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Migration of carrier and trace gases in the geosphere: an overview

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Abstract

The migration mechanisms of endogenous gases in the geosphere are defined in relation to the fluid-rock conditions and analyzed by basic transport equations. Upon examining the geological factors that influence the physical parameters in the equations in porous and fracture media, and considering the widespread high-permeability of deep subsurface rocks, in terms of fracture aperture, (orders of 10^{-2} to 10^{1} mm at depths of thousands meters, as suggested by recent crustal surveys) advection of carrier gases, in its several forms (gas-phase flow, water displacement by gas, gas slugs and bubbles) seems to represent a major migration process. Accordingly, in contrast with early views, the role of gas diffusion and water advection in the transport of endogenous gas to the Earth surface should be strongly minimized in many contexts. In a wide range of geological settings, carrier gases (CO_2, CH_4) may assume a dominant role in controlling transport and redistribution toward the Earth's surface of trace gases (Rn, He). Bubble movement in fissured rocks seems to be an effective way of rapid (gas velocities in the order of 10^{0} to 10^{3} m per day) and long-distance gas migration. The evolution from bubble regimes to continuous phase flow and vice versa, as gas pressure and fracture width change, is the most suitable mechanism towards determining the surface geochemical processes of seismo-tectonic, environmental and geo-exploration relevance. The transport effectiveness of trace gases by a carrier gas has yet to be studied in quantitative terms. It is already clear, however, that further studies on the distribution and behavior of trace gases approaching the Earth's surface may not be meaningful unless accompanied by carrier gas dynamics analyses.

Keywords: Gas migration; Advection; Diffusion; Fractures; Bubbles; Carbon dioxide; Radon

1. Introduction

The origin and migration of subterrestrial gases in the geosphere have been studied in many fields of Earth sciences, both within the framework of exploration and environmental geology. While major aspects of gas genesis and behavior are now completely understood, much confusion and doubts remain over the migration processes. Moreover, some aspects of gas transport mechanisms, studied in gas dynamics and engineering contexts, are generally unrecognized in Earth science literature, and in particular in seismo-tectonic and environmental applications.

In applying gas dynamics rules to the geological context, a first simple consideration we should make is that the gas movement mechanism generally reflects the amount of gas in a given volume of rock (the magnitude and rate of gas production and accumulation) and its chemical reactivity. Subterrestrial gases include highly reactive species (H_2O, CO_2, H_2S, NH_3, H_2, N_2), less reactive (CH_4, and heavier hydrocarbons), and inert, noble gases (mainly He, Rn, Ar). Accor-

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ding to the experience gained with geothermal, petroleum and tectonic prospection, CO_2 and CH_4 can be considered gas carriers due to large amounts in several geological environments (Durrance and Gregory, 1990; Morner and Etiope, 2001). Carbonate metamorphism is the main process responsible for the ubiquitous occurrence of CO_2 in geothermal areas, although mantle-derived, magmatic and organic processes may locally give a significant contribution to the total discharge of CO_2 (Chiodini et al., 2000; Morner and Etiope, 2001). CH_4 may have both organic and inorganic origins, mainly related to hydrocarbon production mechanisms (diagenesis and catagenesis) in sedimentary basins. In geothermal or deep crustal environments, CH_4 may originate primarily from Fischer–Tropsch type reactions (Bougault et al., 1993) and magma degassing. Details on the origin of terrestrial gases have been described, among others, by Sugisaki (1987), Giggenbach (1992) and Klusman (1993). The potential of gas geochemistry in seismo-tectonics has been recently discussed by Toutain and Baubron (1999). Here, we wish to focus on some aspects of gas migration mechanisms in the subsurface, which currently have not been exhaustively considered in seismo-tectonic or environmental applications. We refer to gas migration in a general geological context. We do not discuss the particular case of gas movement in high-pressure and high-enthalpy fluid systems, typical of magmatic environments, for which the reader should refer to volcanologic studies (for example, see Bottinga and Javoy, 1990).

A survey of the available scientific literature reveals a certain heterogeneity and fragmentation of the topics related to gas migration, and even the lack of formal recognition of the main migration mechanisms. In particular, data on gas velocity, an essential parameter due to its relevant implications, are generally ignored. Often terminological confusion makes the understanding of this subject by unspecialized readers difficult. Most gas migration models are based on laboratory studies and computer codes which do not sufficiently take into account phenomena over geological time and space, i.e. processes occurring in real geologic scenarios. One example is given by those generalizations and extrapolations from laboratory scale to field scale of gas flow through low-permeability clay or granite for underground waste disposal (e.g. Volckaert et al., 1993).

In the last decade, however, new gas-geophysical and geochemical studies have allowed us to improve understanding and to suggest alternative views and theories. Accordingly, this paper has attempted to draw a picture of the basic principles and laws governing the migration of gases in porous and fracture media. This has been done by examining the geological factors or processes that influence the physical parameters in the transport equations. The migration mechanisms, diffusion and advection in their different forms, are summarized without rigorous mathematics but by using a carefully controlled terminology, in order to offer a simple reference framework for geological applications to readers unspecialized in gas dynamics. The potential of several gas advection mechanisms, previously considered “unconventional” or uncommon, are re-examined in the light of new data on the permeability of deep rocks, acquired from recent crustal investigations. Thus, emphasis is given to such hypotheses which could be grouped into a single unified approach definable as the “geogas theory”, and derived from field studies (measurements of gas flux, soil–gas and groundwater gas) or laboratory observations of phenomena that naturally occur in the subsurface. Basic principles of gas bubble transport in geological media are examined. Finally, advective velocities in saturated fissured rocks are computed theoretically as a function of the fracture width and compared with available experimental velocities.

2. Gas migration mechanisms

2.1. Main bibliography

The study of gas migration in the geosphere started in the 1930s within the scope of petroleum exploration, when understanding the movement of gaseous hydrocarbons through sedimentary rocks assumed enormous commercial importance. Early studies referred to the dynamic behavior of gaseous compounds associated with hydrocarbon reservoirs (Illing, 1933; Muskat, 1946). The development of mining exploration, particularly uranium research in the 1960s, boosted the knowledge on the dynamics of all terrestrial gases, first of all radon because it is directly associated with uranifeorus mineralizations (e.g. Tanner, 1964).

From the 1970s, the general improvement of geochemical exploration and the technological refinement of analytical instruments meant that a large number of data on Earth degassing could be acquired (e.g. Golubev et al., 1974; Dikun et al., 1975). The first physical models of gas migration, with mathematical equations to different degrees of complexity, have been mainly developed for geothermal prospection (Andrews and Wood, 1972; Stoker and Kruger, 1975), uranium exploration and radon-related environmental radioprotection (Fleischer and Mogro-Campero, 1978, 1979a,b; Fleischer et al., 1980; Mogro-Campero and Fleischer, 1977; Kristiansson and Malmqvist, 1982, 1984, 1987; Malmqvist and Kristiansson, 1984, 1985; Malmqvist et al., 1989; Schery et al., 1982; Soonawala and Telford, 1980; Tanner, 1980; Varhegyi et al., 1986, 1988, 1992; Wilkening, 1980). Migration models have been constrained by an increasing amount of direct observational data from hydrocarbon exploration (MacElvain, 1969; Price, 1986; Klusman, 1993), from studies on the radioactive waste geological disposal (Robertson, 1970; Neretnieks, 1980; Rasmuson, 1984; Thorstenson and Pollock, 1989; Knapp, 1990; Gascoyne and Wuschke, 1990, 1992; Thunvik and Braester, 1990; Hermansson et al., 1991; Rodwell and Nash, 1991; Volckaert et al., 1993; Horseman et al., 1999) and on soil and groundwater pollution (Richter, 1972; Barber et al., 1990). An interesting set of hypotheses on the relationships between outgassing and seismo-tectonics have been reported by Gold (1979) and Gold and Soter (1985). Recently, two-phase flow models have been developed for rock engineering problems (Kostakis and Harrison, 1999) and for studies on hydrocarbon seepage in sedimentary basins (Brown, 2000; Klusman et al., 2000). These approaches have provided new insights and suggested possible magnitudes for gas mass motion in geological media which were underestimated previously. These possibilities, examined in Section 4, have not been sufficiently considered in seismo-tectonic applications.

