions in olivinite of a plutonic massif	Russian Federation	Kugda, 76.4	(Андреева and Молчанов, 1978)
80.7, up to 5.3		In pyroxenites of Kola basic massifs	Russian Federation	Gremiaba, 79	(Соколов, 1971)
		Inclusions in granites and basic syenites of Middle Paleozoic granite massif. Maximum H ₂ in granites	Russian Federation	Ulug-zassky, 80.7	(Андреева and Молчанов, 1978)
81.2, up to 82.7	0.25 0.24	In nephelines and nepheline syenites of Kola basic massifs	Russian Federation	Sakhariok, 81.2	(Соколов, 1971; Петерсилье and Припачкин, 1979)
83.7, up to 47–85	0.7–3	Inclusions in miaskites	Russian Federation	Vishnevogorsk, 82.7	(Петерсилье and Припачкин, 1979)
		Inclusions in granites and syenites of a granite massif.	Russian Federation	Krasny Kamen, 83.7	(Андреева and Молчанов, 1978)
		Maximum H ₂ in granites			
		In dunites 47%, in gartzburgites 67.5%, in gabbroids 85% of Koriaksko-Kamchatskaya orogen region	Russian Federation	Koriaksko-Kamchatskaya orogen, 85	(Велинский, 1978)
85.4, up to 85.8	0.2–10.2	Inclusions in granites, basic syenites and syeno-diorites of a granite massif. Maximum H ₂ in granites	Russian Federation	Syrsky, 85.4	(Андреева and Молчанов, 1978)
86.3	1.51	In olivines of Kola basic massifs	Russian Federation	Afriandsky, 85.8	(Соколов, 1971)
76.7–87	0.63–0.89	Inclusions in nepheline-syenites	Russian Federation	Goryshegorsk, 86.3	(Петерсилье and Припачкин, 1979)
49.9;	5.26;	Inclusions in pyroxenites and peridotites from intrusions	Russian Federation	Monchegorsk, 87	(Петерсилье and Припачкин, 1979)
61.5;	0.56;	Inclusions in:			
87.2;	3.97;	Gabbro from intrusions;			
88.4	11.18	Norite from intrusions;			
		Effusive diabase;			
		Effusive picrite-porphyritic rocks			
90.5		In gneisses of Kola basic massifs	Russian Federation	Olenegorsk, 90.5	(Соколов, 1971)
93.8, up to 99.9	0.3 m ³ /m ³ (up to) of drilled rocks	Gases occluded in rocks. Kola superdeep drilling for 11 km	Russian Federation	Kola superdeep, 93.8	(Войтов, 1990; Карус et al., 1984; Войтов, 1986; Ikorsky et al., 1999)
64–100	0.7–4.1	In apatites and olivines of the Kola basic massifs	Russian Federation	Kovdorsky, 99.9	(Соколов, 1971)
		Inclusions in dunite and meimechite in a plutonic massif	Russian Federation	Gulinsky, 100	(Андреева and Молчанов, 1978)

Table 17
Hydrogen discoveries in inclusions in samples from volcanic rocks.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
19 (av.)		Gas inclusions in andesite formations of the Badjalsk volcanic zone, including Laksky, Stanolirsky and Purilsky complexes	Russian Federation	Badjalsk, 19	(Моисеенко and Сахно, 1982)
19.2 (av.)		Gas inclusions in liparites from Sikhote-Alin' Outer range	Russian Federation	Sikhote-Alin', 19.2	(Моисеенко and Сахно, 1982)
24.1 (av.)		Gas inclusions in basic basalts from Lesser Kuril Ridge	Russian Federation	Lesser Kuril Ridge, 24.1	(Моисеенко and Сахно, 1982)
27.3 (av.)		Gas inclusions in rocks	Russian Federation	Terney, 27.3	(Моисеенко and Сахно, 1982)
34.5, up to	0.63, up to	Gas inclusions in basalts	Russian Federation	Milogradovo, 27.3	(Андреева and Молчанов, 1978)
35–41		Gas inclusions in ignimbrites	Russian Federation	Semyachik, 34.5	(Щека and Гребенников, 2009)
90.4, up to	2.08	Gas inclusions in basalts from different eruptions and craters of Kluchevskoi volcano	Russian Federation	Yakut-gora, 41	(Андреева and Молчанов, 1978)
				Kluchevskoi, 90.4	

store significant amounts of hydrogen (Левшунова, 1982). It has also been reported that hydrogen is relatively abundant (up to 20–30% by volume) in association with anhydrite or gypsum (Smith et al., 2005). In a recent experimental study, sandstones were exposed to pure H₂ to evaluate their properties as potential reservoir rocks for underground storage of hydrogen. It was also shown by the same study that H₂ induced alteration of pore filling anhydrite and carbonate cements (Flesch et al., 2018). Hydrogen has also been observed in organic-rich shales and metapelites (Suzuki et al., 2017). A recent study of H₂ content in the clay-rich rocks of the Cigar lake uranium deposit reported that they are enriched in hydrogen. Measured values reached 0.25 mol per kg which is higher than the methane adsorption capacity of clay rocks (Truche et al., 2018).

There have been several reported instances of hydrogen detected in salt sample inclusions (Table 22). It has been suggested that hydrogen accumulates in salt deposits as a result of the absence of compounds capable of reacting with hydrogen (Smith et al., 2005). Gas inclusions from the German salt deposits in Hesse and Thuringia showed the presence of hydrogen in many samples, reaching maximum concentrations of 32.9% for samples from Thuringia and 26.4% for samples from Hesse (Knabe, 1989).

2.6. Hydrogen dissolved in ground water

A significant number of instances of natural hydrogen as dissolved gas in ground water have been observed. Fig. 6 shows a map with all locations described in this sub-section. The number of such analyses is large enough to allow researchers to look for correlations. In a review of hydrogen occurrence in subsurface fluids in the territories of what was formerly the soviet camp, a map of hydrogen anomalies was prepared from more than 2000 analyses. This study showed that higher hydrogen concentrations were observed in areas associated with recent tectonic activity. In these areas high concentrations of free hydrogen gas was observed in ground water monitoring wells (Shcherbakov and Kozlova, 1986). Another study of 2215 instances of hydrogen detected in ground water showed hydrogen background levels of 50 mL/L in cratons, with anomalous levels of up to 1500 mL/L and even higher associated with deep faults and rift areas (Щербаков, 1985). Statistical studies of hydrogen occurrence in gases dissolved in ground water from Western Siberia showed that 15% of all samples contained hydrogen. Hydrogen concentrations (in ground water) ranged from trace amounts to tens of a percent and there appeared to be a clear increase in the number of instances of hydrogen concentrations increasing with sampling depth (Нечаева, 1968). It was reported recently that there is no evidence or examples of natural springs waters rich in H₂ (Ostojic, 2019). The author precise that measuring of hydrogen is not a part of a routine analysis and is a difficult method, what may explain why there were no discoveries yet.

High hydrogen concentrations were found in ground water sampled from fractured rock in 24 South African wells. Concentrations of dissolved hydrogen were not correlated with depth, salinity, pH, rock type, borehole age, fractured aquifer age or any other measurement, but the highest concentrations were typically found in the deeper, highly saline, non-meteoric, older waters from fractured aquifers (Lin et al., 2005a). Another study showed abnormally high hydrogen concentrations in gases dissolved in ground water from wells in Idaho. Indications were that the hydrogen was associated with a Pliocene age caldera (Sidle and Hydrocarbon, 1982). 45 analyses of ground water from Crimea in Ukraine contained dissolved hydrogen at concentrations ranging from 0.2 to 53.6%, with hydrogen concentrations and total content increasing with depth by an order of magnitude. There appeared to be no correlation between hydrogen concentration and dissolved iron content (Овчаренко, 1967). It is interesting to note that another study from the Volga Region in the Russian Federation reported an opposite finding: that high hydrogen concentrations in ground water were often associated with high iron concentrations (328 mg/L) but

Table 18
Hydrogen discoveries in inclusions in samples from kimberlite pipes.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
40, up to		Inclusions in spherules of quartz and calcite. Proposed origin: endogenic	Russian Federation	Udachnaya, 40	(Яценко et al., 2012a)
56, in average		Inclusions in spherules of magnetite, wustite and native iron. Proposed origin: endogenic	Ukraine, Russian Federation	Priazovsk' pipes, 56	(Яценко et al., 2012a)
29.4–59.0		Inclusions in diamonds	South Africa	Kimberly mine, 43.1	(Melton and Giardini, 1974)
59.2–81.1	0.23–0.7	Inclusions in xenoliths	Russian Federation	Premier mine, 59	
				Obnazhennaya pipe, 81.1	(Петерсилье and Припачкин, 1979)

also with low pH values (Зингер, 1962).

Measurements of dissolved hydrogen in ground water were proposed as a useful way for the monitoring of shallow aquifers contaminated by landfills (Bjerg et al., 1997), solvents and jet fuel (Chapelle et al., 1996). Hydrogen plays the role of a redox indicator positively correlating with pollution plumes. It was suggested that a monitoring well should be allowed to equilibrate for up to 3 months before taking measurements (Bjerg et al., 1997) and that H₂ measurements are more useful than E_h (oxidation–reduction potential) measurements for identifying anoxic redox processes (Chapelle et al., 1996).

Table 23 summarizes reported observances of dissolved hydrogen in ground water.

Hydrogen detections in water samples from hydrocarbon fields are presented in a separate table, Table 24. Two studies appear to show that ground water sampled close to oil fields contain higher hydrogen concentrations than ground water sampled close to natural gas deposits (Зингер, 1962; Нечаева, 1968).

3. Origin

As has been documented in the sections above, hydrogen has been detected in a variety of different environments. Several hypotheses have been proposed by researchers as to the genesis and origin of hydrogen in the Earth's crust.

In summary these hypotheses include:

- degassing of deep-seated hydrogen from the Earth's core and mantle,
- the reaction of water with ultrabasic rocks or serpentinization,
- contact of water with reducing agents in the mantle,
- the interaction of water with freshly exposed rock surfaces,
- decomposition of hydroxyls in the lattice structure of minerals,
- natural radiolysis of water,
- decomposition of organic matter,
- biological activity,
- anthropogenic activities and more.

Some authors have proposed a mixed origin for hydrogen as a combination of several different genetic factors (Angino et al., 1984; Vacquand et al., 2018). Such a large number of proposed explanations for the origin of hydrogen demonstrates on the one hand the ubiquity of hydrogen, and on the other hand a lack of understanding of its' nature and behavior in the Earth.

Indeed, hydrogen being a very reactive element is present everywhere in bonded form with other elements. It is the main element in molecules of water, in many types of minerals, in living beings, organic matter and hydrocarbons. Under specific conditions these materials undergo chemical reactions which give as a product molecular hydrogen. These materials may be transformed by redox reactions, which could be inorganic or driven by living organisms, and also by the action of temperature or radiation. The variety and omnipresence of

hydrogen-containing compounds, together with the variety of mechanisms through which these compounds can be transformed gives way to a very large number of possible explanations for the genesis and origin of hydrogen. This is why it is often difficult to understand which exact mechanisms could be involved in the production of hydrogen gas. Moreover, hydrogen is a very diffusive gas, it is most likely not generated *in situ*. Detection of hydrogen in the crust suggests that there is a constant supply of this gas (Молчанов, 1981). Its high reactivity and mobility, means hydrogen sources must be geologically relatively young (Войтов and Осика, 1982), at least in crustal settings.

The following section critically reviews all possible sources of hydrogen, together with estimates for their hydrogen production potential. I will start with the description of deep-seated hydrogen, as potentially the most important source of natural hydrogen.

3.1. Deep-seated hydrogen

Many studies point to the fact that the presence of hydrogen in samples increases with depth: it is detected more often and in higher concentrations in gases coming from greater depths (Сороченко and Дроздов, 2010). The authors of a 1986 review of hydrogen accumulations concluded that higher H₂ concentrations were observed in abundance in deep and superdeep wells (Shcherbakov and Kozlova, 1986). Another study reported that the number of H₂ detections increased from a few at depths of 500–600 m to tens of detections at 800–1000 m (Войтов, 1971). The amount of hydrogen was reported to increase with depth during the superdeep drilling programs (SG-8) in Kryvyi Rih, Ukraine (Курлов, 2003) and SG-4 in the Ural region of the Russian Federation (Башта et al., 1991).

Such observations have led some scientists to conclude that hydrogen has a “deep-seated origin”. As strict definition for deep-seated hydrogen has as yet to be agreed upon consequently, I propose to use the term “deep-seated” for hydrogen originating from the Earth's mantle or core, but not from crustal processes.

Direct observations of deep-seated hydrogen are difficult for the obvious reasons that drilling into the mantle or core is likely impossible. However, researchers have proposed a deep-seated origin for hydrogen found in soil gas in Kansas (Johnsgard, 1988; McCarthy et al., 1986), in soil gas sampled from the East-European platform (Козлова, 2004; Ларин et al., 2010; Ларин and Ларин, 2007), from kimberlite pipes (Сороченко and Дроздов, 2010), hydrocarbon wells in the Russian Federation (Шевченко and Силкин, 2015), in a chromite mine in Kazakhstan (Лидин et al., 1982; Уханов et al., 1987; Уханов et al., 1984) and for seeps in Khibiny massif on the Kola peninsula (Nivin, 2009; Кривцов et al., 1967; Хитаров and Войтов, 1982).

Gas samples from the Kola superdeep drilling project, the deepest well in the world, are hydrogen rich (Ikorsky et al., 1999; Войтов, 1990). This has led researchers to conclude that the role of deep-seated processes below the Earth's outer crust have not been adequately estimated. Measurements of diffusive flow in Oman by the author of this review and colleagues has demonstrated that the highest hydrogen flow rates were present in layers underlying the peridotites, implying input

Table 19
Hydrogen discoveries in inclusions in samples from orebodies.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
13.8, up to 19, up to	1.1	In rhyolites intrusions. Concentration depends on sample type	Russian Federation	Apatitovaya Mt, 13.8	(Петерсилье, 1964)
21, up to		In microscopic inclusions of fluid in quartz in Precambrian uranium deposits. Mixed with O ₂ . Proposed origin: radiolysis	Canada	Cluff Lake, 19	(Dubessy et al., 1988)
10.5–21.4, (av.)		In microscopic fluid inclusions in quartz in Precambrian uranium deposits. Mixed with O ₂ . Proposed origin: radiolysis	Canada	Rabbit Lake, 21	(Dubessy et al., 1988)
27.4, up to	0.4–0.7	In apatite-nepheline. Concentration depends on sample type	Russian Federation	Suoluav, 21.4	(Петерсилье, 1964)
33, up to	0.6–2.7	In apatite-nepheline and in rhyolites intrusions. Average concentration depends on sample type	Russian Federation	Rasvumchorr, 27.4	(Петерсилье, 1964)
34.6		In crushed porphyric sand diatases of Norilsk nickel field	Russian Federation	Norilsk, 33	(Соколов, 1971; Соколов, 1966a)
4–42.6		Gases from pores in magnetite at Tunguska Podkamennaya river	Russian Federation	Kamyshevsky Baykitnik, 34.6	(Соколов, 1971; Фридман, 1970)
	22–239	In crushed rocks of Kurusaik polymetallic orebody near Karamazar.	Uzbekistan	Kurusaik, 42.6	(Соколов, 1971; Hawkes, 1980; Элинсон and Сазонов, 1966)
3–58		Maximum detected in quartz, minimum in calcite	Kazakhstan	Kempirsai, 58	(Melcher et al., 1997)
69.5, up to		In purified chromite samples from the chrome orebody of Kempirsai Massif	Kazakhstan	Stepninsk, 11.6	(Melcher et al., 1997)
80, up to		In massive ore samples from the chrome orebody of Kempirsai Massif	Ukraine	Kempirsai MOF, 69.5	(Курилов, 2003)
10.8–70.7 in cores 89.8 (up to) in quartz	20(up to) of rock	Gas in cores from the superdeep drilling in Kryvyi Rih, SG-8. Iron orebody in Paleoproterozoic syncline	Russian Federation	Kryvyi Rih superdeep, 80	(Куликова, 1966; Куликова, 1972)
75–89.8	97–134 in cores; 520, up to, in quartz	Gas in core from 216 m borehole in gold orebody. Maximum in Cambrian-Jurassic sandstones. In quartz, near the production zone	Russian Federation	Baleyskoe, 89.8	(Андреева and Молчанов, 1978)
90, up to	2.6–4.4	In magnetite iron ore samples	Russian Federation	Sheregesh, 89.8	(Перевозчиков, 2011; Перевозчиков, 2012)
47.4–91.1		Adsorbed gases at 8–10 m depth in soil over uranium orebody	Uzbekistan	Uchkuduk, 90	(Андреева and Молчанов, 1978)
60.4–93.3	0.9–6.3	In magnetite iron ore samples	Russian Federation	Abagas, 91.1	(Андреева and Молчанов, 1978)
37.8–98.7	1.1–4.1	In magnetite iron ore samples	Russian Federation	Abakan, 93.3	(Андреева and Молчанов, 1978)
68.3–99.6	1.1–52.4	In magnetite iron ore samples	Russian Federation	Krasnoyarskoe, 98.7	(Андреева and Молчанов, 1978)
100	51(up to)	In magnetite iron ore samples	Russian Federation	Tei, 99.6	(Андреева and Молчанов, 1978)
100, up to		Fluid inclusions in chromites chrome orebody	Cyprus	Cyprus, 100	(McElduff, 1989)
		In microscopic fluid inclusions in quartz of Precambrian uranium deposits. Proposed origin: radiolysis	Gabon	Oklo, 100	(Dubessy et al., 1988)

Table 20
Hydrogen discoveries in inclusions in samples from coal basins.

H ₂ , %	Comments	Country	Name of placemark	Reference
11.4	Gas in the samples from the horizon 110 of a coal mine	Russian Federation	Baydaevka, 11.4	(Молчанов, 1981; Гуревич, 1946)
12.7, up to	Gas in coal samples from nickel orebody. Content 0.083 m ³ /t rock	Russian Federation	Talnakh, 12.7	(Фридман, 1970)
18.4	Gas in the samples from horizon 197 in #4 coal mine	Russian Federation	Osinovka, 18.4	(Молчанов, 1981; Гуревич, 1946)
20, up to	40% of all coal samples contain up to 10% H ₂ ; 80% of rock samples contain up to 18% H ₂ in Karagandy coal mines	Kazakhstan	Karagandy, 20	(Соколов, 1971; Соколов, 1966a; Молчанов, 1981)
20–21	Gas from coal samples of Pechora coal basin	Russian Federation	Vorgashor, 21	(Соколов, 1971)
25, up to	Gas in liptobiolites samples from a coal basin. Content 0.5–1 m ³ /t coal	Russian Federation	Razdolnensky, 25	(Гресов et al., 2010)
25, up to	Gas in liptobiolites of Lipovetskoe and Sangarskoe coal basins	Russian Federation	Lipovetskoe, 25 Sangarskoe, 25	(Гресов et al., 2010)
30–35	Gas in cores from wells in Kuzbass coal basin	Russian Federation	Shugurovo, 35	(Молчанов, 1981)
40, up to	Content of H ₂ up to 40% in 95% of rock samples in Donbas coal basin	Ukraine	Donbas, 40	(Молчанов, 1981)
24–64	Gas in raptodissites (coals with high content of leptynite) from Illytchevsk coal field. H ₂ content > 0.5 m ³ /t coal	Russian Federation	Illytchevsk, 64	(Гресов et al., 2010)
76–81	Gas from sandstone samples of Pechora coal basin	Russian Federation	Pechora basin, 81	(Соколов, 1971; Молчанов, 1981)

of H₂ from regions below the ophiolites (Zgonnik et al., 2019).

