[EA]Gas Microseepage as a Source of Seasonal Methane Variation in Martian Atmosphere*

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Abstract

A seasonal pulse of CH_4 to the atmosphere of Mars has been found by the tunable laser spectrometer (TLS) on the rover Curiosity. External sources of CH_4 were originally proposed but have evolved toward a subsurface source. This problem was investigated using a variety of geophysical and geochemical modeling techniques, including deep crustal heat flow, aqueous geochemistry, two-phase buoyant vertical flow of brine and gas, gas hydrate formation, and decomposition near the surface. The deep source of CH_4 and possibly C_2H_6 could be thermogenesis, methanogenesis, or inorganic catalysis.

The chemical evolution of deep, saline formation water favors the formation of either a $CaCl_2$ or $MgCl_2$ brine, contrasting with NaCl brines on Earth. A concentrated brine allows for residual liquid, even at low Martian temperatures. In order to have sufficient pressure for gas hydrate stability near the surface it is necessary to have surface temperatures fluctuate seasonally above and below the freezing point of CO_2 (-78.5°C). A postulated cryosphere thickness of 5000 m was used, with a 50-m unsaturated zone.

The seasonal magnitude of the CH_4 pulse can be variable, depending on the two-phase transport (microseepage) rate from depth, and is highly sensitive to parameters such as porosity, permeability, and thermal conductivity of the surface materials. Some degree of overpressure is probably necessary or the microseepage declines. This supports the existence of an active deep generation process.

Introduction

Mars is approximately half the diameter of Earth with an acceleration of gravity of 0.3794 that of Earth which was used in the proposed modeling. Temperatures are very low because of the distance from the Sun and exhibit a high seasonal and daily variability. The day (sol) is

slightly longer than Earth at 24h 38m. The Martian year is approximately 687 Earth days in length. Atmospheric pressure is approximately 1% that of Earth and is dominated by CO_2. Methane is in the low ppbv range, contrasting with approximately 1.9 ppmv on Earth.

The observed mineralogy and petrology of Mars includes common sulfate, carbonate, and clay minerals, plus a few exotic minerals, along with the observation of more mafic rocks than occur on the surface of Earth. A comprehensive review is provided by Filiberto and Schwenzer (2019) and will not be expanded on here. Early Mars geochemistry may also have included an increased importance of sulfate minerals under more acidic conditions than exist today. Mars is thought to have a thick cryosphere (frozen zone).

Webster et al. (2018) presented results of CH_4 determination in the Martian atmosphere as determined by the TLS instrument on-board Curiosity. Unexpected pulses, or possibly seasonal flows were detected in the first few years since landing in August 2012. A period in 2013 exhibited several high values in the 7 ppbv range (Figure 1). A debate has continued about the source, and two workshops held in 2015 and 2016 discussed the possibilities. This author was a participant and presenter in the second workshop. The results of the workshops were subsequently published (Yung et al., 2018) and favored a subsurface source, but of unknown genesis.

The European Space Agency (ESA) launched an exosatellite (TGO) in 2016, which began orbiting Mars in 2017, and began reporting spectral data in 2018. An unexpected finding was the absence of a CH_4 signal, calling the previous data into question (Korablev et al. 2019). Signal attenuation by spectral interference looking through the Marian atmosphere from above, or atmospheric dust has been considered (Vandaele et al., 2019). Then, on June 19, 2019 another short-term large CH_4 spike of 21 ppbv was measured by Curiosity, three times larger than the 2013 measurements.

Abbreviated Methods

A variety of geophysical, aqueous geochemical, reservoir engineering, and hydrate formation/decomposition methods were used. These are elaborated on in Klusman (2019). It must be pointed out that there has been criticism of the applicability of the aqueous geochemical code (PHREEQC) at low temperatures and high pressures. Although not criticized, the methods used to estimate rock thermal conductivity, gas compressibility, fluid densities and viscosities were developed from algorithms used at ambient temperature → upward. In this application, extension of the algorithms from ambient temperature → downward was used, but the validity is unknown. In the model to be developed, a latitude on Mars where the temperature averages -80° C, with a seasonal amplitude of ±25° C was used as a "best" location. These values result in an appreciable part of the Martian year being above and below the freezing point of CO_2 at the surface, or in the thin unsaturated zone.

 The starting point was a moderately dilute brine in the deep subsurface that would evolve toward a $CaCl_2$ composition with declining temperature and pressure. This selection was intentional in that the viscosity of a concentrated $CaCl_2$ brine has actually been measured down to -25° C and the hydrate stability code includes the effect of $CaCl_2$ destabilization, but not $MgCl_2$ or sulfate-dominated brines (CSM-Gem; Sloan and Koh, 2008).

Results and Discussion

A geotherm was calculated from a groundwater below the cryosphere at +1°C to -80°C at the top of the cryosphere at 50 m depth. The heat flow was estimated at 19.3 milliwatts/m^2 which may soon be supported or refuted by the lander InSight. The model proposes a thermogenic gas cap residing at the base of the cryosphere with a composition of 95% CH_4, 4.0% C_2H_6, with small amounts of C_3-C_5. A "sour" gas of 77% CH_4, 1.0% C_2H_6, 20% CO_2 and 2.0% H_2S was also modeled. The pressure is hydrostatic ("brinostatic") corrected for Mars gravity. During temperature decline during vertical migration, carbonate, sulfate, and clay minerals precipitate, but not chloride minerals, particularly $CaCl_2$ (antarctite or sinjarite).

Figure 2 shows the proportion of gas in the two-phase system in the saturated section at two different pressures (1.00 x hydrostatic and 1.05 x hydrostatic). The proportion of brine is (1.00-proportion of gas). The left side of the diagram shows a gas deficient system with the vertical axis having no free gas phase. At 1.05 x hydrostatic pressure, there is the beginning of the formation of a "gas chimney." The gas phase at -80° C is 0.18028 of the mass of the 2-phase system. The remainder is brine.