2.2. General principles

The main principles of gas migration refer to the relationships between Earth outgassing and geodynamics. Gas migration is strictly related to the existence of the gas source itself (fluid reservoirs such as hydrocarbon pools in sedimentary basins, geothermal fluids in high heat flow regions or fluids linked to magmatic and metamorphic phenomena), and to the existence of preferential routes for degassing. These are zones of enhanced permeability, such as sand horizons within a clayey sequence (migration mainly horizontal), and by tectonic discontinuities such as faults and fracture networks (migration mainly vertical due to buoyancy). The nature of the driving force can change during gas ascent, depending on the physical-geological conditions that the gas encounters. Furthermore, sedimentary basins and their constituent rocks are subject to basin loading, compaction, extensional and compressional stresses, and other tectonic forces that change the driving forces of the fluid flow. Finally, variations in temperature, pressure, mechanical stresses, chemical reactions and mineral precipitation change the gas-bearing properties of geological formations. The interaction of all these factors may lead to time-dependent fluid transport for which gas releases from the Earth, at least on a geological time scale, may be quite variable (Torgersen and O'Donnell, 1991). The high number of interdependent variables involved leads to severe limits on the elaboration of those migration models, which aim to consider the above-mentioned geologic principles.

While the gas volume stored in a rock depends on its porosity, the basic parameter controlling gas motion through the porous media is permeability. Gas permeability is a measure of the ease with which gas may traverse the medium under the influence of a driving pressure. This property depends on the structure of the medium and on the percentage, size and continuity of pores and fractures. The importance of size of pores or fractures derives from the analogies of fluid flow through a capillary tube for which Poisseuille's law is valid:

$$Q = \frac{\pi R^4 \Delta P}{8 \mu L} \tag{1}$$

where Q is the gas flux (m^3/s), R and L are the radius and length of the capillary tube (m), P the pressure difference across length L ($kg/m\,s^2$) and μ is the dynamic viscosity of the gas (kg/m s). The amount of fluid flowing through the tube per unit time is proportional to the fourth power of the radius; hence, if the radius of the tube is doubled, the quantity of flow is increased 16 times. More complex relationships have been developed for geological media (see Cvetkovic

et al., 1999 and references therein, for an exhaustive description). A main finding from laboratory experiments is that the fluid flow rate in fractures with aperture "*d*" may under certain conditions be approximated as proportional to d^3 (cubic law) whereby the fluid velocity is proportional to d^2.

The permeability of porous media is a constant determined only by the structure of the medium and is independent of the nature of the fluid passing through it (Muskat, 1946). Hence, water permeability and gas permeability are the same for a dry medium. Obviously, for a two-phase system gas permeability decreases as the water content increases because the space available for gas is reduced.

In the subsurface a number of forces compete to control gas movement. Basically, the gas movement in the subsurface can be induced by two types of force fields: concentration gradients and pressure gradients. In the first case, a spreading out of gas molecules in a direction tending to equalize concentrations in all parts of a rock system occurs: this is gas "diffusion". In the second case, the whole gaseous mass tends to move from a high pressure zone to the low pressure zone; this mass transport is named "advection". In the geologic environment these two processes almost never act separately; thus, formally, the gas movement should be ascribed to their combination. Nevertheless, the velocity and space scales of advective movements are much higher than the diffusive ones. Diffusion is important only in capillaries or small-pored rocks; advection may assume an exclusive role in larger pores or in fractured media. In the literature the terms "mass transport", "viscous flow", "fluid flow", "air flow", "non-diffusive transport" are also used for advection. Yet some authors improperly used the term "convection" to indicate a pressure-driven transport (e.g. Gurrieri and Valenza, 1988; Nazaroff and Nero, 1988). "Convection" is an advective movement with a pressure gradient generated by geothermal gradients: a warmer gas ascends since it disperses more rapidly and consequently become lighter; at constant volume, a warmer gas is more pressurized. In other words, to say "convection" is to "observe" advection from temperature gradients; it is possible to change this viewpoint, from temperature to pressure, by the equation of state. It is incorrect to name as "convective" something that is not linked to temperature effects, such as normal gas flows linked to buoyancy or to hydrostatic, lithostatic and tectonic stresses. It would, therefore, be opportune to define as "convective" only those motions characterized by advective movements clearly linked to thermal phenomena. Several attempts to consider mass transport from the temperature viewpoint have been made by Lapwood (1948), Mogro-Campero and Fleischer (1977) and Fleischer and Mogro-Campero (1978). Yet, their equations have sometimes been impractical to use, because they require physical parameters (such as the Rayleigh number, the height of convective cells, the thermal conductivity of the medium) that are difficult to assess.

Diffusion and advection can be examined by transport equations without rigorous mathematics, i.e. assuming realistic limitations on the nature of the fluid and porous medium; these limitations are those frequently adopted to solve practical problems.

2.3. Diffusion

The diffusive movement is described by Fick's law, for which gas flux is directly related to the concentration gradient and to a constant:

$$F = -D_{\mathrm{m}}\,\nabla C \quad \text{where} \quad \nabla = \frac{\delta}{\delta x} + \frac{\delta}{\delta y} + \frac{\delta}{\delta z} \qquad (2)$$

or as one-dimensional form along *z*-axis:

$$F = -D_{\mathrm{m}}\,\frac{\mathrm{d}C}{\mathrm{d}z} \qquad (3)$$

where D_{m} is the molecular diffusion coefficient (m^2/s), dC is the variation of gas concentration (kg/m^3) along dz (m). The molecular diffusion coefficient is a constant of the specific gas; it only changes with temperature, pressure and the physical nature of the substance through which the molecular motion takes place. In the rock pores, this substance is generally water or air (or gas mixture). For each gas, therefore, the diffusion coefficient in water (D_{mw} or simply D_{w}) must be distinguished from the diffusion coefficient in the air (D_{ma} or simply D_{m}). Furthermore, considering gas diffusion in porous media it is necessary to take into account that the volume, through which gas diffuses, is reduced and the average path length between two points is increased. In the literature, the frequent lack of a precise reference to the type of diffusion coefficient can lead us to confuse the following three different processes: "molecular" diffusion of gas in

Table 1
D_m, D_w and mean values of D_e and D (cm^2/s) for Rn, He and CO_2[a]

	D_m (25 °C)	D_w (25 °C)	D_e	D
Rn	0.12	1.37×10^{-5}	0.03–0.05 soil, 2×10^{-6} saturated soil	0.0074 soil
He	0.7	2.12×10^{-5}	4×10^{-4} limestone, 10^{-9} saturated rocks	
CO_2	0.15	1.95×10^{-5}	0.02–0.03 soil	0.007 soil

[a] Sources—Rn: Nazaroff (1992); Porstendorfer (1993); Schery and Petschek (1983); He: Lerman (1979); Pandey et al. (1974); CO_2: Lerman (1979); de Jong (1973); Richter (1972).

a fluid; "interstitial" diffusion of gas in a medium; "global" diffusion of gas in a medium. These three processes must be associated with different coefficients with different significance and magnitude (Table 1). The molecular diffusion coefficient has already been described. It is also named "interdiffusion coefficient" (Lerman, 1979) or "binary" coefficient (Nazaroff, 1992) as it only refers to the interaction between diffusing gas and host fluid. Interstitial diffusion is defined by the "effective" diffusion coefficient (D_e):

$$D_e = D_m n \tag{4}$$

where n is the effective porosity of the medium (%). It describes the diffusion considering the gas molecule motion through a porous structure. Global diffusion is defined by the "apparent" diffusion coefficient (D), known in the literature also as "true" or "bulk" coefficient; it includes the effects of porosity and tortuosity of the medium. For soil, most of authors agree to define this coefficient as (e.g. Lerman, 1979):

$$D = D_e n = D_m n^2 = D_m \frac{n}{\tau} \tag{5}$$

where τ is the tortuosity of the medium. In conclusion, $D_m > D_e > D$.

