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Composition of Gases in the Earth's Upper Mantle

ABSTRACT. *There is considerable evidence suggesting the continuous release of gases from deeper parts of the Earth. A review is given of geological data pertinent to deep gas compositions, emphasizing information of relevance to upper mantle conditions, and to possible degassing mechanisms. Data from experimental and theoretical studies relating to the existence and composition of upper mantle gases are presented, and information on deep gas compositions from natural rocks, comprising volcanic gases, gases in ocean-floor basalt glasses, in phenocrysts and upper mantle minerals, is reviewed. The available evidence is not decisively in favour of any single upper mantle gas composition. H_2O and CO_2 appear to be the major species, whereas more reduced gases are present in only subordinate concentrations and are of only minor importance for Earth degassing processes. Very low total gas contents, in the order of less than O.1 weight % gases for some upper mantle regions, are indicated, but an upper mantle heterogeneous in its gas content and composition seems likely.*

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Introduction

Approximately 20% of the total volume of unmetamorphosed sediments at the Earth's surface consists of pore water. During subsequent burial of such sediments most of this water (and other gases, e.g. formed from reactions with organic materials present in the sediments) are expelled from the sediments and progressively lost from the sedimentary pile during diagenesis and metamorphism. Therefore most metamorphic rocks at the base of the Earth's crust are low in gases such as CO_2 and H_2O, with the gases bound in minerals such as amphiboles, micas, and carbonates. Partly because of this trend toward lower contents of gases with depth it is less commonly recognized that most geological processes deeper in the Earth's crust and upper mantle have taken place in the presence of, or have been influenced by, gases of various compositions.

Studies of natural rocks document that gases, either bound in minerals

or as a free gas phase, are actually present in the deeper parts of the Earth. Much of this evidence comes from volcanic activity. Water (H_2O) and carbon dioxide (CO_2) are frequently reported as important constituents of the gases released during volcanic eruptions and are therefore often judged also to be the most important gases in the lower crust and upper mantle. Recently, however, hypotheses of the existence of more reduced gases such as methane (CH_4) in the deeper parts of the Earth's crust and upper mantle have been revived (Gold, 1979; MacDonald, 1983) and have questioned the accuracy of the above simple picture of deep Earth gas compositions.

At a theoretical and experimental level the importance of gases for rock forming processes in general is well documented. In the Earth's crust the presence of gases has important implications for mass transport, deformation mechanisms, rheological properties, and for mineral reactions and equilibria. At still deeper levels, in the upper mantle, gases may significantly affect mineral phase equilibria important for the formation and subsequent evolution of silicate magmas. The presence of deep-seated gases and their possible migration to the Earth's surface may furthermore have important implications for the chemical evolution of the Earth's atmosphere and hydrosphere (Cogley and Henderson-Sellers, 1984).

It is the aim of this article to review the available geological evidence for the presence and compositions of gases, and their actual concentrations and distribution in the Earth's upper mantle. Emphasis has been placed as much on the rationale behind the pertinent geological studies as on the obtained results themselves. The greatest importance will be attached to results obtained from studies of gases in natural volcanic rocks, and to degassing phenomena associated with their formation. As a basis for these data a short account of experimental and theoretical constraints on compositions of deep gases will be given.

The Earth's crust and upper mantle

Some major features of the Earth's crust and upper mantle of relevance to this article are shown schematically in Fig. 1.

The crust consists of the region above the Mohorovicic discontinuity which is defined by an abrupt increase in seismic P-wave velocities considered to reflect a change in density of the rocks due to a mineralogical or chemical change or both. The crust generally ranges in thickness from
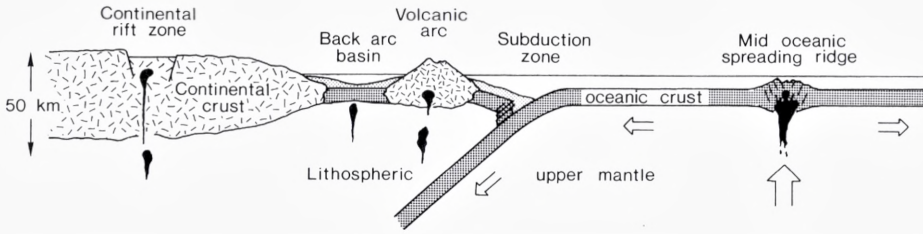
Fig. 1. Schematic cross-section of the Earth's crust and uppermost mantle showing the main large-scale geological features referred to in this article and placed in a plate-tectonic context. Arrows indicate directions of relative movement of the oceanic plate. Mantle derived magmas are shown by black, sediments are light stippled.

about 5-15 km in oceanic regions to 30-50 km in continental regions. Oceanic islands, island arcs and continental margins are examples of transitional crust that exhibit thicknesses of 15-20 km.

The upper mantle extends from the Mohorovicic discontinuity to a depth of about 400 km and comprises the lithosphere and the upper part of the asthenosphere. The lithosphere is between 50 and 150 km thick and forms an upper more brittle part of the upper mantle. The astenosphere extends from the base of the lithosphere and down to about 700 km. The uppermost 50-150 km of the astenosphere is characterized by relatively low seismic-wave velocities and forms the low-velocity zone. The astenosphere deforms plastically. These differences in physical properties of the lithosphere and astenosphere are reflected in the plate tectonic model, where the Earth's surface is considered to be made up of a number of rigid plates which are in motion relative to each other (e.g. Wyllie, 1971). The crust and the lithosphere together form the rigid plates moving on top of the more plastic astenosphere, where the convection cells moving the plates are believed to be concentrated.

New oceanic crust is constantly being formed along mid oceanic rift zones where basaltic melts generated by the upward movement and subsequent partial melting of deep mantle materials are erupted. Generation of magma in the mantle also occurs where older oceanic crust is subducted under continental or oceanic crust, with ascent of the derivative magmas close to the subduction zone and the formation of volcanic island arcs. Continental analogues of island arcs occur in regions (e.g. the Andes in South America) where subduction of oceanic crust occurs beneath a continental mass.

The continental crust is dominated by a variety of different metamor-

Fig. 2. Vertical zonation of a gas-free peridotitic mantle, as inferred from experiments. The beginning of melting of solid mantle is indicated by the peridotite solidus. Curves 1 and 2 indicate the positions of mineral reactions separating depth-regions for spinel-bearing peridotite from plagioclase- and garnet-bearing peridotite (after Wyllie, 1971). Curves C, O and MOR show geotherms for continental (C), oceanic (O) and mid oceanic ridge (MOR) regions, respectively (from Anderson, 1981).
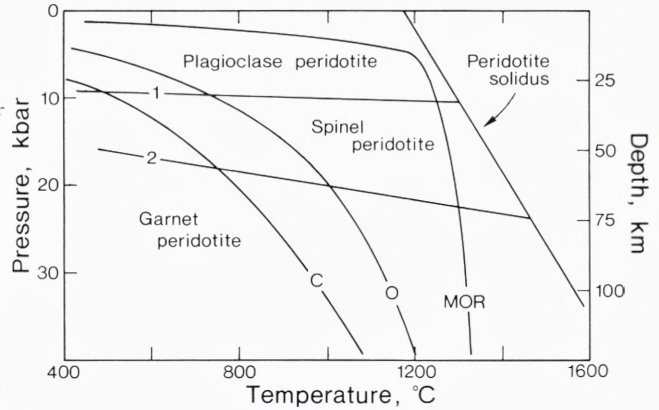
phic and plutonic rock types and a cover of sedimentary rocks of variable thickness. Within some stable continental blocks there are rift systems, which are fault-bounded valleys ranging in width from 30-70 km and in length from a few tens to thousands of kilometers. Such continental rift systems often have associated volcanic activity, with extrusion of lavas originating deep within the upper mantle. Continental rift zones mark the splitting of continental plates and may develop into new oceanic crust.

