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Review Article

Formation of Gas Hydrates at Deep Interior of the Earth and Their Dissipation to Near Surface Horizon

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Methane hydrates occur in diverse geological settings and their origin is puzzling, owing to package of more than 160 times of equivalent volume of methane in ice cage at standard temperature pressure indicating formation at high pressure state. At the core mantle boundary of the Earth, high dense supercritical fluids of Fe with significant amount of O, Ti, Nb, C, H, and other elements exist. Geophysical studies reveal that at the core mantle boundary of the Earth at 2900 km depth, temperature exceeds 4000°C, pressure ranges around 135 GPa and the material present possesses high molar volume 8.8 gm/cm^3. Sudden release of pressure causes opening of vents and supercritical fluid/plasma phase of CH_4 exsolves as finely divided plasma bubbles and rapidly rises up through weak planes. The potential energy of these bubbles is so high; the velocity of ascending bubbles steadily increases with super adiabatic state with minimum frictional energy loss. The rapidly ascending CH_4 plasma bubbles quench with outer skins of H_2 or H_2O while passing through the permafrost or near surface horizons. Again, some bubbles burst into numerous tiny droplets of dense methane into cold seawater near seafloor. The water layer surrounding the tiny bubble is formed as ice-cage on hydrophobic methane, by absorbing or releasing sufficient latent heat energy from freezing water for endothermic formation of methane hydrate. The water envelops as ice cage around CH_4 near surface conditions at ambient temperature and pressure conditions. Numerical analyses of specific heats J/mole for CH_4 and H_2O reveal that such plasma bubbles could form even from upper mantle horizons ~100 km depth but with less potentiality. The charged particles inside the plasma bubble are highly influenced by magnetic and electric fields. Hence most bubbles drive through deep interconnecting fractures towards continental margins of polar region where earth's electromagnetic and gravity intensities are relatively high.

1. Methane Hydrate

Huge reserves of methane hydrate (MH) are discovered in the continental shelves of Arctic Ocean. MH deposits estimated from different places amount to 2500 Gt [1]. These reserves may be sufficient for energy resource for more than 300 years. MH is stable under fairly thermodynamic conditions of high pressure (0.1 MPa to over 120 MPa) and low temperature between −2°C and 24°C [2, 3]. Growth rate of MH is dominated by solubility and adsorption of methane (CH_4) gas filled water cages and CH_4 concentrated at solid liquid interface [4]. MH has a clathrate structure: water molecules form linked cages that enclose individual molecules of low molecular weight gas (e.g., CH_4, CO_2, H_2S, and C_2H_6). It appears that CH_4 and ice are separate phases in the methane hydrate (MH). Chemical composition MH I is $(CH_4)_8$ $(H_2O)_{46}$. It is composed of H 13.06%, C 10.04%, and O 76.90% [5]. The MH I has water 86.59 wt% and methane is only 13.41 wt%. It is stable at 4 to 5°C and 50 bars. Its structural formula is 2(S) 6(L) 46(H_2O) where S represents CH_4, N_2, H_2S, and L for CH_4, H_2S, and CO_2. The MH II, usually found in pore fluids locked up in sediments has the composition of H 13.13%, C 13.04% and O 73.83% and its structural formula is 16(S) 8(L) 136 (H_2O) where S represents CH_4 and H_2S and L includes CH_4, H_2S, CO_2, and C_2H_6 [6]. The latter is composed of 83.13% (wt) of water and only 16.87% of methane like gases. The structural formula of MH is CH_4, and the principal component of natural gas and water is present in higher proportions than CH_4. The presence of traces of H_2S and N_2 indicates that the hydrates were formed at deep seated source. A large amount of CH_4 gas is trapped within a crystal structure of water/ice. It is composed of one mole of CH_4 and 5.75 moles of water. It has a density around 0.9 g/cm^3. The origin MH is puzzling, owing to package of more than 168 m^3 of equivalent volume of CH_4 in its unit volume at STP.

MH is tightly packed with CH_4 and surrounded by H_2O as separate phase. CH_4 and H_2O, respectively, have critical temperatures 190.4°K and 647.1°K, critical pressures 4.6 MPa and 22.06 MPa, and critical densities of 0.162 and 0.322 g/cm^3. CH_4 has molar volume 16.04, density 0.6556 g/L melting point −182°C, and boiling point −161°C while these properties, respectively for water are 18.015 g/cm^3, 1 kg/L. 0°C, and 100°C. CH_4 is the third lightest gas, after H and He in the Universe. CH_4 being the simplest hydrocarbon produces more heat per mass unit (35.7 J K^{-1} mol^{-1}) than other complex hydrocarbons. Therefore, it has has higher diffusivity than water. Pure H_2O bearing fluid inclusions in minerals behave perfectly as diathermal, isochloric, isoplethic systems [7]. H_2O exists as a supercritical fluid above its critical temperature of 300°C in wide range of pressure conditions from 300 MPa to 300 GPa [8]. Experimental studies show CH_4 and H_2O attain solid states of MH at low temperatures and high pressures [3, 4, 8]. Solid CH_4 is produced at low temperatures down to 2.1°K and pressure up to 60 k bars at the Van der Walls Laboratory [9]. Solid CH_4 structure is stable in the pressure range 10–90 GPa. The electronic band structure and density of states show that this structure has not metalized until 90 GPa [9]. Under high pressure CH_4 becomes unstable and it transforms to ethane C_2O_6 at 95 GPa, butane C_4H_{10} at 158 GPa and further carbon and hydrogen above 287 GPa at zero temperature [10]. In this paper, an attempt is made on the possibility of formation of MH from the sources derived from deep interior of the Earth but along the continental margins of higher latitudes by the influences of electromagnetic and gravity forces of the Earth.