The following example can better clarify the significance of D and D_e. The diffusive exhalation flux of radon from the ground is described by the equation (Porstendorfer, 1993):

$$F = D \frac{dC}{dZ} = \varepsilon C_{Ra} \rho \gamma X_d \tag{6}$$

where n is the porosity (%), ε the Rn emanation coefficient (%), C_{Ra} the concentration of ^{226}Ra in soil (Bq/kg), ρ the soil density (kg/m^3), γ the radon decay constant ($2.1 \times 10^{-6}\ s^{-1}$), $X_d = (D_e/\gamma)^{0.5}$ is the diffusive distance (m). It shows that to describe gas diffusion as a global flux across the bulk of the soil, the "bulk coefficient" D must be considered. The same equation also shows that during exhalation radon decays moving through interstitial paths and that in this context the "effective" coefficient D_e should be considered.

In extremely fine porous media and capillaries having small diameters compared with the mean free path of gas molecules (about 0.1 μm at STP), gas diffusion rate is dominated by collision of molecules with the capillary walls (Knudsen diffusion; Wilkening, 1980; Thorstenson and Pollock, 1989).

A diffusing gas, in time t, will cover a diffusive distance:

$$Z_d = (Dt)^{0.5} \tag{7}$$

It means that if we consider He diffusion in water (Table 1) gas may cover 1.3 cm in 1 day, 25 cm per year, 8 m in 1000 years and so on.

Radon may diffuse inside solid lattice, but its diffusion coefficient (Table 1) and its mean life restricts its chance to migrate in this case as well. To calculate the concentration gradient resulting from the diffusion of ^{222}Rn in an isotropic medium, Andrews et al. (1986) have used the following equation:

$$C_x = C_o \exp\left(\frac{-x}{L}\right) \tag{8}$$

where C_x is the concentration of ^{222}Rn at distance x from the origin, in the direction of diffusion; C_o the original concentration of ^{222}Rn; L is the length of diffusion of ^{222}Rn in cm, defined by $L = (D/\lambda)^{1/2}$ where D is the diffusion coefficient of ^{222}Rn and λ the decay constant of ^{222}Rn. This equation shows that only 5% of ^{222}Rn is able to reach a distance of $5L$ from its origin. As the length of diffusion L is 0.7 nm (less than the recoil length), the migration of radon inside its original crystal due to diffusion is quite limited. Andrews (1977) calculated the percentage of ^{222}Rn

generated by ^{226}Ra decay, released from grain-sized rock particles into water as follows:

$$\log(\%\text{Rn release}) = 0.5 \log d + C \quad (9)$$

where d is the diameter of the grain and C is a constant.

Most sedimentary materials with uniform composition (limestone, shales, etc.) were experimentally found to comply with this equation. Even considering that a temperature increase of 10–20 °C tends to double the value of D (Baranova and Novitaskaya, 1949) and in view of the uncertainty in the real values of diffusion coefficients in various geological systems, radon concentrations diminish with distance. The immediate consequence for Earth sciences is the physical impossibility of ^{222}Rn transport over long-distances, in most common geofluids, by diffusion alone. The observed migration of radon over long-distances means that other mechanisms must predominate.

2.4. Advection

The term advection refers to movement of matter under the influence of external forces, namely pressure gradients. In a broader sense, all those movements due to "global" forces are advective (Lerman, 1979): atmospheric precipitation, evaporation, wind, deposition of sediments, groundwater flow, and movements of crustal plates. It is worth noting that caution is needed when applying the term "advection" to gaseous species. Advective migration requires a stream of "free gas", i.e. gravitative forces act only on gases which occur at sufficient concentrations (gas domain). To form a stream of a particular gaseous species, an immense number of atoms of that species must be available at the same location at the same time. The amount of noble gases, such as helium and radon, occurring in the subsurface is many orders of magnitude too small (orders of ppm of He and of 10^{-10} ppm of Rn) to form a macroscopic quantity of gas which can react to pressure gradients and flow autonomously by advection. For such gases the advective movement must be referenced to a "carrier gas" (e.g. CO_2, CH_4, N_2) able to form large domains that can carry the rare gas. More precisely advection could be referred to as "geogas" (Kristiansson and Malmqvist, 1987; Etiope and Lombardi, 1996) which is a gas mixture formed by primary components (carrier gases) and secondary components (rare gases), as will be described in Section 4.

A gas with concentration C (kg/m^3) and velocity v (m/s) results in the flux:

$$F = Cv \quad (10)$$

Its velocity depends on the pressure gradient and on a mobility coefficient related to the geometry of the medium and to gas viscosity. In the case of advection through a dry porous medium, the mobility coefficient depends on the intrinsic permeability of the medium itself, according to Darcy's law:

$$v = -\frac{k \nabla P}{\mu} \quad \text{where} \quad \nabla = \frac{\delta}{\delta x} + \frac{\delta}{\delta y} + \frac{\delta}{\delta z} \quad (11)$$

or in one-dimensional form, along the z-axis, and for a short distance:

$$v = k \frac{\Delta P}{\mu Z} \quad (12)$$

where v is the gas velocity (m/s), k the intrinsic permeability (m^2), μ the dynamic gas viscosity (kg/m s), ΔP is the pressure difference (kg/m s^2) between two points spaced at distance Z (m).

An estimate of advective gas velocity through a planar fissure may be (Gascoyne and Wuschke, 1990):

$$v = \frac{b^2}{12\mu} \frac{\mathrm{d}P}{\mathrm{d}z} \quad (13)$$

where $b^2/12$ is the fissure permeability, b is the fissure width and μ the gas viscosity.

To estimate the gas velocity through a fractured medium (system of intersecting fissures) the "cubic law" could apply (Schrauf and Evans, 1986):

$$v = \frac{b^3}{6d\mu} \frac{\mathrm{d}P}{\mathrm{d}z} \quad (14)$$

where d is the mean distance between intersecting fissures (m).

Restrictions regarding the validity of Darcy equation are related to viscous or laminar flow in which the gravitative influence is negligible. It has been estimated (Bear, 1972) that for a porous medium with mean grain diameter d_G, the gas flux becomes turbulent, and therefore, lies outside the validity field of Darcy's law, when

$$R = d_G v \frac{\rho}{\mu} > 4 \quad (15)$$

where R is the Reynolds number (non-dimensional).

Advective processes can take place in the subsoil whenever pressure gradients between two points occur. Such gradients can be induced by tectonic stresses, variation of lithostatic loading, rock fracturing, localized gas generation, recharge and discharge of aquifers and deep fluid reservoirs and, near the surface, by atmospheric pressure pumping. Also the natural tendency of lighter gases (helium, hydrogen) to ascend, due to their low density, is an advective phenomenon: in fact, a gas with density ρ_1, moves upwards if it is bounded by a gaseous phase with density $\rho_2 > \rho_1$. The lighter gas is subjected to a pressure gradient $\rho_2 g$ and the following equation is valid:

$$v = kg\frac{\rho_2 - \rho_1}{\mu} \tag{16}$$

with g gravity, the term $g(\rho_2 - \rho_1)$ being equivalent to a pressure gradient. It should be outlined that the very existence of a naturally occurring background pressure gradient in the Earth is an index of continuous outgassing.

In shallow rocks the soil gas advection is influenced, and often driven, by atmospheric parameters, such as barometric pressure, wind, air temperature and rain (Klusman, 1993; Hinkle, 1994). Barometric changes of 1000–2000 Pa over a period of 1–2 days produce advective velocities of the order of 10^{-4} cm/s within a soil with permeability of 10^{-12} m^2 (Clements and Wilkening, 1974).

2.5. The general equation of transport

In the light of what has been reported above, the total flux of gas is given by

$$F = -nD_\mathrm{m}\,\nabla C + vC \tag{17}$$

or as one-dimensional form:

$$F = -nD_\mathrm{m}\,\frac{\mathrm{d}C}{\mathrm{d}z} + vC \tag{18}$$

where $nD_\mathrm{m}(\mathrm{d}C/\mathrm{d}z)$ is the diffusive term and vC the advective term.

