

## Isotopic fractionation of methane in the stratosphere and its effect on free tropospheric isotopic compositions

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**Abstract.** Kinetic isotope effects (KIEs) for the oxidation of CH<sub>4</sub> by OH, Cl, and O(<sup>1</sup>D) were incorporated into a 2D model of the atmosphere to examine how sensitive the carbon isotopic composition of CH<sub>4</sub> in the free troposphere is to three influences: realistic stratospheric chemistry and transport, tropospheric Cl chemistry, and use of new, experimentally-determined KIEs for the OH and O(<sup>1</sup>D) sinks. At steady-state, our results indicate that stratospheric chemistry and transport enrich tropospheric δ<sup>13</sup>CH<sub>4</sub> by 0.5 to 0.6‰, tropospheric Cl chemistry as modeled enriches δ<sup>13</sup>CH<sub>4</sub> by ~0.3‰, and the new KIE for the OH sink depletes modeled global δ<sup>13</sup>CH<sub>4</sub> by >1‰. Ignoring the stratosphere (and Cl chemistry in general) in models therefore happens to partially compensate for use of the previously accepted KIE for OH when comparisons with observations of free tropospheric δ<sup>13</sup>CH<sub>4</sub> are made. In contrast, including only one of these influences increases the error relative to including none. Thus, all 3 effects are of sufficient magnitude to warrant their inclusion in inverse models in order to reduce uncertainties in the CH<sub>4</sub> budget.

### Introduction

Over the past 200 years, methane mixing ratios in the troposphere have more than doubled from 0.7 to 1.78 ppmv [e.g., Etheridge *et al.*, 1998], reflecting changes in its sources and/or sinks. Uncertainties in the global distributions and strengths of the sources of this chemically and radiatively important trace gas render predictions of how anthropogenic activities and climate change may alter the amount of CH<sub>4</sub> in the atmosphere that much more uncertain [e.g., Houweling *et al.*, 1999].

Because the different sources of CH<sub>4</sub> (e.g., wetlands, rice paddies, termites, natural gas escape, etc.) have distinct <sup>13</sup>C/<sup>12</sup>C ratios (or δ<sup>13</sup>C values, where δ<sup>13</sup>C = [(<sup>13</sup>C/<sup>12</sup>C)<sub>sample</sub> - (<sup>13</sup>C/<sup>12</sup>C)<sub>standard</sub>] / (<sup>13</sup>C/<sup>12</sup>C)<sub>standard</sub> \* 1000), measurements of δ<sup>13</sup>C of CH<sub>4</sub> in the troposphere, along with CH<sub>4</sub> mixing ratios, have been used to constrain inverse models that attempt to deduce individual source strengths and their spatial and temporal distributions [e.g., Fung, *et al.*, 1991 (FUNG91); Hein and Crutzen, 1997 (HEIN97)]. Current uncertainties in individual source strengths from inverse models are estimated to be as

large as 50% [HEIN97], due in part to sparse measurements of δ<sup>13</sup>CH<sub>4</sub>. Long-term observations of δ<sup>13</sup>CH<sub>4</sub> at the surface are becoming increasingly available [e.g., Quay *et al.*, 1999], however, which should decrease uncertainties due to undersampling of the atmosphere.

In addition, all of the various CH<sub>4</sub> sinks are now known to have substantial kinetic isotope effects (KIEs), some of which have not been included in earlier inverse models or may not be included accurately in more recent models. Oxidation of CH<sub>4</sub> by OH, Cl, and O(<sup>1</sup>D) accounts for ~95% of the total sink. Because the rate constants for the <sup>12</sup>CH<sub>4</sub> isotopomer are larger than those for <sup>13</sup>CH<sub>4</sub> (i.e., [k<sup>12</sup>CH<sub>4</sub>/k<sup>13</sup>CH<sub>4</sub>] > 1), the isotopic composition of the remaining CH<sub>4</sub> in the atmosphere becomes heavier as CH<sub>4</sub> is oxidized. The discovery of a surprisingly large KIE in the reaction of Cl with CH<sub>4</sub> [Saueressig *et al.*, 1995; see Table 1] motivated research into CH<sub>4</sub>'s stratospheric sinks [e.g., Bergamaschi *et al.*, 1996 (BERG96); Gupta *et al.*, 1996 (GUPTA96)] due to the abundance of atomic Cl in the CFC-perturbed stratosphere. Observations and 2D models indicate that Cl accounts for approximately 15% of the total CH<sub>4</sub> oxidation in the stratosphere [Sugawara *et al.* 1997 (SUGA97); BERG96]. Even a relatively small flux of this <sup>13</sup>C-enriched CH<sub>4</sub> into the troposphere could alter the balance of sources and sinks derived by inverse models that do not include this stratospheric effect. In this study, we examine the influence of chlorine chemistry, as well as the significance of newly measured KIEs for OH and O(<sup>1</sup>D), on the carbon isotopic composition of CH<sub>4</sub> in the free troposphere. These results are then used to assess whether their inclusion in inverse models has the potential to significantly alter the magnitude or distribution of deduced CH<sub>4</sub> sources.