2. Mode of Occurrence

The mode of occurrences of MH in diverse geological settings [11] is the major problem facing the study of origin of gas hydrate deposits. Recent bottom simulating reflector (BSR) explorations of hydrocarbon reveal that huge quantities of gas hydrates occur in the following geological settings:

(i) under the cover of permafrost [12],

(ii) continental shelves of high latitudes around Polar Regions [12],

(iii) mid Oceanic Ridges [13],

(iv) ceep-sea hydrothermal vents [13, 14],

(v) island arcs, subduction zones and active continental margins of China, Taiwan-Luzon Island arcs [15],

(vi) passive continental margins [11, 16],

(vii) CH_4 plumes at Hydrate Ridge-Monterey Bay [17],

(viii) emissions of disc like CH_4 bubbles from the Abraham Lake, Alberto, Canada [18, 19],

(ix) active methane discharge on Hydrate Ridge on the Cascadian accretionary margin, Oregon [20] gas and fluid venting at the Makran accretionary wedge of Pakistan [21],

(x) seep gas composition similar to that of gas sequestered in gas hydrates [22],

(xi) CH_4 ebullition sites that occur throughout the Arctic region [17],

(xii) at some marine seeps, massive, relatively pure gas hydrate occurs in seafloor mounds and in shallow sub-seafloor layers occurring at upper continental slope depths,

(xiii) seepage along fault planes of the continental slope in the northwest Gulf of Mexico,

(xiv) sublacustrine mud-volcanoes seeping out MH from freshwater Lake Baikal [23],

(xv) along the continental margins of India, particularly the Krishna-Godavari offshore basin [11, 24],

(xvi) seeps of MH bubbles create carbonate rock formation and reefs by reaction between methane and seawater [25],

(xvii) CH_4 like gases migrates upward through networks of fractures with elevated pore-fluid salinities into deep offshore oceans near Korea along the active continental margins [26],

(xviii) migration of CH_4 from depth along geological faults, followed by precipitation, or crystallization, on contact of the rising gas stream with cold sea water [27],

(xix) hydrothermal venting of methane gas bubbles from mantle horizon to the Arctic seafloor is entrapped into the growing ice-bergs and form as permafrost during the course of several decades of duration [13],

(xx) thermohaline circulation promoted by differences in density, temperature and salinity of the Arctic Ocean waters [13],

(xxi) microbial CH_4 can be formed where labile organic carbon is available in onshore and offshore continental margins [11].

Warm and cold currents have a major impact on formation and dissipation of gas hydrates. In the process of freezing, the salt in seawater is expelled as brine. Approximately one-third of the Arctic Ocean is underlain by continental shelf, which includes a broad shelf north of Eurasia and the narrower shelves of North America and Greenland.

3. Mineral Phase Transitions at Interior of the Earth

Temperature and confining pressure increase with depth. In the upper mantle, along the subduction zones, serpentinization of ultrabasic rocks [28] is reported. At the temperature around 900°K and pressure corresponding to 600 km, CH_4 bearing serpentinized zones are recognized by acoustic emissions which are absent in unaltered ultrabasic rocks [28, 29]. Temperature difference near phase boundary results in density anomaly. Dissociation of carbonates particularly siderite would release methane in significant amount [30] at the pressure range between 5 and 11 GPa and temperature between 500 and 1500°C at depths ranging between 150 and 400 km. Upper mantle consist mostly of olivine, pyroxene, spinel-structure minerals, and garnet; [31] typical rock types are thought to be peridotite, dunite, and eclogite. Between ~400 km and 650 km depth, olivine is not stable and it is replaced by high pressure polymorph is wadslevite and or ringwoodite. Below this depth of about 650 km, all of the minerals of the upper mantle begin to become unstable. The most abundant silicate perovskite mineral, have structures like those of the oxide mineral perovskite followed by the magnesium/iron oxide or ferro-periclase [32]. In the lower mantle post perovskite phase modification results with release of FeO down to the core. The perovskite is expected to react with liquid iron to produce metallic alloys (FeO and FeSi) with nonmetallic stishovite (SiO_2) and perovskite at the pressure 140 GPa [33]. High density of reaction products relative to lower mantle (particularly in D'' layer) moves downward to liquid CMB layer. Such changes in mineralogy may influence in density changes and they may absorb or release latent heat as well as depress or elevate the depth of the polymorphic phase transitions for regions of different temperatures. The slow and steady formation of high pressure polymorphs creates vacant sites in the lower and upper mantle by changing the rheology of the mantle material. This leads to structural deformation in the mantle horizon leading to fault movements and earthquakes. Increasing temperature and pressure from surface to down to the Earth, states of materials in the mantle widely vary, though they represent layered structures. Heterogeneity in the mantle may be due to partial melting of mantle and magma generations. Ascending and upwelling of volatile materials of light elements from magma also cause depletion of these elements from the mantle. The rock in the upper mantle has a relatively low viscosity. The lower mantle is under tremendous pressure and therefore has a higher viscosity than the upper mantle. At elevated temperatures and pressures, conditions that permit some minerals to behave like soft plastic, that if they are stretched or squeezed, they become flattened or elongate without breaking as ductile material. Under high confining pressures, coordination numbers of minerals increase by reducing vacant sites in the lattices of minerals. This phenomenon induces void spaces within mantle. At an optimum level residual stress accumulates in the mantle and the stress is released as creep and faults. It is inferred that these cracks and faults discontinuously extend from crust to top of CMB. Such types of paleo-faults or creeps are filled with viscoelastic mantle materials. These fault planes are weak planes as they are frequently reactivated repeatedly by the tectonic forces induced by phase transitions of mantle minerals with release of huge quantities of heat energy from the CMB. Sudden release of pressure due to creeping and faulting void spaces are developed, and at the state of 4000°C at CMB with release of pressure from 135 GPa to <1 MPa, vapourization of volatile light materials such as H, He, CH_4 and H_2O may be released from the liquid phase at CMB. A high pressure carbon bearing phase is formed by recombination of CO_2 with other oxides at *P-T* conditions close to the lower mantle geotherm. This behavior might be due to a strong thermodynamic stability of the new carbon bearing phase. An increase in the ionic character of C–O bonds at high pressures and temperatures indicate presence of carbonate carbon di oxide (i-CO_2) near the Earth's core-mantle boundary conditions provides insights into both the deep carbon cycle and the transport of atmospheric CO_2 to anhydrous silicates in the mantle and iron core [34]