The general equation of transport, in terms of mass conservation, may be written in more or less complex forms, depending on the assumption and limitations adopted. In most cases the migration models, and their relevant equations, used for practical problems can follow criteria of simplicity and acceptable approximation. This follows from Muskat (1946), who thought it to be inappropriate to apply the mathematical rigour of certain physical laws to complex geologic reality. It is possible, therefore, to consider one-dimensional equations for laminar, steady-state flow through dry, homogeneous and isotropic porous media.

Hence, the following general transport equation is obtained:

$$nD_\mathrm{m}\frac{\mathrm{d}^2C}{\mathrm{d}z^2} - v\frac{\mathrm{d}C}{\mathrm{d}z} + \alpha - \omega = 0 \tag{19}$$

where α is the generation rate of gas and ω the rate of removal of gas from the stream (as a result of adsorption by the rocks, dissolution by groundwater, microbiological consumption and, for radon, radioactive decay; for this last case $\omega = \gamma C$).

At this point we can define the several forms in which gas can migrate advectively and diffusively depending on the condition of the gas–water–rock system. Fig. 1 shows the possible mechanisms with an indication of the rock and fluid properties controlling gas flow and velocity.

2.6. Diffusion forms

1. In dry porous media (i.e. soil, consolidated or unconsolidated rocks) gas diffusion occurs in the interstitial air (gas-phase diffusion). Eq. (2) can be applied.
2. In saturated porous media, gas diffuses in water (water-phase diffusion) but with a velocity much lower than those of diffusion in air (Eq. (2) with D_w; see Table 1). Gas concentration in water, and consequently the concentration gradient, is controlled by Henry's law, i.e. by temperature, pressure and, for CO_2, pH.

2.7. Advection forms

1. In dry porous or fractured media gas flows through interstitial or fissure space (gas-phase advection). Eq. (11) can be applied.
2. In saturated porous media two possible phenomena may be distinguished: gas dissolves and is transported by groundwater (water-phase advection) or gas flows displacing water (gas-phase advection). In the water-phase advection, gas being in solution, moves at the same velocity as water; hence,

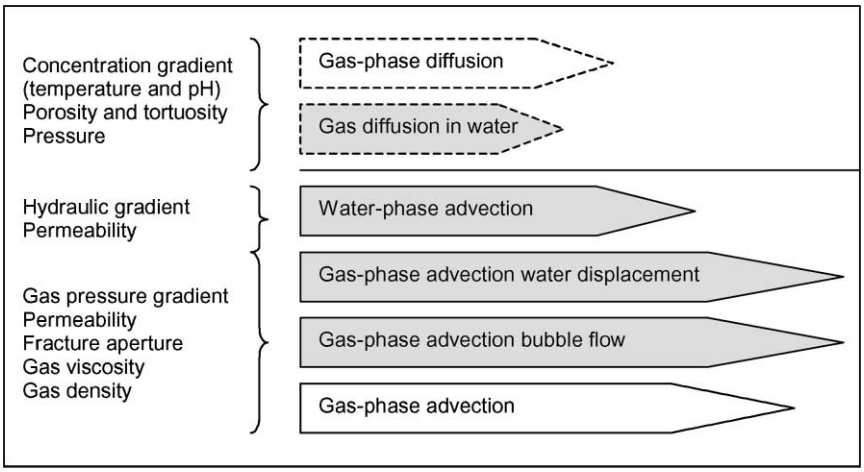

Fig. 1. Gas migration forms in dry (white arrows) and saturated (grey arrows) geological media. Left side lists the main rock and fluid properties controlling the several mechanisms. Length of the arrows represents, qualitatively, the attainable relative velocity as discussed in Section 4.3.

Darcy's equation in the form used in hydrogeology is valid:

$$v = Ki \tag{20}$$

where K is the hydraulic conductivity of the medium (Darcy) and i the hydraulic gradient. Long-distance (basin scale) fluid migration over geological time scale is the subject of copious literature (Pueyo et al., 2000).

Concerning gas-phase advection, as gas can flow through a water-saturated medium, it must have a pressure (P_g) above the sum of hydrostatic pressure (P_w) plus capillary pressure (P_c). Hydrostatic pressure is given by the height of the piezometric surface (H_w) from the point considered ($P_w = \rho_w g H_w$). Capillary pressure is linked to the interfacial tension of water (σ) and to the pore throat radius (r) according to Laplace equation ($P_c = 2\sigma/r$). Studies on gas flow through clayey rocks (Volckaert et al., 1993) effectively demonstrated that if

1. $P_g < P_w + P_c$, gas enters the medium only by diffusion.
2. $P_g > P_w + P_c$, two-phase flow occurs, with water displaced by gas.
3. $P_g = P_{fr} >> P_w + P_c$, gas fractures the rock (P_{fr} is the pressure at which fracture starts and corresponds roughly to the lithostatic pressure).

When gas pressure P_g reaches P_{fr}, gas flow will occur through fracture planes thus generated. If, however, $P_{fr} < P_w + P_c$, then the gas flow only occurs in the fracture and there will be no migration of gas in the rock matrix. Due to the very high permeability of the fracture it can be considered a volume increase, in which the gas is stored without flow. The pressure can rise and, thus, bring about a propagation of the fracture network. If, on the contrary, $P_{fr} > P_w + P_c$ the gas will flow in the fracture and from the fracture towards the matrix (Geneste, 1992). It should be noted that both hydrostatic and lithostatic pressure, when the pressure strikes on the gas (as occurs in a "gas cap"), can act as driving forces for the gas itself.

So water displacement occurs when $P_g > P_w + P_c$ and it can be at a different scale depending on the dimension of advancing front of the gas with respect to the type of water-bearing medium (homogeneous porous medium, single fracture, etc.). For example, within a saturated fissure, gas totally displaces water if the fluid strip has a size similar to the fissure width (Gascoyne and Wuschke, 1992). Eq. (13) can be used considering as a pressure gradient the difference of density between gas and water. On the contrary, if gas moves as a tiny strip, with a size lower than that of the fracture width, or moves as an intermittent flow (i.e. P_g varies in time from values above to values below the displacement threshold $= P_w + P_c$) or, finally,

exsolves from water by oversaturation, gas bubbles form (Etiope and Lombardi, 1996). The equations for bubble motion are described in Section 4.2.

3. Specific features of radon migration

The application of the diffusive and advective laws for Rn must include the decay term. An exhaustive treatment of Rn migration equations is reported by Varhegyi et al. (1986) and Martinelli (1998). Here, some features on Rn dynamic behavior are outlined.

The distribution of the radon released at a water–rock interface into the water flowing through the intergranular spaces depends on its diffusion in the fluid and on the water flow rate. As a result of the slowness of this process, diffusion is of primary importance in determining the dispersion of radon in large volumes of water, in particular, in the case of primary high-permeability aquifers where flow velocity is presumed to be reasonably high.

According to Andrews (1977), radon concentration in water (Bq/m^3) passing through a porous radon-emanating rock is

$$\mathrm{Rn} = \frac{Ar\,\mathrm{Ra}}{f}\left[1 - \exp\left(\frac{-x}{v}\right)\right]\exp\left(\frac{-x'}{v'}\right) \qquad (21)$$

where Ra is the radium content of rock; r the rock density and f its fractional pore space; v and v' are the transport velocities of water within the aquifer and after leaving it, respectively and x and x' are the distance covered within the aquifer and after leaving it, respectively. Factor A is the ratio of radon released into water against the radon generated within the rock and depends on pore-size distribution and mineral composition of the rock. This equation was found to give a satisfactory estimate of the radon content in fluids in common aquifers if the hydrodynamic parameters were adequately known (Gorgoni et al., 1982).

The increase in ^{222}Rn concentration in the host fluid, as a function of time t, is given by

$$\delta C = Q\delta t - \lambda C\delta t \qquad (22)$$

where Q is the number of atoms entering the fluid per unit of time and λ is the decay constant of ^{222}Rn. Integration of the equation gives

$$C = \frac{Q}{\lambda} \qquad (23)$$

when $t >> 1/\lambda$. This means that in a stationary fluid, or one which can only move a few meters a day, the ^{222}Rn concentration is determined by the ratio between the supply and decay rate.

