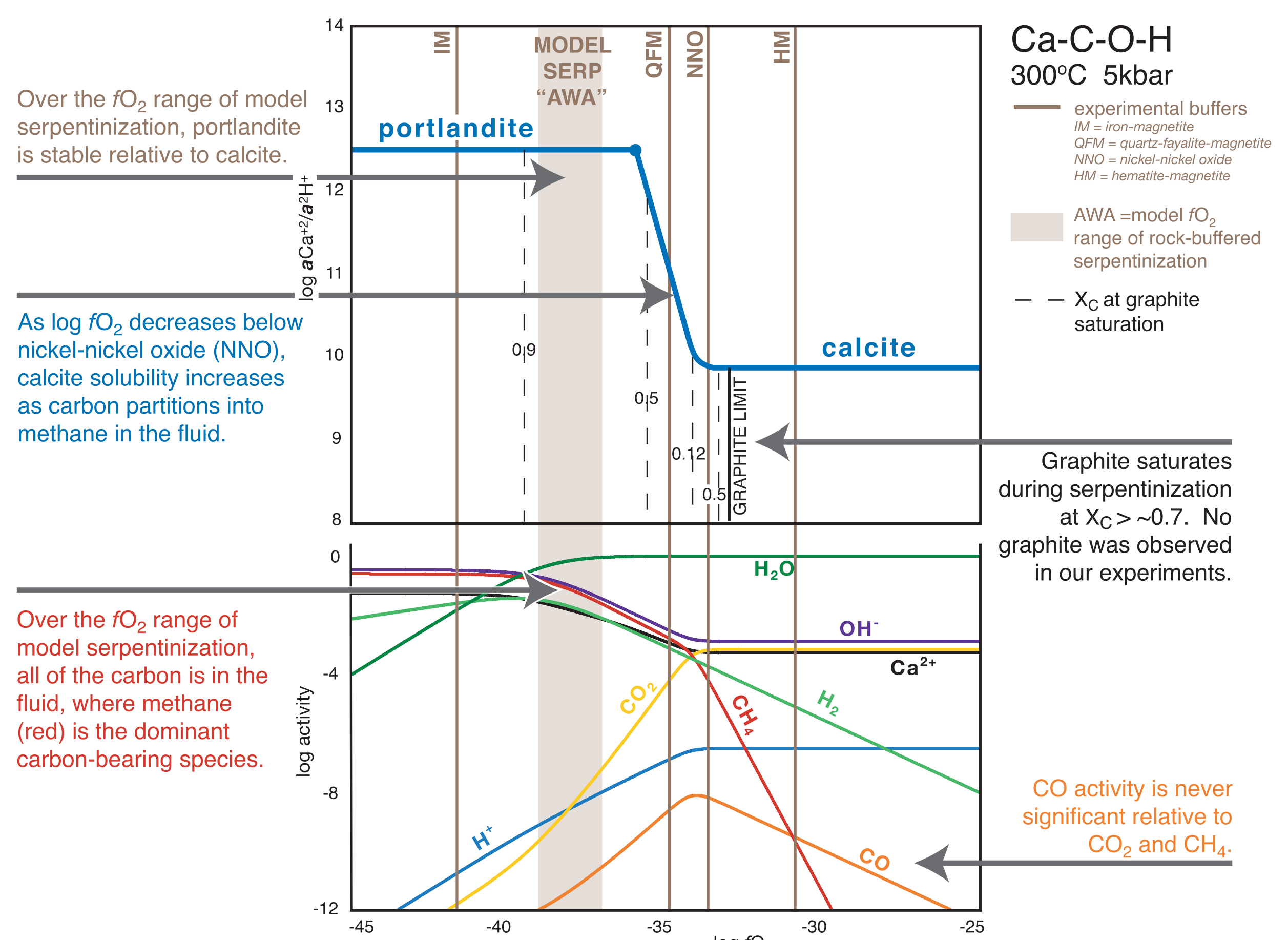


### ABSTRACT

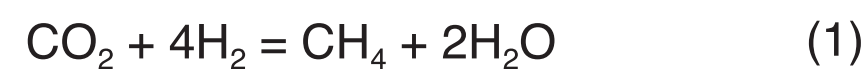
Water-rock interaction is often proposed as a mechanism for generating CH<sub>4</sub> on Mars [1,2]. However, the physical chemistry of hydrothermal methanogenesis is poorly understood. Field and experimental studies suggest that reduced C-O-H fluids do not readily achieve equilibrium, owing to the slow kinetics of CO<sub>2</sub> reduction to CH<sub>4</sub> [3]. Furthermore, serpentinization experiments have not reproduced observed [CH<sub>4</sub>] measurements in terrestrial seafloor springs [9]. Most hydrothermal experiments to date have investigated methanogenesis via formic acid decomposition, a process that requires a transition metal catalysis to produce methane-rich fluids [4,5]. We present experimental evidence for a rapid methanogenetic process that does not require a catalyst: calcite reduction by a hydrogen-rich fluid. At 500°C, 10 kbar, we reacted isotopically labeled calcite and pure water at an *f*O<sub>2</sub> approximately equal to that buffered by serpentinization. After 3 days, our experiment generated approximately 1000 times the amount of methane as low pressure formic acid experiments. The mass of calcite required to sustain a modern Martian atmospheric methane mixing ratio