

Notes for a History of Gas Geochemistry

Guodong Zheng^{1,2}, Giovanni Martinelli^{*2,3}, Yanxin Wang¹, Shun Li⁴, Xiangxian Ma²

1. School of Environmental Studies, China University of Geosciences, Wuhan 430078, China

2. Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China

3. INGV National Institute of Geophysics and Volcanology, Palermo 90146, Italy

4. College of Information Engineering, Shenyang Open University, Shenyang 110003, China

 Guodong Zheng: <https://orcid.org/0000-0002-8137-6477>;

 Giovanni Martinelli: <https://orcid.org/0000-0001-9541-5142>

ABSTRACT: During ancient times, human interest in naturally-occurring gases was religious, while it was scientific in the historical age and industrial in modern times. Gases were also utilized for practical purposes and more than 3 000 years before present day, Chinese populations made use of methane for salt extraction while in the 17th century it was observed that native Americans ignited methane seepages. The development of human thinking on gases followed the fundamental steps that characterized the natural sciences during the 18th century scientific revolution that was based on significant improvements in analytical methods. These improvements are still ongoing while present-day scientific publications evidence the spread of the field of interest and more cooperation with geophysical sciences to solve common interest problems. The existence of proper meetings and dedicated scientific journals confirms that gas geochemistry has ended this pioneering phase to enter a more mature condition.

KEY WORDS: history of earth sciences, gas geochemistry, isotopic analysis, carbon dioxide, noble gases, earthquakes, hydrocarbons.

0 INTRODUCTION

In very ancient times, human interest in naturally occurring gases was solely religious, while it was scientific in the historical age and industrial in modern times. Gaseous hydrocarbons played a central role in the Zoroastrian religion, inspiring the construction of the methane-fuelled fire temples in Azerbaijan, Iran and Irak. In Greece, temples were built around burning springs, such as in the Mount Parnassus area. More than 3 000 years before present day, Chinese populations made use of methane for salt extraction (Fig. 1), while in the 17th century, French explorers discovered that native Americans ignited methane seepages (Paoloni, 1976 and references therein). Carbon dioxide exhalations were exploited in ancient Greece in oracular cults focused on caves (Pfanzt et al., 2014 and references therein; Piccardi et al., 2008 and references therein). The development of human thinking on gases followed the fundamental steps that characterized the natural sciences during the scientific revolution of 18th century that was based on an improvement in analytical methods. The purpose of present paper is to better highlight most relevant steps of evolution of gas geochemistry during historical times.

*Corresponding author: giovanni.martinelli15@gmail.com

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1 BIRTH AND DEVELOPMENT

1.1 The First Steps Taken by Gas Geochemistry Starting from Chemistry and Physics

Georgius Agricola (1494–1555), a German scholar and scientist known as “the father of mineralogy”, wrote the first book about mining technology in the mining district of Freiberg, the famous “De re Metallica” (Agricola, 1556). He was the first to state that natural gas emission sites and springs are suitable pathfinders for detecting mineralized fault zones. An interesting overview of springs, geogas and the first analytical methods is presented in his third volume: “De natura eorum, quae effluunt ex terra” (1546). Jean Baptiste Van Helmont (1577–1644) recognized the existence of discrete gases and identified carbon dioxide in Belgium in the 17th century. This was an important step forward in analytical technology. Its application in geosciences occurred a few years later. Freiberg University in Germany was involved in these findings as well, with Wilhelm August Lampadius (1772–1842), the inventor of the first gas streetlamp, playing a very active part (Heinicke and Martinelli, 2005). In this case as well, technicians played an important role in the applications of gas analysis (e.g., CO₂) for geochemical purposes, in particular in the characterization of different springs or spas, their water and gas composition. During the 18th century interest in the identification of the chemical stones of matter triggered an interest in naturally occurring gases. In 1776 Alessandro Volta (1745–1827) identified methane in Italy from the gaseous seepages of sediments. William Henry in Great Britain accurately identified the chemical composition of methane in 1803, and in the first half of 19th century industrial methane