$$20\left(\mathrm{Mg}_{0.25}\mathrm{Fe}''_{0.75}\right)\mathrm{CO}_3 = 20\,\mathrm{Mg}_{0.25}\mathrm{Fe}'''_{0.30}\left(\mathrm{C}_3\mathrm{O}_9\right)_{0.233} + 3\mathrm{Fe}_3\mathrm{O}_4 + 6\mathrm{CO}\ \{\text{or } 3\left(\mathrm{C}+\mathrm{CO}_2\right)\} \qquad (1)$$

A large amount of iron concentrates as a result of intracrystalline reaction between iron and carbonate, producing high pressure polymorph of carbonate. Further increase of pressure magnetite and nanodiamonds crystallize [34]. The developments high dense mineral polymorphs in the lower mantle induce cracks, creeps and faults in the lower mantle. Residual stress accumulated by the phase transition and contraction of lower mantle and d'' horizon may be caused for the change of state of certain zone of weak planes from viscoelastic to brittle/ductile state. Along these weak planes, due to sudden release of pressure, creeps may be induced [35].

4. Creep

As rock is heated its ability to deform elastically is gradually lost. It can deform plastically at lower stresses. Rocks at deeper levels tend to deform plastically rather than elastically during tectonic movements. But over longer periods they can deform plastically (creeping). At deeper depths rocks retain permanent strains when they deform plastically. Such rocks tend to deform plastically once the temperature exceeds 70% of the melting temperature. Highly competent layers, embedded in lower competent material will form buckle folds and can tend to creep. Lower competent rock-types can distort more easily so commonly pick out a rock cleavage. Due to variations in temperatures and confining pressures some rocks attain strain softening and others attain strain hardening and these processes lead to creep. During the course of younger deformations, it is easier to deform along preexisting creep than to deform the surrounding rocks. It is a weak zone that nucleates further deformation. At high pressure and temperature, the rocks at the lower mantle by phase transitions begin to yield creep. The failure process involves some shearing mechanism. If stresses induce creep, the creep produces heat. A temperature increase often occurs and contributes to strain softening. Solid-solid phase transition occurs preferentially along the plane of maximum shear stresses and if this transition occurs suddenly, it is likely to radiate to produce acoustic emission. As pressure and temperature increase, brittle materials sequentially transformed into ductile, elastic and viscoelastic state and finally attain fluid stage depending upon prevailing differential pressure and temperature. Fault/creep controls on concentration and dispersion of chemical elements due to deformation of rocks and mineral grains. Along the creep planes Si and Fe often increase due to bleeding of K and Na. The stable order of elements from compressional creep to shear plane is Si-Fe-Mg-Ca-Al-K-Na in accordance with the order of ionic radius from small to large. Generally CMB remains in a reduced state owing to presence of H, He and CH_4. Extensional creep is generally in the oxidation environment due to extension and dilatancy, the porosity and permeability enhance. So, H_2, He_2, CH_4 like gases stores along these planes. Primordial H and He were trapped and stored in the Earth's interior as H and He-solutions and compounds stable only under ultrahigh *PT* conditions [36]. The explosive chain reactions of H, He and their compounds are triggered by decompression within fault zones [36]. Water is a catalyst accelerating explosive reactions thousand fold. Volcanoes spewed H, CO and CH_4 into the atmosphere because their magma source from the vicinity of upper mantle was much reduced [37].