is 8x10<sup>5</sup> kg/yr [from 6]. If carbonates make up 0.0001 wt% of a 50 km thick Martian crust, then enough exists to supply atmospheric methane for billions of years. However, a hydrogen source is also needed. Serpentinization and radiolysis are possibilities, but remain speculative pending definitive observations. Although our experiments were performed at deep crustal conditions, we predict that calcite reduction will occur favorably at lower pressures; future experiments will address this.

### EQUILIBRIUM THERMODYNAMICS: calcite is unstable at low *f*O<sub>2</sub>



#### KEY REACTIONS

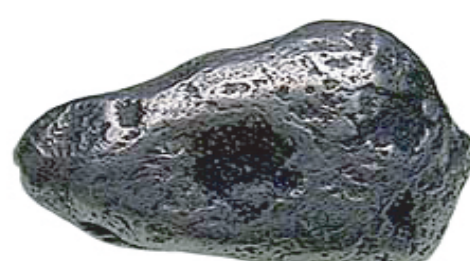
An increase in *a*H<sub>2</sub> drives both of these reactions to the right, consuming CO<sub>2</sub> & calcite and generating methane.



### THE ABIOTIC HYDROTHERMAL METHANE PROBLEM

Experimental studies of abiotic methanogenesis during serpentinization have not been able to reproduce field measurements of serpentine hosted springs. Furthermore, both field and experimental measurements show methane concentrations far below predicted equilibrium values (see table at right, from [3]).

	<i>log</i> [CH <sub>4</sub> ] (mmol/kg)	
	<i>predicted</i>	<i>observed</i>
seafloor springs	-1	-2.5
serpentinization experiments	+4	-5



Catalytic: awaruite (Ni<sub>3</sub>Fe)