There are also indirect arguments for a deep-seated origin for hydrogen. Some researchers argue for a deep-seated origin because the presence of hydrogen is associated with fault zones (Войтов, 1971; McCarthy et al., 1986; Овчаренко, 1967) and riftzones (Сывороткин, 2002). When helium and hydrogen anomalies were studied in different investigations it was shown that the concentrations of both gases correlate, which, according to the authors, suggests a deep-seated origin for these gases (Перевозчиков, 2011; Гусев, 1997). Another indicator for the deep-seated nature of hydrogen is the synchronous and rapid behavior of widely separated, on the order of thousands of kilometers, seeps (Сывороткин, 2009). Some authors relate this unstable nature of deep seated hydrogen seeps to the geodynamic behavior of the Earth (Voitov and Rudakov, 2000). It was suggested that the isotopically-light hydrogen, observed in the study, is an indicator of its deep-seated origin (Уханов et al., 1987). In another study of hydrogen occurrence in coal basins the authors propose that in places where hydrogen is found at anomalously high concentrations it could be of a deep origin (Гресов et al., 2010). Other studies point out that because of the very diffusive nature of hydrogen its detection in the crust suggests that there is a constant supply of H₂ from depth (Молчанов, 1981).

Various works suggest the version of a mantle source for hydrogen. It has been suggested that the origin of the gas in the Khybny Massif is at least partially related to gas influx from the subcrustal layers (Nivin, 2009). Mantle outgassing was proposed as one of many possible sources for hydrogen-rich gas in Kansas (Coveney et al., 1987). A general analysis of the evolution of different Earth fluids has concluded that mantle fluids are much more chemically reduced than those of the crust (Перчук, 2000). Recent experiments have shown that hydrogen is soluble in minerals under mantle conditions (Yang et al., 2016). The authors suggest that significant amounts of hydrogen could be present in the Earth's mantle under reducing conditions. Analyses of metal inclusions in diamonds derived from depths equivalent to that of the Earth's mantle showed the presence of hydrogen, confirming that it is present in the mantle (Smith et al., 2016). Also, it has been demonstrated that the Earth's upper mantle and large portions of asthenosphere are metal-saturated. In such case, the main fluid should be

hydrogen-rich (Rohrbach et al., 2007).

It seems increasingly accepted that the lower mantle is reduced such that C-O-H fluids will be dominated by CH₄/H₂O/H₂ rather than CO₂/H₂O. What seems less clear and pertinent to this review are the conditions at which H₂ > H₂O, i.e. the redox conditions that would sustain reservoirs of genuinely hydridic fluids. Rohrbach et al. (Rohrbach et al., 2007; Rohrbach et al., 2011) state that CH₄ ± H₂ occur with iron saturated fluids and that the metal saturated lower mantle is likely to have a redox state between IW (iron-wustite buffer)–0.5 and –2. This range of conditions suggests gradients exist in the lower mantle between reduced fluids that still contain significant water (relative to H₂) and genuinely hydric fluids (H₂/CH₄/and other hydrides?) that must exist, based on, for example discoveries of metal inclusions in diamonds (Smith et al., 2016), occurrences of moissanite (SiC) (Di Pierro et al., 2003) and various silicides (Muszer, 2014; Геворк'ян et al., 1969; Яценко et al., 2012b). A heterogeneous distribution of hydrogen in the lower mantle (c.f. the crust), possibly influenced by hydrogen fluxes from the core, would therefore be possible. Recent experimental work (Bali et al., 2013) shows that water and hydrogen can be immiscible at mantle conditions and this provides another mechanism for creating heterogeneity in the distribution of hydrogen, at least in the upper mantle.

Isotopic studies of hydrogen suggest that the mantle contains hydrogen and that the mantle supplies it to crustal rocks i.e. "surface" rocks. This is because δD values of measured hydrogen are isotopically light (have less deuterium), similar to the primordial δD values of the Solar System. This was pointed out by the observation of very low δD values in Hawaiian xenoliths (Deloule et al., 1991) and in a study of anomalies in D/H (deuterium to protium) ratios of pore waters in sediments from the Norwegian Sea (Lawrence and Taviani, 1988) (in the Section 2.2 the examples are given illustrating mantle contribution of fluids into crustal settings of the North Sea). The work of unravelling the isotopic record of the mantle is still ongoing. Recent studies (Clog et al., 2013; Loewen et al., 2019) suggest values of δD –60‰–75‰ or lower.

A review of hydrogen in the deep Earth concluded that a significant quantity of hydrogen could be retained in the transition zone, lower

Table 21
Hydrogen in sedimentary or metamorphic rock inclusions.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
5.2–19.7	175–460	Crushed Cretaceous argillites from the well #118. Depth 1580–1582 m.	Russian Federation	Igrim, 19.6	(Несмелова and Позогина, 1963)
56, (av.)		Inclusions in spherules of magnetite, wustite and native iron. Proposed origin: endogenic	Ukraine, Russian Federation	Ilyinets crater, 56 Kara crater, 56	(Яценко et al., 2012a)
66.6, (av.)		Inclusions in glass spherules with perovskite, native iron, silicides, moissanite and titanium oxides. Proposed origin: endogenic	Ukraine	Boltysh Crater, 66.6	(Яценко et al., 2012a)

Table 22
Hydrogen discoveries in inclusions in samples from salt deposits.

H ₂ , %	Content, cm ³ /kg	Comments	Country	Name of placemark	Reference
17.2 (av.)	0.49	Gases from salt-bearing strata from well #10153. Depths 251–998 m.	Kazakhstan	Inder, 17.2	(Зорькин et al., 1984)
23.9, up to		Gases sampled from sylvinite samples from 41.4 m	Belarus	Starobinskoe, 23.9	(Черепеников and Рогозина, 1964)
26.7 (av.)	0.32	Gases sampled from salt-bearing strata from well #88. Depths 1046–2826 m.	Kazakhstan	Kenkyak, 26.7	(Зорькин et al., 1984)
1.1–32.6		Gases extracted from carnallite from Bereznikovskii salt mine. Concentration in free gas of mine: 7.8%. Proposed origin: reaction of newly formed elements with water	Russian Federation	Berezniki, 32.6	(Savchenko, 1958)
6–34		Gases in sylvinite samples	Ukraine	Kalush, 34	(Ковалевич and Сворень, 1975)
34.6, up to		In carnallite from Solikamsk potassium field	Russian Federation	Stebnyk, 34 Solikamsk, 34.6	(Savchenko, 1958)

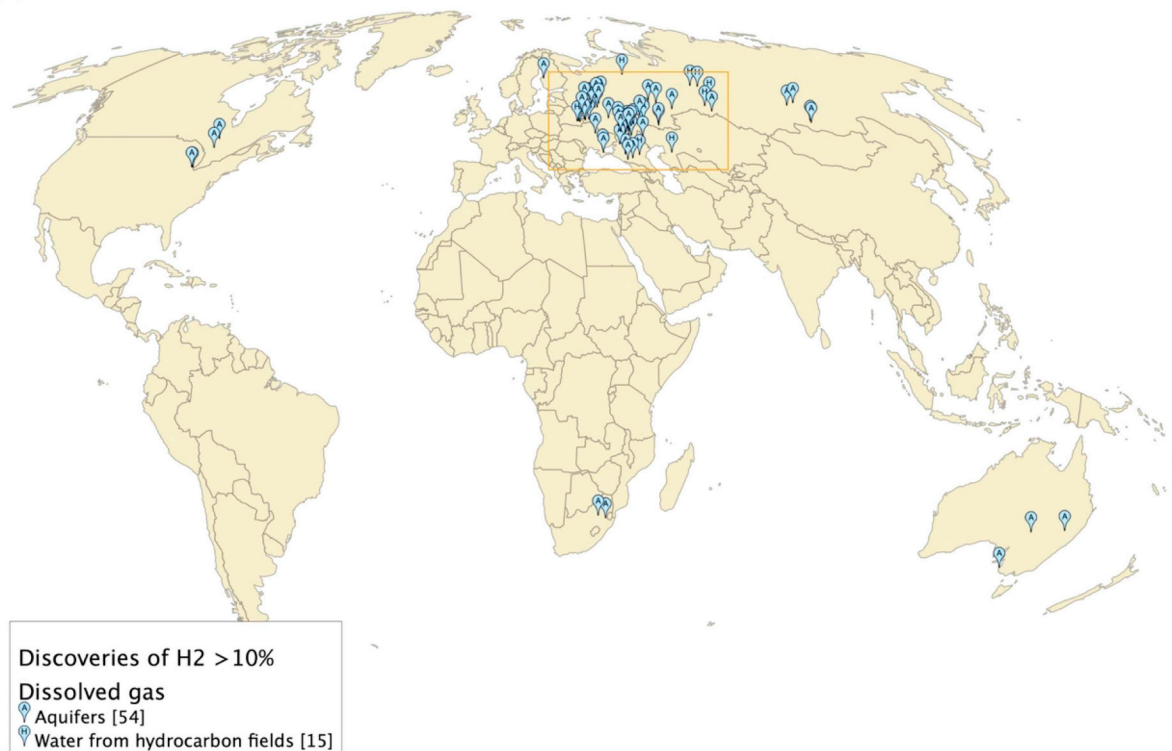
mantle or core (Williams and Hemley, 2001). It was suggested that presence of hydrogen could be responsible for the anomalous electrical conductivity of the asthenosphere (Karato, 1990). Recent studies indicate that a large quantity of hydrogen can be stored in the mantle in the form of hydrated minerals (Schmandt et al., 2014). A very recent discovery of first natural hydride (VH₂) proves the presence of hydrogen-dominated fluids in the mantle (Bindi et al., 2019) and should attract more attention for this topic.

Several works suggest a core source of hydrogen. Hydrogen allows for resolution of the so-called core deficit problem the Earth's core, which is about 10% lighter than Fe-Ni alloy at the same pressure and temperature (Poirier, 1994; Isaev et al., 2007; Yagi and Hishinuma, 1995; Murphy, 2016; Rumyantsev, 2016). It was reported that adding 1% by wt of hydrogen to the core resolves this issue (Poirier, 1994). Studies suggest that iron hydride is stable under the Earth's mantle and core conditions (Isaev et al., 2007). A review of deep-seated hydrogen estimates that the core itself could contain, in the form of hydrides of iron, up to 100 times more hydrogen than in the hydrosphere (Williams and Hemley, 2001). A recent study proposed that the core might contain 80 times more hydrogen than of the mass of all hydrogen in the ocean (Ikuta et al., 2019). One report suggests that an FeH_{0.14} composition for the inner core produces a reasonable agreement with seismic observations (Murphy, 2016). For the outer core an alloy of Fe_{0.88}Si_{0.12}H_{0.17} containing 0.32 wt% hydrogen was reported to match density and seismic profiles (Tagawa et al., 2016). However, there doesn't appear to be a consensus in the literature on the question of what element is responsible for the core density problem and different research teams propose admixture of different elements like carbon, silicon, sulphur, oxygen, etc. The idea of hydrogen as a main light element in the core has not received more attention because it does not altogether support traditional views on the Earth's formation, which postulate that it was accreted from volatile-depleted material (Harry et al., 2010). From this viewpoint reduced species are expected to be present in only minor quantities in the upper mantle (Apps and Van De Kamp, 1993). However, in this model the origin of volatiles, and especially water, remains unclear and is still debated (Harry et al., 2010; Morbidelli et al., 2012).

The discussion on how hydrogen could arise in the Earth's core is open. It has been proposed that the Earth could have accreted a large quantity of hydrogen during its formation. When discussing hydrogen sources some authors are specifically referring to the flow of “primordial hydrogen”, which they hypothesize to have been present in the Earth since its formation (Gilat and Vol, 2005; Gilat and Vol, 2012; Walshe, 2006; Walshe et al., 2005; Larin, 1993). As to possible mechanisms, some studies show that it is possible that hydrogen was likely incorporated into iron during an early stage in the Earth's evolution (Rumyantsev, 2016; Iizuka-Oku et al., 2017). Others propose a reaction of iron with water yielding separate phases of iron oxide and iron hydride (Yagi and Hishinuma, 1995; Fukai, 1984; Fukai and Suzuki, 1986; Okuchi, 1997; Mao et al., 2017). Another idea is based on the discovered relationship between the ionization potential of elements and their distribution in Solar system. Calculations show that the primordial Earth's composition was highly enriched in hydrogen (Larin, 1993). The Earth therefore could have stored some portion of this hydrogen in its interior. This hypothesis was proposed by Vladimir Larin (Ларин, 1973) and developed into a fundamental study of primordially hydrogen-rich Earth years later (Larin, 1993; Ларин, 2005; Ларин, 1991). The underlying idea was recently re-examined using the methods of statistical physics to confirm that the initial bulk composition of the Earth was hydrogen-enriched (Toulhoat et al., 2015). Hervé Toulhoat et al. have suggested that the inner Earth may have contained 5.1 wt % of hydrogen in bonded state in the form of hydrides (Toulhoat et al., 2015). This number is of the same order as previous estimates of 0.61–4.72 wt% (Larin, 1993; Williams and Hemley, 2001; Сывороткин, 2002).

The idea of a hydrogen-enriched Earth is not completely new. It was

A



B

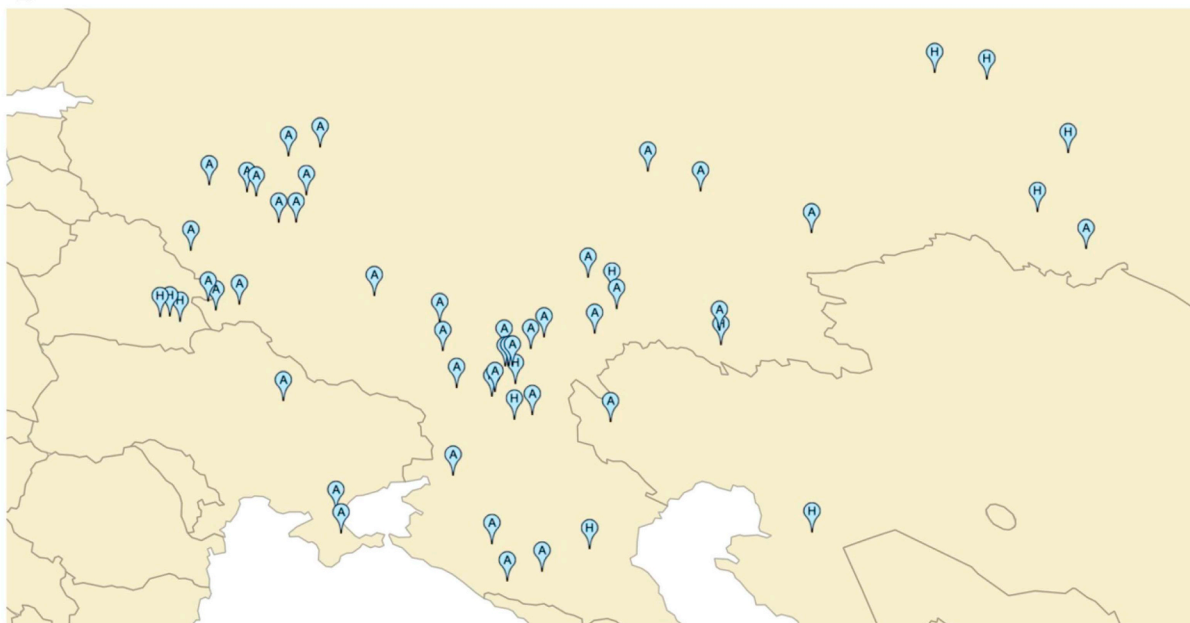


Fig. 6. (a) Map of hydrogen detections in dissolved gases in various environments at concentrations > 10% vol. Note: the high density of placemarks across Eastern Europe and Northern Asia is due to the fact that researchers from these regions were looking for hydrogen more frequently, and not because these regions are richer in hydrogen. The area highlighted by the orange rectangle is shown on the (b). Data on each placemark are available in the corresponding tables of this section and in a .kmz file provided in the Supplementary Information. (b) A detail map of the area highlighted by the orange rectangle on the (a).

first hypothesized at the beginning of 20th century by Vladimir Vernadsky (Вернадский, 1960). Later authors also speculated on the formation and evolution of an initially hydrogen-enriched Earth (Маракушев and Маракушев, 2008a; Семененко, 1990; Маракушев, 1999). The controversial nature of these works probably explains why they have not got much attention. However, they illustrate the interest of scientists in the idea of a primordially hydrogen-rich Earth and its potential to explain various geologic and terrestrial phenomena.

Taking into account the considerations from this section, natural H₂ can be classified into two groups: primary hydrogen (stored in the mantle or the core and progressively degassed to the surface), and secondary hydrogen (produced in the mantle or the crust by various chemical reactions), which is more general than the assumption that natural hydrogen is only produced from water (Молчанов, 1981).

Table 23
Hydrogen discoveries in water samples.

H ₂ , %	Content	Comments	Depth, m	Country	Name of placemark	Reference
0.05–10.3	7410 µmol/L (for the sample with highest concentration 10.3%) 216.9 cm ³ /L	In waters from fractured Precambrian shield rocks in well #DR548. Value of $\delta D = -706\text{‰}$; c (He) = 3%. Proposed origin: unknown, probably radiolysis Water from Early Riphean horizon of Lubimskaya well #3-L; c (He) = 0.5% In water from Lower Cambrian dolomites and anhydrites from well #1-bis Gas from ground water	3200 2984–3004 1210–1215	South Africa Russian Federation Russian Federation Russian Federation Finland	Driefontein, 10.3 Lubimskaya, 10.7 Elovka, 11.1 Kulomzin, 11.2	(Sherwood Lollar et al., 2007; Sherwood Lollar et al., 2006) (Мухин, 1970) (Пиковский, 1963) (Levshounova, 1991)
10–11.1			407		Ylistaro, 11.4	(Sherwood Lollar et al., 2014; Sherwood Lollar et al., 1993b)
11.2			2825	South Africa	Mponeng, 11.5	(Sherwood Lollar et al., 2007; Sherwood Lollar et al., 2006)
11.4		Water from migmatitic biotite, plagioclase gneiss and associated mica and amphibolite schists. In ground water from fractured Precambrian shield rocks in well #MP104. Value of $\delta D = -684\text{‰}$; c (He) = 12.3%. Proposed origin: unknown, probably radiolysis Water from Devonian deposits in well Zvenigorodskaya #3; c (He) = 0.9% In deep waters from Paleozoic deposits of Kaliminskaya field, Zhivetsky horizon, well #2 TsBI; c (He) = 0.7%	788–900 2797–2803 1138–1400	Russian Federation Russian Federation Russian Federation Russian Federation	Zvenigorodskaya, 11.8 Kaliminskaya, 12 Boenskaya, 12.1	(Мухин, 1970) (Стадник, 1970) (Мухин, 1970)
12	540 cm ³ /L		3176–3182	Russian Federation	Gorno-Vodianaya, 12.5	(Стадник, 1970)
12.1	84.2 cm ³ /L	In deep waters from Paleozoic deposits of Gorno-Vodianaya field, Voronezhsky horizon, well #14 In fracture waters from Precambrian shield rocks in a well. Value of $\delta D = -725$ to -737‰ . Proposed origin: serpentinization In water from Low Cambrian, diabases in the well #1-0	2072	Canada	Timmins, 12.7	(Sherwood Lollar et al., 2014; Sherwood Lollar et al., 2007)
0.1–12.7			2608–2615	Russian Federation	Zayarsk, 13.2	(Пиковский, 1963)
13.2			1140–1142	Russian Federation	Peschany Umet, 14.5	(Стадник, 1970)
14.5			1521–1529 (well #32); 1504–1511 (well #69); 1500 (well #12)	Russian Federation	Uritskaya, 15.4	(Стадник, 1970; Зингер, 1962)
6.5 (well #32); 8.8 (well #69); 15.4 (well #12)	1082 cm ³ /L in the well #12	Uritskaya field, Tulskey horizon, wells #32, #69, #12 Dissolved gases in waters. In the well #32 hydrogen-producing bacteria was detected				
15.73	553 cm ³ /L	In deep waters from Paleozoic deposits of Petrushinskaya field, Voroblevsky horizon, well #7 Devonian aquifer well Chapligninskaya #1-Ch; c (He) = 0.6%	2727–2737	Russian Federation	Petrushinskaya, 15.7	(Стадник, 1970)
15.9	25.7 cm ³ /L		678–690	Russian Federation	Chapligninskaya, 15.9	(Мухин, 1970)
16.2	293 cm ³ /L	In deep waters from Paleozoic aquifer of Novo-Kubanskaya field, Evlanovsko-Livensky horizon, well #12 Gases associated with Artesian water	2114–2128	Russian Federation	Novo-Kubanskaya, 16.2	(Стадник, 1970)
15.7–16.5				Australia	Coonanna, 16.5	(Woolhough, 1934)
16.7	739 cm ³ /L	In deep waters from Paleozoic aquifer of Rahmanovskaya field, Zhivetsky horizon, well #12 Gases dissolved in waters of sediments	2924–2962	Russian Federation	Rahmanovskaya, 16.7	(Стадник, 1970; Зингер, 1962)
2–17	18–29 cm ³ /L			Russian Federation	Pochep, 17	(Соколов, 1966a)
17.4	244 cm ³ /L	In deep waters from Paleozoic deposits of Grazhdanskaya field, Nizhneschegrovsky horizon, well #91 Associated with Artesian water from upper zone of the Mungyer well Lower Cambrian dolomites aquifer, in the well #1-R	2446–2449	Russian Federation	Grazhdanskaya, 17.4	(Стадник, 1970)
17.4			918–968	Australia	Mungyer, 17.4	(Woolhough, 1934)
10.6–18.7			1498–1500	Russian Federation	Ust'-Kut, 18.7	(Пиковский, 1963)
18.9		Water from Earlypaleozoic aquifer. Redkino well #2		Russian Federation	Redkino, 18.9	(Мухин, 1970)