5. Primordial Methane

Formation of the carbon atomic nucleus requires a nearly simultaneous triple collision of alpha particles (^{4}He nuclei) at very high pressure and temperature conditions within the core of the Earth. Further, nuclear fusion reactions of ^{4}He with ^{1}H produce ^{5}Li and ^{8}Be are produced by nuclear fusion of ^{4}He with ^{4}He at required temperature and pressure conditions [38]. However, in this triple alpha process, the elements formed ^{5}Li, ^{8}Be and ^{11}B are rarely stable and decay almost instantly and back to elements of smaller nuclei. Presence of intense H, CO and CH_4 keeps the CMB in a reduced state. Primordial CH_4 in the Earth's core is reported by Gold [39]. Both CH_4 and H_2O are greatly soluble in the materials present in CMB till they reach the state of their critical densities. Hence, they dissolve in the CMB materials till they attain a state of equilibrium, possibly all available CH_4 and H_2O. Solvent power of supercritical fluid of CH_4 and H_2O increases with increasing temperature to the extent of a given density of 8.8 g/cm^3 at CMB. Further, mole factions of CH_4 and H_2O from the materials of CMB having 8.8 g/cm^3 are also increased at this equilibrium state with CH_4 and H_2O. On the basis of the density of Fe_7C_3 at inner core conditions, Mookerjee et al. predicted that the maximum possible carbon content of the inner core is around 1.5 wt% [40]. Carbon in the Earth's core can generate large perturbations by the flux of lighter elements from the CMB [41]. Presence of significant amount of C in the inner core creates electromagnetic fields in the Earth [42]. At elevated temperatures carbon, reacts with oxygen to form CO and will reduce such metal oxides as iron oxide to the metal. High temperature plasma H will diffuse into iron carbide and combine with carbon to form tiny pockets of CH_4 at internal surfaces like grain boundaries and voids. The CH_4 collects in the voids at high pressure and initiates creeps and cracks in the iron carbide present at the lower mantle or at the inner core. Iron carbide is present in significant proportion at the inner core of the Earth. The plasmatic hydrogen is diffused into the iron carbide and combines with carbon to form tiny pockets of CH_4 at internal surfaces like grain boundaries and voids. At high pressures CH_4 stored in the voids and grain boundaries of iron carbide. The explosive chain reaction of H and He compounds triggered by decompression within fault zones and upward moving microplumes of CH_4 will be accompanied by additional release of energy. This will also cause decomposition of H and He compounds and release of fugitive elements such as H, O, C, N, Cl and F. Further detonation-induced synthesis of H_2O, CO_2, CH_4, H_2S, HCl and other compounds [36], methane plasma behaves like a fluid with zero viscosity. High pressured mantle gases and supercritical fluids or plasmatic bubbles inflate and weaken any accessible faults reducing static friction across their walls. Frequent triggering of earth quake tremors initiate cracks in the iron carbide and release methane from the voids and intergranular boundaries of iron carbides. The released methane forms as plasma bubble which ascends rapidly because of its light weight, supercritical fluid/plasma state with zero viscosity. Primordial H and He accumulated the excess energy during Earth's accretion by endothermal formation of solutions in solids and liquids. Concentrated flux of hotter than mantle and He from the core will generate liquid magma by the process of volatile flux melting and warm the wall rocks producing heat focusing effect. H and He do not cool adiabatically under decompression. The local increases in discharge of energy and heat together with the fluxing and decompressing action of volatile components would cause local fusion at seismic discontinuities. Ultrahigh *PT* conditions during accretion enhance the progress of endothermic reactions of formation of H and He compounds and solid solutions, which provide efficient cooling and produce more compact components than the re-actives [36].

6. Methane Plasma Bubbles

Suddenly released CH_4-plasma bubble has electron and proton which are not bound together, resulting in very high electrical conductivity and high emissivity. The charged particles are highly influenced by magnetic and electric fields. The ionized gas could then become plasma if the proper conditions for density, temperature and characteristic length are met (quasineutrality, collective behaviour). As an interpenetrating CH_4 plasma fluid its solubility at CMB increases with increasing density of CH_4 to 8.8 molar volume/cm^3 at the existing confining pressure over 135 GPa and the temperature above 4000°C. CH_4 plasma, may pass through solids in the lower mantle d$''$ layer [43, 44]. It may diffuse faster in a solid matrix than a liquid, yet possess a solvent strength to extract the solute from the solid matrix [10]. Molar volume of methane decreases with increase of pressure. Under ultra high pressure at 200 GPa the molar volume of methane decreases to one third of its volume [10]. Before generation of MH, it appears to be remained as supercritical fluids of CH_4 and H_2O. Due to the large compressibility of supercritical fluid, small changes in pressure can produce very substantial changes in density, which, in turn, affect phase equilibrium boundary shifts and at favourable environment, MH forms

Table 1: Increase of specific heat energy J/mole in the interior of the earth.

GPa	T°C	H	He	CH_4	H_2O
0	300	8652	12480	10707	22611
0.3	500	14420	20800	17845	37685
3.4	1800	51912	74880	64242	135666
18	2000	57680	83200	71380	150740
40	2500	72100	104000	89225	188425
88	3500	100940	145600	124915	263795
160	5500	158620	228800	196295	414535
238	5800	167272	241280	207002	437146
321	6000	173040	249600	214140	452220
358	6200	178808	257920	221278	467294

as compressed supercritical CH_4 locked in an icy crystal lattice of water. Hydrogen bonding in water is so strong that it actually forces the crystal structure of the ice to take up a larger volume than the same amount of liquid water occupies. It prevents leakage of highly compressed CH_4 from the structure of MH. Table 1 represents specific heat energy J/mole calculated for the elements of H, He, CH_4 and H_2O for the temperature listed in the column T°C [36]. The specific heat energies (J/mole) increase as the temperature increases (Tables 1 and 2). Figure 1 shows relative specific energy potential of H, He, CH_4, and H_2O from the ground surface to inner core temperature and with corresponding pressure condition. Owing to sudden drop of pressure from 358 GPa to <1 MPa, the differential energy potential is calculated to corresponding temperature without any changes. In the Figure 2 the specific energy potentials of CH_4 and H_2O are calculated for the corresponding temperatures when sudden drop of molar volume (density) of CH_4 and H_2O suddenly decreased to their critical densities (molar volume at critical temperature and pressure) when these components attaining the state of supercritical fluid stage. Were Figure 3 shows the calculation of specific heat energy at their differences between maximum confined pressure at CMB 8.8 gm/cm^3 and critical density state CH_4 and H_2O respectively of 0.162 and 0.322 g/cm^3. Then the excess energy is converted to excessive temperature rise by dividing their specific heat energy/J mole. The results show that the temperature at 100 m deep in the earth is sufficient to make plasma bubbles of CH_4 and H_2O.

However plasma bubbles derived from deep seated sources especially from CMB has more potential for rapid ascent with dense packing of CH_4 with water cages. Compared to CH_4 plasma H_2O have more specific energy potential to higher level ascent from deep seated source. However CH_4 has lower molar volume, and the initial formation of CH_4 plasma bubble is surrounded by H_2O. Further the latter has higher solubility than CH_4. CH_4 has lower solubility; hence, it is released earlier than H_2O plume. CMB increases both by increase of temperature and density referred to as molar volume g/cm^3. At CMB both temperature and density of CH_4 are, respectively, 4000°C and 8.8 g/cm^3 while critical density is 0.162 g/cm^3 and critical temperature is only 48°C. Therefore, CH_4 has very high kinetic energy for upward movement. H, He and CH_4 gases do not cool upon adiabatic expansion. Such high pressured gases inflate and weaken any accessible creep or fault and reduce static friction across its walls. Continuous tremendous degassing of primordial H, He and CH_4 from Earth's interior. According to Gold that CH_4 is one of the primordial gases prevailed at the interior of the Earth and outgassing largely through faults [39]. When quantity of heat energy is balanced with by the products of specific energy of the substance and temperature differences,

$$Q = Cm\Delta T \tag{2}$$

for constant molar volume.