The formation of a hydrate requires water and a gas phase. In this system, there may be four phases formed at the top of the saturated section depending on temperature and pressure, vapor, hydrate, $CaCl_2$ salt, and ice. The composition of the hydrate is dependent on the proportions of molecular gases, CH_4 and C_2H_6, which act as stabilizers. The proportion of salt(s) acts as a destabilizer for the hydrate. The temperature near the surface is dependent on the solar-induced thermal wave penetrating from the surface. The penetration of the thermal wave is dependent on time and the thermal conductivity, density, and heat capacity of the rock in the unsaturated zone (Figure 3). Note that the thermal wave is both attenuated and delayed in time with increasing depth.

The "sour gas" composition results in liquefaction a short distance into the cryosphere, so a CO_2-rich brine cannot participate in the proposed model.

The stability of a hydrate is determined by both temperature and pressure. Since the atmospheric pressure on Mars is approximately 1 kPa, a way is needed to increase the pressure in the unsaturated zone, assuming that is there is true interconnectivity in the pores space, the pressure at the base of the unsaturated zone is almost equal to that at the surface. The approach used is, as temperatures drop below the freezing point of CO_2, solid CO_2 fills the pore space, increasing the pressure to that determined by the density of solid CO_2 (CO_2-static pressure). The required pressure was determined by constructing a table for the full temperature range in Figure 3 and using a "table look-up" method to determine if a hydrate is stable, and the proportion of the four phases in the system. The minimum depth of hydrate formation was determined to be 9.0 meters.

A pore space volume fill rate of 0.01/degree Ls was used and the volume of brine + gas phase moving into the unsaturated zone was 4.932 g/m^2/degree Ls. The porosity was 0.01, thermal conductivity 2.1 watts/mK, specific heat 1.0 kJ/kg·K, rock density 2.7 g/cm³ (1.025 in Mars gravity). The proportion of pore space filling with time is shown in Figure 4. The seasons are opposite between hemispheres on Mars as they are on Earth. Figure 5 shows the same pore space hydrate filling/decomposition for the Northern Hemisphere. Figure 6 shows the calculated

flux for the hydrate components a Northern Hemisphere location. Clearly, there is a rise in flux in the Spring, carrying through the Summer, declining in the Fall and "zero" in the Winter. The expression is more of a "hump" rather than a "spike."

Figure 7 is a summary figure which shows the precipitation of carbonate, sulfate, and clay minerals in the groundwater and into the cryosphere during brine migration and cooling. If there is thermogenesis operating or in the final extant phase, the C_{3+} hydrocarbons will remain at the base of the cryosphere as hydrates or a condensate reservoir. The CH_4 and C_2H_6 pass through the cryosphere in the gas phase (Siberian effect; author's term).

If thermogenesis is not the source of CH_4 at the surface, but methanogenesis is the source, a number of possible reactions must be considered. Oehler and Etiope (2017) and Etiope and Oehler (2019) discuss a variety of possibilities in detail. It is not clear whether CH_4 can be directly produced by serpentinization of mafic/ultramafic rocks, but H_2 can be produced. Hydrogen can also be produced by radiolysis. Hydrogen can then be utilized by methanogenic bacteria utilizing the CO_2-reduction pathway. This pathway has also been observed by Klusman (2006) in a Wyoming oilfield. It is also unclear whether CH_4 can be directly produced by abiotic, low-temperature catalysis. Microbial sulfate reduction (anaerobic CH_4 oxidation) can also occur in the deep subsurface on Earth (Klusman, 2003). This mechanism will consume CH_4, whatever its source, and is not necessary for this model. Hydrogen sulfide will not pass through to the surface due to temperature limitations.

Figure 8 shows an expanded view of Figure 7 with a focus on the unsaturated zone. The arrows show the direction of flow and relative magnitude in Summer (red) and Winter (blue).

Returning to Figure 7, an impact crater is shown on the surface. In the absence of a seasonal pulse of CH_4, but a distinct spike, another process must be considered. If the hydrate formation process has operated in the past, but is currently extinct at a particular location, Figures 3 and Figure 8 must be considered together. They both show an unsaturated zone down to 36-40 m depth. In the seasonal model of Figure 4, Figure 5, and Figure 6, the zone from 9-36 meters is seasonally filled with hydrate. If the process is extinct, repeated solar thermal waves will remove any and all hydrate to the depth of 36 meters.

Fresh impact craters on Earth typically have a depth 0.10 to 0.20 times the diameter. Using an impact that excavates a crater 1000 m (1.00 km) in diameter and using a depth of 150 m, the bottom 114 m will be filled with hydrate. Using a porosity of 0.01 filled with hydrate and $CaCl_2$ salt, a volume of 9.0×10^5 m^3 of hydrate and salt is determined. Determining the composition of the hydrate calculated from the "look-up" table at -80° C, give the proportion of CH_4 at 0.0853, C_2H_6 at 0.0742, H_2O (ice) at 0.804. This translates to 14,000 tonnes of CH_4, 12,000 tonnes of C_2H_6, and 137,000 tonnes of H_2O blasted into the Martian atmosphere. The CH_4 and C_2H_6 will be dispersed around the planet to be detected by the TLS instrument on the rover Curiosity. The H_2O will rapidly fall out as snow. The dispersed $CaCl_2$ will be dispersed in the near-field with rock debris, where the $CaCl_2$ may be oxidized at the low-temperature surface of Mars to chlorate and perchlorate salts (Toner et al., 2015).

Returning to Figure 2, the left vertical axis shows the situation if no 2-phase flow occurs, that is, no gas phase, but only an aqueous phase. No hydrate forms as only CH_4 and C_2H_6 to the limits of brine solubility are present. Low temperatures increase solubility of gases, but high ionic strength of the brine decrease solubility of molecular and gaseous species. This would be the situation if the NOMAD instrument on the ESA-TGO satellite is correct ("no CH_4 detected").

If the thermogenic gas model is correct, and the C_2H_6 is enriched in the hydrate over that in the deep reservoir, C_2H_6 should be detectable by the TLS instrument on the rover Curiosity. To the extent of knowledge of the author, this measurement has not been made, but only CH_4 measured. If the biogenic model is correct, only CH_4 should be present in either a seasonal or an impact generated gas peak.