Whereas samples of the Earth's crust are easily accessible for collection and study, samples of the upper mantle are more fragmentary in nature and essentially consist of the melted portion of the mantle erupted as lavas and the solid fragments of presumed mantle rocks (xenoliths) they occasionally take with them. Although studies of available mantle samples have established the heterogeneous character of the upper mantle (Dawson, 1981) there is a general agreement that the rock type peridotite forms a substantial part of the upper mantle, the major mineralogy being olivine, two pyroxenes (ortho- and clinopyroxene), plus an aluminous phase changing from plagioclase to spinel and then to garnet with increasing depth (pressure), as visualized in Fig. 2.

Experimental and theoretical constraints on deep gas compositions

The gas-free peridotitic upper mantle of Fig. 2 is contradicted by several observations on natural rocks. The occurrence of amphiboles and mica in upper mantle xenoliths brought to the Earth's surface by kimberlitic magmas and alkaline lavas demonstrates that water at least locally is present in the mantle (Dawson and Smith, 1982). Similarly, carbonates as inclusions in garnet and olivine in deep mantle samples indicate the presence of CO_2 (Dawson, 1980). Additional evidence for the potential importance of gases other than CO_2 and H_2O is given by analyses of the volatiles released during volcanic eruptions (Nordlie, 1971). H_2O, CO_2, SO_2 and H_2 are the main volcanic gas components and although such gases may not represent the actual gas speciation in a deep gas phase the importance of some species in the system C-O-H-S is clearly indicated (Fig. 3).

Partly because H_2O and CO_2 after all are considered to be the most important geological gases, partly because of experimental difficulties in controlling exactly the gas species composition in multispecies fluids at high temperatures and pressures practically all experiments have focussed on the influence of H_2O and CO_2 on mantle phase relations. In keeping with these conditions most of the data presented in subsequent sections deal with gas species within the subsystem C-O-H (front of Fig. 3).
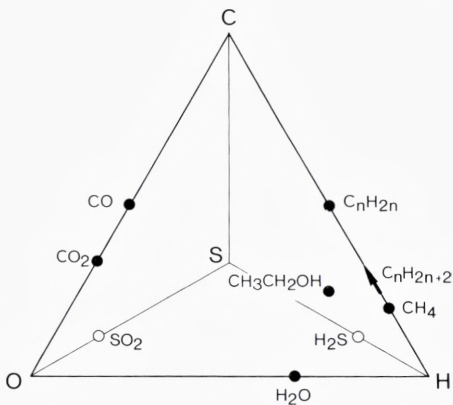

Fig. 3. Main gas species reported present in minerals and rocks of upper mantle derivation plotted in the C-O-H-S system.

A peridotite-CO_2-H_2O upper mantle

The generalized phase relations for peridotitic mantle containing CO_2 and H_2O are given in Fig. 4.

Addition of H_2O and/or CO_2 to the dry system causes temperatures for beginning of melting of peridotitic mantle to decrease from those when no gas is present (Mysen and Boettcher, 1975; Wyllie, 1979). The beginning of melting curves (solidii) for three conditions of gas concentrations are sketched in Fig. 4 (left diagram). Under sub-solidus conditions addition of H_2O and CO_2 allows the formation of hydroxyl bearing minerals and carbonates, respectively. From Fig. 4 (left diagram) the mineral assemblages present at various depths can furthermore be determined by following the three geothermal gradients, representing the main geological settings, through the various mineral reaction and melting curves of Fig. 4. Mantle cross sections so derived are shown in the three columns to the right in Fig. 4 for an intermediate gas content of 0.3 weight % H_2O plus 0.1 weight % CO_2 and *a priori* considered to reflect plausible mantle gas concentrations (Olafsson, 1980).

Fig. 4. *Vertical zonation of a peridotite-CO_2-H_2O upper mantle. The left pressure-temperature diagram shows solidus curves for peridotite-CO_2-H_2O for the volatile contents stipulated in the diagram and compared with geotherms from Fig. 2. The curve C-/C+ (= carbonates/free CO_2) indicates a sub-solidus carbonation reaction (Wyllie and Huang, 1975; 1976). Other abbreviations as in Fig. 2.*

The three right columns show vertical cross-sections for a peridotite-CO_2-H_2O mantle with 0.4 weight % volatiles (0.3 wt.% H_2O + (0.1 wt.% CO_2) for continental (C), oceanic (O) and mid oceanic ridge (MOR) regions. Mineralogical zones, and depth ranges for existance of a free gas phase (light stippled) and partial melting of mantle are indicated. Uppermost in the sections are indicated the average thicknesses of continental (irregular strokes) and oceanic (heavy stippled) crust, and ocean. Diagrams based on data in Mysen and Boettcher (1975) and Olafsson (1980).
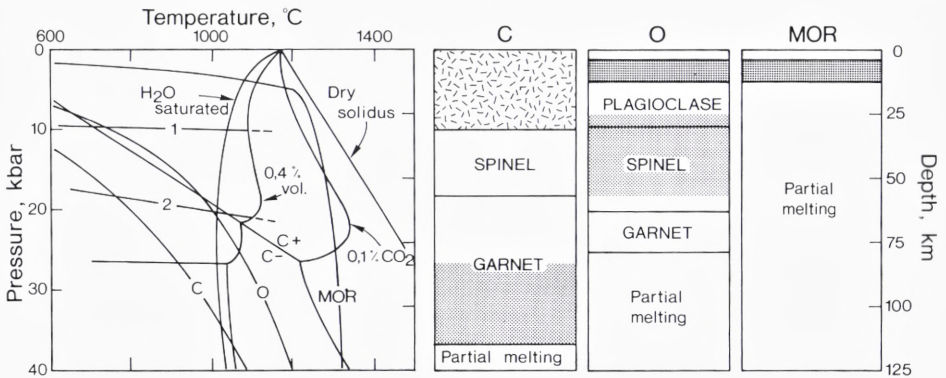
An important result indicated by the three mantle cross sections (Fig. 4) is that upon increasing the geothermal gradient (from continental towards mid oceanic ridge regions) a decrease in both the depth to partial melting of mantle and to regions with the possible existence of a free gas phase takes place. Thus, beneath stable continental crustal regions a free gas phase may exist at depths between 80 and 130 km, due to the break-down of the OH-bearing phase phlogopite, and resulting in a H_2O-rich gas phase. The CO_2 under continental areas is stored in carbonate. In oceanic regions, because of the higher geothermal gradient, melting occurs at shallower depths and a free gas phase may exist within the depth range 25-55 km and have a more intermediate CO_2-H_2O composition (Wyllie, 1979). Under mid-ocean ridge regions a free gas phase, very rich in CO_2, may exist close to the surface and partial melting occurs at all depths greater than about 20 km.

The carbonation reaction (C-/C+) in Fig. 4 is actually only one of three sub-solidus divariant carbonation reactions identified in the model system CaO-MgO-SiO_2-CO_2 by Wyllie and Huang (1975; 1976). According to these model reactions it takes about 5 weight % CO_2 to react away all the clinopyroxene in a normal mantle peridotite, and about 23 weight % CO_2 to transform a peridotite completely into coesite-garnet marble. In some garnet kimberlites (Dawson, 1980) all clinopyroxene and most of the olivine appears to have reacted away and thus indicates that high CO_2 concentrations, at least locally, can occur in the upper mantle.

Amphibole is formed in peridotite by reaction with water. Up to about 0.4 weight % H_2O can be stored in amphibole-peridotite, and up to about 5 weight % CO_2 in dolomite-peridotite without loosing one or more of the principal peridotite minerals.

The results obtained from Fig. 4 furthermore rest on the assumption that any gas species is only stoichiometrically incorporated into minerals such as amphiboles, micas and carbonates. Studies have, however, indicated that species within the system C-O-H may be incorporated at levels of tens to hundreds of parts per million into stoichiometrically volatile-free minerals such as olivine, pyroxene and garnet (e.g. Freund et al., 1980; Aines and Rossman, 1984), and that amphiboles from mantle xenoliths may contain up to about 0.1-0.5 weight % carbon-bearing gas species in addition to water (Matson and Muenow, 1984). Therefore a free gas phase may not exist even though it would be predicted from experimental studies.