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Table 23 (continued)

H ₂ , %	Content	Comments	Depth, m	Country	Name of placemark	Reference
19.2	52.6 cm ³ /L	Devonian aquifer, in Zhavinskaya well	920–923	Russian Federation	Inzhavinskaya, 19.2	(Мухин, 1970)
19.5	17.8 cm ³ /L	Early Riphean aquifer, Klintsovskaya well #5808; c (He) = 0.5%	739–755	Russian Federation	Klintsovskaya, 19.5	(Мухин, 1970)
18.4–20.1	91.2 cm ³ /L	Residual soil ground water in crystalline basement, well #3345 in Strugova Buda	553	Russian Federation	Strugova Buda, 20.1	(Мухин, 1970)
18.8–20.5		Lower Cambrian dolomite and limestone aquifer, well #1-R	540–550	Russian Federation	Schukina, 20.5	(Пиковский, 1963)
20.9	312 cm ³ /L	Deep Paleozoic aquifers Kuleshovskaya field, Nizhebashkirsky horizon, well #59	1779–1784	Russian Federation	Kuleshovskaya, 20.9	(Стадник, 1970)
22.2	832 cm ³ /L	Deep Paleozoic aquifers Bagaevskaya field, Bobrikovsky horizon, well #12	1620–1622	Russian Federation	Bagaevskaya, 22.2	(Стадник, 1970)
8.86 (well #26); 16.4 (well #82);		Kudinovskaya field, Bobrikovsky horizon, well #26	1744–1760 (well #26);	Russian Federation	Kudinovskaya, 22.3	(Стадник, 1970)
22.3 (well #93)		Nizhebashkirsky horizon, well #93	2824–2850 (well #82); 1407–1474 (well #93)			
24.2	360 cm ³ /L	Pashysky horizon, well #82	1063–1075	Russian Federation	Rybinskaya, 24.2	(Мухин, 1970)
23.3–25	754 cm ³ /L	Devonian–Lower Carboniferous aquifers, well Rybinskaya #5-R	1063–1065	Russian Federation	Sokolovaya gora, 25	(Стадник, 1970; Зингер, 1962)
25.4		Deep Paleozoic aquifer of Sokolovaya gora field, Bobrikovsky horizon, well #33	917	Federation	Robe, 25.4	(Headlee, 1962; Woolnough, 1934)
25.6		Fresh water beds in Jurassic sediments from the Robe well		Australia	Belleville, 25.6	(Headlee, 1962; Newcombe, 1935)
26.0		In fresh water aquifer		USA	Washtenaw, 26.0	(Headlee, 1962; Newcombe, 1935)
26.4	187.5 cm ³ /L	Fresh water aquifer J. Polasky 1 well. Proposed origin: mixed, mostly inorganic	583–600	Russian Federation	Kuvshinskaya, 26.4	(Мухин, 1970)
27		Devonian–Lower Carboniferous aquifer, Kuvshinskaya well	3350	Kazakhstan	Aralsor superdeep, 27	(Соколов, 1971)
28	1129 cm ³ /L	Gases dissolved in water from the superdeep drilling SG-2	2174–2184	Russian Federation	Lemeshkinskaya, 28	(Стадник, 1970)
13.5–29.5	28.7–58.2 cm ³ /L	In deep waters from Paleozoic aquifer, Lemeshkinskaya field, Evlanovsko-Livensky horizon, well #16	614–640	Russian Federation	Smolenskaya, 29.5	(Мухин, 1970)
25–30		Devonian aquifer Smolenskaya well #2; c (He) = 1.1–2.1%		Russian Federation	Chesnokovka, 30	(Щербаков et al., 1972)
30, up to		Well water. Proposed origin: deep from basement		Russian Federation	Hudesskoe, 30	(Фридман, 1970)
10.5–32.1		In waters of a copper mine	540–552	Russian Federation	Borisoglebskaya, 32.1	(Мухин, 1970)
18–31.9	89.7 cm ³ /L	Aquifer in residual soil in crystalline basement, Borisoglebskaya well	2027–2033	Russian Federation	Pereyasavl-Zaleskaya, 31.9	(Мухин, 1970)
32.8 (well #319); 11.6 (well #445)	879 cm ³ /L in the well #319	Dissolved gases in ground water Lower Riphean aquifer, well #1-P in Pereyasavl-Zalesk; c (He) = 0.7%	638–655	Russian Federation	Bahmetievskaya, 32.8	(Стадник, 1970)
34.7		Deep paleozoic aquifer Bahmetievskaya field, Vernebashkirsky aquifer, well #319; Bobrikovsky aquifer, well #445	964–966	Russian Federation	Furmanovskaya, 34.7	(Стадник, 1970)
Up to 36.3 1.7–37.7		Deep Paleozoic aquifers of Furmanovskaya field, Vernebashkirsky aquifer, well #21	1077–1082	Russian Federation	Sahaidakske, 36	(Шорохов, 1960; Зингер, 1962)
47.5		Sparkling water from Triassic aquifer	2892–2914	Ukraine	Henicheska, 37.7	(Овчаренко, 1967)
		Gases in aquifers from the well #5. Proposed origin: deep-seated	1755–1790	Russian Federation	Sherbakovskaya, 47.5	(Стадник, 1970)
		Deep Paleozoic aquifer of Sherbakovskaya field, Sakmarsko-Artinsky horizon, well #19				

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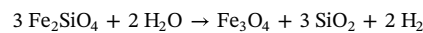
Table 23 (continued)

H ₂ %	Content	Comments	Depth, m	Country	Name of placemark	Reference
41.5 (well #53)	1306 cm ³ /L in the well #53; 946 cm ³ /L in the well #39	Deep Paleozoic aquifer of Zhimovskaya field, Tulskey horizon, wells #53, #641, #39	1027–1029 (well #53)	Russian Federation	Zhimovskaya, 49.1	(Стадник, 1970; Фроловская, 1964; Зингер, 1962)
14.2 (well #641)			1044–1049 (well #641)			
49.1 (well #39)			1050 (well #39)			
1.8–53.6		Gases in aquifers from the well #6. Proposed origin: deep-seated	2836–2858	Ukraine	Nyzhnohirska, 53.6	(Овчаренко, 1967)
9.9–57.8	96 L/day	Fractured Precambrian shield aquifer Copper Cliff well #CCS4572. $\delta D = -637$ to -738 ‰; $c(He) = 2.6$ – 6.7 ‰. Proposed origin: serpentinization	1333	Canada	Sudbury, 57.8	(Smith et al., 2005; Sherwood Lollar et al., 2014; Sherwood Lollar et al., 1993a; Sherwood Lollar et al., 2007; Sherwood Lollar et al., 2006; Sherwood Lollar et al., 1988)
60.6 (well #790)	561 cm ³ /L in the well #31	Deep Paleozoic aquifer of Rodionovskaya field, wells #790 and #31, Kungursky horizon	850–884 (well #790)	Russian Federation	Rodionovskaya, 60.6	(Стадник, 1970; Зингер, 1962)
14.7 (well #31)			1350 (well #31)			
76 (well #4); 6.2 (well #10)	153 cm ³ /L in the well #4	Deep Paleozoic aquifer of Klenovskaya field, Dankovo-Lebediansky horizon, wells #4, #10	1795–1810	Russian Federation	Klenovskaya, 76	(Стадник, 1970)

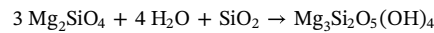
3.2. Serpentinization

Serpentinization is a metamorphic process in which mainly ultra-basic rocks are oxidized by water into serpentine producing hydrogen. It is generally considered that ultramafic rocks are the main constituents of the Earth's mantle explaining why serpentinization as a process attracts so much attention from Earth scientists. It has been well studied with many works published (see for example, these articles (Vacquand et al., 2018; Suzuki et al., 2015; Mayhew et al., 2013) and references therein). A comprehensive review of the serpentinization literature will exceed the scope of this article and has already been done in cited works therefore only a resume of the current literature is presented herein.

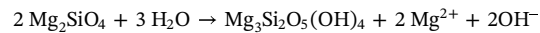
A typical mantle rock is peridotite which is mainly composed of the mineral olivine. This is a mineral which is likely to react with water. Olivine, (Mg,Fe)₂SiO₄, is a solid solution series between forsterite (Mg₂SiO₄) and fayalite (Fe₂SiO₄). Iron in the fayalite has the oxidation state Fe²⁺, which allows it to react with water. During the reaction iron oxidizes to Fe³⁺ and hydrogen in water reduces to H₂⁰:



Forsterite is often the dominant mineral in the structure of olivine. It reacts with excess silica to give serpentine:



Forsterite can also react with water to give serpentine and magnesium hydroxide, which drastically increases the pH of the solution:



It has been reported that serpentinization is most active in the temperature range of 200 to 310 °C (McCormick and Bach, 2009). At lower temperatures, the rate of reaction becomes very limited, and at higher temperatures the reaction rate rapidly decreases because of thermodynamic constraints. While some authors suggest that hydrogen could be produced by low-temperature reactions, a recent rigorous study demonstrated that hydrogen generation in such experiments is also generated by contamination from commonly used reaction vessels which were also generating hydrogen when compared to control experiments done without minerals (McCormick and Donaldson, 2016).

It should also be noted that the alteration of peridotites to serpentine decreases the permeability of the rock which inhibits further access to water (Apps and Van De Kamp, 1993). It is also useful to mention that some authors consider hydrogen to not only be the product of serpentinization but also to be a reagent producing "structural" water in serpentine (Юркова et al., 1982; Юркова and Воронин, 2008). This important point requires further study.

Serpentinization has been well studied in places where outcrops of mantle material are exposed at the surface. Mantle comes close to the surface in rift zones, but these are mainly situated beneath oceans. Rare, but more accessible locales are the ophiolite belts, where oceanic crust with underlying mantle is uplifted and exposed above the sea level. Table 1 summarizes documented locations of hydrogen-rich gas seeps associated with ophiolitic outcrops. Estimates of present-day hydrogen flow from oceanic crust serpentinization are on the order of 0.8–1.3 * 10¹¹ mol/year (0.16–0.26 Tg/year) (Canfield et al., 2006). Other studies have made the assumption that 10% of the seafloor is serpentine, to derive a maximum possible annual flux of H₂ equal to 0.38 Tmol/year (0.76 Tg/year) (Sleep and Bird, 2007). In other studies authors used drill-samples of oceanic crust to obtain hydrogen flux values of 4.5 ± 3.0 × 10¹¹ mol H₂/year (0.89 ± 0.6 Tg/year) (Bach and Edwards, 2003). Applying a recently derived estimate by this author et al. for hydrogen flow from the Semail ophiolite in Oman (Zgonnik et al., 2019) to the total surface area of the ophiolites throughout the world (Vacquand, 2011) we obtain 0.18–0.36 Tg/year, which is in the same order of magnitude as the above cited estimates. It was also suggested that olivine might function as a source of hydrogen for

Table 24
Hydrogen detected in water sampled from hydrocarbon fields.

H ₂ , %	Content	Comments	Depth, m	Country	Name of placemark	Reference
10.9	1163 cm ³ /L of total gas	Dissolved gas in ground water from Jurassic strata. Velichaevsko-Kolodeznoe oil field	3160–3164	Russian Federation	Velichaevsko-Kolodeznoe, 10.9	(Зорькин, 1989)
11.2		Dissolved gas in water, Luginetskaya field, well #159	2224–2232	Russian Federation	Luginetskaya, 11.2	(Молчанов, 1981)
13.1		Dissolved gas in water from Devonian strata. Rechytskoe oil field	2423–2438	Belarus	Rechytskoe, 13.1	(Зорькин, 1989)
12.2–14.2	139–230 cm ³ /L of total gas	Dissolved gas in water from Carboniferous strata. Mukhanovskoe oil field	2208–2138	Russian Federation	Mukhanovskoe, 14.2	(Зорькин, 1989)
9.1 (well #2)		In deep water in oil-gas field from the hydrocarbon free horizon in the wells: #2 of Olsko-Serpukhovskiy horizon and #3 of Vereisky horizon in Katchalinskaya field	2858–2878 (well #2)	Russian Federation	Katchalinskaya, 15.8	(Стадник, 1970)
15.8 (well #3)			2456–2460 (well #3)			
16.4		Dissolved gas in water from Devonian layers of Ostashkovichskoe oil field	2835–2855	Belarus	Ostashkovichskoe, 16.4	(Зорькин, 1989)
5.1 (well #5)	270 cm ³ /L of total gas	In deep water in contact with gas from wells #5 and #82 of Nizhnebashkirsky horizon in Abramovskaya hydrocarbon field	534–535 (well #5)	Russian Federation	Abramovskaya, 18.2	(Стадник, 1970)
18.2 (well #82)			2399–2407 (well #82)			
21.0		Dissolved gas in water from Bolsherechenskaya field, well #3	3145–3250	Russian Federation	Bolsherechenskaya, 21	(Молчанов, 1981)
28, up to		Dissolved gas in water from Ayyuvinskoe hydrocarbon field		Russian Federation	Ayyuvinskoe, 28	(Соколов, 1966a; Молчанов, 1981)
11.2 (well #21)	650 cm ³ /L in the well# 48;	In deep waters from Paleozoic deposits of Korobkovskaya field, Nizhnebashkirsky horizon, wells #48, 50	1780 (well #21)	Russian Federation	Korobkovskaya, 30.6	(Стадник, 1970; Зингер, 1962)
22.3 (well #48)	571 cm ³ /L in the well# 21	Bobrikovsky horizon, well #21	1439–1447 (well #48)			
30.6 (well #50)		Water in contact with hydrocarbons	1447–1466 (well #50)			
33.9		In deep water in contact with oil-gas from the well #6 of Turneisky stage in Startitskaya field	1345–1352	Russian Federation	Startitskaya, 33.9	(Стадник, 1970)
37.7		Dissolved gas in water from Proterozoic strata of Davydovskoe oil field	3490–3500	Belarus	Davydovskoe, 37.7	(Зорькин, 1989)
58.0	286 cm ³ /L of total gas	Dissolved gas in water from Meglonskaya field, well #1	2727–2734	Russian Federation	Meglonskaya, 58	(Молчанов, 1981)
24.2–86.6		Dissolved gas in water from Severnaya field, well #101	2329–2595	Russian Federation	Severnaya, 86.6	(Молчанов, 1981)
90–98		Hydrogen dissolved in oil well water	2450	Kazakhstan	Gagarinskaya, 98	(Перевозчиков, 2011)

energy applications (Schuiling, 2013).

Total estimated hydrogen flux from the global mid-ocean rift system is 0.12 Tg/year (Welhan and Craig, 1979). In comparison with ophiolites this number looks rather low. Other authors used $H_2/{}^3He$ and ${}^3He/$ heat ratios to estimate a global H_2 flux for slow-spreading ridges to obtain 89×10^9 mol/year (0.18 Tg/year) (Charlou et al., 2012). Estimated hydrogen flux from slow-spreading ridges of about 16.7×10^{10} mol/year (0.33 Tg/year) are published in (Cannat et al., 2010). Later study gave a close estimate of 19×10^{10} mol/year (0.38 Tg/year) (Keir, 2010). Another more recent work integrated in their model the spreading rate and demonstrated that hydrogen generation is higher, in the order of $\sim 10^{12}$ mol/year (Worman et al., 2016).

Moreover, hydrogen is produced exclusively by oceanic crust. Recent studies suggest that production of hydrogen from the Precambrian has been underestimated. The authors of the study estimated that the hydration process (reactions of rocks with water) may contribute $0.2\text{--}1.8 \times 10^{11}$ mol per year (0.04–0.38 Tg/year) (Sherwood Lollar et al., 2014).

Mantle rocks are not the only rocks which react with water to produce hydrogen. Basalt-water reactions were also shown to be possible (Stevens and McKinley, 2000). A study of samples of basaltic oceanic crust from the Integrated Ocean Drilling Program (IODP) demonstrated that they were enriched in hydrogen (Lin et al., 2014). The entire basaltic layer of the oceanic crust may contribute 17×10^9 mol H_2 /day (12.6 Tg/year) (Holloway and O'Day, 2000). Other authors estimated the global flux of H_2 from basaltic oceanic crust could result in 3.75 Tmol/year of H_2 (7.5 Tg/year) (Sleep and Bird, 2007). Another study suggests that hydrogen can be produced by the reaction of water with Fe^{2+} -containing minerals at the depths of 10–15 km. The permeability of microcracks in excess of 10^{-14} cm² can extend to depths of 15 km. According to the authors of this study such permeability is enough to permit substantial fluid movement. It is estimated that basaltic rock in equilibrium with water should contain 7 ppm of H_2 by weight. This is equivalent to 75 cm³ per kg of rock or 12 L H_2 per L of water in equilibrium with the rock (Hawkes, 1980). However, some works suggest that basalt-groundwater interaction can not produce large quantities of hydrogen because the surfaces of water-mineral contacts quickly become de-activated by their reaction products (Anderson, 1998).

Other minerals, containing Fe(II) could yield H_2 in reactions with water. It was shown that siderite could generate hydrogen under certain conditions (Milesi et al., 2016).

This question related to water consumption should be addressed in detail, as the majority of currently considered geologic sources of hydrogen imply a reaction of water with minerals speculated to be the only source for natural hydrogen (via serpentinization or other reactions discussed below). Because this reaction is irreversible, it is necessary to estimate the rate of water consumption. With a hydrogen production rate on the order of 23 ± 8 Tg/year via different geological mechanisms (Table 25), assuming all of them are consuming water, the entire hydrosphere (1.4×10^{24} g) would be consumed in a time frame of 6.6 ± 3 billion years. Of course, some portion of hydrogen produced is recycled back to water abiogenically and/or via biological consumption (bypassing through organic compounds), but oxygen still remains bonded in rocks. Therefore, the processes of hydrogen generation through water reaction with rocks can be seen from another perspective: as a process by which surface oxygen from water is redistributed through burial in rocks.

3.3. Other reactions in minerals

Several other mechanisms have been proposed to explain how hydrogen may form in rocks. A frequently cited article suggests that hydrogen can be produced from the reaction of water with fresh rock surfaces along active fault zones (Wakita et al., 1980). Recent friction experiments on rocks showed that fault systems may produce hydrogen

during rock displacement along fractures (Suzuki et al., 2015). However, the chemical reactions taking place are not fully explained. Other articles propose that hydrogen is generated in a reaction between free radicals on fresh rock surfaces with water (Sugisaki et al., 1983; Wiersberg and Erzinger, 2008). Yet such reactions must simultaneously produce oxidized species such as peroxides or oxygen in addition to hydrogen. The pathways of oxidized compounds are not addressed. Moreover in the laboratory, rock samples taken from the fault zone with the highest observed hydrogen concentration were incapable of generating H_2 (Sugisaki et al., 1983), which puts into question the proposed mechanism for hydrogen generation. More recent laboratory experiments with different types of dry and wet rocks showed that hydrogen was generated (Hirose et al., 2011; Hirose et al., 2012), however, the authors did not explore the possible mechanisms for this process and the role of oxygen in the reaction chain. The authors used their results to estimate annual global hydrogen flow generated by rock friction during earthquakes. They concluded that it is equal to 2.3×10^2 mol/m²/year, which gives 235,000 Tg of H_2 per year, which appears to be an unrealistic value, given that it is 3–4 orders of magnitude greater than all other geological estimates combined together (see Table 25). Moreover, such a rate of production would appear to have consumed all available water on Earth in only 0.2 million years.