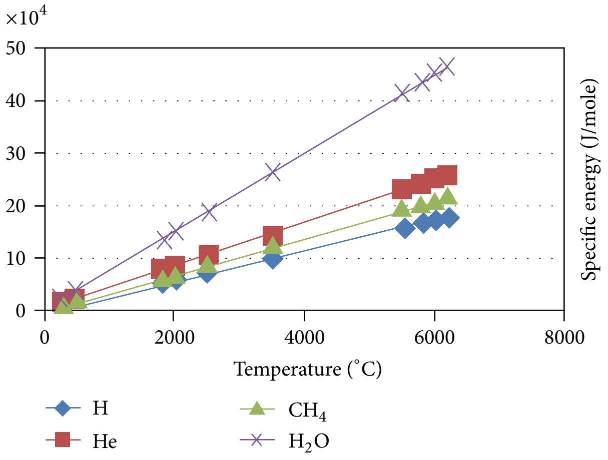

Figure 1: Relative specific energy potential for emission of plasma bubbles at various temperatures conditions from interior of the Earth. Components of relative lower solubility potential H, CH_4, are diffused out initially from the CMB.

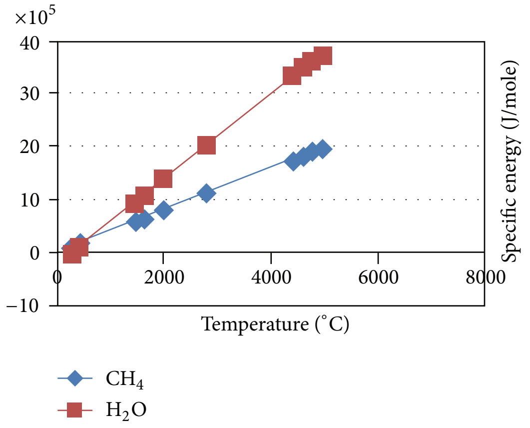

Figure 2: CH_4 plasma bubble is released out initially, relative to its lower solubility and is molar volume in the CMB materials, though plasmatic H_2O has higher specific energy potential per mole and having higher solubility factor than CH_4 at the deep interiors of the Earth. Plasma is an ionized gas comprised of ions and free floating electrons that can create and respond to magnetic and electromagnetic fields.

Table 2: Transformation of specific heat energy J/mole from plasmatic ions of CH_4 and H_2O to supercritical fluids in the interior of the Earth owing to sudden drop of pressure (Jules Thompson effect).

GPa	T°C	CH_4	CH_4	H_2O	H_2O	CH_4	H_2O	CH_{4ex} J/m	H_2O_{ex} J/m	T°C + CH_4	T°C + H_2O
0	300	2212	120133	−1797	−49207	117921	−47407	115709	−45610	3242	−605
0.3	500	3368	182947	3060	83615	179579	80460	176211	77400	4937	1026
3.4	1800	10884	591241	34627	969826	580356	911592	569472	876966	15956	11629
18	2000	12041	654055	39483	1079038	642014	1039459	629974	999976	17651	13260
40	2500	14931	811091	22939	1410845	796159	1359125	781228	1336187	21889	17719
88	3500	20713	1125163	75906	2074460	1104450	1998458	1083736	1922552	30365	25494
160	5500	32277	1753307	124471	3401690	1721030	3277123	1688753	3152652	47317	41806
238	5800	34011	1847529	131756	3600775	1813517	3468923	1779506	3337168	49860	44253
321	6000	35168	1910343	136612	3733498	1875175	3596790	1840008	3460178	51555	45884
358	6200	36324	1973157	141469	3866221	1936833	3724656	1900509	3583188	53250	47516

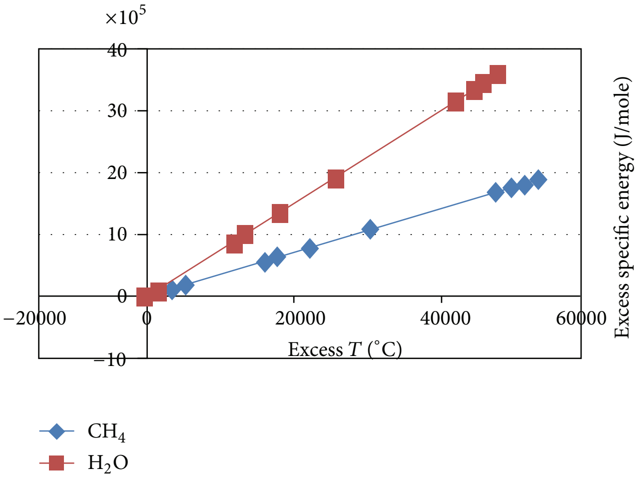

Figure 3: The excessive specific energy (J/mole) potential may be expended for keeping the methane bubble in plasmatic state during ascent to higher levels from CMB. However the rate ascending so rapid, the bubble will maintain its plasmatic state till it reaches the near surface condition with very limited loss of heat energy.

The formula is restated when mass is transformed critical density releasing heat specific energy into as

$$Q = C\Delta mT, \tag{3}$$

keeping T and P at critical states, where, Q = quantity of heat, C = Specific heat of the substance J/mole, m = mass, ΔT is the temperature variation between the two states and Δm = the mass difference between the two states.