The lander InSight landed on Mars in November 2018. The seismometer was quickly deployed and is operational. A marsquake was detected on April 6, 2019, too early to be a cause of the June 19, 2019 CH_4 spike detected by Curiosity, whether by tectonics, meteorite impact, or unknown cause. The heat flow probe on InSight has not yet been emplaced and may be in trouble.

Summary and Conclusions

A model is proposed that at this point in time is qualitative, but backed by quantitative modeling to the extent possible, with limitations posed by lack of low temperature laboratory measurements of important parameters. The overall important result of the PHREEQC modeling is that the aqueous system does not completely solidify when taking the modeled composition down to -80ºC at a relatively low surface pressure but forms a saline brine that may be sulfate-rich, or chloride-rich depending on the starting composition. This allows the 2-phase buoyancy mechanism for gas transport to operate, even at low permeabilities expected for the Martian cryosphere.

The depth and thickness of the frozen zone is unknown and can only be speculated until InSight potentially provides heat flow data, allowing calculation of geotherms for the subsurface. A thickness of 5 km was used in the development of the proposed model.

Possible reactions and processes to produce CH_4 in the deep subsurface of Mars have been recently discussed in detail by other authors. Residual thermogenesis is possible, though C_3-C_4 will be retained at depth. Hydrogen produced from serpentinization of mafic rocks, or by radiolysis can be utilized by methanogens, producing CH_4 by the known process of CO_2-reduction. The extensive known characteristics of microseepage on Earth, particularly pressure requirements suggest, and may require an active source of CH_4 at depth on Mars. The produced CH_4 from the Martian subsurface migrates upward due to buoyancy, flowing directly to the atmosphere as microseepage during the summer, but retained in the unsaturated zone in winter as a hydrate.

The unsaturated zone temperatures were estimated from the seasonal solar temperature wave and the thermal conductivity of rocks. Hydrate formation in the unsaturated zone is a critical part of the model and downward diffusion of CO_2 from the atmosphere in the winter was invoked to seasonally provide a pressure increase. Hydrate can then form at depths that are constrained by P-T conditions. During spring, the CO_2 pore filling sublimes, allowing hydrate decomposition and a Spring-Summer pulse to the atmosphere. The formation of methane hydrates seasonally in the unsaturated zone is a place of storage, not the ultimate generation of CH_4.

An episodic release of CH_4 to the atmosphere is also possible by meteorite impact fracturing the unsaturated zone and upper part of the cryosphere. This may be recognized as a "marsquake" and a punctual gas pulse. Despite uncertainty in many parameters, "all roads lead to Figure 7."