During displacement of rocks along faults friction creates fresh surfaces which can allow water to contact and react with Fe(II)-containing minerals. Hydrogen has been generated in the laboratory by combining water with fine minerals, crushed in situ with a mill (Молчанов, 1968; Голосов et al., 1966). Even after 7 weeks of grinding, hydrogen was still being produced. The authors of this study propose that the hydrogen generated is the result of a reaction between Fe particles (formed in the iron mill) with water (Голосов et al., 1966) and from the reaction of Fe (II)-containing minerals (Молчанов, 1968). One of the authors developed the idea and published an entire book (Молчанов, 1981) proposing that hydrogen could form naturally when minerals are ground together in fault zones. However, the possibility that the released hydrogen could be either pre-existing hydrogen stored in pores or hydrogen migrated along faults from depth, and not generated by friction, was not evaluated.

Cataclasis is a term applied to the crushing of minerals during metamorphism. Laboratory experiments performed to investigate the effects of crushing on wet granite and quartz samples demonstrated that hydrogen can be generated as a result of cataclasis (Saruwatari et al., 2004; Kita et al., 1982; Parkes et al., 2018). However, hydrogen has also been generated in experiments crushing synthetic materials like pyrex, alumina and silica (Kita et al., 1982; Parkes et al., 2018). More surprisingly, high values for generated hydrogen have been reported in experiments where samples were dry milled without water, and the authors have not addressed the issue of possible sources of hydrogen generated in these experiments. Another study obtained hydrogen by crushing rock samples from the Arctic and Antarctic and making them react with 0°C water (Telling et al., 2015). Based on analyses of fluid inclusions in rocks from fault zones the authors of another study proposed that hydrogen is formed by brittle fracturing (McMahon et al., 2016). Nevertheless, the authors of the aforementioned studies do not address the fate of any excess in oxygen produced by the reactions of water with free radicals which were proposed as a mechanism for the generation of hydrogen. This question was not addressed because half-reactions were used rather than balanced full equations. Assuming that water reacts with silica or that silicates give off hydrogen, excess in oxygen can yield either unstable peroxides or molecular oxygen. Another part of the water molecule in the mechanism proposed by the authors yields hydroxyl groups in silicates. However, as already pointed out in other research, exposed mineral surfaces quickly become de-activated in natural environments by reaction products, principally silica gels. Such gels limit the diffusion of water to the underlying unreacted surfaces and reduce their capacity to produce H_2 (Anderson, 1998).

Hydroxyl groups are at the core of another mechanism, which was

proposed as an explanation for the release of hydrogen when the rocks are under stress. It was suggested that H_2 could be formed by the reaction of two hydroxyl groups, forming H_2 and a peroxide anion O_2^{2-} , which in turn would make a peroxide bridge between two silicon atoms in silicates (Freund, 1984; Freund et al., 2002). Based on the results of laboratory experiments the authors estimate that this mechanism could produce 0.005 m^3 of H_2 per m^3 of rock. In comparison, the serpentinization process can produce 20 m^3 H_2 per m^3 of rock. Although peroxy bonds were observed in pure synthetic compounds, there is a lack of evidence for them in natural rocks (Kubatko et al., 2003). Probably because peroxides are unstable compounds and should quickly decompose giving off O_2 . It was later suggested that peroxy bonds break under stress, producing according to the paper's authors terminology "positive holes" (chemically equivalent to O^-), which rapidly propagate to unstressed rock. As the "positive holes" cross the rock-water boundary, the rock turns into a hydrous silica gel and cations are released, leading to the dissolution ("electrocorrosion") of the rock (Freund and Freund, 2015; Scoville et al., 2015; Balk et al., 2009). However, the fate of any remaining oxygen after the breakage of peroxy bonds, remains unclear.

3.4. Water radiolysis

Radiolysis of water is often cited as a possible source of hydrogen. The energy from radioactive decay is high enough to break apart molecules of water into their component parts, oxygen and hydrogen, and the Earth's crust contains significant quantities of radioactive elements, mainly U, Th and K. This idea of rock alterations by ionizing radiation was proposed in 1930's by V. I. Vernadsky (Vovk, 1982). According to some authors, no other known H_2 -generating mechanism can produce large amounts of hydrogen (Lin et al., 2005a).

Ionizing radiation provokes excitation and ionization of molecules, which leads to an increase in their reactivity and the formation of free radicals, the most reactive chemical species. For example, a single, 1 MeV α -particle can ionize 10^5 molecules as it loses energy (Dubessy et al., 1988). When this energy is passed to water molecules, they can decompose to give H_2 and H_2O_2 , which will quickly decompose to O_2 and water. It has been estimated that only 1% of the total energy from the radiogenic decay is absorbed by pore water. The rest is absorbed by the mineral matrix and converted to heat. Thus, H_2 yield is proportional to the rock porosity filled with water (Lin et al., 2005b). In a book dedicated to the role of radiolysis in geochemistry even smaller numbers are given: only a small amount of radioactive energy (0.002–0.06% in igneous rocks and 0.03–0.6% in clays) is consumed to transform the chemical potential of compounds while most of the energy is dissipated as heat. In multicomponent systems radioactive energy is distributed between all components, thus only a part of it is used in the radiolysis of water (Bobk, 1979). In a recent experimental study it has been shown that the action of γ -radiation on hydrogen-containing molecules and mixtures, including water solutions, produces H_2 . Note, that higher hydrogen yields were observed for brines compared to pure water (Wang et al., 2019). Nevertheless, some researchers have developed models for hydrogen generation through radiolysis without making a single H_2 measurement (Blair et al., 2007).

Estimates for possible hydrogen production from these mechanisms vary greatly. One author estimated the volume of radiolytically dissociated water in the sedimentary section to be about 0.026 m^3 per year (it is possible that this is a typing error and the author meant km^3 , even in this case the value is not very high: only $0.00032 \text{ Tg } H_2$ per year) (Vovk, 1982). The book on water radiolysis gives a much higher value: $0.24 \cdot 10^{23} \text{ g}$ during the period of $4 \cdot 10^9$ years (6 Tg/year) (Bobk, 1979). Recent estimates for radiolysis reactions in continental Precambrian crust give H_2 generation rates of $0.16\text{--}0.47 \cdot 10^{11} \text{ mol per year}$ ($0.03\text{--}0.09 \text{ Tg/year}$) (Sherwood Lollar et al., 2014).

It is very important to keep in mind that during water decomposition by radiolysis hydrogen is not the only product. Transformation of

the energy of radioactive decay in water/rock systems has the effect of oxidants being simultaneously produced with reducers like hydrogen, i.e. components with opposite chemical properties (Vovk, 1982). In the case of water decomposition, this should mainly be hydrogen peroxide, H_2O_2 , which should quickly decompose to O_2 . Indeed, experiments with irradiation of water/mineral mixtures consisting of the most common rock-forming minerals resulted in the generation of a hydrogen-oxygen gas mixture with O_2 concentrations of up to 30–35% (Bobk, 1979). One should therefore expect to find nearly stoichiometric proportions of H_2 to O_2 gas at locations where water radiolysis is thought to have occurred, but this is not the case. Oxygen has not been measured in studies exploring chemical composition of inclusions (Parnell and Blamey, 2017a). Moreover, pure hydrogen was detected by Raman spectroscopy in fluid inclusions in quartz from a Precambrian uranium deposit in Oklo, Gabon while fluid inclusions from two other Precambrian uranium deposits (in Canada) are almost pure oxygen (Dubessy et al., 1988). If the origin of these gases is radiolysis, the stoichiometry of the gas mixtures (no oxygen in the Oklo inclusions and no hydrogen in the samples from Canada) can not be explained.

In another study hydrogen yield was estimated for the entire residence-time of water in an aquifer, which was expected to range from 3 to 80 million years. Comparisons of calculated values with measured H_2 concentrations in natural environments show numbers of the same order of magnitude (Lin et al., 2005b). However, hydrogen is a very mobile gas, so its diffusion rate should have been taken into account, which was not done. The analyses of inclusions in rocks of different age show no correlation between hydrogen concentration and the age of the rock (McMahon et al., 2016) while another study has opposite conclusions, that Precambrian samples contain more hydrogen than younger ones (Parnell and Blamey, 2017a).

When making estimates of hydrogen generation over geological time, one should always account for hydrogen diffusion. Because hydrogen is continuously leaving the reaction zone, the oxidation state of the remaining fluid should increase (Dubessy et al., 1988). Estimated O_2 production in the crust from water radiolysis during a period of $4 \cdot 10^9$ years gives $1.91 \cdot 10^{23} \text{ g}$ – a quantity large enough to oxidize the entire Earth's crust (Bobk, 1979). Many studies citing water radiolysis as a possible source for natural H_2 do not address a probable concomitant increase in oxygen and therefore omit to propose a pathway for any oxidized species produced by radiolysis. Hydrogen peroxide has not been detected in rock samples considered to have been exposed to the action of ionizing radiation (Lin et al., 2005a). Examples of other hyper-oxidized compounds in the crust are extremely rare and limited to two peroxide uranium minerals (Kubatko et al., 2003).

Another mechanism for hydrogen generation related to the radioactive decay of elements is connected to the change in valence of atoms. During radioactive decay isotopes transform into new elements with other chemical properties. Such elements may be more or less reactive with respect to their parent atoms. In fact, the cumulative reactivity of new atoms to parent atoms exceeds 0.5 times the reactivity of parent isotopes. This excess reactivity is mainly caused by the accumulation of ^{40}Ca and ^{87}Sr formed from ^{40}K and ^{87}Rb . New elements could react with water, producing hydrogen. Th(IV) and U(IV), in their turn, while becoming Pb(II) also liberate one additional atom of oxygen, thus increasing the oxidation state of the medium. According to the authors of the study, the quantity of hydrogen generated should be comparable to that of radiogenic helium, because radioactive decay of Th and U produces helium. For 100 km^3 of crustal rock, the estimated annual production of H_2 by this mechanism is equal to 0.15 m^3 H_2 (Savchenko, 1958).

One separate case should be discussed in more detail. As is shown in Tables 12 and 22, high concentrations of hydrogen are systematically detected in potassium salt deposits. It is commonly proposed that hydrogen may have a water-radiolysis origin because of K and Rb radioactive decay (Bobk, 1978; Parnell and Blamey, 2017b). In carnallite and sylvinites, irradiation from ^{40}K acts on water molecules generating

hydrogen, which fills the pore spaces, sometimes reaching pressures on the order of megapascals (Vovk, 1982). At the same time, produced oxidizing species transform iron to hematite which lends a red color to the salt (Savchenko, 1958). However, observed H_2/Ar ratios and carnallite/sylvinite H_2 concentration ratios don't support this idea (Bobk, 1978). Another article provides an additional argument against a radiation-induced origin for hydrogen in K and Na minerals. In this article describing experiments done on blue sylvinite, which has its coloration as a consequence of ionizing radiation, no detections of hydrogen were reported (Морачевский et al., 1937).

An alternative mechanism for hydrogen generation in salt deposits has been proposed. It was noted that the volumes of hydrogen extracted from salt samples were higher when the salt blocks were dissolved in water compared to crushed salt samples (Bobk, 1978; Nesmelova and Travnikova, 1973). In potassium deposits the radioactive isotope ^{40}K undergoes branching decay with the formation of ^{40}Ar (12%) and ^{40}Ca (88%). The Calcium-40 cannot be completely transformed into chloride and accumulate in the crystal structure of the salt minerals in its metallic state. During dissolution, elemental calcium readily reacts with water yielding molecular hydrogen (Nesmelova and Travnikova, 1973). Another study proposed that in addition to ^{40}Ca , ^{87}Sr formed from ^{87}Rb could also react with water to give hydrogen. However, there are some discrepancies between the calculated and observed quantities of hydrogen (Savchenko, 1958). The author of another study suggests that reaction of ^{40}Ca with water is not the only mechanism generating hydrogen. The author proposes that water radiolysis is also involved at the same time (Bobk, 1979). Another reaction is possible during the dissolution of carnallite for the extraction of trapped gases. It has been proposed that some hydrogen could be formed by the reaction of the F-centers of the carnallite crystalline structure (created by the action of ionizing radiation) with water (Bobk, 1978).

Some other processes related to water radiolysis should also be taken into account. Noble gases form during the radioactive decay of certain elements. Helium-4 is produced in the radioactive decay chain reactions of U and Th, and radioactive K decomposes to ^{40}Ar . These gases should be present together with hydrogen if water radiolysis takes place in connection with the decay of those elements. Taking into account the above rates for the conversion of radioactive energy to hydrogen ($\leq 1\%$), the quantity of 4He should greatly exceed the quantity of H_2 . Indeed, some studies note, that the quantity of hydrogen produced by water radiolysis could not exceed the quantity of radiogenic helium (Savchenko, 1958). Moreover, any estimate of hydrogen production from radiolysis should take into account the rate of recombination of oxidized and reduced species, formed by the action of high energy particles on water.

Therefore, water radiolysis never happens as a separate reaction, but rather as a complex of connected processes. Being focused on explaining hydrogen generation, researchers often appear to have forgotten or omitted the consideration that radiolysis generates oxidizing chemical species at the same time. When hydrogen volumes are significant it is not possible to attribute its origin to water decomposition driven by radioactive decay. Indeed, it has been shown that radioactive decay is insufficient to produce the measured volumes of hydrogen (Стадник, 1970).

3.5. Biological activity

Biological activity is often used as an explanation for the origin of natural hydrogen in natural gas samples. H_2 can be produced biologically by the anaerobic decay of organic matter (Morita, 1999), fermentation (Conrad, 1996) and by nitrogen fixing bacteria (Morita, 1999; Conrad, 1996; Conrad and Seiler, 1980). In the laboratory and with sufficient substrate many different bacteria will generate hydrogen, as shown in the next overview (Nandi and Sengupta, 1998). Although it is true that microorganisms may produce hydrogen *in vitro*, the fact is that in nature hydrogen-producing bacteria always co-exist

with a suitable hydrogen-utilizing organism (Nealson et al., 2005). Thus, all biologically produced hydrogen is rapidly converted to other compounds (Morita, 1999; Gregory et al., 2019). Moreover, hydrogen producers can not exist without hydrogen consumers because hydrogen inhibits their activity (Hoehler, 2005). A recent comprehensive review combined the knowledge of microbiology in environments with elevated hydrogen content (Gregory et al., 2019).

This topic deserves particular attention not for the production of hydrogen, but for its consumption. Two mechanisms for hydrogen decomposition are possible: by microorganisms and by the soil itself (Conrad and Seiler, 1981). Uptake of hydrogen by soil is responsible for a loss of about 80% of atmospheric hydrogen (Constant et al., 2010; Rhee et al., 2006). Maximum H_2 production and consumption activity was found in the surface layer of soils, where most of the microbial biomass is located (Conrad, 1996). Indeed, it was reported that hydrogen production by the soil itself was not observed, and the production rate of H_2 was shown to be negligible compared to its' consumption rate (Conrad and Seiler, 1985). It was proposed, that non-biological processes are more important than microbial activity in H_2 decomposition (Conrad and Seiler, 1981).

In studies of different soil types it was found that production of H_2 in wetland soils is intensive, but most of the produced hydrogen is immediately converted by methanogens to CH_4 (Conrad, 1996). In upland soils which are oxic soils, hydrogen is mainly produced by nitrogen-fixing bacteria and consumed by abiotic enzymes rather than by microorganisms, while in wetland anoxic soils, hydrogen is produced by bacterial fermentation and consumed by methanogens, sulfate reducers, denitrifiers, ferric iron reducers and Knall gas bacteria (Conrad, 1996; Seiler and Conrad, 1987). It has been reported that most hydrogen is consumed within 1 cm of point sources, and its presence significantly decreases the soil's capacity to oxidize other reduced gases like CH_4 and CO (Piché-Choquette et al., 2018).

The hypothesis that ambient atmospheric concentrations of hydrogen are not sufficient for bacterial growth (Conrad, 1996) while enzymes remain active to rapidly consume hydrogen from the air, remained for decades the basic assumption of many soil uptake studies. However, later Constant et al. identified an aerobic microorganism (*Streptomyces* sp. PCB7) that can consume H_2 at tropospheric ambient mole fractions, and suggested that active metabolic cells could be responsible for the soil uptake of H_2 rather than extracellular enzymes (Constant et al., 2010). They showed that uptake activity at ambient H_2 levels is widespread among the streptomycetes abundant in a broad variety of settings including desert soils, forests and peatlands. They postulated that specialized H_2 -oxidizing actinobacteria are responsible for the most important sink term in the atmospheric H_2 budget (Constant et al., 2010). Recently it was discovered that some microorganisms in Antarctica use only atmospheric H_2 as an energy source (Ji et al., 2017).

Therefore, soils are the primary sink in the atmospheric H_2 budget. It was proposed that the consumption rate of hydrogen by soils is strongly influenced by soil moisture and only slightly by its temperature (Conrad and Seiler, 1985). In more recent studies it has been shown that the maximum hydrogen uptake by moderately humid soils takes place at 30°C (Ehhalt and Rohrer, 2011). It is interesting, that soil remains active in the uptake of hydrogen at temperatures below freezing, temperatures at which hydrogenase, the enzyme responsible for hydrogen consumption, remains active. This fact mitigates in favor of H_2 uptake by living bacteria (Ehhalt and Rohrer, 2011).

Hydrogen consumption by soils drastically increases with concentration. When the concentration of H_2 rises to its lower explosive limit or LEL ($\sim 4\%$) the consumption rate by soil increases by up to 1000 times (Sukhanova et al., 2013). This can be explained by the existence of two metabolically diverse groups of H_2 -oxidizing microorganisms displaying different kinetic rates for H_2 consumption (Constant et al., 2010). To predict a soils capacity for hydrogen uptake, based on the results of experiments, it was proposed that total carbon

content and relative abundance of H_2 -oxydizing bacteria be used (Khdhiri et al., 2015). It was reported that hydrogen can also be oxidized in the rootzone or rhizosphere (Conrad, 1996). A measure of the strength of soil uptake for hydrogen is called deposition velocity, which ranges from 0.06 to 0.22 $cm\ s^{-1}$ depending on the soil type (Chen et al., 2015). Hydrogen deposition velocities for various ecosystems were collected (Ehhalt and Rohrer, 2009). Estimates of hydrogen uptake by soils vary from: 120 Tg/year (Hawkes, 1980), 56 ± 41 Tg/year (Novelli et al., 1999), 90 ± 20 Tg/year (Conrad and Seiler, 1981; Conrad and Seiler, 1980; Seiler and Conrad, 1987), 88 ± 11 Tg/year (Rhee et al., 2006) and 60^{+30}_{-20} Tg/year (Ehhalt and Rohrer, 2009).

Estimates are available for the production of hydrogen by biological processes. Given that soils are the main sink for hydrogen, it is difficult to differentiate the amount of hydrogen that goes into the atmosphere from that consumed by microorganisms and soil enzymes. It has been suggested that the microbial production of hydrogen in soils plays only a minor role in the hydrogen atmospheric budget (Conrad, 1996). Based on field studies of hydrogen emissions from nitrogen-fixing legumes (Conrad and Seiler, 1979), total H_2 from biological N_2 fixation is estimated to be on the order of 2.4–4.9 Tg/year (Conrad and Seiler, 1980). This number seems to be much higher than earlier estimates for total biological H_2 production from paddy soils, enteric fermentation of animals, upland fields and forests which totals to 0.017 Tg per year (Koyama, 1963). Indeed, recent work suggests that 97% of hydrogen produced by nitrogen-fixing bacteria is removed from the soil by microorganisms and soil activity before entering atmosphere (Chen et al., 2015).

In its turn, the fermentation of organic matter does not give high yields of hydrogen. The possibility of hydrogen being generated by the fermentation of complex organic molecules was evaluated with calculations of the Gibbs free energy of fermentation, however, it was concluded that microbial fermentation is unlikely to be the generating mechanism for observed high hydrogen concentrations (Lin et al., 2005a).

