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The study of non-hydrocarbon gases and its implications for natural hydrogen and helium exploration

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Natural gases may contain significant amounts of non-hydrocarbon components such as N_2, CO_2, and H_2S. The prediction of non-hydrocarbon contents, which may range from traces to nearly 100%, remains one of the major challenges in energy gas exploration. Many aspects regarding origins and accumulation mechanism of nonhydrocarbon gases in deep subsurface reservoirs are still debated. The present state of understanding is summarized in Table 1.

The discovery of surface emanations of natural gases rich in H_2, has prompted speculations about commercial reservoirs of “natural hydrogen”, and several mechanisms have been proposed.

1. Hydrogen (H_2) generation by serpentinization of olivine:

This is a viable and active process that has persistently fuelled chemoautotrophic life throughout much of Earth's history. The reaction of water with ferrous iron consumes oxygen and releases H_2. Most known occurrences are in Mid-Ocean hydrothermal areas and surface-near water-ophiolite environments, which typically lack efficient seals and structural traps.

2. Thermal liberation of H_2 from sedimentary organic matter (disproportioning):

Sedimentary organic matter carries its “own” hydrogen, deriving from water splitting and “H-fixation” during photosynthesis. Laboratory experiments show that large amounts of H_2 are released during *open* system pyrolysis. But only marginal quantities are observed in *closed* system pyrolysis, due to the high reactivity of hydrogen.

3. Liberation of H_2 during thermal decomposition of ammonium clays/feldspars:

Ammonium clays/feldspars are the most likely sources of N_2-rich gases in the deep subsurface. The ammonium hydrogen is derived from water splitting during nitrogen fixation by *nitrogenases*. Thermal/hydrothermal decomposition of NH_4^+-bearing minerals producing N_2 should release significant quantities of H_2. Bleached hematite layers in the vicinity of N_2-rich gas reservoirs may result from reduction of ferric iron by H_2 or NH_4^+. Data from N_2/CO_2-rich natural gases in German Lower Permian reservoirs document H_2 contents of up to 4%. These were, however, attributed to corrosion and have never been examined systematically.

Correlation of He and N_2 contents of natural gases:

Helium contents of natural gases appear to correlate more clearly with N_2 contents than with concentrations of other gases. This could indicate a common source but also similar dependencies on temperature and burial history.

Table 1: Proposed sources of non-hydrocarbon natural gases

Gas	**Proposed sources/origin:**
N_2	“Inorganic” (organic origin): ammonium-rich clay minerals
	Organic: pyrrolic/pyridinic organic compounds
	Inorganic: nitrates (hypothetical)
	Inorganic: mantle (hypothetical)
CO_2	Inorganic: carbonate metamorphism and hydrolysis
	Organic: thermal decarboxylation, thermochemical sulfate reduction
H_2S	Organic: “Bacterial” Sulfate Reduction (BSR) Inorganic: Thermochemical Sulfate Reduction (TSR)
H_2	Inorganic: Serpentinization (water splitting by oxidation of ferrous iron)
	Organic: Decomposition of organic matter (disproportioning)
	Organic/inorganic: Decomposition of ammonium clay minerals