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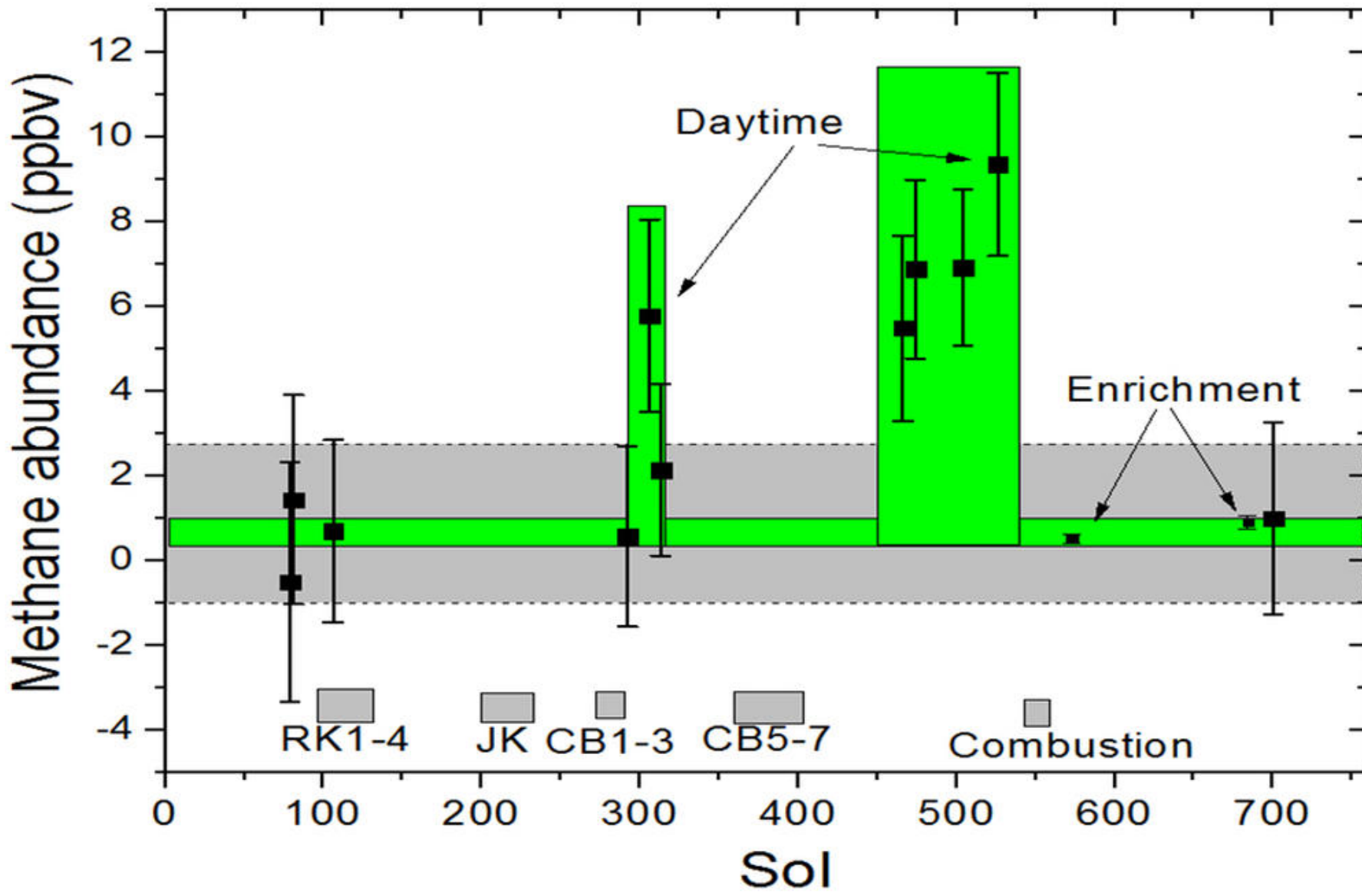
Figure 1. Martian atmospheric CH$_4$ as measured by TLS instrument on rover Curiosity.
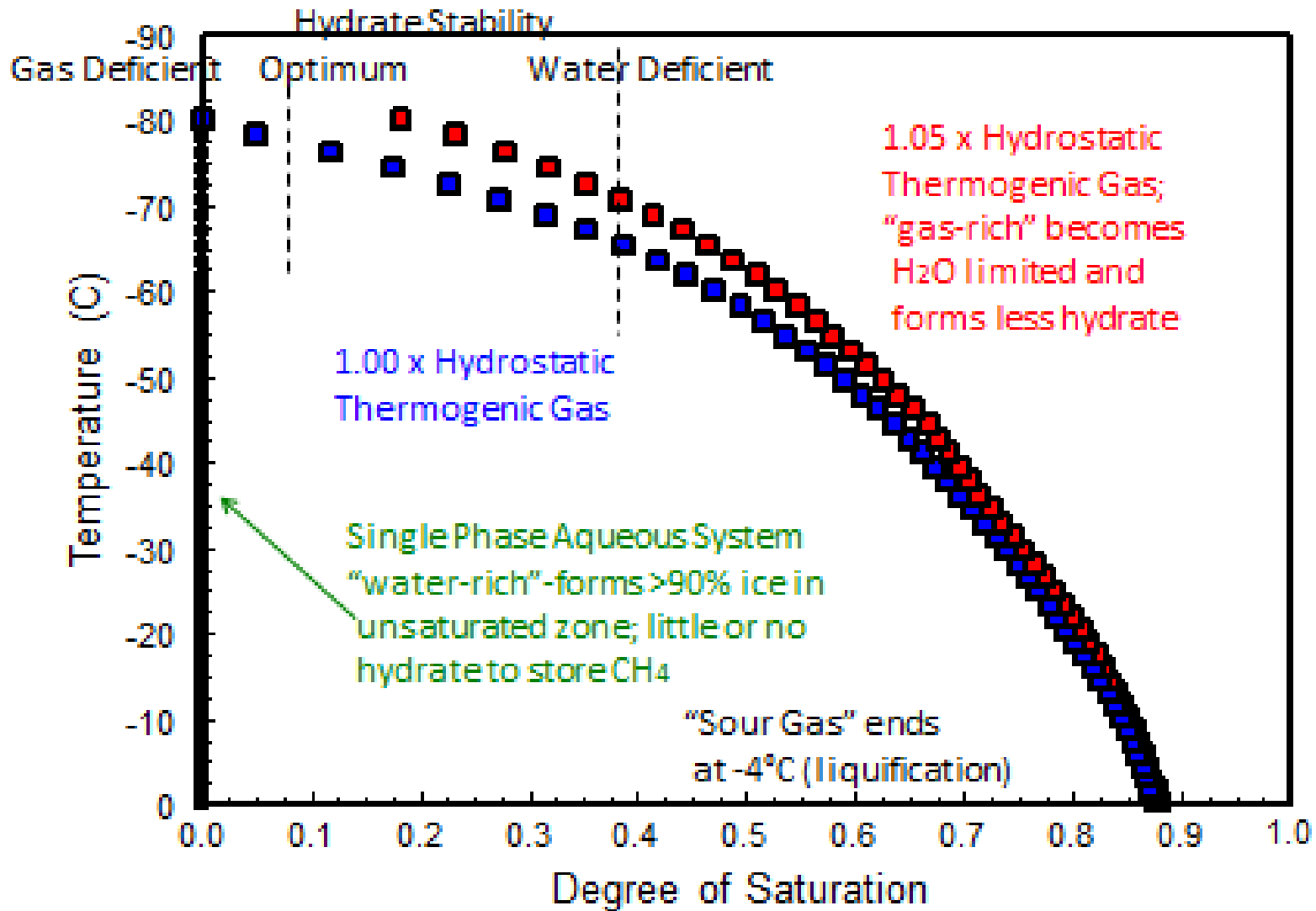
Figure 2. Degree of gas saturation with temperature (depth) on the vertical axis.