Under sudden release of pressure, adiabatic temperature rises to attain an equilibrium state with its potential heat energy; numerous tiny plasmatic bubbles of CH_4 are fractionated from the prevailing liquid at the CMB. Outer skin of plasmatic CH_4 bubble is quenched, generally double walls and outer wall are filled with H_2 as layer and sometimes, the outer shell may be filled with H_2O as layer. A small decrease in pressure causes a large decrease in the density of the super critical phase of methane and water. The flexible thin outer wall is pulling in while the CH_4 plasma inside of it is pushing out. Sphere shaped bubble takes up a very little space and hold a lot of methane in the plasma. Under sudden decrease of pressure and rise of temperature with existing heat capacity, numerous tiny plasmatic methane bubbles are released. Methane is released out in the form of dense supercritical fluid emulsion from CMB due to sudden thermal turbulence. Numerous bubbles of CH_4 rapidly rise with high velocity at the rate of 100 to 200 m/s without any significant loss of heat energy as that in the case of most volcanic eruptions from deep-seated source. The outer skin of the plasma bubble becomes flexible, elastic, and hydrophobic and it can hold the shape of a bubble of H_2O or H_2 when CH_4 is blown into it. The stretchable skin is made up of plasmatic fluid of H_2 or H_2O formed by oxidation of CH_4. The thin wall skin of the bubble is pulling-in, while the CH_4 inside of it is pushing-out.

7. Ascending of Plasma Bubbles

Since plasmatic CH_4 dissolved in the liquid materials at CMB, has a low degree of thermal turbulence in the upper horizon of CMB, numerous CH_4 plasma bubbles are fractionated. Frequent earth quake tremors less than the intensity of 3 in Richter's scale, might have induced fractionation of pure CH_4 bubbles. The quenched elastic bubble wall of H_2 surrounding the CH_4 core is more impervious to CH_4 and prevents the escape of dense CH_4. The oxidation of H_2 during upward ascent causes formation of H_2O skin which is hydrophobic to CH_4 present at the core of the bubble. The rapidly upward ascending plasmatic CH_4 plasma bubble, with zero viscosity and insignificant loss of frictional energy makes its continuous path by widening and interconnecting discontinuous creeps (Figures 4(a) and 4(b)). A plume generally maintains same diameter till its eruption at the surface [45]. Adiabatic processes can occur in an extremely short time, so that there is no opportunity for significant heat exchange. Adiabatic changes in temperature occur due to changes in pressure of CH_4 H_2, and H_2O while not adding or subtracting any heat. The rapid ascent of bubbles widens the conduit to a

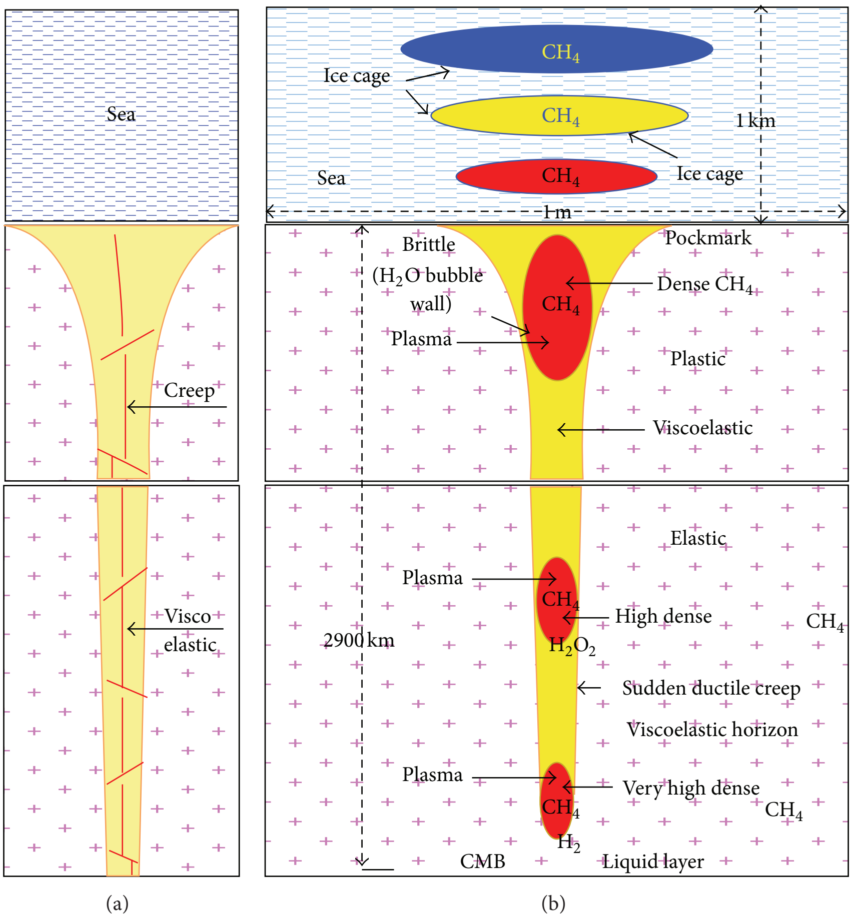

Figure 4: (a) Development of discontinuous creep from lower mantle to ground surface mainly due to mineral phase transformations and release of energy during earthquakes and tectonic movements. Rapidly ascending of micro-plumes and CH$_4$ plasma bubbles create a continuous conduit path by interconnecting discontinuous creeps and fractures on their way. (b) The plasma bubble is thermally insulated by H$_2$. Pressure suddenly drops from 135 GPa to <1 MPa at about 4000°C from the state of CMB. Plasma bubble enlarges its size occupying entire width of the narrow conduit. The outer skin of H$_2$ shell surrounding the CH$_4$ plasma is oxidized to H$_2$O at higher levels. The hydrophobic CH$_4$ is protected by quenched H$_2$O. After entry of seafloor sediments H$_2$O shell is get freeze slowly and form ice cage. Surrounding en-masse of coldwater and sediments at low temperature prevents escape of trapped CH$_4$ inside the MH. Disc like CH$_4$ rises up from the pockmark owing to confining pressure of water column.