Fig. 5. Solubility relations for CO_2 and H_2O in basalt and albite melts. (A) Solubility of CO_2 and H_2O in basalt melt along the basalt-CO_2 and basalt-H_2O solidus curves, respectively, as a function of pressure (/depth). Data from Wyllie (1979) and Spera and Bergman (1980). (B) Solubility of CO_2 and H_2O in albite melt at 1450 °C as a function of pressure. Data from Burnham and Davis (1974) and Mysen et al. (1976)

(C) Solubility of CO_2 and H_2O in ($CO_2 + H_2O$)-saturated albite-melt at 1450 °C and 20 kbar as a function of the mole fraction of CO_2 (X_{CO_2}) in the system (from Mysen, 1976).

(D) Compositions, in terms of mole fraction of CO_2 (X_{CO_2}), of coexisting vapour and melt in equilibrium with albite at 1050 °C as function of pressure at CO_2 and H_2O saturation of the melt (from Eggler and Kadik, 1979).
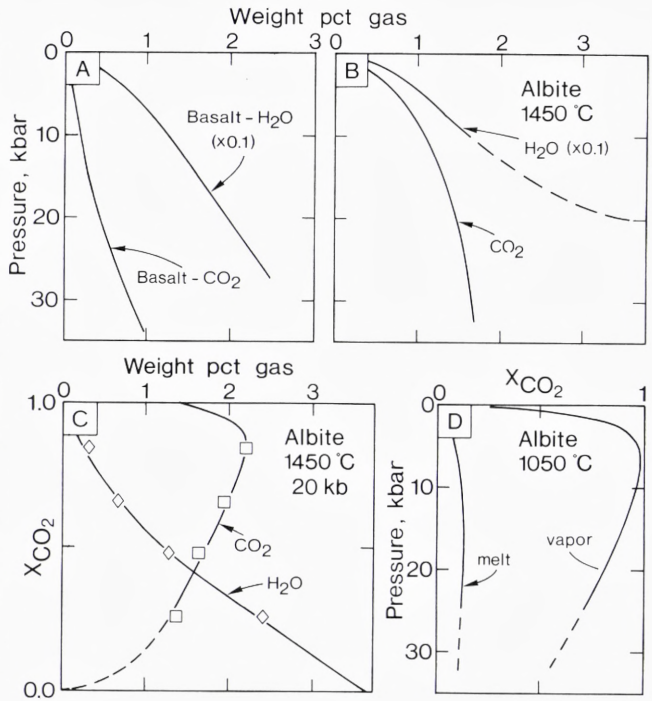
Solubilities of gases in upper mantle melts and minerals

The most important features concerning the solubilities of H_2O and CO_2 in melts at temperatures and pressures relevant to upper mantle conditions are shown in Fig. 5.

On the basis of the results presented in Fig. 5 the following general comments regarding the role of CO_2 and H_2O for melting of upper mantle rocks can be given:

(1) At the same temperature, pressure and melt composition 3-10 times as much H_2O as CO_2 can dissolve in the melt. At pressures of about 20 kbar, corresponding to a depth of 65 km, about 20 weight per cent H_2O and only about 0.5 weight CO_2 can dissolve in tholeiitic basalt melt (Fig. 5,A). Higher solubilities are found for alkali basalt melt compositions (Mysen et al., 1976).

(2) The solubilities of both CO_2 and H_2O are positively correlated with pressure (Fig. 5,B) whereas the correlation with temperature ap-

pears to be linear or at lower pressures possibly negative (Rai et al., 1983).

(3) The presence of H_2O affects CO_2 solubilities; about 20-30% more CO_2 dissolves in hydrous than in H_2O-free silicate melts (Fig. 5,C).

(4) In the presence of a mixed (CO_2 + H_2O)-gas phase, because of the very different solubilities of CO_2 and H_2O in any melt composition, the gas phase is strongly enriched in CO_2 over gases dissolved in the coexisting melt (Fig. 5,D).

A consequence of this fractionation of gases (Fig. 5,D) is that partial melting of a (CO_2 + H_2O)-bearing peridotite may result in enrichment of the residual mantle in CO_2 whereas the melt will be enriched in H_2O. Thus partial melting may result in preferential depletion in H_2O in the magma-forming regions of the upper mantle and thereby create a mantle that is heterogeneous with respect to gas components. Furthermore, although the gas composition of the derivative melt will be highly enriched in H_2O any gas exsolved at lower pressures from the melt because of gas saturation will be highly enriched in CO_2 and differ considerably in composition from the initially dissolved gas phase. Using albite as a model (Fig. 5,D) almost pure CO_2 would exsolve from a (CO_2 + H_2O) saturated melt in the pressure range 5-10 kbar.

Considering the high CO_2 and H_2O concentrations needed to saturate a melt at upper mantle conditions, it appears realistic to conclude that most, if not all, melts formed in the upper mantle are unsaturated in H_2O and CO_2, with complete and instantaneous absorption of any free gas phase by the magma in the magma-forming regions (Kadik and Lukanin, 1973).

Studies of the solubility of CO_2/carbon in minerals coexisting with a CO_2 gas at mantle conditions are few and the results inconclusive. Mysen et al. (1976) found solubilities of carbon in olivine and diopside at 20-30 kbar to be 7-10 ppm. Such low carbon solubilities would preclude storage of any significant amounts of carbon (dioxide) in the upper mantle within crystalline silicates and suggest that any mantle CO_2 is stored in a gas phase, in carbonates, in the form of graphite/diamond, or in silicate melts. However, much higher carbon contents, in the order of 500-2000 ppm, have been obtained by Mathez (1984) and Freund et al. (1980) for mantle olivine, and carbon contents of 140-400 ppm have been obtained on kaersutites from mantle xenoliths (Poreda and Basu, 1984).

Experimental data on solubilities of gases other than CO_2 and H_2O are scarce and at best available only for conditions not representative for the upper mantle. Eggler et al. (1979) measured the solubility of CO_2-CO

volatile mixtures in equilibrium with graphite in various melt composi-
tions at pressures of 20–30 kbar and 1700 °C and observed slightly higher
solubilities than for CO_2 alone. Extrapolating available data on other
gases to a pressure of 2 kbar enables comparison with the solubilities of
CO_2 and H_2O, and the following solubilities (in weight %) were obtain-
ed: He (0.0043%), Ar (0.0071%), Ne (0.0126%), N_2 (0.037%), CO_2
(0.55%), and H_2O (4.4%), with data from Kirsten (1968) and Kesson
and Holloway (1974).

Sulfur behaves slightly different than CO_2 and H_2O in that sulfur
solubility decreases with increasing pressure and increases with increas-
ing temperature and total FeO-content of a silicate melt (Wendlandt,
1982). In the range 20–30 kbar sulfur solubilities are in the order of 0.1–
0.25 weight %.

Gas species composition of a free C-O-H upper mantle gas phase

Evidence for the oxidation state of the upper mantle is not decisive in
favor of any single value. Information has essentially been obtained
from, either thermodynamic and experimental studies relating to chemi-
cal compositions of coexisting minerals in upper mantle xenoliths (e.g.
Eggler, 1983), or direct intrinsic oxygen fugacity measurements on man-
tle minerals (e.g. Arculus and Delano, 1980). Whereas results from the
latter type of approach suggest a strongly reduced upper mantle (with
oxygen fugacities corresponding to the iron – wüstite buffer), results
from the former method of study indicate slightly more oxidized condi-
tions, with oxygen fugacities corresponding to the quartz – fayalite –
magnetite buffer assemblage. The actual oxidation state of the upper
mantle is important as the species composition of a free gas phase will be
very dependent on the actual oxygen fugacity level.