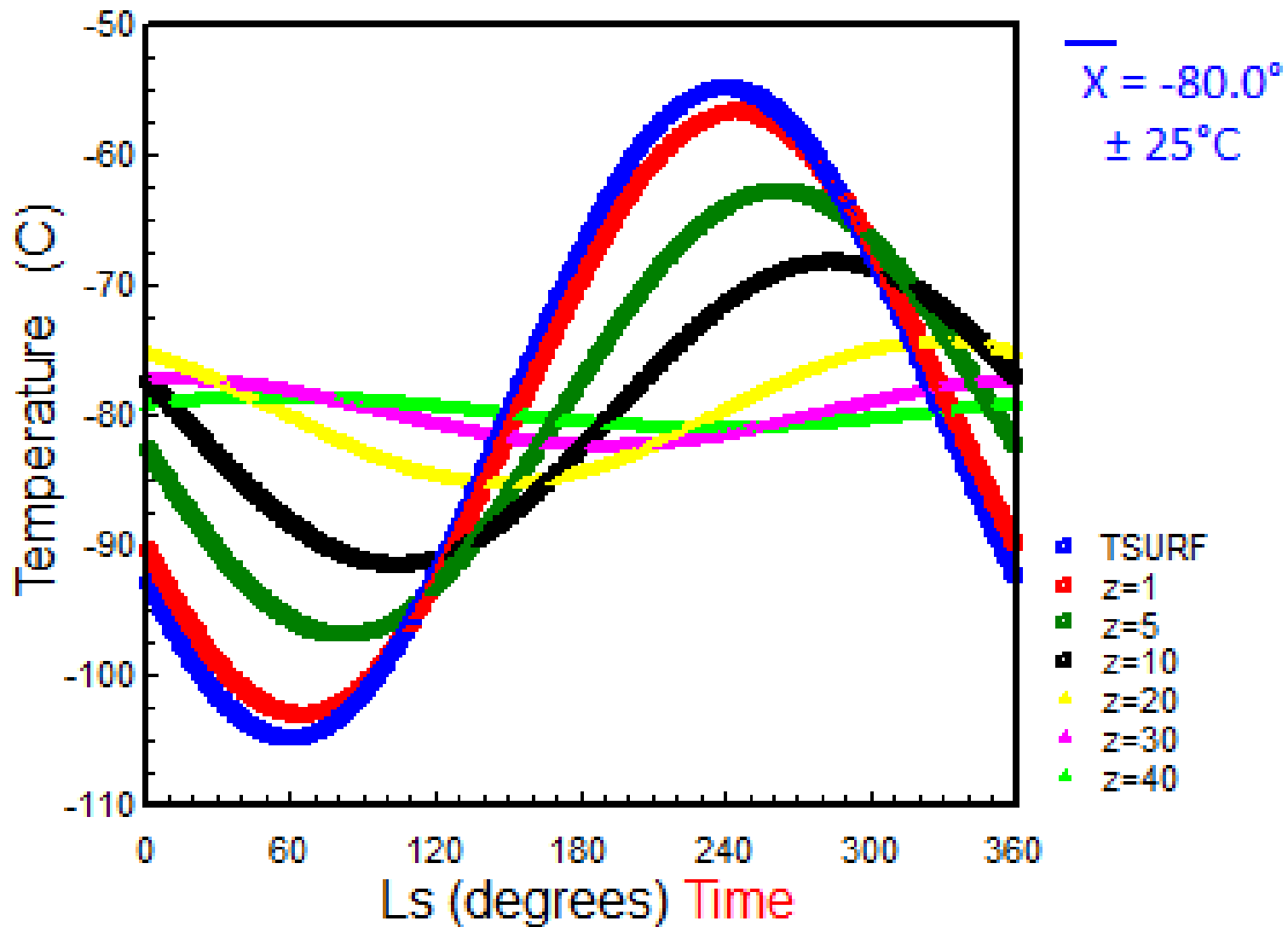Figure 3. Solar temperature waves from the surface to a depth of 40 meters for a Southern Hemisphere location with a surface mean temperature of -80° ± 25° C. The Ls axis is not temperature, but a longitude of the sun at noon for a Northern Hemisphere based longitudinal system.
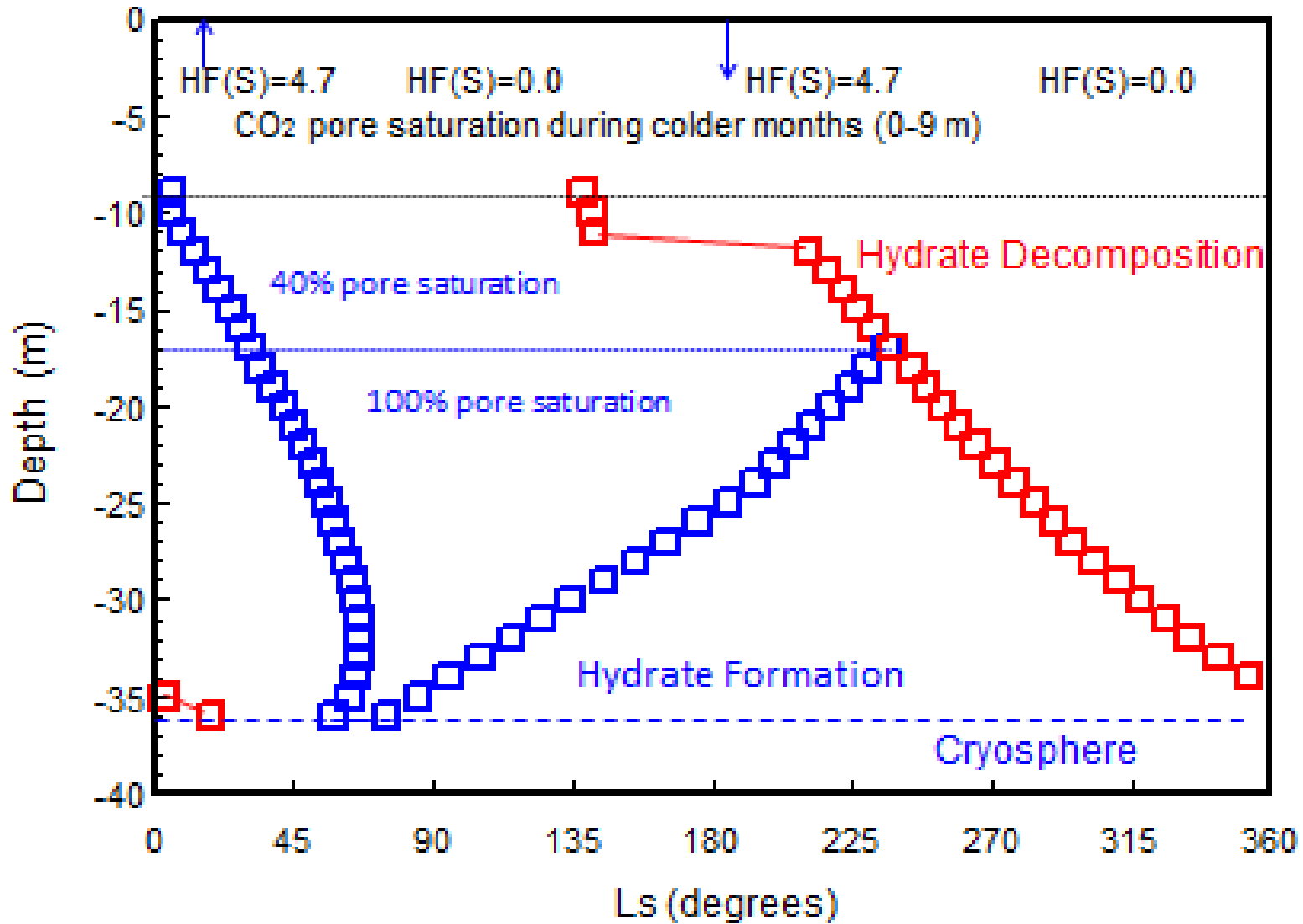
Figure 4. Formation/decomposition of hydrate with season as expressed as Ls for a southern hemisphere location. The HF(S) is the surface