Gascrossing saturated porous media can dissolve in the water. Flowing gas can, therefore, lose significant amounts of energy without going through the water body as a gas-phase.

^{222}Rn transport over long-distances requires the presence of a relatively fast-moving advective fluid. Whatever the origin of the gases, in particular in geological situations, they may reach the Earth surface at rates which sometimes create anomalous degassing areas. These gas flows are precisely those which may serve as fast carriers for radon. Grammakov (1936) computed the concentration of ^{222}Rn transported by a gas carrier at a velocity v at distance z from a surface with concentration C_o by the following equation:

$$C = C_o \exp\left\{\left[\left(\frac{v}{2D}\right) - \left(\frac{v^2}{4D^2} + \frac{1}{D}\right)^{1/2}\right]z\right\} \qquad (24)$$

Simple calculations demonstrate that, where a component for advective transport exists, even if it is only a few meters per day, migration by diffusion is negligible. On the other hand, it is evident that a small gas flow significantly increases the radon transport to shallow depths.

Radon gas is moderately soluble in water, with which, by means of Van der Waals forces, it forms structures of the $Rn{\cdot}6H_2O$ type (clathrates) (Nesmeyanov, 1974). In these compounds, the radon atom is evidently polarized by the strong dipole of the water molecule. In this way we may explain why the water-solubility of the noble gases increases with the atomic number. High pH values (pH 7–12) destabilize clathrates and destroy them, with the consequent passage of radon from the liquid to the gas-phase (Gasparini and Veltri, 1987).

The process activated by pH variations is, thus, similar to the one due to temperature variations and these processes must be borne in mind when evaluating experimental data. Variations in fluid velocity may also influence radon concentrations (Andrews et al., 1986).

The concomitant presence in natural fluids of these processes (effects due to variations in pH, temperature, velocity) may give rise to situations which are extremely complex to interpret and which compels

researchers in this field to adopt particular sampling strategies, increasing the number of experimental points both in time and space. A correct understanding of transport phenomena, thus, becomes especially important.

The most common mathematical formulations in this field come mainly from Andrews and Wood (1972) and Stoker and Kruger (1975). Andrews (1977) developed his mathematical treatment on water-dominated systems. His equation is mainly employed in hydrogeological and geothermal studies, in cases of low-enthalpy hydrothermal circuits.

The mathematical treatment developed by Stoker and Kruger (1975) is widely applied in the high-enthalpy, vapor-dominated, geothermal systems, and in assessing radon anomalies in concomitance with volcanic or seismic events. Stoker and Kruger (1975) estimate the radon concentration in natural fluid by the following equation:

$$\frac{C}{\varepsilon} = \frac{1}{\varphi}\left[1 - \exp\frac{\lambda\varphi\pi h}{Qr_e^2 r_w^2}\right] \quad (25)$$

where C (Bq/m^3) is the radon concentration, ε the radon-emanating from the rocks, λ the decay constant of ^{222}Rn; r_w (cm) the radius of the cylindrical fracture of height h (cm) within a rock of given porosity φ; r_e (cm) is the radius of the circular ring of rock (which comprises the r_w fracture) from which radon diffuses into the fracture. Finally, Q (cm^3/s) is the flow rate.

Stoker and Kruger (1975) introduced the concept of radial flow, artificially generated in the geothermal systems penetrated by a drilled well, but also occurring in natural systems such as volcanoes. Radial flow with passage from laminar to turbulent conditions is typical of large steam reservoirs, perturbed by drilling, or of volcanic systems containing large quantities of gases under pressure, flowing through conduits or faults (Martinelli and Ferrari, 1991). This explains why Stoker and Kruger's model can be applied to the monitoring of geodynamic phenomena, such as volcanic eruptions and earthquakes.

Further refinements of the above model have been proposed by D'Amore et al. (1978) who examined the possibility of radon generation at various depths in geothermal systems. These models may be applied to any subterranean gas fluid, independently of its origin: methane gas wells have also shown behavior similar to that of geothermal wells (Nesmeyanov, 1974).

It is interesting to note that the models of Andrews and Wood (1972) were originally formulated to describe the behavior of radon in liquids with laminar regimes. Similarly, the models proposed by Stoker and Kruger (1975) mainly describe the behavior of radon in vapor-phase fluid and, in any case, in the presence of large quantities of gas. These models have had important consequences in understanding problems connected with the presence of radon in geodynamic systems.

Many radon anomalies in subterranean fluids coincident with seismic or volcanic events were described in the scientific literature during the 1970s. The various research groups tended to interpret these anomalies according to the most popular model of that time, i.e. that of Andrews and Wood (1972). This model predicts the generation of radon anomalies essentially through variations in the velocity of liquid-phase fluids.

If the dilatancy theory (Stoker and Kruger, 1975) holds, then Andrews and Wood's approach sounds promising. Unfortunately, however, the only radon anomalies described by this approach turned out to be normal cyclic trends of radon in the waters of cold or hot springs closely connected with meteorological events, such as the recharging of hydrogeological circuits.

The model proposed by Andrews and Wood (1972), although extremely convincing, did not clearly state that it is difficult to fit radon anomalies connected with geodynamic events into models which only contemplate the liquid-phase and the laminar-type flow only. In other words, it is not only the variation in fluid velocity which produces the anomalies reported in the scientific literature of the 1970s from China, USSR, etc. Only in the early 1980s did Soviet literature begin to report that other geochemical parameters—mainly gases, may also change together with radon.

Stoker and Kruger (1975) were the first to supply useful information to researchers in this field, who then started to monitor other parameters such as CO_2, H_2, etc. These measurements showed that radon spikes were not caused simply by flow variations; other phenomena could also give rise to instantaneous variations. The presence of carrier gas bubbles in fluids was, thus, recognized as the cause of many of the phenomena observed.

4. The "geogas theory"

In the previous paragraphs it has been shown that the mechanisms of gas migration in the subsurface can be considered as being due to diffusive or advective processes. For a long time most authors had considered diffusion as an important process of Earth degassing (e.g. Newton and Round, 1961) and groundwater flow as a main mechanism for long-distance transport of trace gases and radionuclides. But since the 1970s new data on gas behavior appeared in the literature and some authors reassessed the effective role of diffusion and water advection in geological environments. Gingrich and Fisher (1976) and Mogro-Campero and Fleischer (1977) were the first to report long-distance radon transport (>100 m): radon concentrations measured at the ground surface have been found to be too high to be accounted for solely by gas diffusion from the subsurface. Diffusion does not allow radon to be transported for distances over about 10m before the decay of the Rn atoms has reduced the concentration to a level which is indistinguishable from the background, even if the Rn source is strong. Anomalous concentrations of radon, or other gases, in relation with seismic events (King, 1978) or with deep-seated geothermal (Cox, 1980) or hydrocarbon (Armstrong and Heemstra, 1973) reservoirs are further evidence of gas transport processes hardly supported by diffusive or groundwater flow models. Until recently the scientific literature has been enriched by observations whose common theme is the difficulty in explaining long-distance Rn transport, or in general the occurrence of endogenetic gas at surface, as a result of diffusion (McCarthy and Reimer, 1986; Reimer, 1990; Duddridge et al., 1991; Durrance and Gregory, 1988; Etiope and Lombardi, 1995; Varley and Flowers, 1993). At the beginning of the 1980s, Kristiansson and Malmqvist (1982) proposed a new hypothesis for radon transport: they considered that radon movement is linked to the existence of a naturally occurring microflux of gas (geogas), which is mainly enhanced in crustal faults. This gas flow is advective and is accomplished as "microbubbles" when the geogas crosses an aquifer. Subsequently, this hypothesis was found to fit a large amount of experimental data. The literature now suggests that all these experiences may be grouped into a single unified approach definable as the "geogas theory". This theory may include the following features.

(a) *The widespread occurrence of a microflow of gas*: The ascent of a microflow of gas through faults and fractures in the crust is a quite common phenomenon, playing an important role in the Earth's outgassing (Dikun et al., 1975; Gold and Soter, 1985; Etiope, 1999; Morner and Etiope, 2001). This ascending microflow not only occurs in tectonically active areas (seismic, volcanic areas) but also in stable areas (sedimentary basins, shields, forelands; Baubron et al., 1991).