It is interesting to note, that termites and some Protozoa can also produce H_2 . However, nothing has been published on higher organisms which metabolize hydrogen (Conrad, 1996). Estimates show that termites may emit up to 200 Tg of H_2 per year (Zimmerman et al., 1982), which is very high number, when compared to other sources of H_2 (see Table 25) and is considered to be too large by other authors (Ehhalt and Rohrer, 2009). Most of this hydrogen may be rapidly consumed *in-situ* by symbiotic methanogens. It was suggested that only a portion of the produced hydrogen could be released to the atmosphere, on the order of 1 Tg per year (Ehhalt and Rohrer, 2009).

Ocean waters have often been reported to be supersaturated with hydrogen relative to its atmospheric concentration (hydrogen concentrations are higher than equilibrium with the atmosphere) (Bullister et al., 1982). The waters of the Caspian Sea were reported to contain up to 7.3 $cm^3\ H_2/L$ (Levshounova, 1991) with no explanation for the source of this gas. Some Atlantic waters are supersaturated by a factor of three (Schmidt, 1974). This means that the ocean should be a source of this gas to the atmosphere. Estimates for hydrogen production in oceans are 3 ± 2 Tg/year (Novelli et al., 1999), 4 ± 2 Tg/year (Seiler and Conrad, 1987) and 6 ± 3 Tg/year (Ehhalt and Rohrer, 2009). Recent work, based on isotopic measurements of hydrogen dissolved in oceanic waters suggests that it is possibly produced by nitrogen fixing organisms with input from a “significant different source” (Walter et al., 2016). The authors suggest that it may be of photochemical origin, but it is also just as likely that the source may be geological. Indeed, another study suggests that concentrations of hydrogen do not undergo diurnal variations, which appears to eliminate the photochemical and biological hypotheses for hydrogen sourcing (Bullister et al., 1982).

There are experimentally proven examples for the absence of hydrogen producing microorganisms in samples from wells with high hydrogen content, such as in this reference (Войтов and Осика, 1982). Another study checked deep water samples for the presence of

hydrogen-producing and hydrogen-consuming bacteria. For 13 probes containing dissolved hydrogen almost no biological activity was detected (Стадник, 1970). No bacterial activity was detected in hydrogen-rich water in aquifers close to petroleum deposits (Зингер, 1962). Only one paper indicated that hydrogen in a small number of samples originated from biological activity in drilling mud (Несмелова and Рогозина, 1963).

It should be noted that any hydrogen in samples from very deep wells where temperatures and pressures are likely too high to sustain life are unlikely to be the result of bacterial activity (Войтов and Осика, 1982). However, there are a growing number of examples of hydrogen-based deep microbial communities, living at great depths in the ocean and in fractures in the Earth's crust (see the Section on 5.2 Hydrogen and life). Estimated rates of hydrogen consumption by such organisms are not yet available, but it is probable that hydrogen consumption rates are higher than the diffusion rate. In which case low hydrogen concentrations in the majority of environments can be explained by the action of biological activity (Fedonkin, 2009).

3.6. Atmospheric hydrogen

An average hydrogen concentration in the atmosphere has been estimated to be 0.531 ppm (Novelli et al., 1999). However, average hydrogen concentrations vary between the equator and poles, reaching 545 ppb at the equator, compared to 535 ppb at 88°S and 490 ppb at 80°N (Ehhalt and Rohrer, 2009). Global trends of hydrogen concentration show either an increase of 3.2 ± 0.5 ppb per year (Morita, 1999) or a decrease by 2.3 ± 0.5 ppb per year (Novelli et al., 1999). It has been suggested that such discrepancies are related to the large inter-annual or intra-annual variability in H_2 mixing ratios (Ehhalt and Rohrer, 2009). Recent studies have shown that the global mean δD value of atmospheric H_2 is about +130‰ (Batenburg et al., 2011) and values for different sources of hydrogen are reviewed in (Ehhalt and Rohrer, 2009). The total volume of H_2 in the atmosphere is estimated to be around 155 ± 10 Tg (Novelli et al., 1999), while different estimates range from 76 to 172 Tg (Price et al., 2007).

Atmospheric chemistry is complex, and a detailed description of reactions is beyond the scope of this paper. More information can be found in this comprehensive review of tropospheric hydrogen (Ehhalt and Rohrer, 2009) and in these books (Hewitt and Jackson, 2009; Warneck, 1999).

Hydrogen, being the lightest of all gases, readily escapes the Earth's gravitation, and in combination with its high reactivity, makes its residence time in the atmosphere very short. Estimates range from 4 to 7 years (Schmidt, 1974), 2–3 years (Novelli et al., 1999), 1.9 years (Bullister et al., 1982; Price et al., 2007) and even 1.4 years (Rhee et al., 2006). A recent review of hydrogen in the troposphere proposes a 2 year residence time (Ehhalt and Rohrer, 2009). Such short-term residence times imply that there is a constant supply of hydrogen to atmosphere. Researchers have proposed possible sources for atmospheric hydrogen to be anthropogenic, biological and water photolysis (Schmidt, 1974), as well as the oxidation of methane and other hydrocarbons and also oceans and soils (Warneck, 1999). The annual supply of hydrogen to the Earth's atmosphere from all sources was estimated to be on the order of 40–130 Tg/year (Adushkin et al., 2006). Other estimates give values of 81 Tg/year (Warneck, 1999), 73 Tg/year (Price et al., 2007) and 76 ± 14 Tg/year (Ehhalt and Rohrer, 2009). However, none of these estimates take account of geologically supplied hydrogen.

In addition to terrestrial sources of hydrogen, atmospheric hydrogen includes hydrogen produced *in situ* by photochemical reactions. Note that, according to (Berkner and Marshall, 1966), photodissociation of water is not a significant source of hydrogen to the atmosphere. This is as a result of not only the limited transfer of water to high altitudes through freezing, but also because oxygen in the atmosphere acts as a barrier to the photodissociation of water. A variation of only 0.001%

from the present day oxygen concentration in atmosphere is enough to stop the H_2O photodissociation (Berkner and Marshall, 1966). The main reaction producing hydrogen in the atmosphere is oxidation of methane and other hydrocarbons, which passes through a photodissociation of formaldehyde step (Warneck, 1999). Estimates from the oxidation of methane yield $23 \pm 8 \text{ Tg H}_2/\text{year}$ and $18 \pm 7 \text{ Tg H}_2/\text{year}$ for other hydrocarbons (Ehhalt and Rohrer, 2009). Yields calculated by other authors are available in the same study. While the oxidation of CH_4 is considered to be the main source for H_2 and CO in the atmosphere, observed increases in CH_4 and CO have not been accompanied by a corresponding increase in H_2 , which begs the question as to the mechanism proposed (Ehhalt and Rohrer, 2009).

As has been shown above, the residence time of hydrogen in the atmosphere is likely to be very short because it is rapidly consumed by different processes and it also escapes into space. Another study gives estimates for the total consumption rate of hydrogen by the atmosphere, or its' consumption by various so-called "sinks" at a rate of 70 Tg/year ($784 \cdot 10^9 \text{ m}^3/\text{year}$) (Warneck, 1999). In the Section 3.5 Biological activity of this review it was shown that soils are very efficient at consuming hydrogen. However, biologic activity is not the only important sink for this gas. Atmospheric sinks include oxidation by hydroxyl radicals and escape into space. Photolytic oxidation was estimated to consume 10 Tg/year (Hawkes, 1980) and $8 \pm 3 \text{ Tg/year}$ (Seiler and Conrad, 1987). More recent studies give a higher number of $19 \pm 5 \text{ Tg/year}$ (Ehhalt and Rohrer, 2009; Novelli et al., 1999). Photolytic oxidation is of great significance because it affects the ozone cycle. It is described in more detail in the Section 5.3 Atmosphere.

The escape of hydrogen from the atmosphere is an extremely important aspect of this review because it is by this mechanism that the Earth loses part of its mass (discussed in the Section 5.1 Hydrogen as a component of Earth degassing). The three generally accepted mechanisms for hydrogen escape from the atmosphere are: thermal, non-thermal and polar wind (Yung et al., 1989). Thermal escape is also called "Jeans escape", which is described by a Maxwell distribution accounting for the kinetic energy and mass of a molecule determining its velocity. The less massive is a molecule of gas, the higher is the average velocity of the same molecule at a given temperature, and the higher is the likelihood of that molecule reaching the Earth's gravitational escape velocity. It is for this reason that hydrogen escapes more readily from the atmosphere than any other gas. Models have shown that the escape of hydrogen from the Earth's gravitation at 100 km of altitude occurs by conversion of H_2 into atomic hydrogen in the thermosphere (Hunten and Strobel, 1974). Non-thermal escape involves collisional processes energizing hydrogen species above thermal energies. Polar wind is a term defined to explain the movement of charged particles along the lines of the Earth's magnetic field. Hydrogen escape is also controlled by its source and the effectiveness of upward transport (Yung et al., 1989). The Earth's geocorona, detected in 1968 by the observations from the OGO-5 spacecraft, is composed mainly of hydrogen atoms, and was also photographed by Apollo 16 Moon landing expedition. A recent study demonstrated that a "geotail" composed of hydrogen atoms extends beyond the orbit of the Moon (Baliukin et al., 2019). Because of the pressure generated by the Solar wind radiation, the geocorona is compressed on the day side and extended on the night side of the planet forming a hydrogen "tail" downwind the planet.

The calculated that hydrogen escape rate from Earth to space is $1\text{--}4 \cdot 10^8 \text{ atoms/cm}^2\text{s}$ (Hunten, 1990). Using the data from the article ($5 \cdot 10^{26} \text{ atoms/s} = 10^8 \text{ atoms/cm}^2\text{s}$) we obtain $0.8\text{--}3.3 \text{ kg/s}$. The author states that the most probable value is $2.8 \cdot 10^8 \text{ atoms/sm}^2\text{s}$, which is equivalent to $2.3 \text{ kg H}_2/\text{s}$ (0.07 Tg/year) (Hunten, 1990). This is close to other estimates of $3 \text{ kg H}_2/\text{s}$ (0.09 Tg/year) (Catling and Zahnle, 2009) and $8 \text{ kg H}_2/\text{s}$ (0.25 Tg/year) (Белов et al., 2009). Another article suggests that the mean escape rate of hydrogen from the atmosphere cannot be much more than about $2 \cdot 10^8 \text{ cm}^{-2}\text{s}^{-1}$ (equivalent to $2.4 \text{ kg H}_2/\text{s}$ or 0.08 Tg/year) (Brinkmann, 1971). It is very close to the estimated daytime flux of hydrogen based on *in situ*

measurements from the Atmosphere Explorer C satellite, equal to $3.2 \pm 1 \cdot 10^8 \text{ atoms/cm}^2\text{s}$ (equivalent to $2.6 \pm 0.8 \text{ kg H}_2/\text{s}$ or $0.08 \pm 0.03 \text{ Tg/year}$) (Breig et al., 1976). It is also interesting to note that observations of Venus and other planets show hydrogen escaping from their atmospheres. The calculated escape ratio for Venus is $0.2\text{--}2.7 \cdot 10^7 \text{ atoms/cm}^2\text{s}$ ($0.02\text{--}0.22 \text{ kg/s}$, $0.0005\text{--}0.007 \text{ Tg/year}$) (Hunten, 1990).

Because it is assumed that the main mechanism for hydrogen generation is related to reactions of water, an important element in estimates for hydrogen loss that should be addressed are losses of hydrogen to space. These losses are well defined, therefore there should also be (as a result of these losses) a contingent decrease in planetary water volumes, the main hydrogen-containing compound on the surface of the Earth. Taking estimates of current hydrogen loss to space from Table 25, and a mass for the hydrosphere of $1.4 \cdot 10^{24} \text{ g}$ and that the oceans started to appear 4.4 Gyears ago (Wilde et al., 2001), we can obtain a cumulative total loss of water from the hydrosphere of $0.64\text{--}2.25 \text{ Tg water/year}$, which amounts to a cumulative loss of $2.8\text{--}9.9 \cdot 10^{21} \text{ g}$ ($0.2\text{--}0.7 \%$) of the total ocean volume since the ocean's initial formation. However, isotopic studies of deuterium to hydrogen (D/H) ratios in water samples from rocks and ocean water lead to higher percentages for the reduction in ocean volume through time. The studies suggest that 26% (Pope et al., 2012) to 36% (Yung et al., 1989) of the present ocean volume may already been lost. Indeed, some studies suggest that hydrogen losses in early Earth history of the Earth were much greater, up to $1\text{--}5 \cdot 10^{14} \text{ H}_2 \text{ molecules cm}^{-2} \text{ s}^{-1}$ (Pepin, 1991), which is 6 orders of magnitude greater than present day loss estimates (see the Section 3.6 Atmospheric hydrogen). Such processes may have depleted the Earth of water contributing to the oxidation of its surface because the oxygen from original water would remain at the Earth's surface.

On the other hand, there is the possibility of hydrogen being trapped in the form of protons from the Solar wind by the Earth's magnetic field. It was estimated that the mean flux of protons penetrating over one pole is $10^{24} \text{ protons/s}$ with variations of one order of magnitude (Hardy et al., 1989). Assuming all protons recombine to H_2 , this gives 0.8 g/s (0.000025 Tg/year), a negligible number compared to estimates of hydrogen escape rates.

3.7. Volcanoes and hydrothermal systems

Hydrogen is the third most prevalent volcanic emanation after water and CO_2 . The current hypothesis used to explain its presence depends on the nature of the lava, because the composition of the gases are in thermal equilibrium with molten rock (Соколов, 1971). A concentration of 1% H_2 is expected at equilibrium temperatures of around 500°C with an FMQ (Fayalite, Magnetite, Quartz) buffer (Arnorsson, 1985). It has been reported that in geothermal fluid systems the mole fraction of hydrogen $x(\text{H}_2)$ is usually lower than 10^{-3} at 200°C (Arnorsson, 1985). However, as shown in examples from Tables 5 and 6, hydrogen concentrations in volcanic gases and hydrothermal systems may be much higher than theoretical water equilibrium concentrations indicating that other sources are involved. Many studies suggest hydrogen is at the origin of volcanic activity. They are discussed in the Section 5.1 Hydrogen as a component of Earth degassing.

Simple thermal decomposition of water is improbable because the equilibrium of the reaction is unfavorable for hydrogen generation. The water decomposition reaction is non-spontaneous except at very high temperatures. Even at $1000\text{--}1500^\circ\text{C}$ the percentage of thermally dissociated water is low. It begins to become significant at the higher temperatures of $2000\text{--}3000^\circ\text{C}$ and low pressure (0.1 bar) (Соколов, 1966b; Lede et al., 1983).

Calculated estimates of H_2 released by volcanoes were only based on the assumption that H_2 and CO_2 are in equilibrium with the FMQ buffer. Flow values of $4.8 \pm 3.6 \cdot 10^{12} \text{ mol/year}$ ($9.6 \pm 7.2 \text{ Tg/year}$) were estimated by (Holland, 2002). Hydrogen flow from the most

active volcano in Antarctica, Erebus, was estimated at 30 g/s (0.001 Tg/year) (Moussallam et al., 2012) and for Mt. Etna in Europe at 0.00065 Tg/year (Aiuppa et al., 2011). Hydrogen fluxes from subaerial volcanoes is estimated at $0.9\text{--}3.4 \times 10^{11}$ mol/year (0.18–0.7 Tg/year), and from mid-ocean ridge volcanoes at $0.07\text{--}0.27 \times 10^{11}$ mol/year (0.02–0.05 Tg/year) (Canfield et al., 2006). Another study indicates that annual hydrogen flow from subaerial volcanoes is poorly understood and estimates it at 0.24 Tg/year (0.24 Tg/year) (Stoiber, 1995).

Isotope studies show that hydrogen released from hydrothermal systems at mid-ocean ridges is of volcanic origin. Using $\delta^{13}\text{C}$ data for the coexistence of methane with carbon dioxide in hydrothermal fluids from the East Pacific Rise, showed that these gases could have been in isotopic equilibrium only at temperatures between 550 and 750°C. The study states that “at such high temperatures, neither methane nor hydrogen could be generated by olivine or enstatite hydrolysis because these minerals are thermodynamically stable with respect to their hydrolysis products. The dissolved gases in high-temperature hydrothermal vents are therefore the products of the degassing of molten or quenched basaltic magma with an oxidation state in the region of the FMQ buffer” (Apps and Van De Kamp, 1993). However, as has been shown in the Sections of this paper 3.1 Deep-seated hydrogen and 5.1 Hydrogen as a component of Earth degassing, the hydrogen derived from such places could be of a deeper origin.

Decomposition of hydrogen sulfide has been mentioned in some studies as a possible source of hydrogen. One study, where hydrogen was discovered in fumarole gases from the Mt St Helens volcano in the USA, suggests that hydrogen was produced by the reaction of H_2S with water (Evans et al., 1981). One more study suggests that hydrogen may come from the reaction of various sulfides with water and atmospheric oxygen (Молчанов, 1968). The authors propose that hydrogen could be generated through a similar process to that which results from the crushing and grinding of minerals (Молчанов, 1981). On closer inspection this study reveals that the hydrogen detected was most likely a by-product of the reaction of hydrogen sulfide with copper in the mill reaction chamber. Indeed, in all runs, where H_2S solution was added, yields of hydrogen were much higher than in experiments where no H_2S was used. For this reason, hydrogen generation data from sulfide reactions appear to be ambiguous with regard to whether the hydrogen generated was due to natural causes or experimental error.

Decomposition of H_2S was suggested as a possible source of hydrogen in a study of the isotopic compositions of hydrogen from hydrocarbon wells in the Russian Federation. It was shown that in some cases the δD of free hydrogen was equivalent to the δD of water from some aquifers, but in other cases the δD was too low to originate from ground water (Зыкин, 2009). However, the mechanism used to explain the presence of hydrogen as being derived from H_2S is likely valid in only a few rare cases, because H_2 has been detected mainly in H_2S -free zones, indicating that hydrogen is not likely to be related to the processes of H_2S decomposition (Войтов and Осика, 1982).

3.8. Decomposition of organic matter

Several studies mention the decomposition of organic matter as a possible source of hydrogen without going into details and providing solid arguments. One interesting study shows that ground water close to petroleum deposits is richer in hydrogen than ground water close to natural gas deposits. The authors hypothesize the origin of this hydrogen to be the result of the decay of organic matter (Зингер, 1962). Laboratory experiments show that hydrogen, up to 10.9%, forms during the thermal decay of kerogen at 300°C (Богомолов, 1976). However, at such temperatures in the natural environment the hydrogen generated would immediately be consumed in reactions with oxygen-containing compounds to produce water which is thermodynamically more stable.

Burning of biomass is considered by some studies as an important source of hydrogen and it is estimated to give 20 ± 10 Tg H_2 /year (Seiler and Conrad, 1987) or 16 ± 5 Tg H_2 /year (Novelli et al., 1999).

The most recent review gives a value of 15 ± 6 Tg/year (Ehhalt and Rohrer, 2009) for hydrogen produced from the burning of biomass.

There are numerous discoveries of hydrogen in coal basins (see Table 25). The highest hydrogen concentrations were observed for coal samples associated with the final stages (V–VI) of coal maturation (Гресов et al., 2010). Indeed, it is likely that hydrogen in coal basins is related to coal metamorphism. Total hydrogen on a global basis produced from coal fields is estimated to be around 0.0014 Tg/year (Koyama, 1963), a very low number when compared to other sources.

3.9. Anthropogenic sources

Some studies suggest that hydrogen in the atmosphere comes from automobile tailpipe emissions (Barnes et al., 2003). Some authors even consider the combustion of fossil fuels as a major source of atmospheric H_2 (Ehhalt and Rohrer, 2009; Novelli et al., 1999; Warneck, 1999) which is not the case, as shown in the Table 25. Calculated anthropogenic hydrogen emissions are in the range of 4.28–5.13 kg/year* per person for the population of the North-East USA (Barnes et al., 2003). Other studies have estimated anthropogenic emissions of H_2 to be 20 ± 10 Tg/year (Seiler and Conrad, 1987; Warneck, 1999), close to further estimates of 15 ± 10 Tg/year (Novelli et al., 1999). The most recent review gives value of 11 ± 4 Tg/year (Ehhalt and Rohrer, 2009).