### Model Details and Rate Coefficients

The LLNL 2D chemical-radiative-transport model calculates zonally averaged distributions of chemically active trace species in the troposphere and stratosphere and has been used in numerous ozone assessment studies [e.g., Kinnison *et al.*, 1994; WMO, 1999]. The processes represented include (a) thermal kinetic chemical reactions with rate constants based on climatological zonal temperature distributions, (b) photolytic chemical reactions, (c) advection and diffusion driven by climatological zonal average temperature, radiative transfer of energy, and orographic forcing, (d) surface emission and in situ production of active trace constituents, and (e) removal of active species by dry and wet deposition. For this application, the model treats 63 chemically active species in 188 photochemical reactions without using "family" chemistry. The model domain extends from pole to pole and from the surface to 85 km. The horizontal resolution is 5° in latitude, and the vertical coordinate is logarithmic in pressure with an approximate resolution of 1.5 km.

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**Table 1.** Experimentally-determined carbon kinetic isotope effects (KIEs) for gas-phase CH<sub>4</sub> sinks

Reaction	KIE (k <sub>12</sub> /k <sub>13</sub> )	Reference
CH <sub>4</sub> + Cl	1.043exp(6.455/T)	Saueressig <i>et al.</i> [1995]
CH <sub>4</sub> + OH	a) 1.0054: (273-353K)	a) Cantrell <i>et al.</i> [1990]
	b) 1.0039: (296K)	b) Saueressig <i>et al.</i> [1999]
CH <sub>4</sub> + O( <sup>1</sup> D)	c) 1.001: (297K)	c) Davidson <i>et al.</i> [1987]
	d) 1.011: (296K)	d) Saueressig <i>et al.</i> [1998]

For this study, isotope-specific reaction rate coefficients for CH<sub>4</sub> oxidation (Table 1) were incorporated into the model. Recently, both experiment [Crowley *et al.* 1999, Tyler *et al.* 2000] and theory [Roberto-Neto *et al.* 1998] have yielded similar values to that of Saueressig *et al.* [1995] for the KIE for Cl+CH<sub>4</sub>. In contrast, the most recent experimentally-determined KIEs for OH and O(<sup>1</sup>D) fall outside the margin of error for the previous KIEs used in atmospheric models and have not yet been confirmed by additional experiment [Saueressig, *et al.*, 1998; 1999]. (The decrease in the OH KIE and the increase in the O(<sup>1</sup>D) KIE are related in that OH was generated in the experiments by O(<sup>1</sup>D)+H<sub>2</sub>O.) Like Cl, the KIE for OH is expected to depend on temperature but has not yet been determined at temperatures of importance in all regions of the atmosphere. To isolate the effects of using the more recent OH and O(<sup>1</sup>D) KIEs as well as inclusion of a realistic stratosphere on predictions of surface δ<sup>13</sup>CH<sub>4</sub>, 5 scenarios using differing combinations of KIEs (detailed below) were run and compared.