In Fig. 6 the influence of the oxidation state for the compositions of a
free C-O-H gas in equilibrium with graphite/diamond is given for
pressure-temperature conditions corresponding to the upper mantle in
the Lesotho kimberlite province (Fig. 6, A). Oxygen fugacities calculated
from the chemical compositions of coexisting olivine, pyroxene and
oxides in high-pressure xenoliths from various kimberlites and perido-
tites from the upper mantle are shown in Fig. 6, B (Eggler, 1983). Values
cluster between the quartz – fayalite – magnetite and magnetite – wüstite
oxygen buffer curves and are nearly centred on the oxygen fugacity
values defined by the coexistance of enstatite – magnesite – olivine –
graphite/diamond (Eggler et al., 1980). These relatively oxidized condi-
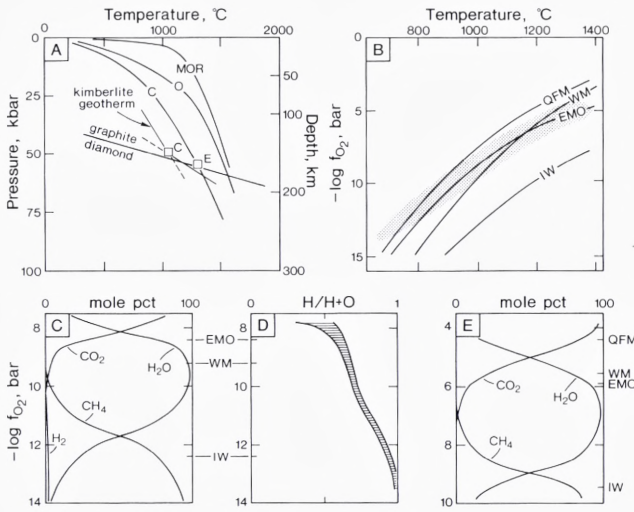tions may be interpreted as representing the oxidation state of the sub-

*Fig. 6. Gas species composi-
tions of a free C-O-H gas
phase as function of tempera-
ture, pressure and level of
oxidation of the upper man-
tle. (A) Pressure-tempera-
ture diagram showing geo-
therms (C, O and MOR)
from Fig. 2 and the inflected
sub-continental geotherm
proposed for the Lesotho
kimberlite province (Boyd,
1973). Graphite-diamond
stability curve from Bundy et
al. (1961). Boxes C and E
indicate the pressure-temper-
ature conditions of diagrams
C-D and E, respectively.*

*(B) Oxygen fugacity-temperature relations for the Lesotho upper mantle, for the pressure-
temperature relations given by the inflected geotherm from diagram A. The stippled field shows the
oxygen fugacities and temperatures inferred from mineralogical studies (Eggler, 1983). Oxygen
fugacities defined by synthetic mineral assemblages, considered relevant to upper mantle conditions,
and in equilibrium with graphite/diamond are shown by curves. QFM: quartz – fayalite –
magnetite; WM: wüstite – magnetite; EMO: orthopyroxene – magnesite – olivine; IW: iron –
wüstite.*

*(C) Gas species compositions at 1023 °C and 50 kbar of a free C-O-H gas phase in equilibrium
with graphite as a function of the oxygen fugacity (from Ryabchikov et al., 1981). Oxygen
fugacity levels defined by the mineral assemblages in diagram B are indicated. (D) Molar H/(H +
O) ratio of the gas compositions in diagram C as a function of oxygen fugacity.*

*(E) Gas species compositions at 1223 °C and 56 kbar of a free gas phase in equilibrium with
graphite/diamond as a function of oxygen fugacity (from Eggler, 1983).*

continental source regions for alkaline magmas and possibly subconti-
nental upper mantle in general.

The species composition of a gas phase existing at these temperatures
and pressures as a function of the oxygen fugacity is shown in Fig. 6, C-
E. At oxygen fugacities corresponding to those proposed from the natu-
ral upper mantle mineral assemblages the gas will essentially be a mix-
ture of CO_2 and H_2O. Only at significantly lower oxidation levels
(around iron – wüstite buffered oxygen fugacities) do more reduced gas
species such as CH_4 take the place of CO_2.

The results in Fig. 6 indicate that if a gas exists in the upper mantle its

composition and oxidation state is most probably buffered to (H_2O + CO_2) -rich mixtures.

Although sulfur is not considered in the above presentation, results will not change significantly with addition of sulfur to the system. Calculations by Mitchell (1975), based on estimates of the sulfur fugacity from sulfide minerals found in kimberlites, show that for all reasonable sulfur fugacity levels any sulfur-bearing gas species in the C-O-H-S system such as H_2S, S_2 or SO_2 would only be present in concentrations 2-3 orders of magnitude less than H_2O, CO_2, and CH_4.

Gases in natural rocks of upper mantle derivation

Most of the evidence for the presence of deep gases and their composition is related to magmatic activity, most dramatically evidenced by the often explosive release of gases accompanying volcanic eruptions. The volcanic eruption itself is, however, only the final result of a series of events starting with partial melting of upper mantle, and the initial composition of any involved deep-seated gas phase may have been significantly changed in response to changes in temperature, pressure, composition and oxidation state of the magma during its ascent to the surface, and from mixing with ground and surface waters. Samples representing various intermediate stages in this sequence of events (Fig. 7) have, however, been preserved for study and a review of the data obtained from studies on such samples is presented below.

Compositions of volcanic and geothermal gases

Volcanic gases are generally considered to provide the most complete information on bulk gas composition because of the complete exsolution of all gases from silicate melts at atmospheric pressure.

Opportunities for field collection of volcanic gases are necessarily sporadic and involve serious access, collection and gas contamination problems. Available data are furthermore largely restricted to relatively quiet basaltic eruption thereby possibly biasing the obtained data. Gerlach and Nordlie (1975a; b; c) reviewed the then published volcanic gas compositions and attempted to remove the changes caused by atmospheric and meteoric water contamination, and reactions of the high-temperature gases with the sampling equipment from the analyses. Representative examples of such restored volcanic gas analyses are given in Table I.

Stage A
Partial melting of the upper mantle and subsequent removal of the melt fraction.
Parts of non-melted mantle may be picked up by the melt as nodules/xenoliths

Stage B
Possible entrapment of melt inclusions in the phenocrysts

Stage C
Formation of gas and gas-glas inclusions in phenocrysts

Stage D
Formation of gas-filled vesicles in the residual glassy matrix formed by quenching of the melt upon eruption
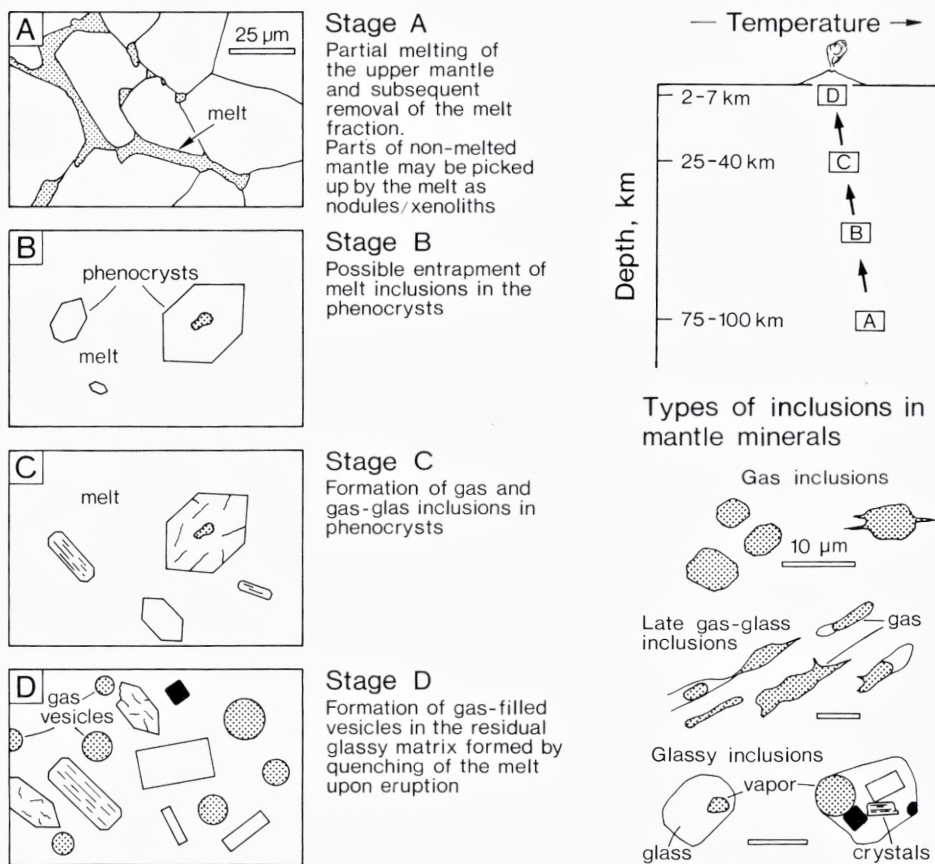
Fig. 7. Schematic representation of stages (A to D) of possible entrapment of gases in gas and melt inclusions in minerals in mantle-derived magmas, in gas vesicles and in the glassy matrix of volcanic rocks. Corresponding approximate depth and temperature conditions (to stages A-D) are sketched in the top-right figure. Sketches of the types and morphologies of inclusions in minerals from mantle nodules are shown in the lower-right part of the figure.