heat flow in W/m^2. Note that on Mars, the greatest proportion of heat flow is from solar input, not deep-sourced heat flow, just as occurs on Earth.
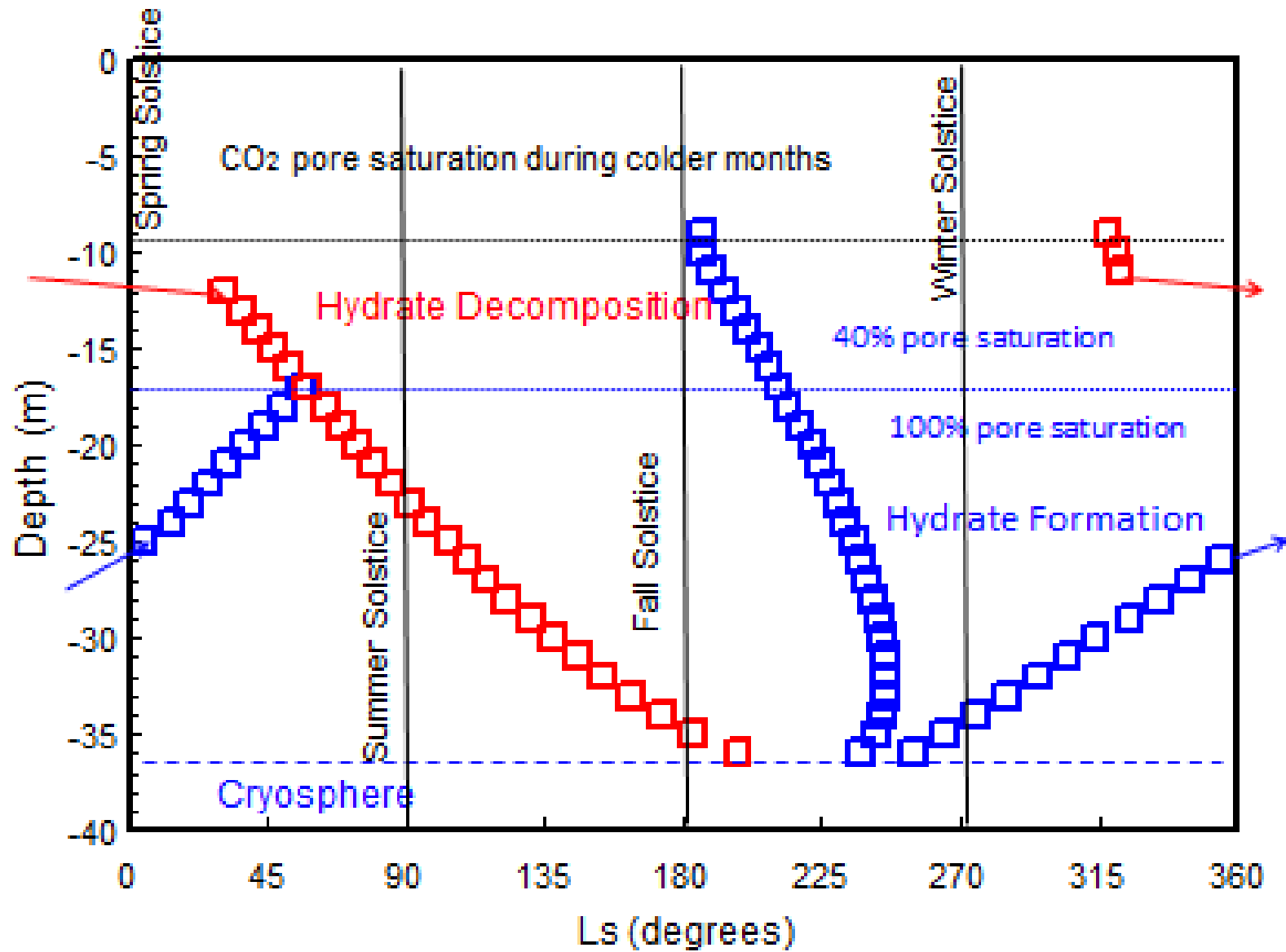
Figure 5. Formation/decomposition of hydrate with season as expressed as Ls for a Northern Hemisphere location. The beginning of each season is added to the figure.
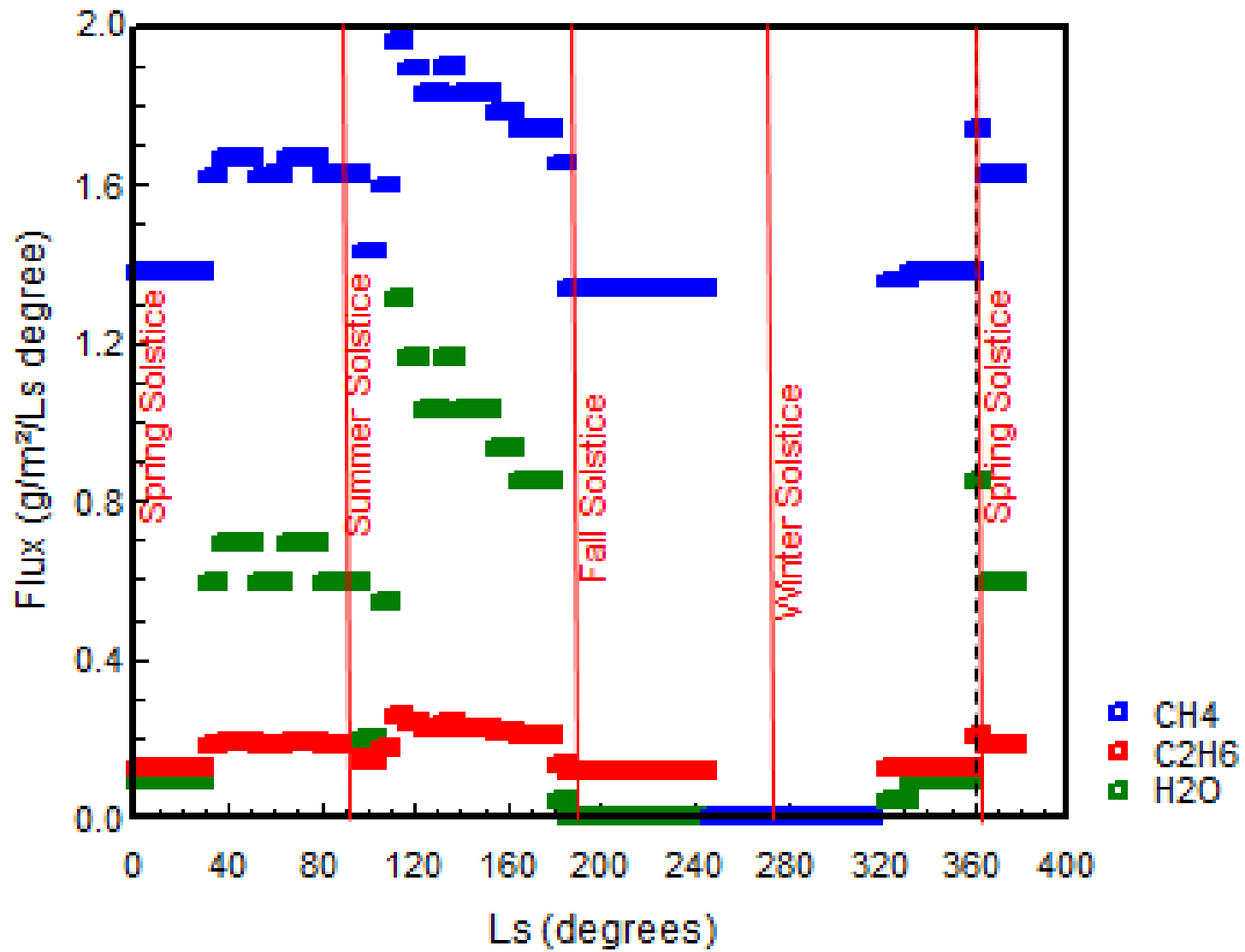
Figure 6. Calculated flux of CH₄, C₂H₆, and H₂O for a Northern Hemisphere location with season.