(b) *Advecting multicomponent gas*: This microflow regards advective movement of a mixture of naturally occurring gases (geogas), formed by carrier gases (CO_2, CH_4, N_2) which transport rare gases (He, Rn; Malmqvist and Kristiansson, 1984; Durrance and Gregory, 1990; Etiope and Lombardi, 1995). Because a gas can move by advection, i.e. to be responsive to gravitative forces, it must have a sufficient amount of mass (it must form a "gas domain", as suggested by Gold and Soter (1985)). In the subsurface rocks the amount of rare gases, such as Rn and He, is many orders of magnitude too small to form a macroscopic quantity of gas which can flow advectively. Thus, such gases must be carried by a macroscopic flow of another gas which is moving upwards. Previously, Dikun et al. (1975) suggested that the occurrence of helium anomalies at the surface and their duration can only be explained by an ascending carrier gas.

High Rn emissions are generally related to U-rich soils and bedrock; accordingly Rn-prone areas and radioprotection zoning are basically focused on granitic and volcanic environments. Nevertheless, it is not rare to find locally, above fault zones, soil–gas Rn much higher than the level imputable to U decay in the ground (Ball et al., 1991; Etiope and Lombardi, 1995; Guerra and Etiope, 1999). Moreover, Rn and CO_2 in soil are often directly correlated both in time and space (e.g. Etiope and Lombardi, 1995; Heinicke et al., 1995). There is no doubt that this is a strong evidence of trace gas transport by carrier gas.

(c) *Rapid gas upflow*: A large number of case histories have produced evidence for long-distance transport of radon that cannot be explained by simple gas diffusion or groundwater flow models (Gingrich and Fisher, 1976; Mogro-Campero and Fleischer, 1977, 1979; Fleischer and Mogro-Campero, 1979a,b;

Fleischer et al., 1980). In fact, as previously mentioned, in order for radon to reach the surface before decaying, it must be transported upwards at a rapid rate, which, in itself, is possible only if a rapidly ascending carrier gas exists. Gas migration at relatively high speed can be due to (Fig. 1):

- pressure-driven continuous gas-phase flow through dry fractures;
- pressure-driven continuous gas-phase displacing water in saturated fractures;
- buoyancy of gas bubbles in aquifers and water-filled fractures.

(d) *The bubble flow*: When the geogas microflow crosses groundwater a bubble stream may form. Fault-linked bubble flows can take place in different geological environments (Malmqvist et al., 1989; Sugisaki, 1987 and references therein); the bubble movement has been theoretically and experimentally recognized as a fast gas migration mechanism (Malmqvist and Kristiansson, 1985; Varhegyi et al., 1986, 1992). Microbubbles of colloidal size (radius below 1 mm) are considered by MacElvain (1969), Price (1986) and Klusman (1993) as the main migration mechanism for gaseous hydrocarbons.

(e) *Matter transport by geogas bubbles*: The bubbles seem to be able to pick up and transport trace elements upwards for long-distances (gaseous atoms as well as solid particles) (Kristiansson and Malmqvist, 1987; Pattenden et al., 1981; Walker et al., 1986; Etiope, 1998; Etiope and Zhang, 1998). This mechanism may be responsible, for example, for rapid and long-distance radon transport and for all other phenomena which are not accountable for by gas diffusion or water transport alone. This matter transport can take place by way of following four types of physical mechanism:

- flotation (lifting of solid particles inside the bubble);
- surface-active elements binding on the gas–water interface;
- aerosol transport;
- transport of volatile compounds dissolved in the carrier gas.

Flotation is a well-known physical process (Gaudin, 1957) due to the fact that the specific surface energy is higher between water and gas than between solids and gas. Thus, a microbubble stream crossing crushed rocks can lift fine particles and transport them upwards.

Transport of surface-active elements on a gas–water interface is due to the lower energy level provided by the interface itself than that occurring in solution. Many elements, mainly radionuclides, tend to attach to and concentrate on the bubble surface (Peirson et al., 1974; Pattenden et al., 1981). It has been shown, as an example, that a substantial enrichment of elements can take place on the surfaces of air bubbles that pass through seawater. It was found that foam on the surface water contains up to 600 times more plutonium per unit volume than the sea water (Walker et al., 1986).

Aerosol transport may occur by dispersion of solid and/or liquid particles induced by rapid movement of gas pockets through the rocks.

There are a large number of elements, such as mercury, cadmium, arsenic and lead, that can form alkylated compounds through the action of microorganisms. These compounds are quite volatile (and toxic) and are responsible for much of the dispersion of these elements in the geosphere and biosphere. If such compounds are formed in the fractures of the rocks, they may dissolve in the geogas and be transported to the surface.

All these aspects of the gas transport mechanisms are generally unrecognized in the literature on environmental geochemistry, geo-exploration and seismo-tectonics.

4.1. Permeability and width of gas-bearing fractures

The key parameter constraining validity and potential, in quantitative terms, of the above-described advective gas migration forms is the intrinsic permeability of rocks. In particular, the width of gas-bearing fractures is a direct parameter for bubble flow modeling.

Crust permeability, at a regional scale, has recently been discussed by Manning and Ingebritsen (1999). It appears that a geochemically significant level of permeability can exist throughout the crust. Excluding faulted and fractured rocks, metamorphic and geothermal zones in the upper crust display permeabilities to the order of 10^{-20} to 10^{-16} m^2. These values suggest that mass transport is dominated by advection. In fault zones, at a scale of hundreds of meters to

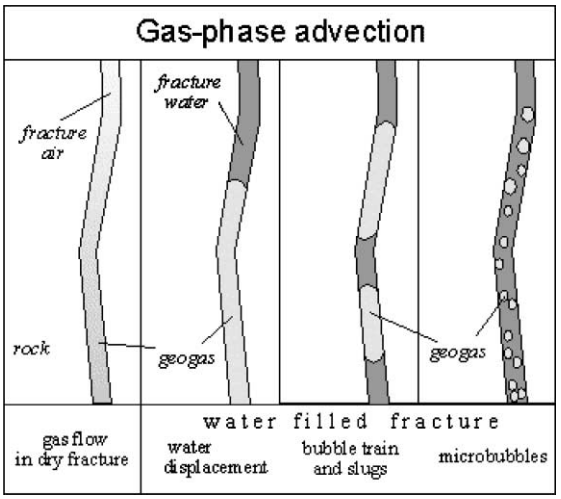

Fig. 2. Schematic picture of gas-phase advection forms. For all forms the flow is controlled by permeability (fracture aperture for bubble flows) and pressure gradients, that may be induced by tectonic stresses, fracturing, variations of lithostatic loading, aquifer or fluid reservoir charge/discharge, local gas production, and barometric pumping near the surface.

kilometers, the permeability is higher than these levels; and is much higher at local (m) scale in fractured rocks. Here, gas-phase migration involving water displacement and bubble flow (Figs. 1 and 2) can be examined by knowing the width of the fracture and its variation.

The width or aperture of a fracture is the distance, at one given point, between the two rough fracture walls. This aperture is obviously highly variable along the same fracture. Possible relationships between fracture width and permeability are given in Eqs. (13) and (14).

The knowledge of the entity and general distribution in the subsurface of such a parameter will provide a direct indication of the real possibilities for rapid and long-distance gas migrations in bubble form. Values of fracture aperture at depth vary from 10 to 50 μm for low-permeability argillaceous rocks, to several cm for large fissures in geothermal systems and carbonate (karst) environments.

Fracture width in clayey rocks ranges between 10 and 100 μm (Rodwell and Nash, 1991), while in granitic rocks it is to the order of 400–500 μm (Gascoyne and Wuschke, 1990).