limited extent and the most of energy is expended for rapid upward movement. The plasma bubble reaching near the surface H$_2$ shell is oxidized to H$_2$O shell which is hydrophobic to CH$_4$ thus preventing the escape of dense CH$_4$ packed inside the bubble. Reaching impervious sediment layer below the seafloor though the conduit of a pockmark, the outer shell of water surrounding the plasma bubble gets freeze. The high temperature bubble slowly cools owing to the surrounding en-masse of cold water at 4°C or less than −2°C or at ambient temperature and pressure conditions for the formation of MH. The bubble always tries to take up the smallest amount of space and hold the most of CH$_4$ that it possibly can. The dense supercritical tiny CH$_4$ bubble burst into the en-masse of cold water, ice-cage forms around the hydrophobic CH$_4$ by absorbing or releasing sufficient latent heat energy from the surrounding coldwater layer to maintain its ambient pressure temperature conditions. Larger surface areas of the tiny bubbles are provided far more nucleation points enabling a much faster formation of MH. The lens-shape of the bubble is the best way to take up a little space and hold a lot of CH$_4$, while passing through a narrow conduit produced by the creep. Further, the bubble wall becomes flexible and elastic and it will be flattened in the form of discs very similar to the CH$_4$ bubbles ejected in the Abraham Lake, Alberta Canada [18, 19]. Disc-shaped methane bubbles, often observed in marine sediments, result from growth in a medium that elastically resists expansion of the bubbles and yields by fracture. Discoid bubbles that grow in sediments that obey LEFM grow much faster than spherical bubbles (two- to fourfold faster for the times and conditions tested here) and become more eccentric with time (aspect ratios falling from 0.3 to 0.03 over 8 d of growth). In addition, their growth is not continuous but punctuated by fracture events. Furthermore, under some conditions, LEFM predicts that bubble growth can become arrested, which is not possible for a bubble in a nonresistant medium, even for nonspherical bubbles. Cessation of growth occurs when the dissolved gas concentration gradient near the bubble surface disappears as a result of the increase in bubble gas pressure needed to overcome sediment elasticity [46]. Owing to increase of pressure deep in the Earth, denser mineral phase transition takes place. Formations of such denser minerals voids are developed at the interiors where residual stress energies are stored. Sudden release of such energies by earthquakes followed by numerous aftershocks causes release of numerous bubbles and plumes of CH_4 at CMB. Ascending numerous plumes within a day or two large MH deposits may form in the regions of high latitudes. The latent heat emitted or absorbed during the course of freezing or melting of ice, turbidity, salinity, volume of water/ice, wind speed, warm and cold currents and atmospheric pressure play critical role in the formation of MH entrapped into ice cages [13]. MH can dissociate rapidly due to expulsion of warm fluids from the seafloor, warming of overlying waters, or possibly pressure perturbations. For exploration and exploitation of the resources, it is essential to know the physical properties of MH with its origin and mode of occurrences.

8. Lava Tubes and Bubbles

In Tamil Nadu, India, lava tubes and bubbles of composition of basaltic materials erupted at many places [47]. Similarly Fe, Ti and Nb bearing lava tubes were also erupted in several places as bubbles lava flows without any feeder dykes [48]. From these evidences lava tubes and bubbles may be directly from deep-seated source. The gas trapped in bubble, has a relatively thin glassy outer crust. Inner portion of the bubble wall is coated with glassy exotic material of limu o pele [49]. The Fe-Ti-Nb lava flows scattered at some places of Tamil Nadu indicate that they were directly erupted from the CMB horizon, indicating that some fractures continuously extend up to CMB of 2900 km deep into the Earth. These basaltic bubbles that erupted on the surface have no roots or feeder dykes. The roots hardly extend less than a meter deep and then vanish. Lava bubble formation is very similar to the formation of CH_4 plasma bubbles with similar bubble tectonic mode. The origin of MH is very similar to the eruption of alkali-basaltic basaltic eruptions that took place from the 1996 to 2004 at several places of Tamil Nadu. The holes and pits of various sizes are probably formed by lava erupting onto the seafloor so quickly it traps water beneath it, forming bubbles of steam that eventually collapse as the water cools. The hardened crust then breaks, forming pock marks and glassy black plates of ocean crust with stalactites on their underside [49].