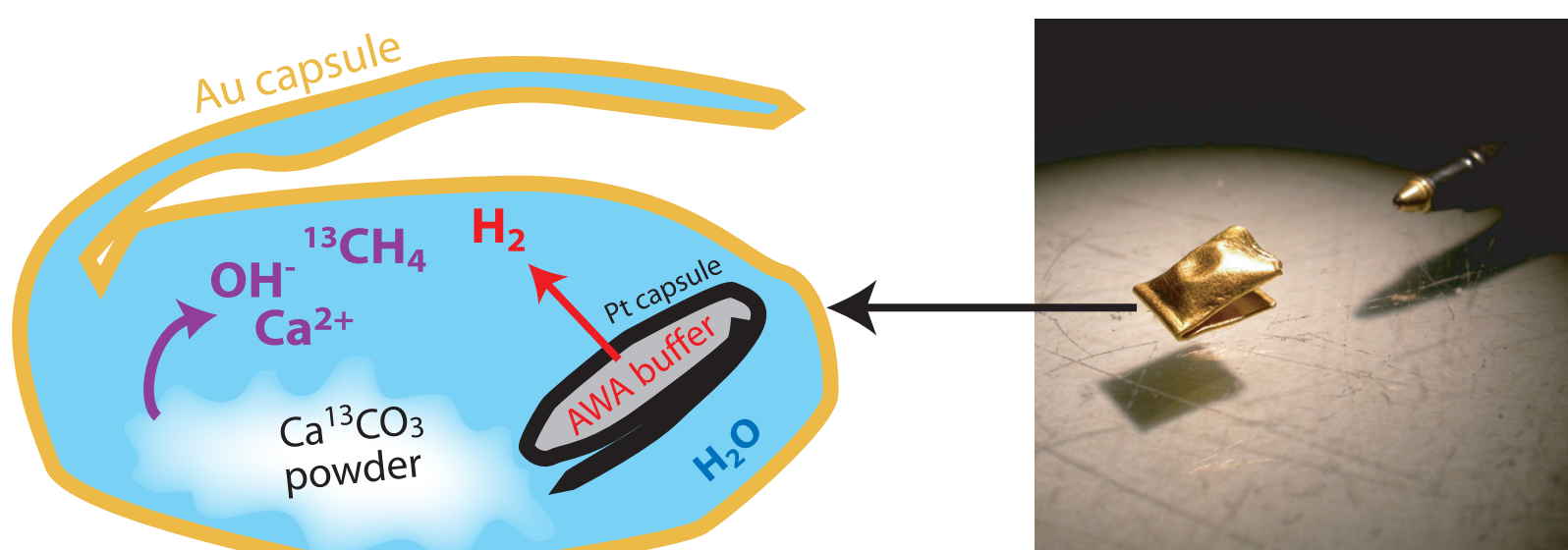
Previous work has focused on formic acid decomposition, and the most methane-rich experimental fluids have required transition metal catalysts. We propose a new mechanism for methanogenesis that does not require a catalyst: calcite reduction by a H<sub>2</sub>-bearing fluid. Since carbonates have been recently detected on the Martian surface, carbonate reduction could be an important process on Mars. The present experiments are required to assess whether and to what extent this process could yield methane.

### EXPERIMENTS: methanogenesis is sluggish...or is it?

We reacted labeled calcite (Ca<sup>13</sup>CO<sub>3</sub>) with pure water and AWA & NNO buffers (see below). Labeled calcite is required to resolve calcite-derived methane from the decomposition products organic contaminants. Experimental conditions: 500°C, 10 kbar, Au capsule.



High pressure apparatus: Boyd-England-style piston cylinder



BUFFERS: *f*O<sub>2</sub> is fixed by equilibrium constants as long as both solid phases are present

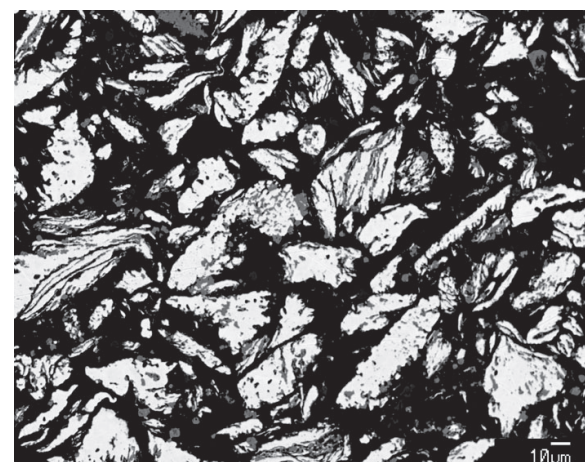
NNO = nickel-nickel oxide  
2NiO = 2Ni<sup>0</sup> + O<sub>2</sub>  
K = *f*O<sub>2</sub>

AWA = awaruite(Ni<sub>3</sub>Fe)-magnetite modeled by varying iron activity via:



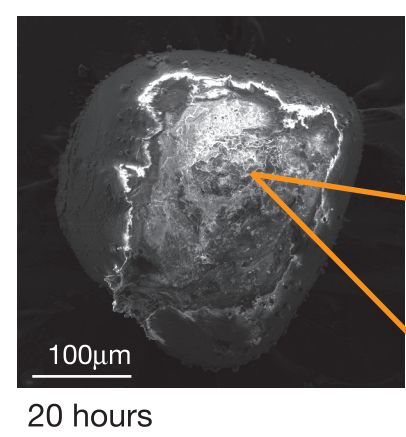
$$K = \frac{f\text{O}_2}{X^3_{\text{Fe in AWA}}}$$

see: [7]