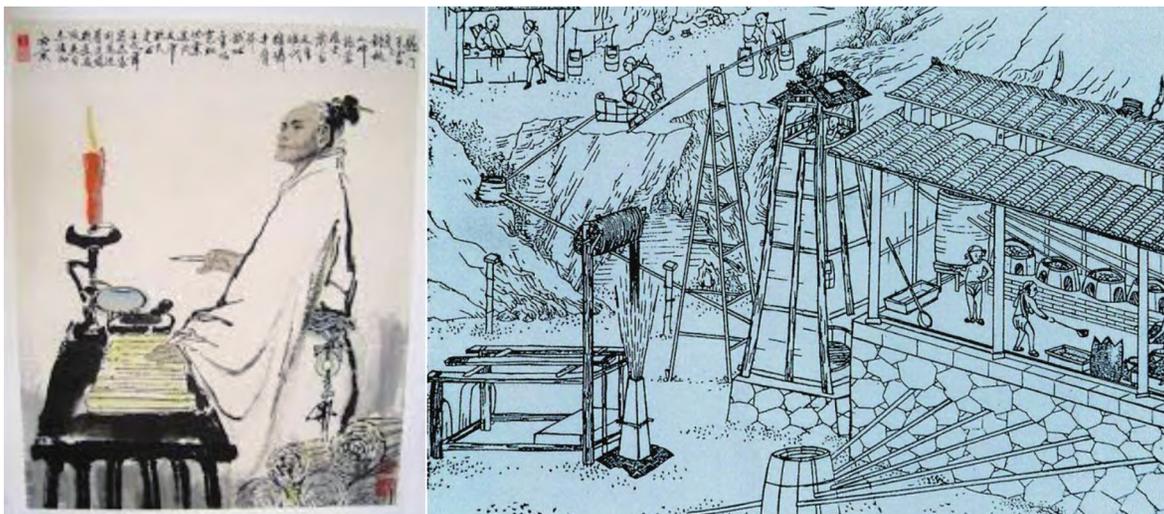


Figure 1. Paintings on the oils and gases extracted from rocks in ancient China. Left: Shen Kuo (1031–1095 A.D.), a famous Chinese traveller. He described “shiyou” (in Chinese, namely oil from stones) in his book *Mengxibitan* (*Dreams Pool Essays*) which was published in Song Dynasty (960–1279 A.D.). Right: sketch showing boiling salts obtained by the boiling of brackish groundwaters by methane burning (Needham, 1986).

extraction began in various locations around the world. In the second half of the 19th century, methane extraction from terrestrial rocks strongly concurred to provide the energy for the industrial revolutions in Europe and the United States. In 1756, Joseph Black (1728–1799) in Great Britain identified the most relevant chemical characteristics of CO_2 in the laboratory and thought that the identified gas was the same as that found in volcanic geological contexts (West, 2015). The investigation of volcanic activities followed. In 1788 the French scientist Dolomieu reported that “the terrible phenomena occurring during volcanic eruptions are produced by the generation of volatile substances”. In 1792 the Italian abbot Spallanzani suggested “the collection and chemical analysis of the gases emitted by volcanoes, to better comprehend their nature and origin”. In his famous book “*Kosmos-Entwurf einer Weltbeschreibung*”, Alexander von Humboldt in Germany described different observed geological phenomena of the world related to different, though mostly CO_2 -emitting sites: volcanoes, springs and fluid emission sites on fault zones (Humboldt, 1845). In 1856 Charles Sainte-Claire Deville in France suggested that: (i) the nature of the exhalations emitted at the same spot changes with the time elapsing from the start of the eruption; (ii) the nature of the exhalations emitted at different spots changes with the distance from the eruptive center (Sainte-Claire Deville, 1856). In 1865 Ferdinand André Fouqué published in France the first chemical data on gaseous volcanic emissions (Fouqué, 1865). Seventy-eight percent of the Earth’s atmosphere is made up of nitrogen, a gas discovered by Daniel Rutherford in 1772 in Great Britain. John Dalton (1793) in Great Britain better contributed to a more complete understanding of the atmosphere as a combination of several gases. Joseph-Louis Gay-Lussac and Jean-Baptiste Biot in France more accurately specified the chemical composition of the atmosphere in 1841. Research into gases in the atmosphere grew rather intense in the 18th century. In 1784 Henry Cavendish in Great Britain noted that a persistent residue was present in the air after the chemical removal of nitrogen and oxygen. This was the first clue toward