When hydrogen was discovered in some wells, it was proposed that it formed as a result of the reaction of water with steel casing (Bjornstad et al., 1994a; Bjornstad et al., 1994b; Chapelle et al., 1997), iron casing (Chapelle et al., 1997), with tubing made of black iron (Bjerg et al., 1997) or equipment used for the extraction of gas and liquid from rock (Левит, 1954). In another example hydrogen concentrations were observed to be rising in monitoring wells over time (Стадник, 1970). When all the water was pumped from the wells, hydrogen concentrations decreased to near-zero. The authors attributed the hydrogen to corrosion processes in the well (Стадник, 1970). However, if hydrogen is generated by reactions of water with metal well casing it should be observed systematically in most wells with iron casing worldwide (assuming, of course, that it was being sampled), which is not the case (Войтов and Осика, 1982). A recent experiment has demonstrated that the generation of hydrogen by reaction of water with steel slag is negligible at neutral pH, but can be stimulated by the addition of acids (Crouzet et al., 2017).

4. Total global hydrogen budget and hydrogen cycle

By combining together numbers from the previous sections it is possible to compare them to get an idea for the total volume of natural hydrogen at the Earth's surface. Table 25 contains the available estimates from the literature and proposes a first approach for defining a global hydrogen cycle.

The first remarkable thing about this table is the wide range in estimates. Different authors sometimes differ by orders of magnitude, as is the case for hydrogen production from the oceanic crust and its basaltic layer. Also, estimates from different studies may overlap, for example, with the values obtained for hydrogen produced from the oceanic crust. Another important point that all currently available estimates are based on the assumption that hydrogen is generated mainly from water reactions with rocks. Therefore, all these estimates and their totals are approximate and obviously should not be taken as definite numbers. Total hydrogen production obtained by the addition of different sources is higher than estimates made by other authors (Seiler and Conrad, 1987; Novelli et al., 1999; Warneck, 1999). However, none of the articles (Seiler and Conrad, 1987; Novelli et al., 1999; Schmidt, 1974) and books (Warneck, 1999) which attempted to evaluate a total planetary hydrogen budget accounted for a geologic source in their estimates!

It should be noted that to date (2019) there has been no comprehensive and systematic attempt to evaluate the total volume of

Table 25
Estimates for sources and sinks of hydrogen in nature.

Sources	$\times 10^9 \text{ m}^3 \text{ H}_2 / \text{year}$	Tg/year ($= 10^6 \text{ t/year}$)	Reference
Geological			
Mid-oceanic rift system	1.3	0.12	(Welhan and Craig, 1979)
	2	0.18	(Charlou et al., 2012)
	3.7	0.33	(Cannat et al., 2010)
	4.3	0.38	(Keir, 2010)
Oceanic crust, by various oxidations	10 ± 7	0.9 ± 0.6	(Bach and Edwards, 2003)
Oceanic crust serpentinization	1.8–2.9	0.16–0.26	(Canfield et al., 2006)
	8.5	0.76	(Sleep and Bird, 2007)
	22.4	2	(Worman et al., 2016)
Ophiolite massifs	2–4	0.18–0.36	based on (Zgonnik et al., 2019)
Basaltic layer of the oceanic crust	84	7.5	(Sleep and Bird, 2007)
	139	12.6	(Holloway and O'Day, 2000)
Precambrian basement	0.45–4.3	0.04–0.38	(Sherwood Lollar et al., 2014)
Volcanoes and hydrothermal systems	108 ± 81	9.6 ± 7.2	(Holland, 2002)
Subaerial volcanoes	2–7.7	0.18–0.69	(Canfield et al., 2006)
	2.7	0.24	(Stoiber, 1995)
Mid-ocean ridge volcanoes	0.2–0.6	0.02–0.05	(Canfield et al., 2006)
Coal metamorphism	0.02	0.0014	(Koyama, 1963)
Deep-seated hydrogen	?	?	
Sub-total for geologic	254 ± 91	23 ± 8	
Estimates for total geologic hydrogen by other studies	67	6	(Gilat and Vol, 2005; Gilat and Vol, 2012)
	6	0.54	(Voitov and Rudakov, 2000)
	0.3	0.027	(Giardini and Melton, 1983)
Atmospheric			
CH ₄ oxidation by OH ^a	257 ± 90	23 ± 8	(Ehhalt and Rohrer, 2009)
Oxidation of nonmethane hydrocarbons ^a	202 ± 78	18 ± 7	(Ehhalt and Rohrer, 2009)
Sub-total for atmospheric	459 ± 119	41 ± 11	(Ehhalt and Rohrer, 2009)
Biological			
Biological N ₂ fixation ^a	27–54	2.4–4.9	(Conrad and Seiler, 1980)
	34 ± 22	3 ± 2	(Ehhalt and Rohrer, 2009)
Burning of biomass ^a	224 ± 112	20 ± 10	(Seiler and Conrad, 1987; Warneck, 1999)
	168 ± 67	15 ± 6	(Ehhalt and Rohrer, 2009)
Oceans ^a	45 ± 22	4 ± 2	(Seiler and Conrad, 1987)
	67 ± 34	6 ± 3	(Ehhalt and Rohrer, 2009)
Anthropogenic emissions ^a	123 ± 45	11 ± 4	(Ehhalt and Rohrer, 2009)
Sub-total for biological	412 ± 106	37 ± 9.5	
Estimates for total biological hydrogen by other studies	0.2	0.02	(Koyama, 1963)
Total for geological, atmospheric and biological	1125 ± 183	100 ± 16	
Estimates for total for all sources by other studies (no geologic sources were taken into account)	974 ± 437	87 ± 39	(Seiler and Conrad, 1987)
	862 ± 179	77 ± 16	(Novelli et al., 1999)
	907	81	(Warneck, 1999)
	448–1456	40–130	(Adushkin et al., 2006)
	851 ± 157	76 ± 14	(Ehhalt and Rohrer, 2009)
Sinks			
Oxidation by OH ^a	90 ± 34	8 ± 3	(Seiler and Conrad, 1987)
	110	9.8	(Hawkes, 1980)
	213 ± 56	19 ± 5	(Ehhalt and Rohrer, 2009)
Uptake by soils ^a	1008 ± 224	90 ± 20	(Conrad and Seiler, 1981; Seiler and Conrad, 1987)
	1344	120	(Hawkes, 1980)
	672^{+336}_{-224}	60^{+30}_{-20}	(Ehhalt and Rohrer, 2009)
	986 ± 123	88 ± 11	(Rhee et al., 2006)
Uptake by oceans	?	?	
Consumption by deep microbial communities	?	?	
Escape to space, estimates	0.8–2.8	0.07–0.25	(Hunten, 1990; Catling and Zahnle, 2009; Belov et al., 2009; Brinkmann, 1971)
Escape to space, estimates based on <i>in situ</i> satellite measurements	0.9 ± 0.3	0.08 ± 0.03	(Breig et al., 1976)
Total sinks	1142 ± 282	102 ± 25	
Estimates of total sinks by other studies	1098 ± 258	98 ± 23	(Seiler and Conrad, 1987)
	840 ± 459	75 ± 41	(Novelli et al., 1999)
	780	70	(Warneck, 1999)
	885^{+336}_{-224}	79^{+30}_{-20}	(Ehhalt and Rohrer, 2009)

^a More estimates from different authors are available in (Ehhalt and Rohrer, 2009; Price et al., 2007).

geologically generated hydrogen. In every study reviewed where a value was given it was not the main subject of the study, but rather a secondary topic (Voitov and Rudakov, 2000; Gilat and Vol, 2005; Giardini and Melton, 1983; Gilat and Vol, 2012). It is interesting to note, that estimates have been increasing by an order of magnitude

every one or two decades which is probably due to progress in an understanding of the widespread occurrence of natural hydrogen. In 1983 total hydrogen volumes were estimated to be 0.027 Tg/year (Giardini and Melton, 1983), in 2000: 0.54 Tg/year (Voitov and Rudakov, 2000) and in 2005: 6 Tg/year (Gilat and Vol, 2005; Gilat and Vol, 2012). For

comparison purposes, the current world industrial production of hydrogen for 2015 was 97.4 Tg (Runte, 2015) and has been projected to grow to 2750 Tg by 2080 at a peak hydrogen economy (Barreto et al., 2003).

This review shows that previous estimates of hydrogen flux produced from geologic sources have largely been underestimated. It is interesting to point out, that the author of the most recent estimates for globally generated total hydrogen, before this review, reached the conclusion that geological sources for hydrogen have been underestimated (Voitov and Rudakov, 2000). It is very likely that current estimates in this review are lower than they should be, because they do not include the data on flux of hydrogen from recently discovered seepages with diffusive flow and for the flux of deep-seated hydrogen from diverse geological settings.

5. Hydrogen and natural phenomena

This section discusses the role hydrogen plays in the Earth's structure, how hydrogen flow influences natural phenomena and how hydrogen can be used for the monitoring of natural environments.

5.1. Hydrogen as a component of Earth degassing

Earth degassing has been proposed as the source for Earth's atmosphere (Хитаров and Войтов, 1985). It is believed that hydrogen played a very important role in this process in the past and that the early Earth's atmosphere was hydrogen-rich (Tian et al., 2005). Hydrogen continues to play an important role if, as this author and others propose, the Earth is constantly degassing hydrogen (Осика et al., 2002; Моисеенко and Сахно, 1982). Some authors describe this process as gas "breathing" (Войтов and Осика, 1982; Войтов, 1975; Шестопалов and Макаренко, 2013). However, a more correct phraseology could be "exhalation". Degassing of the Earth is classified as either "hot" or "cold" by these authors. Hot "exhalation" includes volcanic activity and can be mainly characterized by oxidized gas species. Cold "exhalation", which is sometimes called "cold degassing", is related to gas seeping from surface depressions, faults, gas chimneys, pockmarks, etc. By chemical type, gases from "cold degassing" are mainly reduced. Because of its quiescent nature, cold degassing processes happen in background and are often poorly studied or not studied at all. It is for this reason that volumes of gas from cold-degassed gases have been underestimated (Шестопалов and Макаренко, 2013).

Molecular hydrogen flow is thought to be very irregular and unstable in time (Voitov and Rudakov, 2000; Войтов et al., 1995). It is hypothesized to likely be controlled by the geodynamic activity deep within the Earth's interior and in probable association with preferential vertical permeability pathways (Войтов et al., 1995). Therefore, hydrogen should be an excellent indicator for processes happening in depth (Hernández et al., 2000). Hydrogen mapping should be capable of revealing structural, lithologic and geodynamic features otherwise attributable to previously unidentified causes (Войтов et al., 1995). The extensive review of hydrogen occurrences in the territories formerly part of the soviet camp show spatial distributions of hydrogen detection to be a reflection of Earth degassing via geological structures and formations (Shcherbakov and Kozlova, 1986).

Hydrogen affects the structure and chemical composition of the rocks it passes through (Гуфельд, 2012). It has been reported that saturation of rocks with light gases changes their crystal structure, creates porosity and changes their volume. The authors suggest that the creation of porosity and fracturing at the depths of the Mohorovicic discontinuity ("Moho") could be the result of hydrogen and helium seeping from greater depths. They suggest that below the Moho layer, diffusion of hydrogen and other gases is possible and mainly happens within crystal lattice vacancies and dislocations (Гуфельд, 2012). Another study suggests that at depths where there are no open fractures hydrogen and other fluids migrate via different mechanisms. It has been

shown experimentally that in tectonites the velocity of fluid migration is several orders of magnitude higher than in fractures. The mechanism consists of sliding films of fluid along foliation surfaces in tectonites (Летников, 2000). Propagation of light gases during Earth degassing creates porosity with high internal pressures resulting in lithospheric instability. (Gufeld and Matveeva, 2011). Some researchers have proposed that variations in hydrogen concentration could be responsible for changes in the velocity of seismic waves (Гуфельд, 2012).

It is known that deep faults play a major role in the migration of natural gases and other fluids (Перчук, 2000; Летников, 2000). It is possible that such zones are not only acting as conduits but can also be the result of diagenetic changes in porosity and permeability resulting from the effects of highly chemically reactive gas such as hydrogen. It has been shown experimentally that exposure of non-metallic materials such as calcite, dolomite, antigorite, etc. to hydrogen at low pressure reduces their microhardness and crystal constants. This means that hydrogen diffusion can cause weakening and embrittlement of non-metallic materials. As a result, hydrogen migration along fault zones might indicate not only the location of fault zones, but also the activity of the faults (Su et al., 1992). Another study showed experimentally that the strength of limestone decreases by 1.5–1.7 times with an increase in brittleness after being saturated with hydrogen at 100°C and $P_{H_2} = 8\text{ MPa}$ for 48 h (Levshounova, 1991). Based on the aforementioned experiments hydrogen not only migrates along fractures but it may also affect their development and dispersion.

This property of hydrogen may be at the origin of recently discovered hydrogen seepages described in the Section 2.2 Diffusive flow. It is thought that hydrogen seepages can be identified on the surface by topographic circular to sub-circular shallow depressions. The formation of these circular depressions seen as the result of a process of chemical dissolution (diagenesis) of the rock by hydrogen (Larin et al., 2015; Zgonnik et al., 2015). Hydrogen may react with rocks creating porosity because the products of hydrogen reactions with rock are water and soluble mobile compounds which may tend to migrate away from the reaction zone. The porosity created by hydrogen flowing through hydrogen-enhanced porosity will in turn promote the creation of additional porosity in the form of a preferential hydrogen migration channel. I.e. more hydrogen will create more porosity. As a result, initially diffused flow will concentrate in vertical "streams" or plumes. The origin of hydrogen in such seepages may be related to the degassing of deep-seated or primordial hydrogen (Larin et al., 2015; Zgonnik et al., 2015).

Indeed, some works (Gilat and Vol, 2005; Su et al., 1992; Овчаренко, 1967; Walshe, 2006) refer to a primordial origin as a possible explanation for the observed hydrogen (discussed in detail in the Section 3.1 Deep-seated hydrogen).

The following works cited assume that the Earth has a deep reservoir of hydrogen that has been leaking upwards to the surface, probably episodically, through geologic time. While this is a plausible model it should be noted that it has yet to be generally accepted and the cited works are theoretical. However, these theories propose that should the Earth's interior be rich in hydrogen, which is chemically bonded in the form of hydrides, their progressive decomposition would sustain the continuous degassing of hydrogen over geologic time (Сывороткин, 2002; Ларин, 2005; Бембель et al., 2011). These authors suggest that hydridic fluids from deep within the Earth are very important in mineral systems. The action of hydridic fluids can effectively be used in theories of volcanism, mineral system formation, anoxia, evolution of ocean chemistry, climate change, mass extinction and more. It is suggested that all these phenomena can be explained using a hypothesis of episodic hydrogen flow from the Earth's core (Walshe et al., 2005). Another work points out that flows of hydridic fluid from the Earth's core can sustain a redox gradient between a reduced Earth core and oxidized outer layers. The authors argue that this gradient can be used to explain in simple ways many geologic phenomena (Walshe, 2006). Another study advances the same idea, that hydrogen affects the

character of redox processes in the crust and their intensity (Войтов and Осика, 1982). Ascending hydridic flows from the mantle are proposed to account for the melting of silicates. Others have suggested that hydrogen plays a key role in volcanic activity (Gilat and Vol, 2005; Gilat and Vol, 2012; Портнов, 2003; Портнов, 2010; Персиков et al., 1986; Велинский, 1970). In which case, it may play a dual role: that of a heat-transfer agent (Letnikov et al., 2011) and to release heat while undergoing oxidation (Белов et al., 2009). Others note that hydrogen plays a major role in the volcanic eruption of ignimbrites (Щека and Гребенников, 2009). A recent study proposed that a sudden release and ignition of hydrogen may explain the formation of Libyan desert glass, which are fragments of molten silica found at the surface in Libya and Egypt (Saul, 2019). In one study, it was experimentally shown that hydrogen can affect the process of differentiation of molten rocks (Персиков et al., 1986). It has been theorized that hydrogen could play a role in the formation of outer core plumes (Letnikov and Dorogokupets, 2001). Other works propose that hydrogen rising from depth plays a role in the formation of hydrothermal and ore-forming systems (Павлов, 1977) and also in the formation of "juvenile" water (newly created water in the interior of the Earth) (Войтов and Осика, 1982).

The origin of water on Earth is an extremely important topic but there has yet to be agreement on how it appeared. A widely accepted hypothesis that water was delivered by comets has been criticized and seems to have been ruled out by isotopic constraints (Drake, 2005). Proposed in its place, the hypothesis of so-called "wet accretion" states that water was trapped during the Earth's formation, but does not explain how this water came to be preserved during the assumed stages of the Earth's melting and subsequent heavy bombardment by planetary debris. However, if the Earth was initially hydrogen-rich the origin of water ceases to be an issue but rather becomes a logical consequence of the planet's continual degassing of hydrogen (Larin, 1993). Moreover, the quantity of water should increase with time, even at present, an important point yet to be considered by scientists studying the rise and fall in sea levels over geologic time (an extremely significant point at that, if it these hypotheses prove to be valid).

A recent 632-page monograph describes some aspects of Earth degassing based on an analysis of published sources and research (Шестопалов et al., 2018). Consideration is given to fluid-conducting systems in the crust, characterization of various types of conduit structures created by or facilitating degassing, degassing cyclicity, role of degassing in the generation of oil and gas, its action on climate, evolution of the biosphere and hazards caused by degassing. The authors of the monograph highlight what they believe are the important, but still underestimated impacts of the Earth's degassing of hydrogen and other fluids.

The hydrogen "exhalation" of our planet can be seen as the process of our planet's loss of mass to space (Войтов and Осика, 1982). From a thermodynamics point of view this allows for the characterization of the Earth as an open system (which is exchanging mass and energy with its surroundings) and not as a closed system (which is exchanging only energy). Current planetary models have considered mass exchange to be negligible but in view of the volumes of hydrogen being lost to space discussed in this review this is not necessarily accurate. This point is important for interpretations of terrestrial evolution. It appears that through geologic time the planet is evolving towards more structural ordering (formation of the core, crust, mountains, etc.), i.e. entropy of the planet as a thermodynamic system is decreasing, which contradicts the second law of thermodynamics if the Earth is considered to be a closed system. This is possible only if the planet is considered to be an open system, where mass and energy are being exchanged with its surroundings with a corresponding removal of entropy. Hydrogen lost to space appears to be a good candidate for the role of an entropy removal agent (Larin, 1993; Ларин, 2005).

Taking into account the considerations of this section, the topic of hydrogen Earth's degassing deserves more attention.

5.2. Hydrogen and life

Hydrogen is an excellent source of energy for living organisms (Morita, 1999; Gregory et al., 2019). In microbial systems H_2 transfer creates the basis for organism-to-organism interaction. It is an important mediator for electron transfer, energy regulation and community interaction (Hoehler, 2005). Many bacteria, including the very well-studied *Escherichia Coli*, are able to generate energy through the oxidation of H_2 . As oxidizing agents bacteria can use not only oxygen, but also carbon dioxide, nitrogen, sulfates, nitrates and other electron acceptors (Cammack, 2001).

Many prokaryotic microorganisms use H_2 as an energy source, competing for access to it (Fedonkin, 2009; Schwartz and Friedrich, 2006). They are confined to the base of the phylogenetic tree, which means that hydrogen consumption is one of the oldest and most basic properties of life. Indeed, about 30% of microorganisms have genes encoding hydrogenases, a principal type of enzyme for H_2 metabolism (Colman et al., 2017). A recent study sequenced and classified several thousand of hydrogenases (Greening et al., 2016). They were recovered from all types of environment, indicating that hydrogenases are broadly used and sustain the survival and growth of microorganisms in a variety of ecosystems. This signifies that hydrogen was a primary component of redox chemistry in the first living systems. It also indicates that initial levels of hydrogen in early Earth history might have been several orders of magnitude higher than they are today. Even today hydrogen plays an important role in microbial chemistry (Hoehler, 2005). Studies of microbial communities show that the evolution of life on the Early Earth was related to reactions of H_2 with oxidizing compounds (Fedonkin, 2009; Schwartz and Friedrich, 2006). A strongly reducing atmosphere is much more favorable to the synthesis of bioorganic molecules than more oxidized atmospheres (Miyakawa et al., 2002). Indeed, it was proposed that an Archean atmosphere could have contained up to 30% hydrogen (Wordsworth and Pierrehumbert, 2013). The emergence of life under such conditions would have been much more efficient than in hydrothermal systems (Tian et al., 2005). It also makes it probable that the first organisms used hydrogen rather than light as an energy source (Kral et al., 1998). An analysis of early anaerobic ecosystems shows that an early-Earth hydrogen-based ecosystem may have been dynamic, but not as active as the present marine biosphere (Canfield et al., 2006).