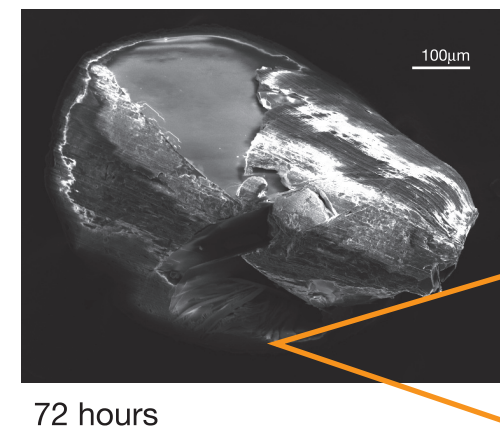


Backscattered image of the products of the AWA buffer mounted in epoxy (black). Awaruite is bright gray; magnetite is medium gray. Starting materials: awaruite and water. Magnetite grew during the experiment. 600°C, 10 kbar, 3 days, Pt capsule, piston-cylinder.

Portlandite forming on single calcite crystals, AWA buffer, 600°C, 10 kbar



20 hours



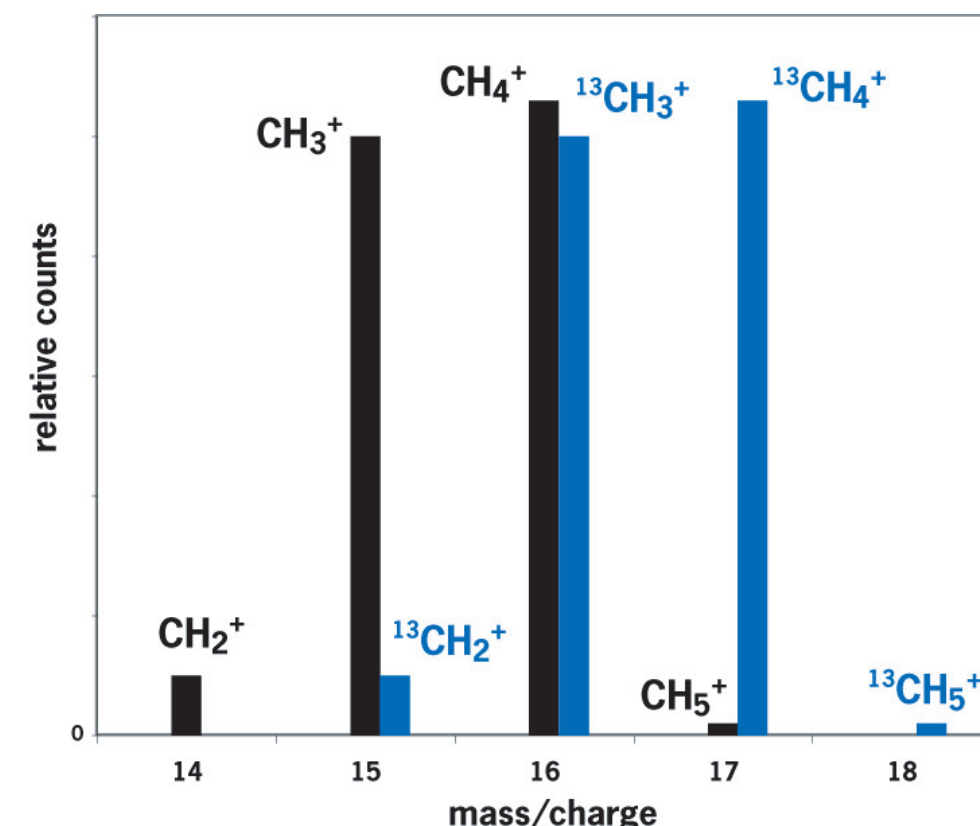
72 hours

### ANALYSIS

Capsules punctured in a gas vial.