Surface   Impact Crater

Unsaturated Zone

-80°C

Permanently Frozen Zone, 2-phase Transport
of Gas and Residual Brine

Impact-induced Fractures

0°C

Possible Gas Cap
Possible C3, C4, Hydrates and/or Condensate Reservoir

Chemical precipitation of $CaCO_3$, $(Ca,Mg)(CO_3)_2$, $CaSO_4$
into veins, fractures, faults, bedded strata at high pH

Zone of possible microbial sulfate reduction
$$CH_4 + SO_4^{2-} \longrightarrow HS^- + HCO_3^- + H_2O$$

Zone of possible methanogenesis
$$HCO_3^- + H^+ + 4H_2 \longrightarrow CH_4 + 3H_2O$$

$$Fe^{2+} + S^{2-} \longrightarrow FeS \text{ or } FeS_2$$

Buoyant gas
migration through
brine-saturated
regolith and up
faults and fractures
that serve as pathways(?)

H_2 production by radiolysis(?), serpentinization(?); CH_4 production by Pt-group catalysis(?)
CH_4, C_{2+} by thermogenesis(?); CH_4 by methanogenesis(?)

Serpentinite Zone(?)
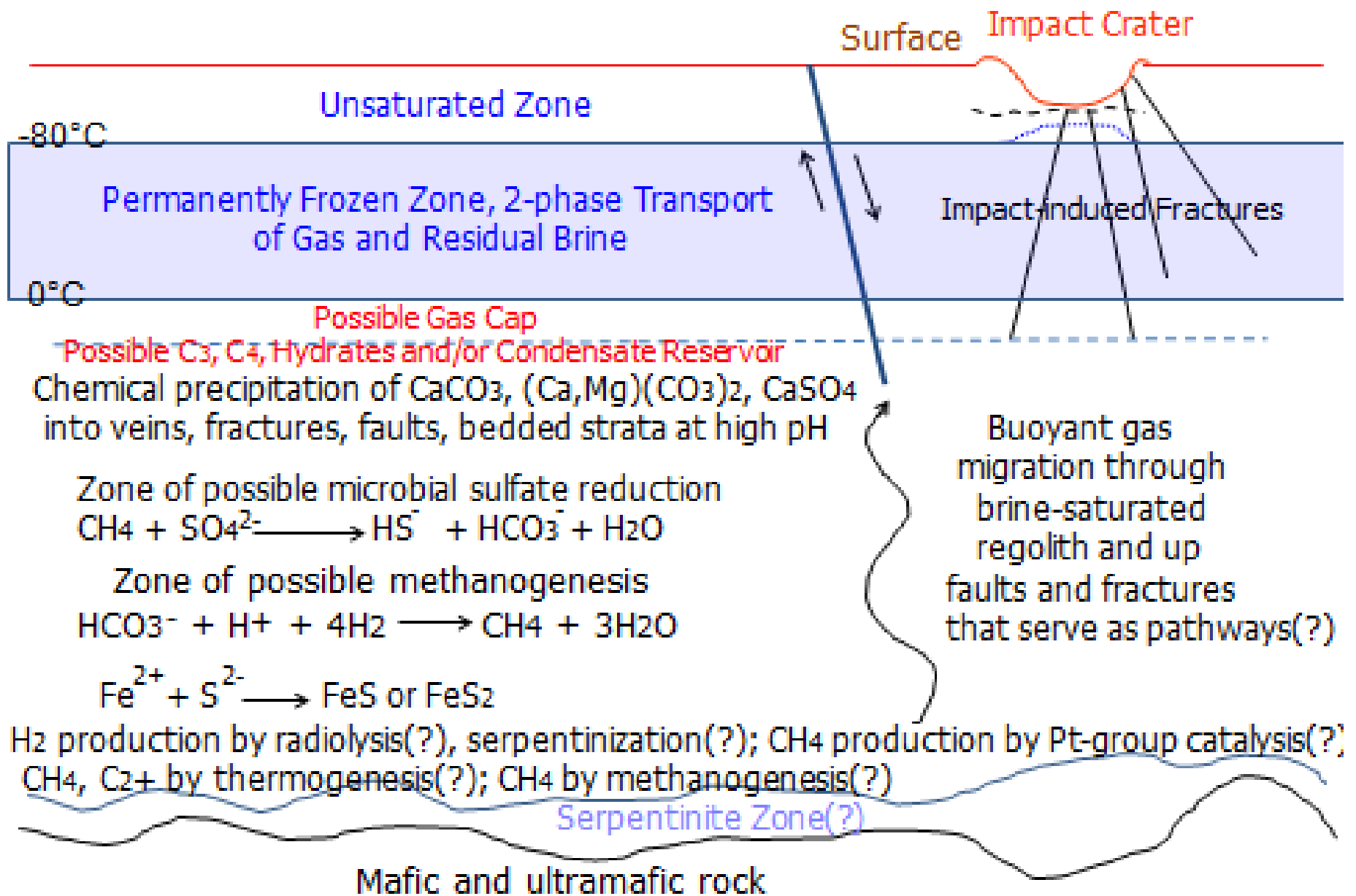
Mafic and ultramafic rock