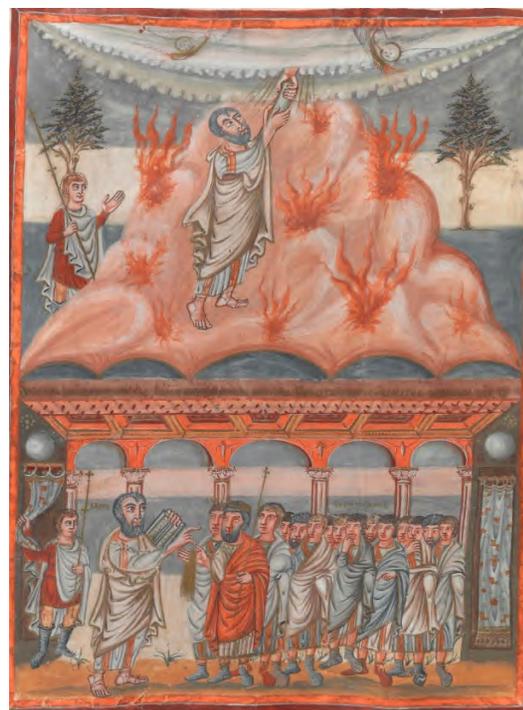


Figure 2. Moses receiving the Law from the Hand of God, and extolling the Law to the people, at the beginning of Exodus. Gaseous emissions marked by fire are visible. Grandval Bible, British Museum, 840 A.D. <https://blogs.bl.uk/digitisedmanuscripts/2018/05/the-spectacular-moutier-grandval-bible.html>

the identification of noble gases. Argon was identified by John William Strutt (3rd Baron Rayleigh) and William Ramsay in Great Britain in 1895, and soon after that Norman Lockyer and William Crookes in Great Britain identified helium. In 1898 William Ramsay and co-workers identified neon, krypton and xenon. The noble gas column of the Periodic Table was completed in 1900–1903 by the identification of the gaseous emanation of thorium and radium as a noble gas, i.e., thoron and radon (Ciardi, 1998).

1.2 Gas Geochemistry as an Independent Scientific Discipline

The physical and technical invention and development of mass spectrometers were a revolution in the analysis of gases and their different isotopes. The geosciences rapidly made use of this tool. Allen (1922) and Jaggar (1940) proposed collections of volcanic analytical data and their first interpretation. Vernadsky (1924) defined outgassing phenomena as “the gaseous breath of the Earth” while Irwin and Barnes (1980) recognized a fundamental role of CO₂ in geodynamic processes along fault zones, in particular in seismically-active regions. In 1948, Aldrich and Nier (1948) reported their first observations on helium isotope composition in terrestrial gases. Further steps ahead in noble gas geochemistry were made possible only after the introduction of new advanced mass spectrometric techniques (Reynolds, 1956). Due to high noble gas depletion in terrestrial materials their isotopic ratios are more variable than other elements and so their peculiar distribution is utilized to track fluid fluxes from the mantle to the crust and from the crust to the atmosphere. Noble gases are nearly always mixed with the three main terrestrial gaseous environments dominated by CH₄, CO₂ and N₂. A knowledge of the abundance of noble gases and their related isotopes has helped to solve many significant problems concerning crustal evolution (Sano and Marty, 1995; Sano and Wakita, 1985; Mamyurin and Tolstikhin, 1984; Butler et al., 1963). Further applications of noble gas geochemistry were found in the age-attribution of geological materials, in research into meteorites, and so on. Mamyurin and Tolstikhin (1984) compared the first steps in noble gas geochemistry to a sort of “desert island”, not born directly from earth sciences but spinning off from advanced technology. Present day applications of noble gas geochemistry are the subject of specialist scientific journals and books (e. g., Ozima and Podosek, 2002; D’Amore, 1977; Vyshemirskii, 1977), among others, introduced gas geochemistry as an autonomous scientific discipline. Giggenbach (1996) summarized the main knowledge on volcanic gases and related geological environments on the grounds of the available data collected in geothermal and volcanic areas. All of the geosphere is being continuously crossed by fluid fluxes that are variable both in their flow rate and their chemical composition. Gas geochemical techniques developed in past 50 years have strongly contributed to better describing gas accumulations, gas fluxes and their geological causes (e. g., Hilton et al., 2013). Specific implications have been rapidly developed in the investigation and study on geological greenhouse gases in last 10–15 years worldwide (Zheng et al., 2021).

2 APPLICATION FIELDS

2.1 Gas Geochemistry in Hydrocarbon Geological Contexts

Alfred Treibs (1936) was the first to discover porphyrins in oil and identified them as derivatives of chlorophyll. This discovery was the starting point of organic geochemistry, which includes organic gas geochemistry. One of the main tasks of organic gas geochemistry is the identification of the factors able to transform biogenic organic matter into hydrocarbons. One of the first surface hydrocarbon prospecting methods by soil gas analysis was patented in 1929 and published in