H_2O, CO_2 and SO_2 are the dominant species in all volcanic gases, generally in that order, and with other gases generally constituting only a few % of the volcanic gas. Thermodynamic calculations show all such gas compositions to be compatible with equilibration of the volcanic gas at oxygen fugacities generally constrained to values between those of the quartz-fayalite-magnetite and hematite-magnetite oxygen buffers, indicating effective buffering of the volcanic gas by the magma (Gerlach and Nordlie, 1975c).

TABLE I. Representative analyses of volcanic gases (mole %) released during eruptions of various basalt types

	(1)	(2)	(3)	(4)	(5)	(6)
H_2O	53.4	69.9	77.1	49.9	45.9	81.1
H_2	0.7	1.6	1.6	0.5	1.6	2.8
CO_2	33.3	17.8	11.7	21.7	45.6	9.3
CO	1.1	0.8	0.5	2.7	2.7	0.7
SO_2	11.3	8.8	7.4	26.9	2.3	4.1
H_2S	0.05	1.0	0.9	0.2	1.4	0.9
S_2	0.02	0.5	0.3	0.2	0.6	0.3
COS	–	0.02	–	–	0.1	–
HCl	0.1	–	0.4	–	–	0.8
T, °C	1175	1020	1020	1075	1020	1125

1. Kilauea, Hawaii, Tholeiitic basalts (from Gerlach, 1980a)
2. Erte'Ale, Ethiopia. 1971 eruption, basalts transitional between tholeiitic and alkaline (from Gerlach, 1979b)
3. Erte'Ale, Ethiopia. 1974 eruption, basalts transitional between tholeiitic and alkaline (from Gerlach, 1979b)
4. Mount Etna, Italy. 1970 eruption, alkali basalts (from Gerlach, 1979a)
5. Nyiragongo, Ethiopia. 1959 eruption, nephelinitic basalts (from Gerlach, 1980b)
6. Surtsey, Iceland. 1964-1967 eruptions, alkali olivine basalts (from Gerlach, 1980c)

Inspection of Table I and Fig. 8, where volcanic gases from various volcanoes are presented in terms of their C/S and C/H ratios, shows significant variations, both between different volcanoes and with time for an individual volcano (e.g. Erte'Ale, Table I). The overall distribution of volcanic gas compositions seen in Fig. 8, except for gases from the Nyiragongo lava lake, was proposed by Gerlach and Nordlie (1975a) possibly to reflect various degrees of degassing of basaltic magmas with a common initial gas composition, with C/H and C/S ratios of about 0.7-1.0 and 0.5-0.9, respectively. Alternatively, the distribution of gas compositions in Fig. 8 could represent true differences in gas compositions between different volcanoes and magma types (Sigvaldason, 1981).

Changes in volcanic gas composition with time for both Surtsey and Erte'Ale have been shown to be due to preferential degassing, especially of CO_2 (Gerlach, 1979b; 1980c). Such preferential degassing renders estimates of the initial bulk gas composition in magmas very difficult.

Degassing of species other than CO_2 from magma bodies has primarily been documented by studies of changes in compositions of gases in

fumaroles in areas with contemporaneous and repeated volcanic activity, such as the Krafla volcanic area in North Iceland. Although the majority of gases encountered in fumaroles on the basis of their chemical and isotopic compositions can be shown to have been leached from nearby non-magmatic rocks, both CO_2 and H_2 degassing from shallow magma chambers could be established (Oskarson, 1978; 1984). Outgassing of other minor species such as helium, radon and nitrogen are occasionally observed as well and may accompany degassing of the major species (CO_2) or occur independently (Oskarson, 1984).

Reduced gases in mid-ocean ridge hydrothermal systems

The discovery of active hydrothermal circulation systems at mid-oceanic ridges with exceptionally high contents of reduced gases such as CH_4 and H_2, and accompanied by high helium contents with $^3He/^4He$ ratios about 8 times higher than atmospheric (e.g. Welhan and Craig, 1979) spurred the search for mantle derived gases in mid-ocean ridge hydro-thermal systems. Studies of the isotopic composition of CH_4 and accom-panying CO_2 and the overall chemical characteristics of these systems suggest that a common, abiogenic and deep origin for both the helium and the carbon in the reduced gases is highly likely (Welhan and Craig, 1982). Although the actual observed concentrations of the various gas species may reflect lower temperature equilibration of originally CO_2 and H_2O rich compositions via a Fisher-Tropsh type of reaction, it is also possible that the CH_4 is leached directly from underlying basalt together with H_2, He and CO_2. The carbon–isotopic composition observed in these mid-ocean ridge hydrothermal systems are very similar to those of
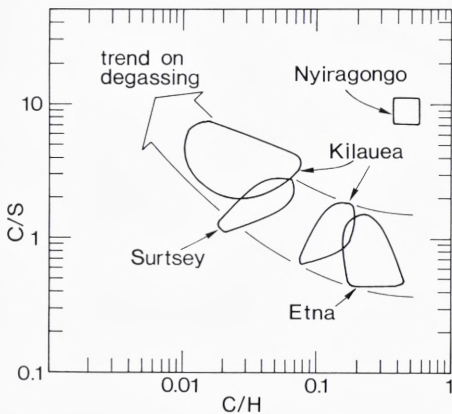

Fig. 8. Atomic C/S versus C/H relations of volcanic gases from various volcanoes as indicated in the figure (data from Gerlach, 1981; and references to Table I). Proposed evolution in gas composition with degassing of magma of a gas with an intial C/H and C/S ratio of about 0.7 and 0.5-1.0, respectively, is shown by the arrow (from Gerlach and Nordlie, 1975a).

Fig. 9. Concentration of CH₄ in Nyiragongo lava lake gas as a function of temperature, assuming equilibration of the gas at a pressure of 1 kbar and oxygen fugacities defined by the mineral assemblage quartz – fayalite – magnetite. The composition of the high-temperature volcanic gas is included in the figure. From Gerlach (1980b).
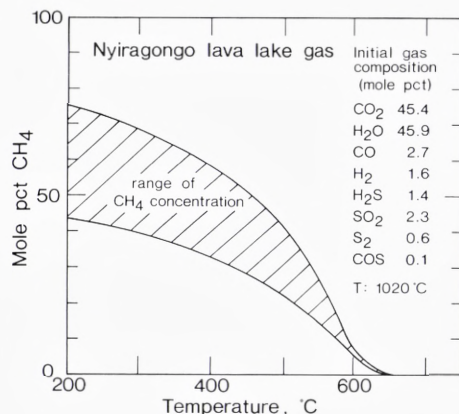
CO_2 found in vesicles in basalts and in the basaltic glass itself from mid-oceanic settings (Pineau et al., 1976; Moore et al., 1977; Pineau and Javoy, 1983; Des Marais and Moore, 1984).

High concentrations of reduced gases (up to 22% CH_4 and 77% CO_2) have been found in lake gases from Lake Kivu, Zaire, and stable isotope analyses (Deuser et al., 1973) have similarly indicated a deep, abiogenic origin for most of the carbon in this gas. The location of Lake Kivu in a continental rift environment (see Fig. 1) characterized by deep-going fault and fracture systems led Gold (1979) to consider the high CH_4 contents as possibly representing degassing from great depths. However, calculations by Gerlach (1980b) on volcanic gas compositions from the nearby Nyiragongo lava lake demonstrated that under conditions of continued buffering of such gas compositions by basaltic rock, at pressures corresponding to depths of about 5-6 km, gas compositions very rich in CH_4 would arise at temperatures below about 400 °C (Fig. 9). Therefore the high contents of CH_4 in Lake Kivu more probably represent lower-temperature equilibration of CO_2-rich gases outgassed from underlying, partially molten magma chambers and not the degassing of CH_4 from depths.

