

Origin of Low Molecular Weight Hydrocarbon Gases During Serpentinization: Insights from Fluid Inclusions in Rodingites

C. Normand*

Saskatchewan Ministry of Energy and Resources, Regina, Saskatchewan, Canada

Charles.Normand@gov.sk.ca

and

A.E. Williams-Jones

Earth & Planetary Sciences, McGill University, Montreal, Quebec, Canada

Summary

Fluid inclusions in rodingites from the Jeffrey mine, Asbestos, Quebec, sample aqueous-carbonic and carbonic fluids interpreted to have evolved during serpentinization of the host harzburgites and dunites. Microthermometric and gas chromatographic analyses indicate that the carbonic phase in both types of inclusion is composed predominantly of methane. Carbon dioxide was not detected. More importantly, ethane, propane, n-butane, n-pentane, and traces of acetylene or ethylene, cyclopropane and isobutane were identified in the majority of the samples analysed, in proportions which suggest that they formed under unusually high total dissolved carbon and hydrogen fugacity, and low water fugacity. The hydrocarbons display a Schulz-Flory distribution for alkanes (excluding methane which is in excess in most samples), with values of the chain-growth probability factor, α , varying from 0.05 to 0.23. These values are generally below the range reported for Fischer-Tropsch-type synthesis, the process commonly invoked to explain the abiogenic formation of higher (carbon number) hydrocarbons in nature. An abiogenic model, which has not been proposed previously, involves reaction of a CO- and/or CO₂-rich fluid with a strongly reducing mineral assemblage comprising native iron or a Ni-Fe alloy to form a metastable mineral assemblage under conditions where the fluid is supersaturated with respect to graphite. Thermodynamic calculations show that a C-O-H fluid in equilibrium with the metastable assemblage cohenite (Fe₃C), magnetite (an ubiquitous mineral in serpentinites) and native iron (or awaruite, Ni₃Fe) yields hydrocarbons with a Schulz-Flory distribution having the range of α values observed in the Jeffrey mine. However, this process of hydrocarbon formation will occur only if the fluid is H₂O-poor and CO- and/or CO₂-rich, a condition which is consistent with the occurrence of cohenite in some serpentinites.

Introduction

Hydrocarbon-rich gases (e.g., CH₄, C₂H₆, and C₃H₈) have been reported from numerous occurrences of serpentinized peridotites in ophiolites (e.g., Fritz et al., 1992) and on the seafloor (e.g., Konn et al., 2009). In some cases, a strong argument can be made for the biogenic origin of hydrocarbons. However, in most other cases of hydrocarbon seeps in serpentinites, there is no obvious organic source, suggesting that the gases (mainly simple alkanes) form as a result of abiogenic processes (e.g., McCollom and Seewald, 2007). Moreover, methane gas from such serpentinites has a distinctively light carbon isotopic signature that is unlikely to have resulted from the thermal maturation or bacterial reduction of organic matter (Welhan, 1988).

A process that may lead to the formation of higher hydrocarbons during serpentinization is a Fischer-Tropsch-type catalytic synthesis (e.g., Lancet and Anders, 1970). Another process that might produce higher hydrocarbons is reaction of a CO₂-H₂O fluid with a mineral assemblage such as magnetite ± awaruite and approach to equilibrium with cohenite. Cohenite (Fe₃C) is reported to occur in retrograde, lizardite-dominant serpentinites (e.g., Shteynberg and Lagutina, 1978), and magnetite is common in all serpentinites. C-O-H fluids that equilibrate or approach equilibrium with the metastable assemblage cohenite + magnetite at elevated pressures and temperatures can include up to 7 mole % of ethane and higher hydrocarbons.