A readily available electron acceptor in many environments is carbon dioxide. Hydrogen together with water and a small amount of minerals is all that simple forms of life would need to exist. Most of them survive by reducing carbon dioxide to produce methane, from whence comes the term "methanogen". Methanogens were reported to be present in every type of soil, and even in dry desert environments (Conrad, 1996). Certain methanogens can consume hydrogen at partial pressures as low as 4 Pa (Kral et al., 1998). However, ambient atmospheric concentrations of hydrogen are not sufficient for their growth (Conrad, 1996) and require an external source of H_2 .

Estimates show that 10–50% of the total methane produced in anoxic soils is synthesized by methanogenic microorganisms from hydrogen (Conrad, 1996). Biogenic methane has been found all over the world (Kotelnikova, 2002). It is produced not only in soils, but in the Earth's crust as well. It has been reported that deeply-buried hydrogen-based methanogenic communities exist within the planet (Chappelle et al., 2002). A large accumulation of methane thought to have been generated by hydrogenotrophic methanogens is believed to exist beneath the West Antarctic ice sheet (Michaud et al., 2017). In deep aquifers chemolithoautotrophic (those obtaining energy from the oxidation of inorganic compounds) microorganisms consume hydrogen to produce methane. These microorganisms greatly outnumber those that could grow on organic compounds (Kotelnikova, 2002). It is interesting to note, that isotopic studies of methane emissions into the atmosphere show that since 2006, biogenic CH_4 has become a main source of this greenhouse gas (Schaefer et al., 2016; Nisbet et al., 2019). This raises the issue of whether there might be a causal link to the possible increase

in planetary hydrogen degassing with an increase in methane, because with added hydrogen, methanogens will generate more methane. Moreover, as hydrogen inhibits the decomposition of methane in the atmosphere (see Section 3.6 Atmospheric hydrogen) the overall quantity of methane will increase, with consequences on climate change.

There are many examples of deep ecosystems using hydrogen as an energy source, the so-called subsurface lithoautotrophic microbial ecosystems (SLiMEs) (Morita, 1999; Nealson et al., 2005). Such communities were discovered in deep basalt aquifers (Stevens and McKinley, 1995). There is strong evidence for hydrogen-driven ecosystems hosted in deep granitic rock aquifers (Pedersen, 1999), for subsurface habitats within serpentinites (McCollom and Seewald, 2013), for hyperthermophilic communities beneath active deep-sea hydrothermal vents (Takai et al., 2004) and for microbial ecosystems in seafloor fault zones (Suzuki et al., 2015). Hydrothermal hydrogen vents are true oases of life in the deep ocean (Геворкян et al., 1990), and hydrogen flow could be used to identify an important feature of an explanation for their existence. Taking into account facts about methanogens, the question arises as to the possible connection between the activity of methanogens on the ocean floor and hydrogen seeps (Mikucki et al., 2003) and the formation of methane hydrate deposits. A recent study reporting hydrogen and helium concentrations in hydrate-bearing marine sediments showed relatively high concentrations of these gases, and in particular, over fault zones (Шакиров et al., 2016), which indicates that hydrogen and helium gases are likely seeping from depth.

Hydrogen-based microbial communities can exist under extreme conditions, such as the +122°C hot springs of mid-oceanic ridges (Colman et al., 2017) or -13°C cold brines of Antarctic lakes (Murray et al., 2012) where no other energy (food) sources are available. The recent discovery of microorganisms in Antarctica that use only atmospheric H₂, CO and CO₂ as an energy source (Ji et al., 2017), greatly extends the limits within which life can exist. It is suggested that similar life forms may exist on Mars and Europa (Gregory et al., 2019; Chapelle et al., 2002). Finally, could it be possible that new life forms are presently appearing in isolation deep within the Earth but in contact with a source of hydrogen? Because if new life appeared once in the past, why would it not be possible for it to be an on-going process?

The existence of a “deep hot biosphere” was predicted in the early 1990's (Gold, 1992). A recent paper comprehensively reviews the state of the art 25 years later (Colman et al., 2017). It was proposed that the total mass of the deep biosphere may be comparable to that of all life at the Earth's surface (Gold, 1992). The model requires a continuous influx of hydrogen to maintain the activity of SLiMEs (Nealson et al., 2005; Fedonkin, 2009). Indeed, genomic studies of deep-living microorganisms show that they have an order of magnitude more copies of the hydrogenase sequence than organisms from surface environments, demonstrating the importance of H₂ in their metabolism (Colman et al., 2017). Another study proposed that the first life forms may have emerged in water-conductive ultramafic rock systems (Hellebrand et al., 2011). Recent discoveries in the genomics of hydrogen-based subsurface Archea provide insights not only on their evolution but on the emergence of life as well (Colman et al., 2017).

For life to exist in deep-earth environments the flow of hydrogen must be continuous, which rules out certain proposed mechanisms for hydrogen generation. For example, for SLiMEs discovered in basalt aquifers, the source of hydrogen proposed was a water-basalt reaction (Stevens and McKinley, 1995). However, other researchers disagree and say that a basalt-groundwater reaction producing hydrogen is not possible under natural conditions. In natural environments, exposed mineral surfaces will quickly become de-activated by their reaction products and reduce their capacity to produce H₂ (Anderson, 1998). The authors suggest that deep subsurface microbial ecosystems would grow on reduced gases if there is a constant supply of such gases from the depth. It has been suggested that rock faulting and continuous deformation of the brittle crust sustains the supply of hydrogen to

maintain the deep-crust habitats (Sleep and Zoback, 2007). The rate of hydrogen consumption by prokaryote organisms is probably greater than the rate of input of hydrogen to a hydrogenotrophic habitat thereby explaining the low hydrogen content in the majority of environments (Fendonkin, 2009). The last remark is very important and should be considered in any study of natural hydrogen.

Because hydrogen is readily used by microbial communities, which are widespread on the Earth's surface and subsurface, they should be taken into account during the design of geology-related projects. For example, it has been proposed that a microbial hydrogen-consuming web can be integrated into the design of underground constructions (such as nuclear waste repositories) to reduce risks associated with hydrogen build-up (Bagnoud et al., 2016). Another work shows that in the presence of sulfates, they can be chemically reduced by hydrogen into a toxic hydrogen sulfide (Boylan et al., 2019). A recent comprehensive review combined many examples on how hydrogen-consuming microorganisms can impact underground projects like gas storage, carbon capture and radioactive waste disposal (Gregory et al., 2019).

Recently, sub-circular depressions were discovered to be seeping molecular hydrogen (see Section 2.2 Diffusive flow). Observations show that soils at hydrogen seep locations lose their humus, reducing their fertility (Суханова, 2012). This effect of hydrogen mediated soil fertility loss has been confirmed though field observations and experimentally in the laboratory. Hydrogen also affects the diversity of microbial communities in soils, decreasing their total mass and increasing the proportion of bacteria in soil (Sukhanova et al., 2013). Another work confirms that at hydrogen seep locations the microbiota of soils is affected. The total quantity and biomass of bacterial cells, as well as fungal spores and the length of fungal and actinomycetal mycelium, are decreased (Polyanskaya et al., 2014). In laboratory tests of soils treated with hydrogen fungal spores numbers decreased to zero after a week and after 2 weeks actinomycetes and fungal mycelium could not be isolated (Polyanskaya et al., 2017). A very recent study confirmed experimentally that treatment of soil samples with hydrogen changes the microbial community and this is probably a major sink for hydrogen seeping from topographic depressions (Myagkiy et al., 2020).

Hydrogen may also affect the biochemistry of higher plants. One study shows that plants growing in the presence of molecular hydrogen in air, change their spectral parameters indicated by an increase in the quantity of chloroplasts and carotenoids (Тимченко et al., 2014). A very recent study on the influence of hydrogen on plants under natural and laboratory conditions demonstrated that prolonged exposure to high concentrations of H₂ led to inhibition or fading of agricultural crops (Sukhanova et al., 2019).

Some researchers, by assuming there is a high flow of deep-seated hydrogen, propose that it may affect the biological productivity of the oceans and paleobasins (Syvorotkin, 2013), speciation and other biological processes (Сывороткин, 2013; Syvorotkin, 2010). Speciation is the evolutionary process by which new living species arise. It was noticed that areas with high biological diversity are also situated over regions of high geologic-tectonic activity, where one might expect higher flows of hydrogen. Such zones, when they are situated close to the equator, are also exposed to maximum solar radiation. Seeps of hydrogen and methane entering the atmosphere damage the ozone layer (see the next Section 5.3 Atmosphere) and increase levels of ultraviolet radiation coming to the surface of the Earth (Сывороткин, 2012a). Areas impacted by high UV radiation from the Sun may undergo higher rates of speciation when compared to other regions of the Earth (Сывороткин, 2013; Syvorotkin, 2010), a hypothesis yet to be verified.

5.3. Atmosphere

Hydrogen in the atmosphere was first detected as a by-product of the liquefaction of air. There is an abundance of atmospheric hydrogen concentration data because during the 1950–70s the atmosphere was

monitored for the presence of tritium, an atomic weapons testing indicator (Warneck, 1999). For estimates of hydrogen concentration in air see the Section 4 Total Global Hydrogen Budget and Hydrogen Cycle.

Research on hydrogen in the atmosphere is still ongoing. For example, in a study (Barnes et al., 2003), hydrogen concentrations were monitored every 24 min for three years above Harvard forest, MA USA. The authors found that hydrogen concentrations in the air change seasonally, with a spring maximum and an autumn minimum. Diurnal changes include a morning minimum and an afternoon maximum. It is interesting to note that their calculated annual emissions over 3 years show a statistically significant decline in H_2 concentrations and that the diurnal hydrogen cycle is opposite to that of CO. These two facts appear to contradict the study author's suggestion that hydrogen in the atmosphere comes from automobile tailpipe emissions. Another study confirms a conclusion that hydrogen is not associated with anthropogenic pollution by showing that H_2 concentrations around polluted areas are not significantly greater than in regions where the air is clean (Novelli et al., 1999). Another similar study conducted near Saint-Petersburg in the Russian Federation discovered that hydrogen concentrations varied greatly when the wind blew from the direction of the city but were almost stable when the wind came from the forest (Образцова et al., 2011). When H_2 soil to air exchange was monitored for 1 year in a rural area of Canada, it was shown that the uptake rate depended on temperature, with the highest values measured at the end of summer and the highest emissions observed at snow-melting time in spring. The average uptake rate was 0.34 mg H_2 per m^2 per day (Constant et al., 2008).

To understand the global budget and distribution of hydrogen in the troposphere, studies were done in both hemispheres of the globe. Air samples were collected from ~50 sites all over the world and from a ship crossing the Pacific Ocean on regular basis. Clearly visible yearly changes in both hemispheres were observed, with a maximum in late winter in the Northern hemisphere (NH) and correspondingly in early summer in the Southern hemisphere (SH). The amplitude in the NH was three times that of the SH, but mixing ratios were lower in the NH (Novelli et al., 1999). The authors of another paper observed seasonal variations in H_2 at high latitudes. Such variations remain unexplained (Warneck, 1999). Seasonal variations in atmospheric hydrogen concentration exhibit several features not found for other trace atmospheric gases (notably CO) (Ehhalt and Rohrer, 2009). Isotopic studies of atmospheric hydrogen in both hemispheres also showed seasonal variations of δD value (Batenburg et al., 2011).

The relative quantity of hydrogen in the atmosphere is low, but because of its high reactivity it has a noticeable impact on some natural processes. Probably the most important consequence of the presence of hydrogen in the atmosphere is the direct impact it has on concentrations of hydroxyl (OH) and ozone (O_3) in the troposphere (Barnes et al., 2003). Many studies indicate that hydrogen participates in the depletion of the ozone layer (Сывороткин, 2002; Сывороткин, 2013; Маракушев and Маракушев, 2008a; Syvorotkin, 2010; Маракушев, 1998a). The below cited works assume a large reservoir of hydrogen is present deep within the Earth and a periodic release of this gas is hypothesized to affect natural processes.

The interpretation of spatial distributions of negative ozone anomalies from a geologic point of view suggests a relationship between these anomalies and rift zones and hot spots (Сывороткин, 2013; Syvorotkin, 2010). The largest ozone anomaly is observed over Antarctica, where three main oceanic ridges merge and the entire continent is surrounded by a rift zone (Pavlenkova, 2009). The hole in the ozone layer above Antarctica has at times been observed to exhibit a tri-lobate shape with the rays radiating from the South Pole in the direction of the mid-ocean rifts: the Atlantic, the East and the West Pacific rises (Сывороткин, 2009). Such a unique configuration can be explained with the concept that ozone depletion is related to hydrogen flux, assuming that it is important enough to make an impact. Other ozone anomalies have been observed over Iceland, the Red Sea, the

Hawaiian Islands and the equatorial Pacific. Continuous observations of hydrogen concentration over a period of 44 months in the Khibiny mountains, showed that there is a relationship between abrupt increases in hydrogen concentration and a subsequent decrease in stratospheric ozone. It is therefore suggested that geologic hydrogen plays an important role in the ozone planetary balance (Сывороткин, 2013; Syvorotkin, 2010). Some studies suggest that hydrogen may be responsible for the formation of noctilucent clouds (Сывороткин, 2002; Маракушев, 1998b; Tromp et al., 2003), which consist of frozen water, the product of hydrogen oxidation at high altitudes.

Based on continuous monitoring of hydrogen in soil gas, the author of another study developed a method for quantitative estimation of hydrogen input into the atmosphere based on ozone data. The method was confirmed by comparing hydrogen ground data concentrations with ozone levels. During sharp increases in hydrogen ground concentrations, ozone levels decreased over the region under observation. It was thereby possible to transform Dobson units (DU) to degassed hydrogen volumes. An increase of 1 ppm H_2 in soil gas, corresponds approximately to a decrease in ozone of 1 DU (Сывороткин, 2013).

Critics of this method say that the estimated total known hydrogen input to the atmosphere is insufficient to affect the ozone layer (Adushkin et al., 2006). However, as has been shown in some examples cited in the Section 5.4 Earthquakes, hydrogen concentrations measured at continuous monitoring sites show abrupt changes in concentration over several orders of magnitude, up to 10^6 times, in a short period of time (Сывороткин, 2013). In such cases, plumes of hydrogen may rise very quickly and reach the stratosphere. Indeed, at epicenters of large earthquakes a reduction in the ozone layer above them has been observed. This seems to confirm that hydrogen is released in large quantities during earthquakes (Сывороткин, 2011).

Hydrogen seepage is a dynamic process which appears to be very irregular in space and time (Сывороткин, 2013; Syvorotkin, 2010). Nevertheless, it is not completely chaotic. Continuous monitoring has revealed periodic changes, related to seasonal and tidal influences of the Moon and Sun (see the Section 2.4 Periodic variations in concentration).

Some researchers have warned that ignoring hydrogen component of Earth's degassing is a significant error when addressing issues such as the destruction of the ozone layer and climate change (Сывороткин, 2010). It is important to note, that H_2 increases the half-life of the greenhouse gas methane (CH_4) via a competing reaction with the hydroxyl radical (Warwick et al., 2004). It has been suggested that hydrogen may be at the origin of significant weather events. In one study the author speculated that an El-Niño event can be caused by hydrogen degassing. El-Niño events form over an active rift system, which is likely producing hydrogen. Periodically, hydrogen seepage increases, which causes damage to the ozone layer which in turn increases air and water temperatures which in turn causes hurricanes. Finally, the flow of reduced gas may render seawater anaerobic, causing mass biota die-offs (Сывороткин, 2012b).

Other studies have proposed that a sudden release of a large quantity of natural gas, including hydrogen, could have been responsible for the mysterious Tunguska event, a large explosion which happened over the Russian Federation in 1908. This event flattened 2000 km^2 of forest. There is an explanation scenario for the 1908 Tunguska event which proposes a 10 Mt natural gas seep from the Kulikovskii crater paleovolcano (Kundt, 2001) with a subsequent high-altitude blast of a giant hydrogen-methane jet and the propagation of a combustion or detonation wave. Such a scenario would explain some of the identified paradoxes and contradictions related to the Tunguska event (Gendugov et al., 2010). Indeed, there is a comprehensive analysis of the 255 article bibliography on the Tunguska event, the authors of which show that, despite the largely accepted comet impact hypothesis, many facts remain unexplained. The authors suggest that a release of methane and hydrogen can explain all the facts of the Tunguska event better than the meteorite or comet impact hypothesis. One

of the hypotheses proposes that on the night of the event a large amount of gas was released, which formed a cylindrical cloud with an explosive concentration of CH_4 and H_2 . This 12 km in length cloud of explosive gas extended up to 3 km in altitude. The ignition of this cloud in its upper part, caused the Tunguska event (Petrov and Shamshev, 2008). According to the authors, this hypothesis is supported by isotopic observations.

Another recent study suggests that hydrogen may be at the origin of other catastrophic natural events. The spatial distributions of wildfires in the Russian Federation were shown in 2010 to correspond to geologic structures. Spontaneous endogenous methane-hydrogen releases from depth were proposed as a possible trigger and back-up for these wildfires (Марин and Скублов, 2011).

Several studies have suggested that a massive implementation of hydrogen technologies may affect atmospheric chemistry and ozone layer integrity (Tromp et al., 2003; Warwick et al., 2004), however, a recent re-examination has demonstrated that the impact would be small when compared to natural variability in stratospheric values for water vapor concentrations (Vogel et al., 2012). Moreover, any impacts resulting from a conversion of the main energy carrier from fossil fuels to hydrogen will largely be off-set by positive effects related to the replacement of fossil fuels and their pollutants (Ehhalt and Rohrer, 2009).

5.4. Earthquakes

Being the lightest of all the gases, hydrogen responds quickly to even minor disturbances in the Earth's crust. Hydrogen will mainly dissipate through fracture zones. Moreover, faults, where high concentrations of hydrogen have been detected, are mostly active. Observed hydrogen anomalies associated with fault movements have either been synchronous or precursory (Su et al., 1992). A systematic study of hydrogen in aquifers shows that H_2 concentrations are inversely correlated with the age of the area's last tectonic activity (Shcherbakov and Kozlova, 1986). Another study shows that hydrogen concentrations in earthquake-associated faults are usually much higher than concentrations in non-earthquake faults (Sugisaki et al., 1983). The recent Wenchuan Earthquake Fault scientific drilling project showed the presence of hydrogen in the wells studied (Fang et al., 2018).

It may be that hydrogen is too diffusive and too reactive to significantly accumulate in geologic traps. However, during earthquakes hydrogen concentrations in fault zones have been shown to increase by several orders of magnitude (Осика et al., 2002). Numerous articles discuss hydrogen as a good earthquake indicator and the possibility of monitoring hydrogen for the prediction of seismic events. Hydrogen concentrations normally vary with time in soils and fractures, sometimes its variation could be up to several orders of magnitude. Hydrogen concentrations respond to even very weak disturbances such as tidal effects, as was described in the Section 2.4 Periodic variations in concentration. However, hydrogen concentrations increase even more drastically during seismic events (Войтов and Осика, 1982). The main reason for this is that tectonic stress causes rocks to release absorbed and adsorbed hydrogen (Giardini et al., 1976; Fong-liang and Gui-ru, 1981).