Gases in vesicles, glassy matrix and melt inclusions in minerals from ocean-floor volcanics

Basaltic magmas erupted onto the sea-floor are generally considered to represent the best material for the study of the composition of the volcanic gas phase prior to eruption and gas saturation. Such melts are rapidly quenched under pressure thereby enabling the retention of dis-
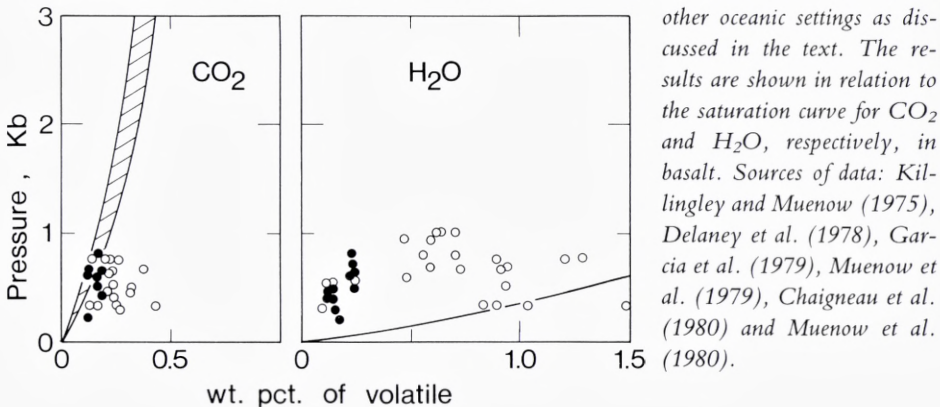
solved gases. Their chemical composition furthermore indicate that mid–ocean ridge basalts represent some of the least evolved mantle derived magmas erupted, and are thus closest in composition to the initially formed melt in the upper mantle.

The presence of vesicles in mid–ocean ridge basalt pillow lavas, however, indicates that these melts were already saturated with a gas phase at the time and pressure of eruption and quenching (Stage D, Fig. 7). Analyses of the gases in these vesicles show that CO_2 is the dominant gas, constituting more than 95 volume % of the gas in the vesicles, indicating that gas saturation of the melt prior to eruption was essentially due to CO_2 (Moore et al., 1977). In addition to CO_2, a sulfur gas was originally present but later reacted to form sulfides now lining the vesicle walls. H_2O, SO_2, O_2 and N_2 constitute the rest of the gas in these vesicles.

Analyses of the gases trapped in matrix glass from rims of the basaltic pillow lavas and of low vesicularity may reflect magma gas contents more closely. Data on the CO_2 and H_2O contents of such glassy matrix material are shown in Figs 10 and 11.

In Fig. 10 the CO_2 and H_2O contents are shown as a function of their quenching pressure (corresponding to their depth of eruption below the sea-floor) and further compared with the basalt-CO_2 and basalt-H_2O gas saturation curves, respectively. The data show that CO_2 saturation of the melts was probably attained in almost all samples prior to quenching.

Fig. 10. Concentration (in weight %) of CO_2 (left diagram) and H_2O (right diagram) in the glassy matrix of basalts quenched beneath the ocean floor shown as a function of the quenching pressure. Filled circles show data for mid oceanic ridge (MOR) basalts, open circles data for basalts from other oceanic settings as discussed in the text. The results are shown in relation to the saturation curve for CO_2 and H_2O, respectively, in basalt. Sources of data: Killingley and Muenow (1975), Delaney et al. (1978), Garcia et al. (1979), Muenow et al. (1979), Chaigneau et al. (1980) and Muenow et al. (1980).

Fig. 11. Concentration (in weight %) of CO_2 versus H_2O in the glassy matrix of basalts from various geological locations and settings as indicated in the figure and discussed in the text. Data from Byers et al. (1984), and references to Fig. 10.
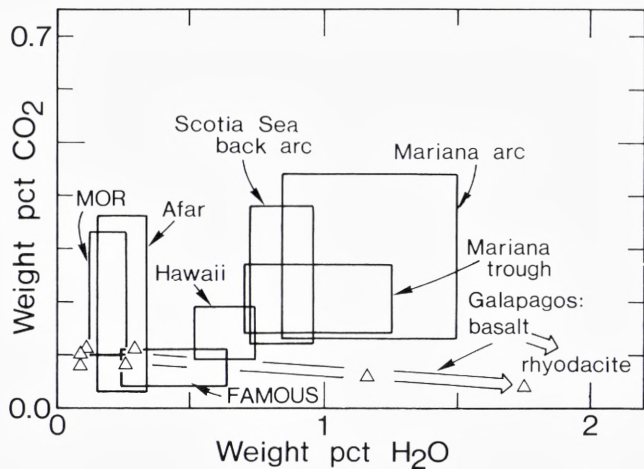
This suggests that the obtained CO_2 contents are the sum of CO_2 in the glass and vesicles, thereby preventing any estimate of the initial CO_2 content of the magmas. These basalts may have degassed a substantial amount of CO_2 and adjusted their actual CO_2 contents to the prevailing pressure prior to eruption and quenching. H_2O contents are, however, always lower than saturation values and may therefore be considered to express the actual H_2O contents of these melts.

In Fig. 11 a distinction between the gas contents in glassy matrix material from basalts of different tectonic setting and compositions has been made. Basalts from mid-ocean ridge areas (MOR, FAMOUS, Galapagos) and from Hawaii thus represent samples of magma believed to have suffered only a small degree of chemical evolution from their initial formation, whereas the remaining samples in Fig. 11 represent basalt types formed and erupted as a result of subduction of oceanic plate. The content of H_2O in the glassy matrix largely follows this distinction: H_2O contents of the glassy matrix in basalts from mid-ocean type of settings are significantly lower than that of subduction-related basaltic glasses. These latter glasses are also richer in elements such as Cl and F (e.g. Garcia et al., 1979), thus favoring models for formation of their magma involving addition of materials (e.g. volatiles) to their source regions from subducted oceanic crust. Such data furthermore show that gases in these tectonic setting may become recycled back to the upper mantle and that such recycling results in heterogeneities in the gas contents of the upper mantle.

The H_2O and CO_2 contents of a suite of glasses, ranging in composition from primitive mid-ocean ridge type basalts through andesite to rhyodacite, from the Galapagos rift have been emphasized in Fig. 11 in order to illustrate the relation between especially the H_2O content of the glasses and their chemical evolutionary stage. However, of most pertinence to deep gas compositions are the gas contents of the most primitive Galapagos basalt glasses (Byers et al., 1983). Total volatile contents for these glasses vary between 0.32 and 0.38 weight %, with 0.09-0.11 weight % H_2O and 0.08-0.11 weight % CO_2. As these glasses contain less than about 1 volume % gas vesicles their gas contents were considered to approximate actual gas contents for these melts. In addition to H_2O and CO_2, hydrocarbons as well as CO were detected, with the most abundant hydrocarbon being CH_4. CO contents were about 0.04 weight %, CH_4 contents < 0.01 weight %. The bulk composition of gases (H_2O: 36 wt. %, CO_2: 40 wt. %, CO: 20 wt. %, and CH_4: < 4 wt. %) in these glasses was considered by Byers et al. (1984) to represent approximately the gas composition of the source region for these melts. Assuming that these melts formed from 25% batch melting and highly incompatible behavior of the gas species, mantle source values of about 0.08 weight % total gases, and about 0.02 weight % of both CO_2 and H_2O are indicated. Such values indicate that very dry mantle may be involved in the generation of magmas along mid-ocean ridges.

