

Auxiliary Material for “Formation of Methane on Mars by Fluid-Rock Interaction in the Crust”

Auxiliary Text

Oxygen fugacity of Martian Crust

The fO_2 of martian basaltic crust, as modeled by shergottite meteorites, is lower and more variable than terrestrial basalts [*Stolper and McSween, 1979; Smith and Hervig, 1979; McSween et al., 1996; Ghosal et al., 1998; Hale et al., 1999; Taylor et al., 2002; Herd et al., 2001; Rubin et al., 2000; Herd et al., 2002; Xirouchakis et al., 2002; Goodrich et al., 2003; Herd, 2003; Wadhwa, 2001; Papike et al., 2004*]. Figure A1 shows that fO_2 of basaltic and lherzolithic shergottites, estimated using mineral equilibria and redox-sensitive trace elements, is between QFM and QFM-4.5, regardless of technique. The variation of ~4 orders of magnitude likely reflects heterogeneous mixing of mantle source-components [*Herd, 2003; Borg et al., 2003*]. Reported temperatures of closure to redox exchange are ~1100 to <500 °C, indicating that fO_2 remains below QFM during cooling to ambient conditions. Provided that the fluid-rock ratio is low, fO_2 during fluid-rock interaction in martian crust will be rock buffered, and therefore most plausibly modeled as \leq QFM. Note that this does not imply or require the presence of the assemblage quartz+fayalite+magnetite, but rather that the variation in chemical potential of O_2 in the system is the same as the QFM equilibrium.

Carbon in undegassed martian magma

Magmatic C delivered to the atmosphere (as CO₂) has influenced martian climate over time [*Jakosky and Phillips, 2001*] potentially including warming sufficient to permit liquid water at the surface [*Baker, 2001*]. Tharsis magmatic CO₂ equivalent to Hawaiian basalt (0.65 wt%) was used to calculate atmospheric CO₂ pressure [*Phillips et al., 2001*], but this value is unconstrained. Carbon in SNC meteorites (36 and 847 ppm in EETA 79001 and Chassigny, respectively [*Banin et al., 1992*]) is a poor guide to initial magmatic concentration because of degassing during crystallization and terrestrial contamination [*Jull et al., 1998*]. In combination with the great uncertainty in the mass of atmospheric C lost to space and to carbonates in the crust, these observations preclude quantitative estimation of the C content of undegassed martian magma.

Carbon isotopes of CH₄ produced by serpentinization

Serpentinization reactions [e.g., *Kelley 1996; Horita and Berndt 1999; Charlou et al. 2002; Foustoukos and Seyfried 2004*] are another possible source of CH₄, and although this is not the mechanism we are focusing on here, it is important to determine whether isotopic or compositional discriminant exists between serpentinization and a magmatic scenario. Because the C source in serpentinization is likely to be HCO₃⁻ derived from dissolution of crustal carbonate [*Bandfield et al. 2003*], the resulting δ¹³C(CH₄) could be quite different from the magmatic case. Extrapolation of equilibrium CO₂-calcite fractionation data [*Scheele and Hoefs, 1992*] yields a carbon fractionation factor $\alpha_{\text{CO}_2\text{-calcite}} = 1.0021, 1.0035, \text{ and } 1.0039$ at 200 °C, 300 °C and 400 °C, respectively.

Equilibrium fractionation factors for CO₂ and CH₄ are $\alpha_{\text{CH}_4\text{-CO}_2} = 0.9670, 0.9758$ and