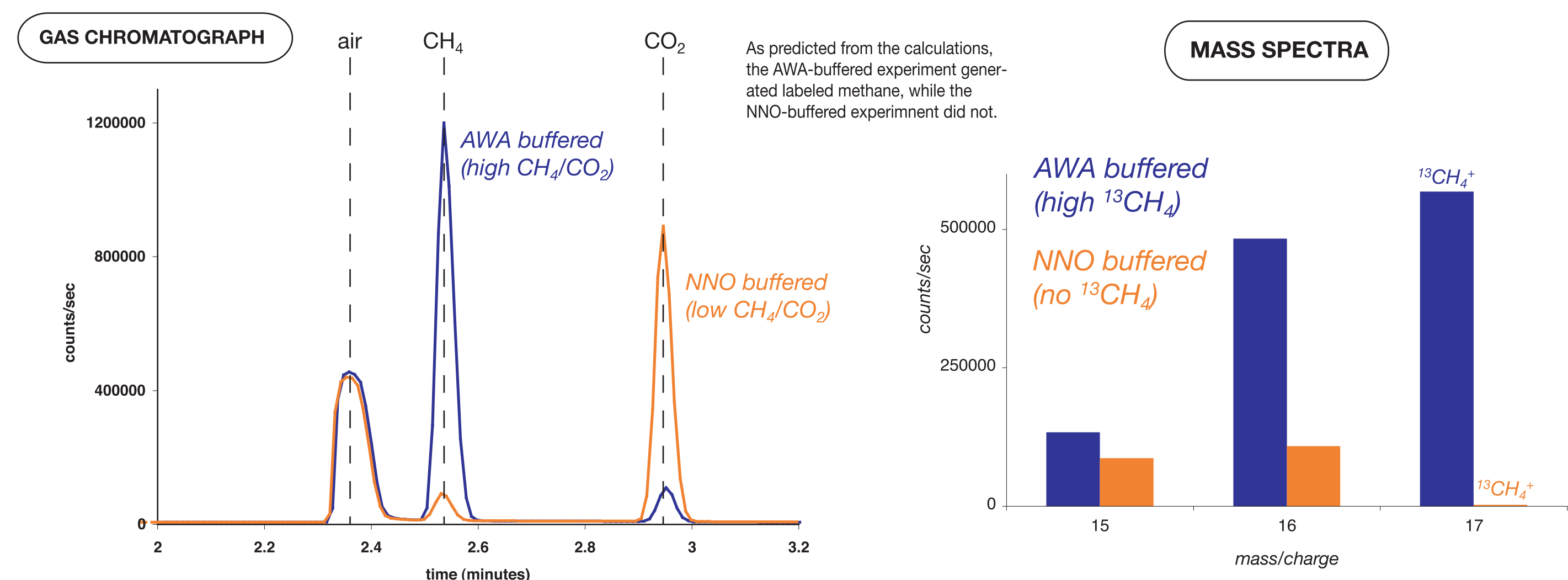
After cooling below -10°C, volatiles were extracted via lockable gas syringe.

Syringe contents were injected into a calibrated GC-MS.



Standard mass spectra for <sup>12</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> were used together with concentration measurements to determine how much Ca<sup>13</sup>CO<sub>3</sub> was converted to <sup>13</sup>CH<sub>4</sub>.