Samples of the gas content of melt compositions at earlier stages (stages C and B in Fig. 7) during ascent of the magma are occasionally preserved as melt inclusions in phenocrysts. Analyses of such melt inclusions show that, whereas the mole percentage of CO_2 in the (residual) glassy matrix varies from about 4 to 38 mole % CO_2 in primitive basalt glasses, the mole percentage of CO_2 in melt inclusions in phenocrysts varies from about 45 to almost 100%. This trend towards higher H_2O contents with evolution of the magma is consistent with the evolution in gas composition of the melt to be expected from solubility data, if gas saturation occurred at some stage after the crystallization of the phenocrysts but prior to eruption. Samples indicative of such gas saturation of the melt prior to eruption are occasionally present in phenocrysts in the form of fluid inclusions.

Fluid inclusions in phenocrysts from lavas and in minerals from upper mantle xenoliths

CO_2 fluid inclusions in phenocrysts from lavas and in minerals from upper mantle xenoliths have been reported from more than 100 different localities worldwide (e.g. Roedder, 1984) and such inclusions appear to be typical of upper mantle derived materials, irrespective of their global tectonic environment. Representative examples of such CO_2-bearing fluid inclusions are sketched in Fig. 7.

In phenocrysts in lavas the CO_2 fluid is often seen to have been enclosed by the growing mineral together with silicate melt and this resulted in a mixed gas-glass inclusion at room temperature. Such simultaneous entrapment of fluid and melt shows that entrapment occurred at temperatures close to those of the gas-saturated solidus, that is temperatures around 1200 °C. The density of a CO_2 fluid in an inclusion will be identical to that of the free CO_2 phase coexisting with the mineral/magma at the temperature and pressure of entrapment. It is possible under the microscope to determine this density from the behavior of the enclosed CO_2 fluid. Knowledge of the density of a CO_2 fluid in an inclusion further enables the construction of the pressure-temperature path along which entrapment of that particular fluid inclusion occurred. If the pressure and temperature conditions indicated by the density (and chemical composition) of the entrapped fluid furthermore are compatible with the conditions of formation of the host mineral/rock, as inferred from other types of geological information, the entrapped fluid will provide information on the fluid conditions during mineral/rock formation.

Densities for CO_2 fluid inclusions in phenocrysts in lavas and in minerals from upper mantle xenoliths have been summarized in Fig. 12,B. Densities for the CO_2 fluid in gas-glass inclusions in phenocrysts have not been separated in Fig. 12,B but are generally less than 0.6-0.7 g/cm³. Such densities indicate entrapment of the CO_2 at pressures from a maximum of 3-5 kbar and down to a few hundred bars (Fig. 12,A). Although such pressures are far from upper mantle pressure values, the results indicate that CO_2 gas saturation in some magmas occurred at considerably greater depths than suggested from Fig. 8.

More common, however, and generally the type of CO_2 inclusions observed in minerals from mantle xenoliths are CO_2 fluid inclusions without any sign of the simultaneous entrapment of a silicate melt phase. Although the densities for such CO_2 inclusions extend to considerably higher values than those of the gas-glass inclusions (Fig. 12,B), estimates of the pressure of entrapment from these densities (to a maximum of
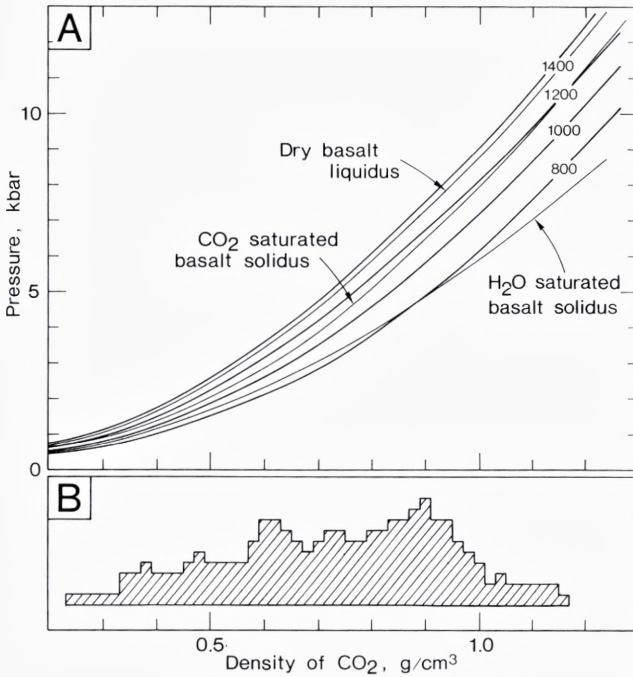
Fig. 12. Conditions for possible entrapment of CO_2 as gas inclusions in phenocrysts in lavas and in minerals from mantle derived nodules. (A) Possible entrapment pressures as function of the density of CO_2 in an inclusion at temperatures given by the selected four geotherms. Temperature-density-pressure curves corresponding to the basalt-CO_2 and basalt-H_2O saturated solidii and the liquidus curve for a gas-free basalt are shown for reference. Diagram based on data from Shmonov and Shmulovich (1974), Wyllie (1979), and Spera and Bergman (1980).

(B) Frequency diagram of CO_2 densities recorded for CO_2 inclusions in minerals from mantle nodules and in phenocrysts from lavas from a large number of localities worldwide. Diagram summarized from data in Roedder (1965), Jones et al. (1983), Murck et al. (1978), Bergman and Dubessy (1984), Roedder (1984), and own data.

about 11–13 kbar; Fig. 12) are almost invariably significantly lower than the pressures indicated by the mineral assemblages in the xenoliths. The fact that no density higher than about 1.2 g/cm³ has been recorded for any CO_2 fluid inclusion in xenoliths, irrespective of depth of formation of the xenolith, suggests that, either the maximum densities recorded reflect the tensile strength of the host minerals and that any inclusion trapped at higher pressure will rupture during ascent of the xenolith to the surface and will be lost, or that the CO_2 fluid inclusions in minerals from mantle xenoliths do not reflect the presence of a free gas phase but owe their formation to some other mechanism.

Electron microscopic studies of μm-sized cavities, considered originally to have contained a gas, in minerals from mantle xenoliths suggest that cavity formation occurred in response to deformations in the mantle prior to incorporation of the xenolith material in the magma, and that cavity formation was due to nucleation and growth of bubbles on crystal

TABLE II. Representative analyses of the volatiles released from minerals on crushing in vacuum (mole %)

	(1)	(2)	(3)	(4)	(5)
H_2O	–	39.6	20.5	–	–
H_2	7.0	19.4	5.0	0.2	54.0
CO_2	16.1	15.5	0.3	–	18.5
CO	74.9	3.8	tr	50.4	–
CH_4	1.2	3.7	64.2	23.0	2.2
C_2H_6	tr	0.03	6.8	–	–
C_3H_8	0.1	–	0.9	–	–
C_nH_{2n+2}	–	–	0.4	–	–
C_nH_{2n}	0.6	–	–	–	–
C_3HOH	–	1.0	–	–	–
CH_3CH_2OH	–	1.0	–	–	–
N_2	0.1	15.9	2.8	26.4	25.2
Ar	–	0.1	0.1	–	–
He	–	1.0	0.03	–	0.005

1. Olivine from lherzolite nodule, Massif Central, France. (from Chaigneau, 1975)
2. Average of 7 natural diamonds, Arkansas, U.S.A. (from Melton and Giardini, 1975)
3. Nepheline from nepheline syenite, the illimaussaq intrusion, south Greenland (from Konnerup-Madsen et al., 1979)
4. Murchison C2 meteorite (from Andrawes and Gibson, 1979)
5. Average of 5 kimberlites, Obnazhennaya, U.S.S.R. (from Lutts et al., 1976.

defects and these later collected to form larger cavities (Green and Radcliffe, 1975; Kirby and Green, 1980). It is, however, uncertain whether such a mechanism can be responsible also for the much larger (5–30 μm) CO_2 inclusions often observed in xenolith minerals. Alternative mechanisms for CO_2 fluid inclusion formation in such material include decarbonation of CO_2-bearing minerals occluded during growth of the host mineral, and precipitation of CO_2 directly from solid solution in the host mineral structure. The apparent lack of observations of decarbonation products in association with the CO_2 inclusions appears to favour the latter mechanism. Freund et al. (1980) reported appreciable amounts of carbon in xenolithic olivine, as atomic carbon in solid solution. Such carbon might exsolve at lower pressures (taking oxygen from ferric iron or other variable-valency elements) and form the CO_2 inclusions.