9. Continental Margins

Continental margins are genetically related to plate margins. Perhaps they appear to be one and the same. Though there are 6 continents Eurasia, Africa, Australia, Antarctica, North America and South America, their margins are marked by either deep fractures ending with edges of mid oceanic ridges or active subduction zones comprised of shallow fractures. Based on this concept of continental drift, plate tectonic models are conceived. The lithosphere is broken up into 7 or 8 major plates and many minor plates. The major plates bounded as edges of major continents. The African plate enclosed with mid oceanic ridges of Atlantic, Australian, Indian and Red sea mid oceanic ridges except northern part whch is a fault bounded Alpine-Himalayan region. The eastern margin of Eurasian plate is marked by subduction zone and its western margin ended with the eastern edges of Atlantic mid those of ocean ridges. These features are very similar to the North American, South American plates, and Pacific plates. There exist some genetic relationships between plate margins and continental margins. Tectonic plates are composed of thin oceanic crust and thick continental crust. Global earth quake epicenters are concentrated along active margins. Active margins are commonly the sites of tectonic activity: earthquakes, volcanoes, mountain building, and the formation of new igneous rock. Because of the mountainous terrain, most of the rivers are fairly short, and the continental shelf is narrow to non-existent, dropping off quickly into the depths of the subduction trench. The passive continental margin is the transition between oceanic and adjoining continental crust. It is constructed by sedimentation above an ancient rift. Continental rifting creates new ocean basins. Major portion of continental margins are surrounded by deeply faulted and rifted volcanic and subducted active volcanic continental margins. Isostasy controls the uplift or downwarp of rifted blocks. The continental crust is stretched and thinned due to plate movements. Active margins are the sites of tectonic activity with narrow continental shelves. The continental margins of the two antipodal large low shear-velocity provinces (LLSVPs) under Africa and the Pacific are favourable locations for the episodic initiation of large thermal upwelling (mantle plume). Mantle plumes from the edges of stable areas with low seismic shear velocity above the core-mantle boundary can explain the surface distribution of most hotspots, LIPs, and kimberlites [50]. Because of isostatic compensation, the continental regions do not correlate with topographic features. Many hydrocarbon reservoirs occur with temporal and spatial relationships in passive margins. The spatial and temporal formation of MH from plasmatic state from deep interior of the earth is more plausible than microbial or thermal dissociation of carbonaceous materials into MH. CH_4 plasmatic bubbles attracted by electromagnetic and gravity fields such bubbles move through interconnecting fractures towards polar region. Most subduction zones trending N-S directions lying along the eastern peripheral portions of Eurasia and America are captured and concentrated towards polar region. Similarly, N-S trending Mid Oceanic Ridges and their interconnecting transform faults guide these bubbles towards polar region.

10. Cooling Earth

The huge quantities of energy released during the course of earthquakes, melting of rock at depth, tectonic and orogenic movements and volcanic and magmatic activities might have been derived by cooling of the Earth ever since its formation estimated about 4500 ma. Earth evolution and dynamics are determined by interior heat production and the heat transport towards the surface. While the core heat is mostly transported outwards by mantle plumes, the sinking of cold, subducted plate material is balanced by a pervasive warm counter flow, transporting the mantle-generated radiogenic heat. Hot lithosphere is generated at the oceanic spreading ridges and efficiently cooled by hydrothermal circulation in the fractured ridge crust. Subduction of oceanic lithosphere is the main cooling agent of the mantle. The highest rates of magma production takes place along divergent plate margins at midocean ridges, which are also the locus of most of mantle degassing. The ultrahigh PT-conditions during accretion enhance progress of endothermic reactions of formation of H and He-compounds which provide efficient cooling and produce end products more compact than the reactive [36]. When, Pacific plate undergoing subduction, the oceanic plate, absorbs huge quantity of heat from the mantle and core. Such type of cooling generates downstreams of cold material that cross outer core and freeze onto the inner core. Convection currents move warm mantle to the surface and send cool mantle back to the core. Blobs of light elements are being constantly released from the CMB. The heat given off as the core cools flows from the core to the mantle to Earth's crust. Earth has an outer silicate solid crust, a highly viscous mantle, a liquid outer core that is much less viscous than the mantle, and a solid inner core. The blobs of light elements will rise through this layer before they stir the overlying outer core. The dense LLSVP and ULVZ reservoirs could have remained largely isolated for most of the Earth's history and stabilized antipodal near the equator by Earth's rotation [50]. Ocean floor sinking into the mantle due to tectonic processes can lead to cooling in the mantle. The inner core of Earth is simultaneously melting and freezing due to circulation of heat in the overlying rocky mantle. During oceanic plate undergoing subduction, the oceanic plate absorbs huge quantity of heat from the mantle and core. Downstreams of cold materials, those cross outer core and freeze onto the inner core and convection currents move warm mantle to the surface and send cool mantle back to the core. Blobs of light elements are being constantly released from the CMB. Over millions of years, Earth has cooled from the inside out causing the CMB to partly freeze and solidify. The inner core has subsequently freeze and for a solid mass [51].

11. Global Warming

When heat energy is dissipated out from the core to land surface, it is warmed up. The release of methane like green house gases by natural dissociation also causes global warming. Global warming causes thermal expansion of the Earth's crust. In areas prone to seismic activity, this can cause submarine earthquakes and landslides. Shockwaves can disturb methane hydrates that are already more vulnerable due to temperature rises of the ocean. During the last 5,000 years, the Earth on average cooled about 0.72°C until the last 100 years, when it warmed about 0.72°C [52].

12. Conclusion

Research is going on the plasma state of a matter. Heat energy is stored or released in a matter when transition from one phase to another, is subjected to considerable debate. At super critical plasmatic state, ions of different combinations and dissociations could release or absorb various amounts of energy potentials to form new material. In addition to pressure, temperature and storage of potential energy in a matter, space, time and the external or internal forces impacting on the matter play a critical role in the dynamic changes or evolution of the matter into different many numbers forms. CH_4 bearing fluid inclusions in minerals [53] are direct evidences for formation of MH bubbles. During estimation of PTX condition of in the trapping of fluid inclusions in minerals, several unknown factors are not considered. Therefore only very approximate results are obtained. The occurrences of rootless lava-tubes of alkali basalts, Fe-Ti-Nb oxides lava tubes, and carbonatite lava occurrences in various parts of Tamil Nadu might be other of evidence for such formation of MH bubbles from deep interior of the Earth. Methane plasma bubbles may be captured by electromagnetic fields and gravitational forces along N-S trending normal fault planes of mid oceanic ridges of passive continental margins and similarly along N-S trending faulted edges of active continental margins towards polar region where ambient conditions are available for the formation of methane hydrate. However, N-S trending passive margins comprised of deep normal faults favour higher concentrations of accumulation of MH as larger deposit than that of active margins. A large deposit of methane hydrate may be formed in a day or two when earthquakes are associated with numerous foreshocks and aftershocks by releasing residual stresses stored by phase transformation of minerals in the deep interior of the Earth.

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