1933 (Laubmeyer, 1933). Meanwhile, an instrument for measuring radon and thoron liberated during the radioactive disintegration of the uranium series elements was invented in the Soviet Union. If microgas seepages exist above hydrocarbon reservoirs they could alter the adsorption of radioactive gases present at the surface, and the instruments were able to detect it (Sokolov, 1933). In the period 1935–1960 in the USA attention was paid to analytical techniques of gases obtained by heating soil sampled in hydrocarbon research target areas (Horvitz, 1985) and to gas geochemistry of samples collected in soils (Philp and Crisp, 1982). The first in-depth isotopic studies of hydrocarbon gases were carried out by Nakai (1960) within the frame of research on hydrocarbons that started in Japan after 1955 (Motojima, 1975). Zartman et al. (1961), Fuex (1977) and references therein, Jones and Drozd (1983) in the USA, May et al. (1968) in East Germany, Colombo et al. (1965) in Italy, Lebedev (1964), and Galimov (1973) and references therein in the Soviet Union the initial basic knowledge of isotope geochemistry applied to gaseous hydrocarbons was developed. Erik M. Galimov (1936–2020), who headed the Laboratory of Carbon Geochemistry at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, explored, among other topics, all the various behaviours of carbon in rocks and in hydrocarbons at various sites in the world, including China, where scientists of the Chinese Academy of Sciences developed their findings. Further research into noble gases in gaseous hydrocarbons was developed in China by Xu Y C (1976), Xu S et al. (2017), who discovered particular accumulation processes of helium and argon in petroleum reservoirs. Noble gases may be utilized to distinguish biogenic and/or abiogenic sources of hydrocarbon gases based on different isotopic ratios.

2.2 Gas Geochemistry in Geothermal and Volcanic Geological Contexts

At the beginning of the 20th century, there was a lively scientific debate about the reliability of volcanic gas analysis as only a few satisfied the condition of air-free collection and analysis by precise methods. Clarke (1916) reviewed previous data and demonstrated that a large number of reactions are possible starting with only water, carbon dioxide and the minerals of magma. Studying variations in the theoretical gas compositions with temperature and those found in natural geothermal gases, Ellis (1957) found that high temperature gas discharges associated with volcanic systems closely approach a state of chemical equilibrium. Furthermore, D’Amore (1977), D’Amore and Nutti (1977) and Giggenbach (1980) published papers dealing with the chemical reactions that may justify the presence of the more common gas species and their relative abundance in geothermal fluids (H₂O, H₂S, NH₃, N₂, CO₂, CH₄). These reactions are used, among others, as geothermometers for identifying the deep temperatures in the main geothermal reservoir.

2.3 Gas Geochemistry in Tectonically Active Geological Contexts

The pioneering data published by Ulomov and Mavashev (1971) in the former Soviet Union, by the Group of Hydrochemistry, the Seismological Brigade of Hebei Province (1975) in China, by King (1986) and references therein in the USA,

by Wakita et al. (1988) and references therein in Japan started the race toward earthquake prediction by geochemical methods in geofluids (Martinelli, 2020). Although no definitive results have been reached to date, research spread toward many fields of tectonics, such as fault location and seismic hazard evaluation (Toutain and Baubron, 1999; Irwin and Barnes, 1980). Soil gas investigation and research have been performed in numerous seismic faults in China with identical results in recent years, especially in the Longmen Mountains fault zone since the huge M_s 8.0 Wenchuan Earthquake on May 12, 2008 and the capital region faults (e.g., Chen et al., 2020; Zhou et al., 2010). Gas geochemistry is at present utilized not only in research about possible earthquake precursors and/or for fault location but also to identify the deep geological driving forces of crustal evolution (Zhang et al., 2021; Pik et al., 2006).

2.4 Gas Geochemistry in Living Environments

Carbon dioxide emitted by volcanoes and by faulted areas influences organismic life. It irritates various species of animals although some species of plants show adaptation to CO_2 atmosphere and to acidic soils (Pfanzen et al., 2004). Furthermore, CO_2 and H_2S emanations may be hazardous for local inhabitants (Tchindjang, 2018; Williams-Jones and Rymer, 2000). Among noble gases transported by carrier gases, radon has been widely used as a sensitive tracer to characterize a variety of processes, including gas exchange rates between air and water, uranium exploration, rocks and the atmosphere of living spaces.

In particular, indoor radon exhalations are related to human health risks. Radon effects are currently studied very often as a radiation (e.g., UNSCEAR, 2008). In spite of this, gas geochemistry considers radon as a noble gas and contributes to the general knowledge of noble gas geochemistry (e.g., Baskaran, 2016 and references therein).

2.5 Gas Geochemistry in Waste Treatment

Waste storage is a matter of concern in risk assessments of industries and for municipal management. Geological disposal techniques imply the knowledge of various scientific disciplines, such as geology, geochemistry and engineering. These disciplines may contribute to improving storage techniques and landfill design. Gas geochemistry has been also utilized to track leakages in power plants or in waste disposal landfills (Langhrey and Baldassare, 2003; Ross and Amter, 1989). The long-term stability of carbon dioxide capture and storage (CCS) is challenging for gas geochemistry.