### PRELIMINARY RESULTS: calcite + H<sub>2</sub> = rapid methane



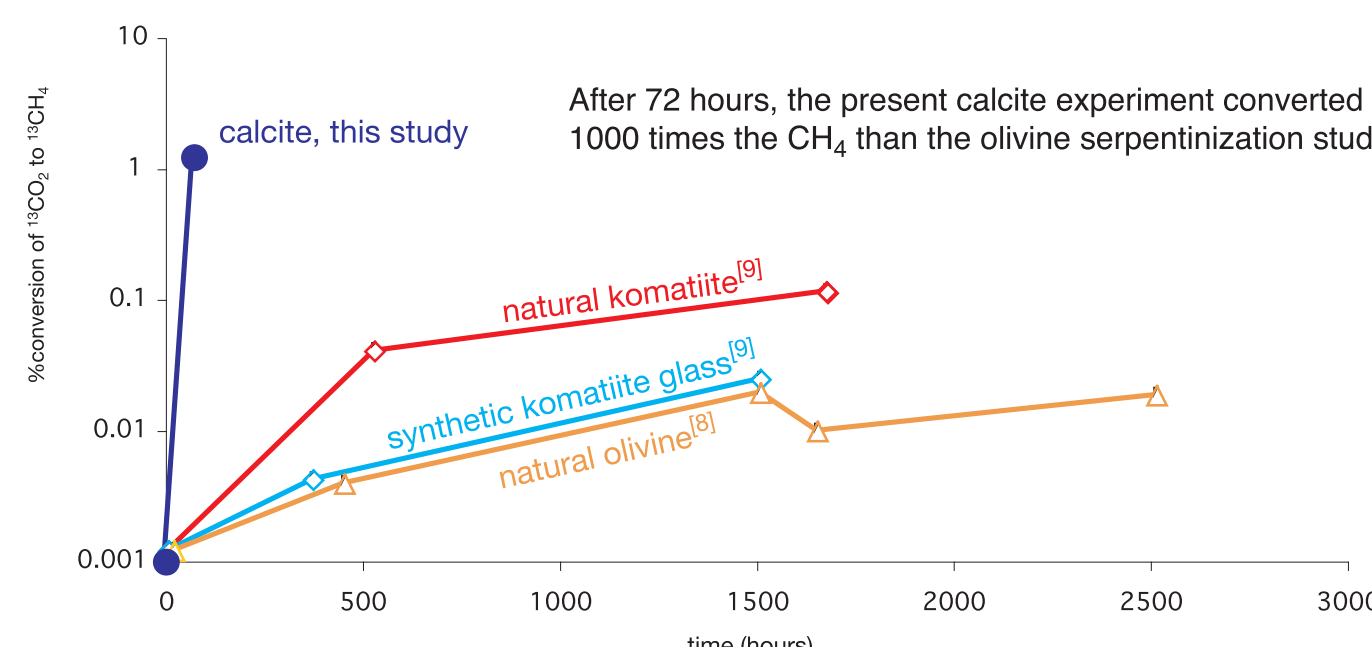
### QUANTITATIVE ANALYSIS

AWA-buffered experiment  
500°C, 10 kbar, 3 days

starting calcite	0.1840 mmoles
<sup>13</sup> CH <sub>4</sub> , 3 days	0.0023 mmoles
[ <sup>13</sup> CH <sub>4</sub> ]	61 mmolal**
%conversion	1.23%
[ <sup>13</sup> CH <sub>4</sub> ]/[ <sup>13</sup> CO <sub>2</sub> ]	~ 10

\*\*For comparison, an olivine serpentinization experiment produced < 0.5 mmolal after two months, 300°C, 350 bar [8]

Comparison of experimental methanogenesis rates between calcite reduction at 500°C, 10 kbar, and formic acid decomposition: at 300°C, 350 bar. Future work: 500°C, 350 bar and 300°C, 10 kbar.



### APPLICATION TO MARS: carbonates are ubiquitous at the surface

The required rate of methanogenesis to maintain the current methane mixing ratio on Mars is 126 metric ton/yr (Atreya et al, 2007). We calculate that the carbon equivalent mass of calcite required to supply this methane is 8x10<sup>5</sup> kg. If carbonates comprise 0.0001 wt% of a 50 km thick Martian crust, then there is enough carbonate to maintain current methane mixing ratios for billions of years. Thus, carbonates are probably not the limiting factor in our hypothesis. Hydrogen, on the other hand, has not been reported on Mars, although the possibilities of serpentinization of the Martian mantle and deep radiolysis [10] remain strong candidates for H<sub>2</sub> sources. The Martian crust is basaltic, so serpentinization--if it is active--is likely to be a relatively deep crustal or upper mantle process. That our experiments were performed at 10 kbar demonstrates that deep methane is possible, although we predict that methanogenesis should also proceed favorably at lower pressures.

### CONCLUSIONS

1. At low *f*O<sub>2</sub>, carbon partitions from calcite to a methane-rich fluid.
2. Hydrothermal reduction of calcite to methane is a rapid process.
3. Such methane may influence the Martian atmosphere if a H<sub>2</sub> source exists.

### REFERENCES

[1] Lyons et al 2005 *GRL* [2] Oze and Sharma 2005 *GRL* [3] McCollom & Seewald 2007 *Chem. Rev.* [4] Horita and Berndt 1999 *Science* [5] Foustoukos and Seyfried 2004 *Science* [6] Atreya et al 2006 *PSS* [7] Sleep et al 2004 *PNAS* [8] McCollom and Seewald 2001 *GCA* [9] Lazar et al in prep [10] Lin et al 2005 *GCA*