0.9817 at 200 °C, 300 °C and 400 °C, respectively [Richet *et al.*, 1977]. For CH₄ formed by serpentinization from crustal C (and assuming isotopic equilibrium) we predict methane to have δ¹³C between -31 ‰, -21 ‰ and -14 ‰ relative to crustal carbonate. If carbonates in ALH84001 and Nakhla, with δ¹³C_{PDB} ~ + 15 to + 55 ‰ [Romanek *et al.*, 1994; Jull *et al.*, 1997], are representative of crustal carbonates, Mars CH₄ produced by serpentinization should be δ¹³C_{PDB} ~ - 15 to + 40 ‰, assuming isotopic equilibrium between 200 and 400 °C. Isotopically light CH₄ (~ -30 to -15 ‰ vs. PDB) may suggest serpentinization and a crustal C source, a magmatic C source (~ -24 ‰ vs. PDB), or a biogenic source. Isotopically very light CH₄ (<< -30 ‰ vs. PDB) may be evidence for biogenic production. Kinetic effects in serpentinization experiments at 200 °C yielded CH₄ with δ¹³C ~ -50 ‰ relative to starting carbonate [Horita and Berndt 1999], ~ 20 ‰ lighter than expected in equilibrium, and so must be considered another possible source of light CH₄. However, carbon isotope ratios of CH₄ in terrestrial MOR vent fluids are not consistent with CH₄ formation by serpentinization at low temperatures (~100 - 200 °C) [Kelley *et al.* 1996; Charlou *et al.* 2002]. A tighter constraint on the crustal carbonate carbon isotope ratio would greatly improve our chances of distinguishing between a crustal and magmatic C source for martian CH₄.

Carbon isotope fractionation during oxidation of CH₄ in the atmosphere

In the atmosphere destruction of CH₄ by gas phase reactions with OH and O(¹D) radicals will preferentially destroy ¹²CH₄, producing a small enrichment of ~ 5 ‰ [Nair *et al.* 2005]. This enrichment is too small to alter the interpreted provenance of the CH₄.

However, hydrogen isotopes are predicted to be strongly modified by atmospheric processes (D enrichment ~ 100 ‰) [Nair *et al.* 2005].

Auxiliary Figure

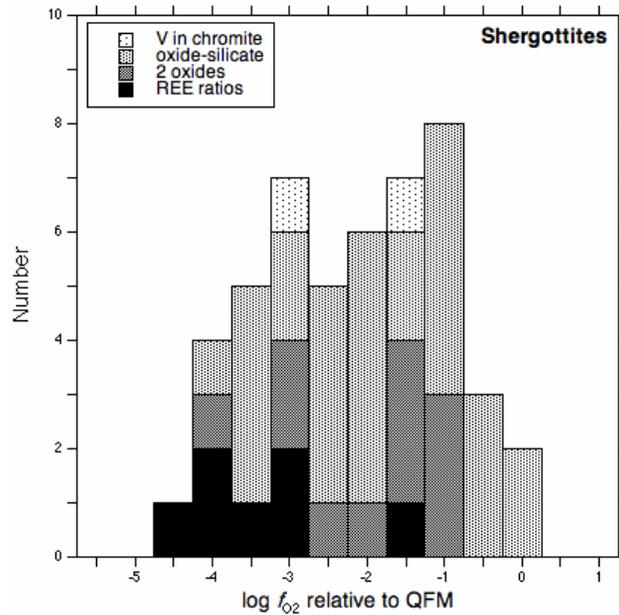


Figure A1. Summary of f_{O_2} of basaltic and lherzolitic shergottites relative to quartz-fayalite-magnetite equilibrium (QFM), based on two oxides [Stolper and McSween, 1979; Smith and Hervig, 1979; McSween *et al.*, 1996; Ghosal *et al.*, 1998; Hale *et al.*, 1999; Taylor *et al.*, 2002; Herd *et al.*, 2001], oxide+silicates [Herd *et al.*, 2001; Rubin *et al.*, 2000; Herd *et al.*, 2002; Xirouchakis *et al.*, 2002; Goodrich *et al.*, 2003; Herd, 2003], REE in pyroxene [Wadhwa, 2001] and V in chromite [Papike *et al.*, 2004]. Typical uncertainty is ± 0.5 log units. REE in pyroxene may give lower values than other methods [McCanta *et al.*, 2004], but the differences are not significant for the purposes of this study.

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