2.6 Geological Greenhouse Gases

The Earth is subjected to climate variations which have affected the evolution of the planet during the geological time. In recent decades, significant climate variations have been observed and, for the first time, attributed to human activities (e.g., IPCC, 2021; Masson-Delmotte, 2021). Ekholm (1901 and references therein) reported that the increasing concentration of CO_2 in the atmosphere is inducing climate changes through a greenhouse mechanism. The earth science scientific community has recognized that most relevant greenhouse gases are CO_2 , CH_4 and N_2O (Lamb et al., 2021 and references therein). These gases are mostly produced by human activities through the utilization

of fossil fuels and the management of intensive agriculture. Greenhouse gases may be monitored by conventional or by satellite techniques (e.g., Xu et al., 2020). Meanwhile a significant fraction of greenhouse gases is produced by geological environment through natural seepages. Gas geochemistry has contributed to the inventory of natural greenhouse gases in all countries (Etiopie and Schwietzke, 2019 and references therein; Fischer et al., 2019 and references therein).

2.7 Carbon Capture and Storage (CCS)

Carbon capture and storage (CCS) aims to prevent the release of CO_2 from heavy industry with the intent of mitigating the effects of climate change is the process of capturing carbon dioxide (CO_2) and storing it (carbon sequestration) for geological times (Sun et al., 2018). CO_2 is captured from large point sources and then stored in an underground geological formations (Wei et al., 2021). The first CCS plant was proposed by Marchetti (1977) and entered commercial service close to Houston (USA) in 1977. CO_2 storage in geological formations has been used in different parts of the world. A great variety of physical processes and chemical reactions (Marini, 2007) are involved in the injection and post-injection phases of carbon dioxide. Monitoring the reservoir for eventual leakages (De Paolo et al., 2013) is critical in the post-injection storage phase. Geophysical and geochemical parameters in the gaseous, liquid and solid phases are commonly utilized to monitor CCS reservoirs. Relevant contributions of gas geochemistry to carbon storage techniques have been reached in the fields of site selection, reservoir engineering and environmental monitoring (Romanak and Dickson, 2022; Akono et al., 2019). Geochemical monitoring techniques include also noble gases and related isotopes (Weber et al., 2021).

2.8 The Support of Gas Geochemistry to Geoheritage and to Geo Tourism

The release of geogenic gases in different forms is an important factor supporting the development of tourism in many regions of the world (Baciu, 2012; Erfurt-Cooper, 2011). Thermal and mineral waters generally contain various amounts of dissolved gases, essential for their biological effects. The use of thermal and mineral baths for therapeutic purposes has a long history (Erfurt, 2021). Beyond their practical use, the ancient civilizations have developed an important element of their culture related to the possible healing properties (e.g., Niewöhner et al., 2013) of dissolved and gaseous geochemical parameters in geothermal waters and muds. All across ancient territories ruins of spas and other facilities dedicated to the use of waters for cleansing, therapeutic bathing and therapeutic inhalations and breathing (e.g., Keller et al., 2014) can be found in almost every place with thermal springs or with muddy pools or with gas emissions. Gas geochemistry strongly contributed during past decades to the knowledge of the origin of utilized geofluids (e.g., Guo, 2012 and references therein). As a general outline, the main therapeutic factors that gave value to these watering places, present in various proportions and combinations in each of them, are as follows: waters with increased contents of dissolved mineral compounds, thermal waters, dissolved and also dry CO_2 , H_2S , radon and thoron. The scientific interest and

scenery of volcanoes, geothermal areas, mud volcanoes, mofettes (Sisto et al., 2020; Soentgen, 2010) etc. are important premises for their inclusion in tourist circuits.