Larger fissures of the order of mm occur along hydrocarbon-bearing fault planes, hot dry rock (HDR) geothermal systems and in crystalline bedrocks near active faults. Vertical hydrocarbon migration is typical of faults whose conductivity and aperture can be enhanced by dilation, refracturing of the mineralized zone, seismic pumping and thermal expansion of water (Hooper, 1991; Sibson, 1981; Hunt, 1979). Wide fissures in hydrocarbon-bearing fault zones are the extension fractures parallel to the greatest principal stress, around compressive faults (Hooper, 1991). Fractures of 0.2–0.5 mm have been reported from arenaceous rocks cored in the Po plain (Italy) during oil drilling, while pores whose diameters range between 0.1 and 0.2 mm characterize the sandy Quaternary aquifers of the southern Po plain (Regione Emilia-Romagna ENI-AGIP, 1998). Fractures of 1–3 mm in Mesozoic carbonates and mineral-filled fractures up to 50 mm have been reported over oil reservoirs (Hunt, 1979). Fractures wider than 10 mm have been discovered at depths of 2000 m in the crystalline (granitic) basement of the San Andreas Fault zone (Barton et al., 1995).

Larger fissures exist, especially near the surface, in geothermal systems where widths of 1–10 cm have been found by visual inspection in boreholes (Elder, 1981).

Finally, very large joint systems and rock voids exist in karst environments; here, water-filled cavernous zones and sinkholes represent the largest rock void structures.

4.2. The bubble migration mechanism

The straightforward description of gas bubbles in natural fluids in the subsoil or related geodynamic events has escaped observation in almost all the specialized literature until recently. Preliminary theoretical studies on gas bubble movement through porous media are reported by Varhegyi et al. (1986). They assumed that groundwater bubbles move in accordance with Stokes' law:

$$v = d^2 g \frac{\rho_w - \rho_g}{18\mu_w} \quad (26)$$

where v is bubble velocity (m/s), d the bubble diameter (m), ρ_w and ρ_g are the water and gas density, respectively (kg/m^3), μ_w is the water viscosity (kg/m s). This equation shows that bubble velocity is directly related to the square of the diameter. When hydrostatic pressure decreases, d increases and bubbles accelerate

with respect to the surrounding water. The equation, so written, is the general form of Stokes' law. In porous media the equation has to be properly modified. Firstly, the d parameter must have an upper limit, somehow related to the structure of the medium. More precisely, it is expected that the maximum size of bubbles is controlled by the minimum cross-section of the migration path through the porous medium. For a fractured rock the bubble size may be related to the minimum distance between the fissure walls. Varhegyi et al. (1986) described a theoretical model to estimate the bubble size (d_B), and consequently its velocity as a function of the medium porosity (n) and mean grain size (d_G):

$$d_B = 1.26 d_G n(n + 0.21) \quad (27)$$

Using this formula it is possible to derive the maximum velocity (bubble size being equal to pore space) of gas bubbles through homogeneous and equigranular porous media. But this kind of media can only be found rarely in nature. The relation between d_G and the true grain size distribution is very difficult to investigate theoretically. It is probable, however, that in case of a wide grain size distribution d_G, as the equivalent mean grain size, is shifted towards the finer sizes and the cross-section available for bubble flow is reduced (Varhegyi et al., 1986). However, the modified Stokes' equation may be used to estimate the order of magnitude of microbubble velocity in geologic media.

This model, however, was developed considering the generic Stokes' law of bubble motion, with bubble diameter as function of rock porosity. For fractured media, the fracture or fissure width determines the maximum bubble diameter to be used in Varhegyi's equation. This very simple model must be considered as a first approach to the derivation of bubbles velocities in geologic environments, as it does not take into account a number of factors occurring under real conditions. Firstly, the velocity given by Stokes' equation should refer to single bubbles in "unbounded" water conditions, when the motion and shape of a given bubble is not perturbed by other bubbles or by the wall effect induced by the fracture. Second, increasing gas fluxes, bubbles can coalesce producing vertically elongated bubbles, called "slugs", and then continuous gas streams within the fracture.

Recently, Kostakis and Harrison (1999) have investigated in more detail the problems and strategy of physical modeling of high flow of gas bubbles in single fractures (slug regime); they also derived basic equations of mass and momentum conservation, and developed a novel procedure for numerical analysis, considering major parameters, such as gas and liquid density, liquid viscosity, wall effect, fracture aperture and boundary pressures.

According to the numerous experiences in bubble dynamics, the main parameters of pipes and capillaries influencing bubble motion are width and inclination (e.g. Kostakis and Harrison, 1999); this is reasonably valid also for natural rock fractures, where, however, fracture wall roughness is also of primary importance. Experimental data show that small bubbles ($d < 0.2$ mm) in contaminated (real) water actually follows Stokes' law (Sangani, 1986). For greater sizes, microbubbles suffer the occurrence of surface-active impurities: the drag coefficient of contaminated systems is higher and, thus, the bubble velocity is lower than that of pure water.

We can identify four main bubble flow patterns as possible circumstances occurring in natural rock fractures, depending on the gas flux and fracture size, in which the velocity of gas bubbles must be examined differently.

1. Bubbles with negligible fracture wall effect: classic equations of single bubble motion can be used assuming there is no perturbation on the bubble flow by the fracture walls. This condition can occur for microbubbles in relatively larger fractures and rock voids.
2. Bubbles rising along a typically narrow fracture whose walls influence the bubble rise (fracture width close to bubble diameter). The bubble velocity (v_w) normalized to the stokes' velocity (v) depends upon the ratio of bubble radius (r) to half width (b) of the fracture (approximated by parallel plates) following (Brown, 2000):

$$\frac{v_w}{v} = 1 - 1.004\left(\frac{r}{b}\right) + 0.418\left(\frac{r}{b}\right)^3 - 0.21\left(\frac{r}{b}\right)^4 - 0.169\left(\frac{r}{b}\right)^5 \quad (28)$$

3. Long bubble-trains and slugs. Increasing gas flux and/or reducing the fracture aperture, bubbles become elongated (slugs) forming a typical bubble-train flow.

4. Bubble plumes in larger rock voids. An additional upwelling fluid velocity should be considered (variable from 10 to 40 cm/s) as an effect of bubbling turbulence (Clift et al., 1978). In large joint systems, water-filled cavernous zones and sinkholes in karst environments, intense bubble plumes can rise without significant wall friction.

At higher gas pressures and fluxes, slugs can be replaced by connected gas streams driven by the pressure gradient. In particular, bubbles coalescencing with a following gas stream would occur if pressure-driven velocity is higher than buoyancy-driven velocity.

Bubble-trains and slug flow can be due to intermittent gas leakages through reservoir–cap rock systems, or be related to the transmission of pressure pulses created by crack propagation due to tectonic (seismic) stresses. This possibility has been recently proposed as mechanism of generation of hydrogeochemical earthquake precursors (Heinicke and Koch, 2000). This work seems to represent the first attempt of examining the role of rapid advection of bubbles in seismo-tectonics.

Continuous phase flow may exist only if a fracture is continuously invaded by large amounts of gas with pressure above hydrostatic plus capillary pressures (e.g. leakage from geothermal or hydrocarbon pressurized reservoirs). Any reduction of gas pressure or fracture width will interrupt the flow and slugs or trains of bubbles will form. As the bubble rise its radius increases and it can be occluded within the fracture. As bubbles occlude, they coalesce to again form longer slugs and then continuous phase gas columns.