Figure 7. Summary model of possible processes operating in the groundwater below the cryosphere, the permanently frozen cryosphere, and the unsaturated zone at the top of the section (Not to scale).
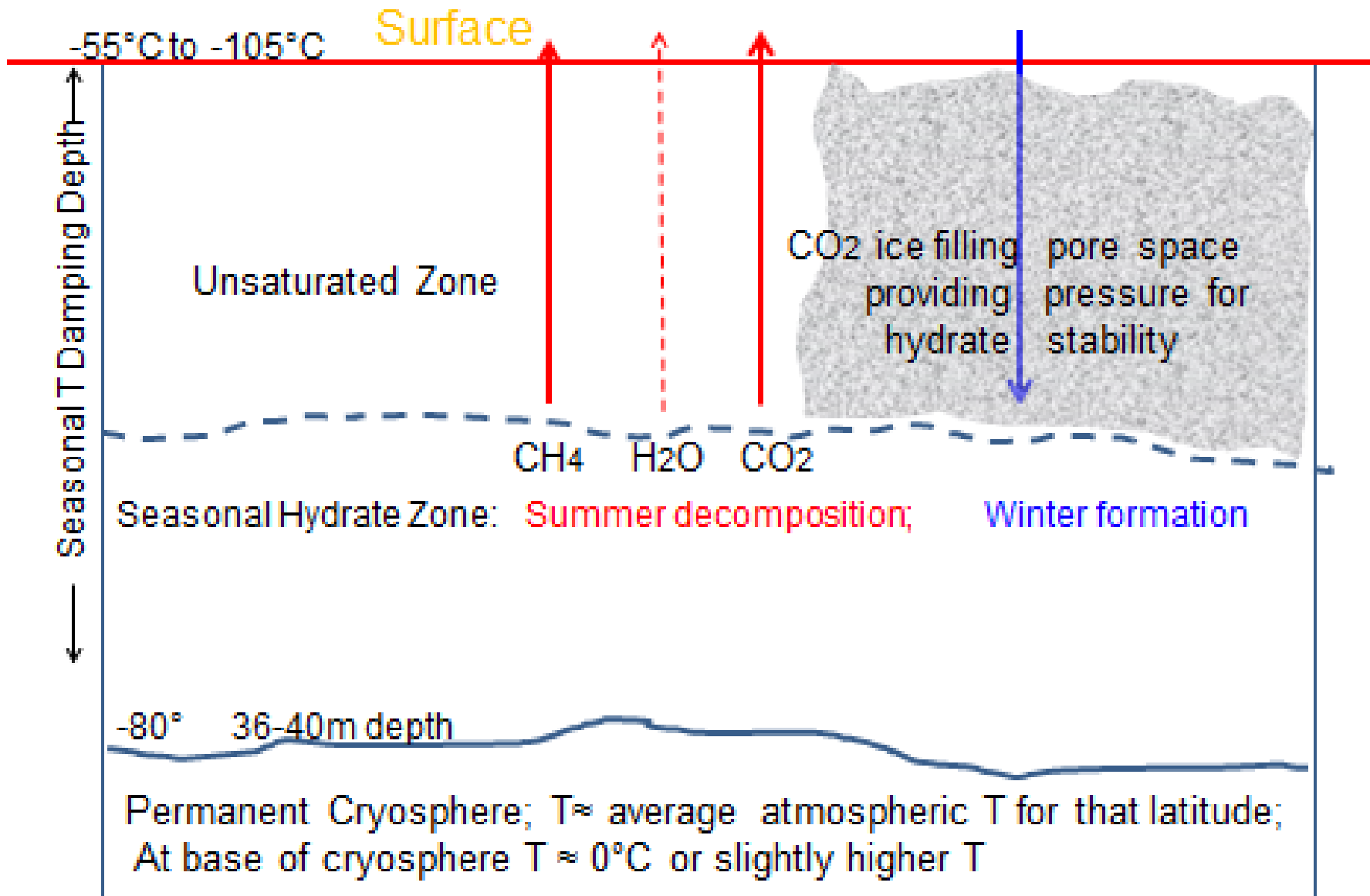
Figure 8. Expanded view of the unsaturated zone showing the seasonal hydrate formation/decomposition zone just above the permanent cryosphere. The upper portion shows CO_2 ice forming in the Winter and sublimation during the Summer.