The composition of these CO_2 fluid inclusions is almost invariably pure CO_2, and all studies indicate that other gases are present in concentrations less than about 1 mole %. Only in one xenolith of wehrlite, with

an andesine-amphibole cross-cutting vein, have CO_2 inclusions containing 8-12 mole % CO been reported from the vein, whereas inclusions in the wehrlite nodule itself were pure CO_2 (Bergman and Dubessy, 1983).

Apart from the CO_2 gas compositions reported for high-density fluid inclusions, more complex gas compositions are frequently reported on other types of upper mantle derived materials such as kimberlites and diamonds. Representative examples of such analyses are included in Table II. Although the carbon isotopic signature of these gases clearly indicate their upper mantle origin, the general lack of recognizable gas inclusions in minerals from these materials when examined under the microscope, makes the actual location of evolved gases somewhat enigmatic. Gaseous constituents may be present in minerals in various forms (e.g. Bibby, 1982): (1) substitutionally or interstitially in the structure, (2) in mineral and melt inclusions or (3) as gaseous inclusions. For example, H, N and O are normally present in diamonds in the first form and in concentrations generally in the range 50-250 ppm although higher concentrations have been reported (Roedder, 1984). Therefore gas analyses such as those given in Table II may well represent the total amount of gases present at various locations in the minerals, and the actual bulk gas compositions reported may be the result of reactions among these gases during the extraction procedure preceding analyses. Thus, these analyses can not be taken as an expression of the gas species composition

Fig. 13. Compositions of gases in minerals and rocks of upper mantle derivation, as indicated in the figure, in terms of (left diagram) atomic C-O-H relations, and (right diagram) molecular (CO_2 + CO)-H_2-total hydrocarbon contents and on a H_2O-free basis. References to data as to Fig. 12 and Table II, and Chemla et al. (1968), Krafft and Chaigneau (1980), and Vakin and Kutyev (1980).
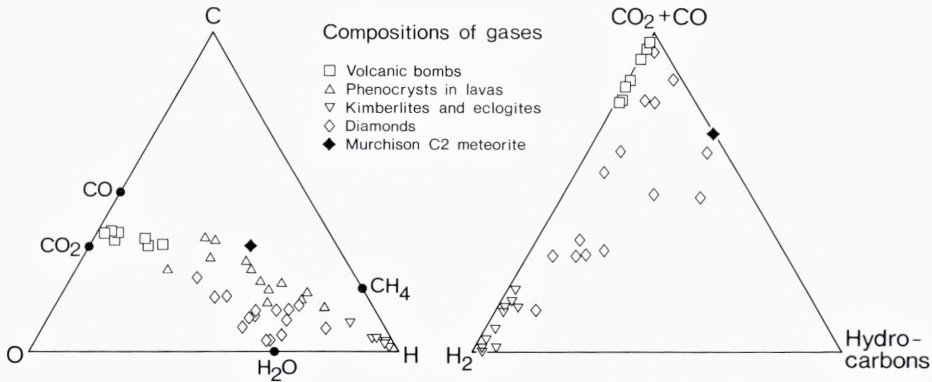
of any deep, upper mantle gas, although their compositions in terms of atomic C-O-H relations (Fig. 13) may be of significance. Except for the generally high contents of reduced gases in materials from the upper mantle such gases are distinguished from those previously discussed in containing high contents of N_2 (Table II). In both respects they resemble analyses obtained on gases from meteorites (Table II; and Yasinskaya, 1967; Fiéni et al., 1978).

Possible degassing along deep faults

High contents of hydrogen (> 3 volume % H_2) have been observed in soils and groundwaters from some areas with active faulting together with significantly increased helium fluxes and higher than normal $^3He/^4He$ ratios (Nagao et al., 1980). Such observations have been taken to document the possible degassing from deep sources of reduced gases together with helium, and in some fault areas other noble gases. Analyses of the D/H ratio indicate that the enrichment in hydrogen, however, is related to formation of molecular hydrogen from chemical reactions between groundwater and the surfaces of silicate minerals created by crushing during the fault movements (Kita et al., 1980). Experimental confirmation of the feasibility of such a mechanism has been given by Kita and Matsuo (1982). However, although no significant degassing of any major species is indicated to take place along fault zones, monitoring of gas compositions of soils and ground waters may prove useful in earthquake predictions.

Concluding comments on deep Earth gases

The actual concentration and composition of deep Earth gases is important because any such gases will represent a reservoir which may have yielded (parts of) the modern hydrosphere and atmosphere by degassing, and may have added nonbiological methane to the biologically produced hydrocarbon and oil deposits. Studies of deep-Earth gas compositions are, however, difficult because true samples from the upper mantle are difficult to separate unambiguously from samples contaminated by sedimentary and atmospheric gases.

The presently available evidence for degassing is mostly linked with helium. Enrichment in ^3He has been established for a number of mantle
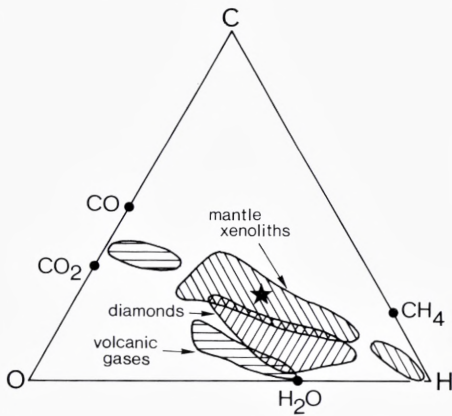
Fig. 14. Summary of the atomic C-O-H relations for gases in minerals and melts considered relevant to deep Earth gas compositions, as discussed in the text and summarized from data in previous figures. The star shows the bulk C-O-H composition estimated from gases in Galapagos basaltic glass matrix (Byers et al., 1984).

derived samples and, when coupled with observations on volcanic and fumarolic gases, CO_2 and possibly some more reduced gases in mid-ocean ridge hydrothermal systems, gas vesicles and the glassy matrix of ocean–floor basalts, clearly demonstrate that volatiles from deep sources are continuosly being added to the Earth's surface. Attempts to quantify this addition of gases to the Earth's atmosphere have been made on the basis of gases in diamonds (Melton and Giardini, 1982) and from noble and rare gas isotope systematics in ocean–floor basalts (Kyser and Rison, 1982; Ozima et al., 1983) but the results vary considerably and more reliable estimates must await further studies.

Estimates of the actual major gas species composition af any deep gas may be attempted on the basis of data from compositions of volcanic gases, gases in rapidly quenched ocean–floor volcanics, or from gas compositions of gases trapped by some mechanism in minerals in mantle xenoliths (Fig. 14). Such estimates vary considerably, both in terms of atomic proportions of C, O, and H, and in terms of the corresponding major gas species compositions. Part of the discrepancy between the various sets of data probably reflects differences in oxidation states during formation of the different materials, but other factors such as solid state diffusion of gaseous constituents, either in elemental form or as gas species, may be important.

Although the possible existence of a free gas phase in some parts of the upper mantle is predicted from experimental and theoretical studies, and will essentially be a mixture of CO_2 and H_2O, actual gas concentrations suggested for some source regions from the gas contents of primitive ocean–floor basalts indicate the possible storage of both C, H and O in

minerals as impurities in the crystal structure or forming solid solutions. Especially the state of carbon in the Earth's mantle is crucial to any hypothesis regarding deep Earth gas compositions. If carbon is present in largely elemental form, much carbon could migrate as a solid phase through the mineral lattices and produce CH_4 and CO_2 only when reducing or oxidizing conditions were encountered (Freund, 1981; Duba and Shankland, 1982). If such mechanisms are operative on an important scale, earlier perceived ideas regarding the actual form of gases in the Earth's mantle and of the processes operating may be highly misleading.

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