One of the stumbling blocks to resolving the issue of the origin of hydrocarbons in serpentinites is that hydrocarbon seeps are open to contamination by air, by mixing with other types of fluids before sampling, or by modification by biological activity. Also, they are potentially sampled at very different conditions of pressure and temperature than those prevailing when they formed. In principle, this problem can be overcome by analyzing fluid inclusions that trapped these hydrocarbons. Unfortunately, serpentinites, especially retrograde serpentinites, rarely contain minerals that are suitable hosts for fluid inclusions. Rodingites, on the other hand, which are composed of minerals that readily trap fluid inclusions (e.g., garnet-group minerals, and vesuvianite), are commonly present in serpentinites, having formed as a result of calcium metasomatism of felsic and adjacent ultramafic rocks by alkaline and SiO₂-poor fluids derived from the serpentinization (e.g., Frost and Beard, 2007). They therefore represent an important carrier of uncontaminated samples of the serpentinizing fluid, and contain hydrocarbon-bearing fluid inclusions (e.g., Schandl et al., 1990).

In this paper, we report the composition of hydrocarbon gases contained in fluid inclusions from rodingitized slate, monzodiorite and granite, and vesuvianite-rich veins of the Jeffrey chrysotile mine, Asbestos, Quebec, and interpret the data in light of mechanisms for the abiogenic synthesis of hydrocarbons in serpentinites. Our data are consistent with a model in which the hydrocarbons formed, during serpentinization, through reaction of a C-O-H fluid with a mineral assemblage containing native iron or a Ni-Fe alloy.

Gas chromatographic analyses of fluid inclusions

The petrographic characteristics of the various types of fluid inclusions present in the samples studied and the corresponding microthermometric data were reported in Normand and Williams-Jones (2007). The gas composition of bulk samples (~ 1 g) of the rodingites was determined with an HP®-5890 Series-II gas chromatograph equipped with a thermal conductivity (TC) detector and a photoionisation (PI) detector connected in series. Volatile species were identified by comparing the retention time of the signal peaks given by the detectors with spectra obtained from gas mixtures of known composition. Water was not quantified as all blanks contained variable proportions of residual water. Details on the apparatus and analytical techniques are given in Salvi and Williams-Jones (1997). The results of the analyses are presented in Table 1.

Water was the principal component detected. Methane was by far the most abundant carbon-bearing species in all samples analysed (> 99 mole % of carbonic species). By contrast, the proportion of CO₂ was below the detection limit (~ 3 nmole). In addition to methane, all the samples contained ethane (C₂H₆) and propane (C₃H₈). Quantifiable amounts of n-butane (n-C₄H₁₀) and n-pentane (n-C₅H₁₂) were present in five of the ten samples analysed. In some samples, there were traces of acetylene or ethylene (C₂H₂ and C₂H₄), cyclopropane (C₃H₆) and isobutane (i-C₄H₁₀). Small proportions of N₂ and/or H₂ and/or CO and/or Ar were detected, but the nature and amounts of these species were not determined. The gas species are similar in all types of rodingite. However, the proportions of C₂+ hydrocarbons are higher in purple vesuvianite and in rodingitized granite.

Table 1. Gas composition of inclusion fluids in rodingites from the Jeffrey mine.

	Sample					
	Ves-1	Ves-3a	Ves-3b	Slate-1a	Gran-1b	Dior-2b
	Gas content (nanomoles)					
CO ₂	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CH ₄	27.374	137.065	225.305	155.846	88.087	17.796
C ₂ H ₆	1.988	3.651	2.126	3.495	3.120	0.235
C ₃ H ₈	0.279	0.707	0.226	0.308	0.304	0.012
n-C ₄ H ₁₀	0.093	0.172	0.039	0.089	0.106	n.d.
n-C ₅ H ₁₂	0.020	0.013	n.d.	0.019	0.024	n.d.
C ₃ H ₆	n.d.	0.042	0.057	present	present	n.d.
i-C ₄ H ₁₀	0.024	0.055	n.d.	present	present	n.d.
α (including CH ₄)	0.17	0.12	0.06	0.11	0.21	0.03
α (excluding CH ₄)	0.23	0.16	0.14	0.19	0.14	0.05

n.d.: not detected; Ves-1: Vug-filling purple vesuvianite from vein; Ves-3a: Vug-filling purple vesuvianite from vein; Ves-3b: Vug-filling colorless wollastonite interstitial to purple vesuvianite; Slate-1a: Orange grossular-diopside vein cutting rodingitized slate; Gran-1b: Orange grossular-diopside rodingite after pegmatitic, feldspar-rich granitic rock; Dior-2b: Diopside-grossular-zoisite rodingite after dioritic rock.