For example, during the Dagestan earthquake in 1970 ($M=6.7$), a 20 fold increase in hydrogen concentrations was observed, and reached values which were 5–6 orders of magnitude higher than normal hydrogen concentrations in the atmosphere (Осика, 1981). Spike-like anomalies in hydrogen concentration were recorded in a 1000 m deep hot water well in Beijing prior to the $M=6.9$ Ninghe earthquake in 1976 (Fong-liang and Gui-ru, 1981). Increases of 3 orders of magnitude in H_2 concentration after earthquakes were observed in the Zuramakent thermal springs in Dagestan (Войтов and Осика, 1982). Weekly measurements of hydrogen concentration in soil gas at five locations situated over the Atotsugava and Ushikubi faults north of Toyama city, Japan, documented outstanding discharges of hydrogen during the

large, $M=7.7$ earthquake in 1983. Hydrogen increases were observed before the earthquake at three locations and simultaneous with the quakes at the other two. Sometimes simultaneous increases were registered at stations situated 50 km apart. It was shown that such changes were independent of meteorological conditions (Satake et al., 1985). Hydrogen concentrations were continuously monitored for a period of 1 year along the Yoro-Ise Bay fault zone in central Japan. Pre-seismic increases were recorded for local microquakes and for moderately large events within a 25 km radius (Ito et al., 1998). Soil gas hydrogen concentrations were monitored continuously for almost a year in Turkmenistan at two locations, one near Ashgabat and a second in the northern part of the country. During the monitoring period in 1994, two earthquakes took place within a 100 km radius of the monitoring locations. At both locations, a continuous increase in H_2 background concentration of 0.2–0.5 ppm per day was observed for several months prior to the earthquakes. A sharp multifold increase of H_2 concentration was observed just after the earthquakes. Aftershocks were preceded by concentration increases, but after each new aftershock the increases in hydrogen concentration were less and less pronounced (Voitov and Rudakov, 2000; Ишанкулиев et al., 1997). Continuous monitoring of hydrogen in soil gas during the period from 1998 to 2000 in Dagestan showed that all seismic events with a magnitude > 5 took place when H_2 concentrations in soil gas were 3–5 times higher than normal background levels (Урдуханов et al., 2002). In the Khibiny Massif anomalous changes in hydrogen concentration were shown to be related to seismic activity. It was observed that before weak seismic events, hydrogen concentrations increased but before significant seismic events, it decreased (Нивин, 2013). Monitoring of H_2 in soil gas at the surface over a mine situated in Khibiny Massif, showed that concentrations of hydrogen increased after seismic events, but also after large explosions in the mine (Федотова and Жукова, 2014). Continuous observations of hydrogen in soil gas in Southern Kamchatka, during the 1999–2004 timeframe, showed a statistically significant correlation (correlation coefficient > 0.99) between hydrogen concentration pulses and earthquakes, with measured hydrogen concentration pulses 2–14 times over background. An earthquake event was detected within a 2–4-week period, following a pulse in hydrogen concentrations (a probability of 0.8 was projected for an earthquake event). An earthquake of magnitude ≥ 5.6 was recorded close to the observation site, and ≥ 7 for earthquakes located at some distance from the hydrogen monitoring location. The authors suggested that it should be possible to predict the position of future epicenters by analyzing the start times of hydrogen impulses at different monitoring locations (Firstov and Shirokov, 2005; Фирстов et al., 2006). In later studies, the same investigators put in place a continuous monitoring system for multiple parameters, including hydrogen, and reported the successful detection of pre-earthquake signals (Shirokov et al., 2011). It was suggested that earthquake epicenters could be detected from hydrogen soil gas measurements. For example, the highest observed values for helium and hydrogen corresponded to the positions of the 1976 and 1984 Gazli earthquakes in Uzbekistan, with 7–7.5 magnitudes, and hypocenters situated at a depth of 20–25 km (Перевозчиков, 2012). Another observation confirmed the release of hydrogen from earthquakes with epicenters marked by a reduction in the ozone layer above them (Сывороткин, 2011) (for comments on this process, see the Section 5.3 Atmosphere). Other atmospheric phenomena which accompany some earthquakes are the so-called “earthquake lights”. Some researchers have suggested that combustible gases, such as hydrogen or methane, are released and ignited during earthquakes. Other peculiar phenomena such as sharp flashes, fireballs and diffusive luminosity may be due to a sudden release of large amounts of gas into the atmosphere (Gold and Soter, 1980).

Taking into account the numerous observations of an abrupt increase in hydrogen concentration during earthquakes, some researchers have proposed that Earth degassing in general and hydrogen in particular, plays an important role in the mechanisms of earthquake

behaviour (Сывороткин, 2011; Gold and Soter, 1980). It has been suggested by some that deep earthquakes can be explained by an abrupt change in hydrogen concentration at depth (Гуфельд, 2012). The amount of energy which can be liberated by the degassing of 6 Tg/year of hydrogen is $2.16 \cdot 10^{17}$ J/year. This is close to the global annual earthquake energy total of 10^{17} – 10^{18} J/year. The authors see the Gutenberg-Richter relation as an energy law, which requires a constant supply of energy (Gilat and Vol, 2005; Gilat and Vol, 2012). In an attempt to explain possible mechanisms for the action of hydrogen in the Earth's crust, one researcher examined the geochemical and geological factors controlling the precursory processes of earthquakes and the occurrence of low- and high-magnitude seismicity. In the list of leading factors contributing to the occurrence of earthquakes, the author proposed degassing of hydrogen (and helium to a lesser extent) and mutual displacements of lithospheric blocks. In the scenario proposed, seismotectonic processes are triggered by physicochemical reactions of hydrogen with rocks which "lock" the boundaries of crustal blocks, thus changing their seismic regimes (Гуфельд, 2007; Gufeld, 2008). If hydrogen plays a major role in earthquakes, non-tectonically induced variations in gas concentration should be recognized in the search for earthquake markers (King, 1986).

It was suggested, that the action of geologic hydrogen could have contributed, or even have been a trigger for the Chornobyl catastrophe (Шестопапов et al., 2018; Шестопапов, 2016) (n.b. correct transliteration from Ukrainian). The Chornobyl region is covered with surface depressions, which have been shown to be releasing molecular hydrogen. It was shown in other studies that soil in such areas may subside (Larin et al., 2015; Zgonnik et al., 2015; Шестопапов et al., 2018), probably as a result of diagenetic action of hydrogen on rock. During the year of the Chornobyl catastrophe many small earthquakes were recorded and one earthquake in particular was registered only 16 s before the catastrophe. It was therefore proposed, that the quake resulted from a soil subsidence may have caused a resonance effect in the building, which housed the reactor, and the resultant catastrophic explosion (Шестопапов et al., 2018; Шестопапов, 2016).

Another process called hydrogen embrittlement may contribute to the weakening of structures. It is well known that some metals become brittle and fracture due to the introduction and subsequent diffusion of hydrogen into the metal. While this is actively studied for industrial applications, no work has been done to draw attention to the possibility that hydrogen present in the sufficient quantities to cause embrittlement of man-made structures. However, some Nuclear Power Plants in the Russian Federation have already started to monitor for H_2 in soil (Шестопапов, 2016). Also, in a recent study, hydrogen mapping was successfully used as a tool to predict rockslides around oil and gas pipelines and storage facilities (Аксютин et al., 2010).

5.5. Oil, gas and minerals

This review summarizing the occurrence of hydrogen in nature shows that hydrogen degassing is likely to be widespread phenomenon in both space and time. In the light of these facts, the claims of some authors, that hydrogen plays a major role in the formation of hydrocarbons should be taken more seriously (Войтов and Осика, 1982; Levshounova, 1991; Маракушев and Маракушев, 2008a; Маракушев and Маракушев, 2008b). In the presence of carbon-containing compounds, hydrogen will reduce and convert them into hydrocarbons (Glasby, 2006). Indeed, it has been reported that measured hydrogen concentrations in gas reservoirs are 25 times less than hydrogen concentrations measured beyond reservoir boundaries (Rodgers and Tyrone-Mt, 1984). This would be consistent with a model which attributes the consumption of H_2 by reactions with carbon-containing material. In other studies, it was also reported that concentrations of hydrogen are inversely related to the concentrations of hydrocarbon in oil fields (Левшунов, 1972). Another study indicates that the hydrogen content of the strata of a known hydrocarbon pool decreases

exponentially as the samples locations decrease from 30 to 0 km from the oil field (Levshounova, 1991). Ground water close to petroleum deposits has been reported to be richer in hydrogen than ground water close to natural gas deposits (Зингер, 1962). Another study shows that ground water samples from aquifers surrounding oil and gas fields, contain dissolved hydrogen at concentrations higher than those in direct contact with the oil and gas fields (Стадник, 1970). These facts suggest that hydrogen is reacting with carbon-containing material, which explains why hydrogen concentrations decrease in the vicinity of oil and gas deposits.

If hydrogen is released from depth, it is unlikely that any portion of it will penetrate upward beyond the hydrocarbon thermogenic zone because the hydrogen will be taken up by reactions with carbon compounds (Apps and Van De Kamp, 1993). Laboratory experiments measuring hydrogen saturation in clastic and carbonate rocks show that rocks can adsorb very large amounts of hydrogen compared to their initial content (24–57 times) and are able to retain this hydrogen over several days. The highest retained hydrogen concentrations were observed in limestones. It was suggested that while it is retained in sediments H_2 promotes a more complete transformation of organic matter into hydrocarbons (Levshounova, 1991; Молчанов, 1981). This published research confirms the need to further evaluate the hypothesis that hydrogen originating from deep in the Earth would play an important role in the genesis of hydrocarbons (Hawkes, 1972). And this idea is supported by conclusions from another study, which proposes that observed increases in H/C ratio in hydrocarbons with age and depth may be related to hydrogen influx at depth (Hawkes, 1980). Another study reported the observation that with depth, reduced forms of carbon become more widespread (Войтов, 1986). Moreover, it has been proposed that it is possible that the organic matter in coal deposits also accepts hydrogen coming from depth, and only in zones of active metamorphism of organic matter is hydrogen produced from organic material (Молчанов, 1981). It has also been proposed that deep life forms may contribute to the generation of hydrocarbons at depth, where free hydrogen and a source of carbon is available (Шевченко, 2017).

A more detailed analysis of the role of hydrogen in the formation of hydrocarbons is beyond the scope of this paper. The reader interested in the role of hydrogen in abiogenic theories for the origin of petroleum can find a lot of information in the next review (Glasby, 2006).

The next several references show how hydrogen plotting can be used in oil and gas exploration. Based on a study of hydrogen concentrations along a transect across the Lost Hills Oil field in California (Jones and Pirkle, 1981) the statement was made that H_2 shows a strong correlation with hydrocarbon anomalies and can be used as a petroleum predictor. Hydrogen concentrations in soil gas were studied above the Ostashkovich oil field in Belarus (Voitov and Rudakov, 2000; Войтов et al., 1997). Hydrogen concentrations were higher where the sampling profile crossed clearly visible fault zones and zones corresponding to the oil-water contact. Similar results were obtained for Yuzhno-Aleksandrovskoe oil field (Войтов et al., 2000) and the Pripyat basin in Belarus (Voitov and Rudakov, 2000). High concentrations of hydrogen, up to 95.2%, were observed in the discovery well for the Elsk field in Belarus (Шопухов, 1960). Anomalously high hydrogen concentrations were found in the Gazli gas field, Uzbekistan (Перевозчиков, 2011; Перевозчиков, 2012). The authors concluded that hydrogen could be used as a marker in the search for new oil fields (Войтов et al., 1997).

In the Sections 2.1 Hydrogen as a free gas and 2.4 Hydrogen in inclusions many examples are given of hydrogen being detected in gas from orebodies and mines. Some authors even state that high concentrations of explosive gases, especially hydrogen, is one of the particular properties of orebodies and mines (Малышев and Айруни, 2005). H_2 was reported to be present along with other explosive gases in metal mines (Harrington and Denny, 1931) and to be one of the main constituents of gas in gold mines (Eschenburg, 1980). The presence of hydrogen is a safety issue for miners. There have been attempts to predict the presence of combustible gases in mines through the

sampling and analysis for hydrogen in occluded rocks but it was shown to be a poor predictor of spontaneous hydrogen releases (Nivin, 2009).

The many instances of the detection of hydrogen associated with orebodies and mines has stimulated researchers to examine whether there is a causal link between hydrogen and mineral ore. For example, in the next cited study the authors compare gold-bearing zones with hydrogen-rich zones and suggest that there is a relationship (Letnikov and Narseev, 1991). They observed an increase in hydrogen concentration with depth and proposed that it can be used as search marker for new mineral veins. By mapping hydrogen concentrations in the Trans-Challis fault system of Idaho and the Carlin trend in Nevada, researchers concluded that anomalous concentrations of hydrogen can be useful in the identification of mineral deposits covered by overburden (McCarthy and Kiilsgaard, 2001; McCarthy and McGuire, 1998). Other studies mention that hydrogen concentrations increase with depth in uranium and rare earth orebodies (Поцелуев, 2010). A hydrogen anomaly was reported to have been detected over the Uchkuduk uranium deposit in Uzbekistan (Перевозчиков, 2011). Some work has been done to suggest that hydrogen may have been active in the formation of certain uranium deposits for which no other reducing agents have been found (Перевозчиков, 2011; Levinson, 1977). It was suggested that hydrogen plays an important role in the formation of native elements and their alloys (Яценко et al., 2012a; Dekov and Damyanov, 1997; Лукин, 2006). Other work has been done which proposes that orogenesis could be related to ascending hydridic fluids acting as vectors for mineral systems (Walshe, 2006; Walshe et al., 2005; Larin, 1993).

Earlier in this article it was shown that high volume releases of hydrogen were discovered in kimberlite pipes (Table 7). Some work has been done to suggest a primary role for hydrogen in the formation of kimberlites (Портнов, 1999), and also in the formation of diamonds (Larin, 1993). Indeed, it should be noted that it has been shown experimentally that diamonds can be grown from methane-hydrogen gas mixtures (Matsumoto et al., 1982). More detailed experiments have shown that diamonds form in the presence of hydrogen-rich fluids in carbon-containing silicates and sulfides at pressures of 50–60 Kbar. In the absence of hydrogen-rich fluid, the P-T conditions necessary for the formation of diamonds are too high for the P-T conditions estimated for their formation depths derived from other indicators (Федоров, 2001). In a recent work the analysis of growth zones in diamonds and concentration of hydrogen in them has been documented. The authors concluded that hydrogen plays a crucial role in the formation of diamonds (Vasilev and Kozlov, 2018).

6. Conclusions

This review clearly shows that molecular hydrogen is present in every type of environment on Earth and often plays an important role in many natural processes. However, its role is underestimated, misunderstood and neglected, which has been the author's primary incentive for this review. A good illustration of the current perception of natural H_2 is the Wikipedia article on hydrogen fuel, stating that “*pure hydrogen does not occur naturally on Earth in large quantities*”. This is clearly not true based on the documented evidence from wells flowing hydrogen with the rate of up to 100,000 m³ per day in East Siberia or the first producing wells in West Africa, where extraction of natural hydrogen has been recorded since 2012 without any apparent decrease in production. The hydrogen flow rate in that West African gas well is high enough to run a generator that produces all the needed electricity for a local village. It is the first case of commercial exploration for natural hydrogen. In 2018, there were 18 exploratory wells drilled in search of hydrogen (Prinzhofer et al., 2018). The first drilling project for natural hydrogen in the USA by Natural Hydrogen Energy LLC successfully ended in the early 2019. Other small and large companies are starting to explore for natural hydrogen in different countries and to test their gas wells for the presence of H_2 . Note that scientists who have reviewed the data and literature on natural hydrogen in the past have stated that “*in the future the extraction and refining of gases containing hydrogen will become a separate branch of industry*” (Shcherbakov and Kozlova, 1986).

While examples such as those cited above may appear rare, it is necessary to mention that these were accidental discoveries. With an intentional search for hydrogen at locations likely to be optimal for the occurrence and production of hydrogen, the chance of finding similar and even greater quantities will be greatly increased. The vast majority of wells worldwide have been drilled in sedimentary basins. But hydrogen is probably too diffusive and too reactive to be trapped in geologic traps for any length of time. Its discovery in significant quantities has shown that it is likely to be more concentrated at depth, with the largest accumulations being found in Precambrian basement, which is seldom targeted during drilling for conventional oil and gas. Moreover, because of preconceptions as to the significance and origin of hydrogen, it is rarely measured by gas analyses. These factors in combination with the fact that hydrogen is colorless, odourless and non-toxic may explain why hydrogen seepages have not been recognized earlier.

It has been shown in this review that hydrogen on the Earth's surface has as yet been insufficiently studied. Some studies on hydrogen only selectively take into consideration just a part from a complex of processes, which are generating and simultaneously oxidizing and reducing chemical species in the geosphere. These are studies on radiolysis and water interaction with fresh mineral surfaces. It is not accurate from a chemical point of view to consider only that part of a reaction where hydrogen is generated and ignore the oxygen side of the equation. Referring to biological process of hydrogen production is used often to explain the source of hydrogen. However, it has been shown in this review that hydrogen is an essential energy source for many simple forms of life, therefore in nature it is mostly consumed rather than produced. The only well-examined process for the occurrence and genesis of hydrogen is serpentinization. Because of this, serpentinization is, in this author's opinion, mistakenly considered as the main (and sometimes the only) mechanism for the natural generation of hydrogen. However, serpentinization is only a small part of a much larger picture which includes a complex hydrogen cycle as part of the many cycles which make-up a dynamic Earth. From a chemical point of view, serpentinization is a redox process between the oxidized surface and a slightly reduced subsurface. Whereas, with increasing depth the redox state of matter becomes more and more reduced and numerous studies propose that the interior of the planet could be hydrogen-rich.

The behaviour and habitat of hydrogen at depth remains almost an unknown subject and researchers should give specific attention to a deep-seated source for hydrogen. Many studies have already demonstrated that the Earth's core and mantle could contain significant quantities of hydrogen stored in the form of hydrides, most likely since the formation of the planet. The progressive decomposition of these hydrides could sustain the observed near surface occurrence of hydrogen, which can impact many processes such as volcanism, the genesis of ores and hydrocarbons, the addition of water to the oceans, microbial life, atmospheric and climatic events, integrity of the ozone layer and much more. Some researchers have suggested that most of the H_2 is seeping from the mantle, but its high chemical activity makes it difficult to clearly determine its' origin. Therefore, it is often mistakenly attributed to other processes (Моисеенко and Сахно, 1982). We should agree that an understanding of the extent and nature of hydrogen as a constituent of the planet is a key to an understanding of the structure, evolution and dynamic state not only of the deep interior of the Earth, but ultimately of the crust, as well of the hydrosphere and biosphere (Williams and Hemley, 2001). Moreover, deep-seated hydrogen could represent an inexhaustible source of energy.

Hydrogen is the most energy-rich of gases and is currently considered to be a good candidate to replace fossil fuels. A recent comprehensive study has reviewed methods for hydrogen production (Nikolaidis and Poullikkas, 2017) and shows that all of the current methods are as yet too expensive to compete with fossil fuels. Therefore, the discovery of substantial sources of natural hydrogen gas would provide a cost-effective boost to a hydrogen economy. Moreover, hydrogen becomes a source of energy, and not its vector, like it is seen currently (Moretti, 2019). At the

moment, exploration for natural hydrogen is in its infancy, where the search for hydrogen shows on the surface may point the way to identifying larger reserves in the subsurface. This is exactly analogous to the situation at the end of the 19th century, when hydrocarbon exploration was just beginning (Smith et al., 2005). Appropriate exploration techniques will be developed to reveal the potential of yet unknown accumulations and seepages (Truche and Bazarkina, 2019). It has been suggested that future exploitation of hydrogen will hinge on the delineation of hydrogen-conducting fracture zones, the presence of possible sealing horizons and the use of appropriate well drilling and completion techniques (Johnsgard, 1988; Шевченко and Силкин, 2015). It is important to note, that unlike natural gas, geologic hydrogen is a carbon-free, sustainable resource, which is constantly being generated underground. The natural processes producing hydrogen have been active since primordial times and will continue for millions of years in the future. Because of this natural hydrogen can be classified as a renewable source of energy. This is why it is sometimes called the clean energy of the future (Truche and Bazarkina, 2019; Белов, 2003). Interestingly, it falls into a global trend toward the less-C/higher-H-content fuels. This trend is observed throughout the history of energy evolution: from coal, through oil, then natural gas and, finally, hydrogen (Ausubel, 2000). In a recent book authors point out that natural hydrogen represents a new source of energy, a rare event in the energy industry (Prinzhofer and Deville, 2015). The title of this book is great as a concluding remark for this review: “*Natural hydrogen, the next revolution? An inexhaustible and non-polluting energy, it does exist!*”.

Declaration of Competing Interest

The author declares no competing interests.

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Appendix B. Supplementary data

Supplementary data associated with this article can be found in the online version, at <https://doi.org/10.1016/j.earscirev.2020.103140>. These data include the Google map of the most important areas described in this article.

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