2.9 Ore Deposit Contexts

Since the late-1980s, with the accumulation of knowledge on gas geochemistry, researchers have studied the noble gas isotopic compositions of ancient ore-forming geofluids (Simmons et al., 1987). Volatile stable isotopes and noble gas isotopes are effective tracers for separating diluted mantle-derived fluids from other types of crustal components, as well as implying magmatic conditions and tectonic settings isotope compositions of C and of noble gases differ significantly across tectonic domains (Zhang et al., 2009 and references therein; Turner et al., 1993). The development of the Earth's atmosphere and hydrosphere was aided by degassing of the Earth's mantle and it continues to affect our global ecosystem. Volatiles have a crucial function in mantle differentiation and development. Mantle metasomatism, magma production, and crust-mantle interactions plays important roles in earth's evolution. Under supercritical conditions, volatiles in the Earth's mantle are in a supercritical state and can transport large amounts of economically significant metals from the Earth's deep interior (Xie et al., 2016 and references therein; Olmez et al., 1986). For instance, pyrite is known as a suitable trap for noble gases (Burnard et al., 1999), because it retains helium over geological periods, in contrast to quartz and feldspar. Further applications of gas geochemical prospections have been carried out in research into sulphide ores. The oxidation of sulphide minerals creates an O₂ demand that is partially met by the overlying soil air, while the acid formed by the oxidation reactions attacks carbonate minerals nearby to release CO₂, a portion of which migrates into the overlying soil pores. Soil air anomalies with a negative O₂ component and a positive CO₂ component may indicate oxidizing mineralization (Lovell et al., 1983 and references therein).

2.10 Hydrogeological Cycle Contexts

The use and management of aquifers require an understanding of aquifer hydrogeology and its dynamics, which can be obtained through years of observations and measurements of precipitation, river flows, etc. Early advances in groundwater hydrology centered on techniques for estimating aquifer storativity and hydraulic conductivity, which led to the establishment of the theory of transient groundwater flow (e.g., Anderson, 2008). Isotope techniques, especially those that can be used to estimate the age of groundwater, contribute to the development of a conceptual framework of aquifer hydrogeology and flow system in a cost-effective manner. The age of groundwater for estimating aquifer storage, the rate of groundwater renewal, and flow velocity can be determined through tritium (von Buttlar and Wendt, 1958) and ¹⁴C analysis (e.g., Aggarwal et al., 2012 and references therein). Brinkmann et al. (1959 and references therein) for first proposed to utilize isotopic carbon composition of carbonatic species derived by CO₂ to estimate the age of groundwaters. Analysis of noble gases can provide additional details about the age of groundwater and the infiltration processes. The concentrations of noble gases in the hydrosphere are governed primarily by the solubility of noble gases

in surface waters. Equilibrium concentrations in surface waters are determined by the water's temperature (T), salinity (S), and ambient atmospheric pressure (P). Consequently, the determination of the concentrations of the five stable noble gases (He, Ne, Ar, Kr, and Xe) in any water sample ought to allow for the reconstruction of the T, S, and P conditions under which the water equilibrated with the atmosphere. Any body of originally meteoric water that has been sealed off from the atmosphere can be seen as a potential archive of past environmental conditions. The most important of these potential archives are groundwaters, which cover a range of residence times from days to millions of years (Wang et al., 2022; Pinti and van Drom, 1998; Mazor, 1972 and references therein).

2.11 Crust-Mantle Interactions: Potential Origin For Hydrogen and Oxygen

Alvarez and Cornog reported that: "We have now adjusted the shims of the 60-inch cyclotron so that it is possible to obtain a steady beam of 24-Mev He⁺⁺ ions. We have compared the isotopic ratio ³He/⁴He of tank (gas-well) helium to that of spectroscopically pure (atmospheric) helium, and find that it is about twelve times as great for atmospheric helium as for the gas-well variety" (Alvarez and Cornog, 1939). The advances in mass spectrometry resulting from the so-called Manhattan Project (1942–1946) during the Second World War (WW2) opened up new opportunities in gas geochemistry in the post-war years (Yergey and Yergey, 2020; Burnard et al., 2013). In 1969 Clarke and coworkers reported that "the excess ³He is due to leakage into ocean water of a remnant of the earth's primordial ³He" (Clarke et al., 1969 and references therein). These pioneering authors opened the door to further researches oriented to a better understanding of mantle degassing processes and to crust-mantle interactions. Important contributions were made up to the period 1960–1985 by gas-geochemical researchers who carried out substantial investigations of the helium isotope abundance in sea water, basalts of oceanic crusts, rocks and gases of mantle origin. As a result, a complete distribution of helium isotopes on the Earth, in the ocean and the atmosphere is now available (e.g., Mamyrin and Tolstikhin, 1984). Present-day knowledge allows us to locate and quantify mantle-derived geofluids in the Earth's crust (Polyak et al., 2020). Active tectonics driven by continental collision maintained an efficient release of noble gases over geological timescales along faults (Zhang et al., 2022 and references therein).