Discussion

Significantly, all samples show a more or less well-defined Schulz-Flory distribution of hydrocarbons for species with more than 2 carbon atoms. The value of α , calculated ignoring methane, varies between 0.05 and 0.23 (Table 1). The α values for fluid inclusions in rodingitized granite and slate, and in vesuvianite, are thus not very different from those for Fischer-Tropsch synthesis using Ni (0.36: Kudo et al., 1993) as the catalyst (although data are not available for magnetite, the α value for this catalyst is likely to be somewhat higher, based on the data for native iron; Kudo et al., 1993). Moreover, Ni-Fe alloys such as awaruite are widely distributed, albeit in small amounts, in the Asbestos serpentinites. On the other hand, the α values for hydrocarbons in rodingitized diorite are too low to reflect Fischer-Tropsch catalysis on the surface of a metal alloy, but too elevated to be explained as having been formed in equilibrium with a stable mineral assemblage in the system Mg-Fe-Si-C-O-H. Equilibrium precipitation of graphite would limit fO_2 and fCO_2 to conditions that do not permit C₂+ hydrocarbons to form in concentrations detectable by available analytical techniques.

In principle, C₂+ hydrocarbons can be produced from C-O-H fluids, if the fCO_2 and fH_2 are high enough. However, in practice, this is not possible at equilibrium because saturation of the system with respect to graphite buffers the these fugacities to much lower values than required. On the other hand, cohenite, (Fe,Ni,Co)₃C, which is metastable with respect to graphite in the system Fe-C at T < 350 °C, has been reported to occur as sub-micron diameter grains in low temperature lizardite-chrysotile-type serpentinites (Shteynberg and Lagutina, 1978). This indicates that cohenite forms during serpentinization, and suggests exceptionally high fCO_2 and fH_2 , i.e., conditions that would allow C₂+ alkanes to form.

Serpentinization is typically accompanied by the formation of magnetite and Ni-Fe alloys, and the production of H₂ which drives the system to highly reducing conditions and may even saturate it with hydrogen (Klein and Bach, 2009). Low activity of water at a serpentinization front will serve to increase the bulk carbon concentration of the fluid and even lead to effervescence of a carbon-rich fluid, an effect that would be promoted by the accompanying increase in the ionic strength of the fluid and the conversion of CO₂ to CH₄. This fluid would be H₂O-poor and CO₂- or CH₄-rich. We propose that effervescence of a CO₂-rich fluid and its reaction with magnetite + awaruite is a plausible mechanism for cohenite and higher hydrocarbon formation.

The presence of cohenite formed at low temperatures in serpentinites is direct evidence that this process does take place in nature. A CO₂-rich fluid that infiltrates a serpentinite containing

awaruite or native iron and magnetite may become buffered with respect to fO_2 but not fCO_2 until cohenite forms, provided that crystallisation of graphite is inhibited. It is important to note, however, that increase in fCO_2 along the native iron + magnetite or awaruite + magnetite fO_2 -buffers does not need to result in the formation of cohenite for higher hydrocarbons to form in proportions that would be easily detectable by means of gas chromatographic analysis.

Conclusions

Previous studies invoking an abiogenic origin for hydrocarbons in serpentinites have proposed that they are the result of Fischer-Tropsch synthesis. This hypothesis predicts that the hydrocarbons will have a Schultz-Flory distribution with a chain growth probability factor, α , >0.3 . However, although the hydrocarbons trapped as fluid inclusions in rodingites of the Jeffrey mine display this distribution, the value of α is significantly less than 0.3. We propose that this can be explained by a model in which a C-O-H fluid reacts with Ni-Fe alloys (and magnetite) at elevated fCO_2 , and support this conclusion with thermodynamic calculations showing that the reaction not only produces higher hydrocarbons with a Shultz-Flory distribution, but the range of α values is consistent with that determined for the JM Asbestos deposit.

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