4.3. Analysis of gas velocity

Theoretical gas velocity as a function of the fracture width can be calculated from Eq. (13) for continuous gas-phase flow between parallel plates and Eq. (26) for bubble flow in the Stokes regime, assuming that the bubble diameter is less than the fracture width. In Fig. 3, velocity curves have been plotted for reference conditions corresponding to a subsurface depth of 1000 m (fluid properties are described in Fig. 3). The pressure gradient is assumed to be density-driven,

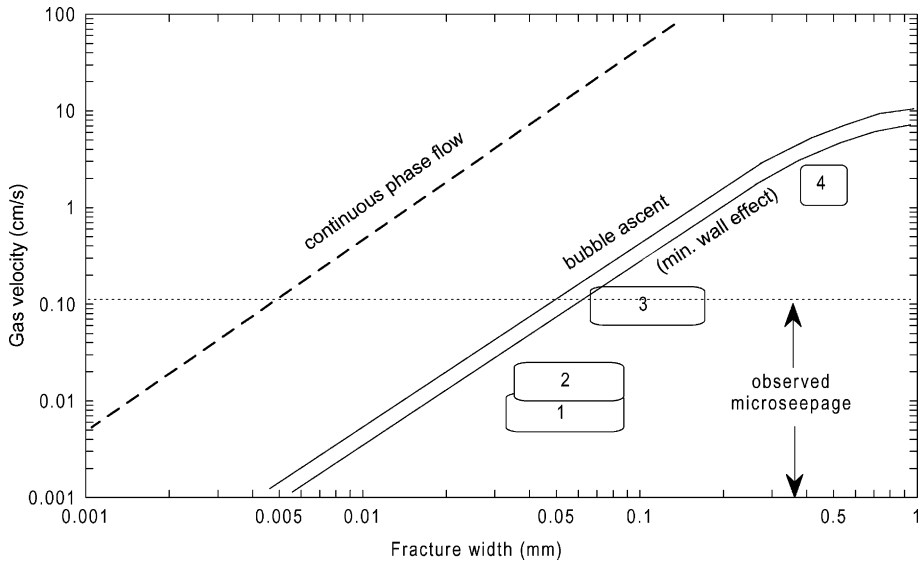

Fig. 3. Gas velocity vs. fracture width. Theoretical velocities of continuous gas-phase flow and bubble flow (Eqs. (13) and (26)) are computed for fluid properties at depth of 1000 m (38 °C and 10 MPa; water density 1000 kg/m^3; water viscosity 0.0009 Pa s; gas density 100 kg/m^3; gas viscosity 0.000015 Pa s). The wall-effect bubble velocity is computed (Eq. (28)) for $r/b = 0.74$, which provides the maximum velocity. Experimental data: (1) Rn in igneous rocks (Kristiansson and Malmqvist, 1982); (2) He in low-permeability saturated faulted clays, gas path length: 22 m (Etiope et al., 1995); (3) He in medium permeability (highly consolidated) clays, gas path length: 35 m (Duddridge et al., 1991); (4) He in high-permeability saturated faulted granite, gas path length: 117 m (Gascoyne and Wuschke, 1990). The range of observed microseepage velocities is taken from Brown (2000).

due to simple buoyancy of gas within water. Bubble velocity is computed both without wall effect (no correction factor in the Stokes equation, condition '1' of Section 4.2) and with wall effect (condition '2' of Section 4.2), as reported by Brown (2000), considering a velocity attenuation as function of the ratio of bubble radius to fracture width (Eq. (28)).

Experimental data on in situ gas velocity are very difficult to obtain. Very few examples, coupled with fracture data, are available in literature. They come primarily from field gas injection tests, (generally performed as part of studies on the geological disposal of radioactive wastes) where the injected gas has a pressure equal to hydrostatic pressure plus capillary pressure. Some conservative estimates of velocity, with unknown fracture aperture, were made by evaluating the effects of subsurface pressure changes on surface geochemical signatures of hydrocarbon seepage (Brown, 2000). In special cases related to gas vents, velocities can be estimated measuring the flux of gas emitted: 150–300 m per day were estimated conservatively for gas rising through mud volcanoes (Martinelli and Ferrari, 1991).

Theoretically, the continuous phase gas migration is the fastest mechanism, as already demonstrated by Brown (2000). In fact, the velocity of the continuous phase flow is controlled by the viscosity of gas (Eq. (11)), while the viscosity controlling bubble ascent is that of water, that is about 60 times that of gas under the reference conditions assumed. Bubble velocity ranges from 0.001 to 10–20 cm/s for fractures of a few millimeters. Microbubbles of colloidal size (radius below 1 μm), considered by MacElvain (1969) and Price (1986) a favorable mechanism of hydrocarbon gas transport, should have very low velocities in the order of 10^{-6} to 10^{-5} cm/s. The observed gas velocity range instead in the order of 10^{-4} to 10^{0} cm/s (0.1–2000 m per day). Fig. 3 suggests that these velocities can be easily reached by continuous phase flows at any fracture width and by bubbles within fractures larger than 0.01 mm. For larger fracture apertures and voids in the order of cm, microbubble plumes may reach velocities of the order of 10^{4} m per day. Bubble-trains and slugs can have velocities intermediate between microbubbles and continuous gas flow, depending on the wall effect. Heinicke and Koch (2000) have observed that hydrogeochemical earthquake signals can be due to CO_2 slugs rising through water-filled faults at velocities of about 7–8 cm/s (6000–7000 m per day). The conclusion of Brown (2000) for which the gas bubble ascent cannot account for observed microseepage velocities is, therefore, valid only for bubbles of colloidal size. Considering the possible large values of fracture width within the crust, as discussed in Section 4.1, rising bubbles can effectively account for the rapid and long-distance gas migration rate observed.

Moreover, field injection tests indicate that aquifers do not constitute a barrier for gas migration, nor do they reduce the gas velocity. In fact, under the same injection pressure gas through saturated rock moves faster than gas in dry rock. This is due to the higher buoyancy developing between gas and water (Eq. (26)) than between gas and gas (Eq. (16)). This fact, already observed in the laboratory (Etiope and Lombardi, 1996) is an important indication of the potential of the bubble and gas stream motion through aquifers and water-filled fractures.

5. Conclusions

The main conclusive remarks of this overview can be summarized as follows.

1. Recent crustal surveys suggest the widespread occurrence of high-permeability deep subsurface rocks. Fracture aperture can be in the order of 10^{-2} to 10^{1} mm at depths of hundreds and thousands of meters. These sizes are sufficiently high to allow for advective migration of large amounts of gas.
2. Accordingly, the dominant gas migration mechanisms in fractured rocks may include: pressure-driven continuous gas-phase flow through dry fractures; pressure-driven or density-driven continuous gas-phase displacing water in saturated fractures; buoyant movement of gas bubbles in aquifers and water-filled fractures, either as slugs or microbubbles. Predicted movement of microbubbles of colloidal size are less rapid than observed velocities. The most likely process is the evolution from bubble larger than 0.01 mm to continuous phase flow and vice versa, as gas pressure and fracture width change. Advective velocity of gas range mainly in the order of 10^{0} to 10^{3} m per

day. For high-permeability, fractured rock, whose fracture aperture or voids are in the order of cm, microbubble plumes may reach velocities of the order of 10^4 m per day.

3. Diffusion, whose velocity is on average in the order of 10^{-4} to 10^{-2} m per day, can be important in a small spatial scale and a large time scale (e.g. in the primary migration of hydrocarbons). Water advection cannot account for the fast vertical gas migration observed, nor the surface gas-geochemical anomalies, unless for rare conditions of high-velocity resurgent water.
4. Migration of carrier gas by bubbles can be considered an important transport mechanism governing distribution of carrier (CO_2 and CH_4) and trace (Rn, He) gases over wide areas on the Earth surface. Above fault zones, Rn and CO_2 in soil are strictly correlated and Rn may reach unexpected concentrations, higher than the level attributable to U decay in the ground.
5. The velocities and long-distances attainable suggest that gas advection in water-filled fractures can be an important process for the propagation of seismicity-linked geochemical anomalies from the focal zone to the Earth surface. Soil–gas anomalies and chemical changes in groundwater, observed during seismic events, can be attributed to gas carrier dynamics. For example, CO_2 lowers pH, while CH_4 increases pH by stripping CO_2.

The "geogas" theory basically proposes a re-evaluation of several concepts on gas migration and behavior in the geosphere, previously underestimated or improperly applied. The occurrence and abundance of carrier gases, such as CO_2, in many geological environments, and the capabilities of bubble transport, represent primary factors in controlling long-distance movements, behavior and distribution of rare gases on the Earth's surface. The role of micro-fractures and related gas advection, for example, is underestimated in seismo-tectonics, underground waste disposal studies, radioprotection zoning and geological exploration. The transport effectiveness of trace gases by carrier gas has yet to be studied in quantitative terms. It is already clear, however, that further studies on the distribution and behavior of trace gases on the Earth surface may be not significant if not accompanied by analyses of carrier gas dynamic.

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