2.12 Atmospheric Evolution and its Chemical Composition

Brown (1952) has been one of the first researchers to utilize noble gas composition to understand the early stages of the Earth's atmosphere. During the first two billion years of the Earth's existence, atmospheric oxygen levels were extremely low. Not until at least 500 million years after the evolution of oxygenic photosynthesis, and possibly as early as 3 billion years ago, did oxygen levels during the Great Oxidation Event reach appreciable levels. Thereafter, marine carbonates experienced the Lomagundi event, a large positive fluctuation in carbon isotope ratios (Catling, 2014, and references therein). In an anoxic atmosphere, the loss of O₂ due to continental oxidative

weathering is negligible; therefore, the dominant sinks on O_2 in the Archean must have been reactions with volcanic and metamorphic reductants, such as reducing gases (H_2 , CH_4 , CO , SO_2 , and H_2S) and dissolved reducing cations (e.g., Fe^{2+}) in direct communication with the atmosphere. In the redox chemistry of the atmosphere, the chemical adversaries of O_2 are hydrogen-containing reduced gases (such as CH_4 and H_2). Eguchi et al. (2020) demonstrated that a tectonic transition that resulted in increased volcanic CO_2 emissions about 2.5 billion years ago have led to increased deposition of both carbonates and organic carbon (organic C) via enhanced weathering and nutrient delivery to oceans. Increased burial of carbonates and organic C increased the delivery of carbon to subduction zones and allowed for the accumulation of atmospheric oxygen. Eguchi et al. (2020) found that a tectonic transition can simultaneously explain the Great Oxidation and Lomagundi events. This tectonic transition may explain how the Earth became oxygenated allowing for the proliferation of complex life on the surface. Noble gases have contributed significantly to our understanding of the origin of Earth's volatiles, the structure of the mantle, and the long-term degassing of the mantle. Although the differences between the MORB mantle and the plume mantle cannot be solely explained by recycling atmospheric volatiles, noble gases derived from the atmosphere have been injected and incorporated into both mantle reservoirs throughout Earth's history (e.g., Mukhopadhyay and Parai, 2019).

2.13 Oceanic Evolution

Approximately 50 to 150 million years later, the water vapor of the Earth's secondary atmosphere condensed to form the oceans. In equilibrium with a CO_2 -dominated atmosphere, the ancient ocean was likely more acidic and anoxic than it is today (Rubey, 1951 and references therein). As in modern seawater, halite dominated the chemistry of the Archean ocean, but the total concentrations of elements such as halogens were higher. These concentrations can be explained by a mantle-buffering effect on ocean chemistry as a result of large-scale hydrothermal interactions with the oceanic crust (e.g., Pinti, 2005). Metals are mobilized and transported by oxidized brines with moderate temperatures (80–250 °C) and moderate-to-high salinity (10 wt.%–30 wt.%), limiting their maximum age to 2.4 billion years ago. Transport along faults, either during rifting or basin inversion, concentrates these fluids at oxidation-reduction interfaces such as distal-facies black shales, where metals precipitate (Hoggard et al., 2020). The distribution, accumulation, and circulation of oxygen and hydrogen within the interior of the Earth determine the geochemical evolution of the hydrosphere, atmosphere, and biosphere.

Two end-members of the oxygen-iron (O-Fe) system, the oxygen-rich atmosphere and the iron-rich core, overlap the entire pressure-temperature composition range of the planet. The interactions between O and Fe determine the formation of the Earth, the separation of the core and mantle, and the development of the atmosphere. Iron's multiple oxidation states regulate the oxygen fugacity and oxygen budget, with hydrogen playing a crucial role in the reaction between Fe and O. The mineral goethite, $FeOOH$, which is concentrated in bog iron ore, decomposes under the conditions of the deep lower mantle

to form FeO_2 and release H_2 . The reaction could result in the accumulation of dense FeO_2 -containing patches in the deep lower mantle, the upward migration of hydrogen, and the separation of the oxygen and hydrogen cycles. This hydrogen, in principle, could be the precursor of abiogenic methane (Hu et al., 2016).

3 CULTURE OF GAS GEOCHEMISTRY: MEETINGS AND PUBLICATIONS

Over the past fifty years, scientists' and scholars' studies in gas geochemistry have been chiefly communicated at IUGG, AGU, EGU and AAPG scientific meetings. In spite of its growing scientific importance, a kind of ancillary role has been commonly attributed to gas geochemistry in modern times, also as a result of more visible advances in the scientific disciplines benefiting greatly from mass media popularization such as Geology, Geophysics and Geochemistry. Nevertheless, different opportunities for scientific exchanges have been independently established over the past three decades. Among these, a series of International Conferences on Gas Geochemistry (ICGG) have been held. The first partly official meeting was held in 1982 in the research center of the Commissariat à l'Energie Atomique of Fontanay-aux-Roses (Paris), organized by P. Zettwoog. Scientific communications were not published in a single book, but in various different scientific journals, thus some of the participants promoted the 1st International Colloquium on Gas Geochemistry, held in Mons, Belgium in 1990 and organized by J. M. Charlet, L. Dejonghe and P. Doremus (see Table 1 for a complete list). The 16th conference will be held in the Canary Islands, Spain. In order to improve academic exchange and collaboration opportunities for domestic scientists in China, a Professional Board for Gas Geochemistry was set up under the aegis of the Chinese Society for Mineralogy, Petrology and Geochemistry in 2018 and a special celebration symposium in China for isotopic techniques and related implications in earth sciences is organized every two years with more than 400 participants at each event. Each edition of the International Conference on Gas Geochemistry was followed by the publication of most of the relevant papers presented at the meetings in scientific international journals in special issues. This approach will be followed by local meetings as well.

4 CONCLUSIONS

The history of gas geochemistry is to some extent the result of technical inventions combined with a growing interest in earth sciences. In very ancient times, human interest in naturally occurring gases was only religious, while it was scientific in the historical age as well as the industrial age in modern times. The development of human thinking on gases followed the fundamental steps that characterized the natural sciences during the 18th century scientific revolution that was based on an improvement in analytical methods. The current trends confirm that Earth, Energy and Environmental Sciences are the most promising fields for the application of gas geochemistry and noble/rare gas geochemistry, as they are more related to technological advancements than to a straightforward geological knowledge. A more direct cooperation with geophysical sciences is still needed to solve the increasingly challenging problems in which gas geochemistry is involved.

Table 1 List of international conferences on gas geochemistry since 1990

No.	Place	Organizers	Time	References
1	Mons, Belgium	J. M. Charlet, L. Dejonghe P. Doremus	1990	http://biblio.naturalsciences.be/rbins-publications/memoirs-of-the-geological-survey-of-belgium/pdfs/msgb-1992-32x.pdf
2	Besançon, France	A. Chambaud, D. Klein, Rebetz M., C. Dubois	1993	https://books.google.it/books/about/Gas_Geochemistry.html?id=MpMQAQAAMAAJ&redir_esc=y Supplement to Volume 16 (1994) of Environmental Geochemistry and Health
3	Amritsar, India	H. S. Virk	1995	Virk H. S. (Ed.) 1997. Rare gas geochemistry, applications in Earth and Environmental Sciences. Guru Nanak Dev University, Amritsar, 372 p
4	Rome, Italy	P. F. Biagi, G. Ferrara, G. Martinelli	1997	https://www.sif.it/riviste/sif/ncc/econtents/1999/022/03-04
5	Debrecen, Hungary	I. Hunyadi	1999	https://aleph.omikk.bme.hu/F/?func=find-b&request=000154036&find_code=SYS&adjacent=N&x=27&y=11&filter_code_1=WLN&filter_request_1=&filter_code_2=WYR&filter_request_2=&filter_code_3=WYR&filter_request_3=
6	Cuernavaca, Mexico	N. Segovia, M. Mena, Y. Taran	2001	http://revistagi.geofisica.unam.mx/index.php/RGI/issue/view/50
7	Freiberg, Germany	J. Heiniche	2003	https://www.annalsofgeophysics.eu/index.php/annals/issue/view/236
8	Palermo, Italy	F. Italiano	2005	https://www.annalsofgeophysics.eu/index.php/annals/article/view/4434?articlesBySameAuthorPage=2
9	Taipei, Taiwan	T. F. Yang	2007	https://onlinelibrary.wiley.com/toc/14688123/2008/8/4
10	Cluji, Romania	C. Baciú	2009	https://onlinelibrary.wiley.com/toc/14688123/2010/10/4
11	San Diego, USA	D. Hilton	2011	https://www.sciencedirect.com/journal/chemical-geology/vol/339/suppl/C
12	Patras, Greece	G. Papatheodorou	2013	https://www.ufr-team.com/international-conference-gas-geochemistry/
13	Chengdu, China	Y. P. Wang	2015	https://www.sciencedirect.com/journal/chemical-geology/vol/469/suppl/C10.1016/j.marpetgeo.2017.08.023
14	Wrocław, Poland	A. Solecki	2017	https://wggg.pwr.edu.pl/fcp/PGBUKOQtTKlQhbx08SlkTUA1QX2o8DAoHNiwFE1xVSH9RFVZ-pCFghUHcKVigEQUw/_users/code_gB1YUPhBYUQvSvQciAwIUVwQCBDpICakXRzUN/konferencje/icgg14/book_of_abstracts_xiv_icgg_cover.pdf
15	Palermo, Italy	F. Italiano	2019	https://www.frontiersin.org/articles/10.3389/feart.2022.936733/full

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