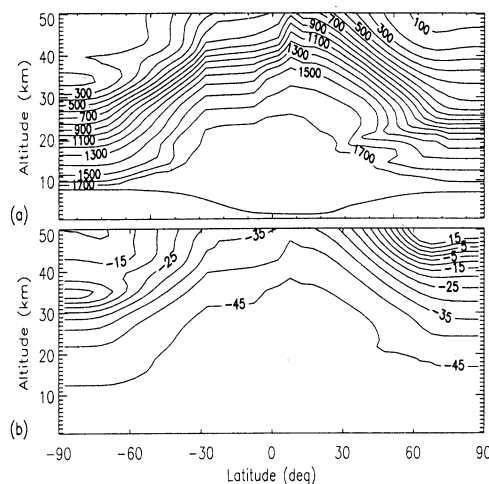
Each scenario began with the same initial conditions. Surface CH<sub>4</sub> fluxes were chosen to give mixing ratios of ~1800 ppbv at the surface for a total flux of 535 Tg/yr (an average from FUNG91 and HEIN97). A uniform value for δ<sup>13</sup>CH<sub>4</sub> of -52.16‰ (on the PDB scale) for the surface sources was used, as in GUPTA96. Each scenario was run for 50 years, at which point the values for δ<sup>13</sup>CH<sub>4</sub> for all grid cells had converged to steady-state to within 0.005‰/yr. Atomic Cl concentrations were simulated using a 1990 chemical inventories emission set; current CFC levels are about 10% higher [WMO, 1999]. The soil sink for CH<sub>4</sub>, with a KIE of 1.012 to 1.025 [Snober, *et al.*, 2000], is not included. Because we are examining the relative δ<sup>13</sup>CH<sub>4</sub> changes when the gas-phase KIEs for the sinks are altered and when the stratospheric Cl sink is included or excluded, lack of a soil sink will not affect interpretation of the differences in δ<sup>13</sup>CH<sub>4</sub> between the scenarios.

A number of sensitivity studies were run. Altering the KIE for Cl within measured uncertainty (1.043±0.25

**Table 2.** KIEs for scenarios testing the relative effect on δ<sup>13</sup>CH<sub>4</sub> in the free troposphere

Scenario	KIE for CH <sub>4</sub> + OH	KIE for CH <sub>4</sub> + Cl	KIE for CH <sub>4</sub> + O( <sup>1</sup> D)
1	1.0054	1.043exp(6.455/T)	1.001
2	1.0054	1 (strat only) <sup>a</sup>	1.001
3	1.0054	1 (trop and strat) <sup>a</sup>	1.001
4	1.0039	1.043exp(6.455/T)	1.011
5	1.0039	1 (strat only) <sup>a</sup>	1 (strat only) <sup>a</sup>

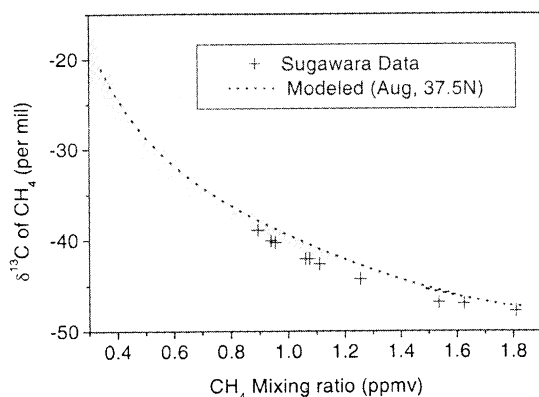
<sup>a</sup> For KIEs of "1," the fractionation was removed in the stratosphere ("strat only") or in both the troposphere and stratosphere ("trop and strat").

**Figure 1.** (a) Modeled CH<sub>4</sub> mixing ratios for August in ppbv. (b) Modeled δ<sup>13</sup>CH<sub>4</sub> for August in ‰ (PDB-scale) using the KIEs of scenario 1.

exp([6.455±6]/T)) had little effect on modeled δ<sup>13</sup>CH<sub>4</sub> throughout the stratosphere (< 0.5‰), but larger changes resulted in significant departures from the observed δ<sup>13</sup>CH<sub>4</sub>:CH<sub>4</sub> relationship from SUGA97. Using the KIE for OH of 1.010 from Davidson *et al.* [1987] showed marked disagreement with stratospheric observations. Importantly, changes in the OH KIE as small as 0.0001 led to significant (~0.1‰) changes in calculated free tropospheric δ<sup>13</sup>CH<sub>4</sub>. Altering the source fluxes to reflect more realistic latitudinal gradients in both isotopic composition and source strength did not change the relative δ<sup>13</sup>CH<sub>4</sub> differences between scenarios at steady-state in the free troposphere, as expected given the rudimentary eddy diffusion-dominated tropospheric transport in the model. As an additional check on the model results for the influence of the stratosphere on δ<sup>13</sup>CH<sub>4</sub> in the troposphere, a simple box model was used. In an analysis similar to Luz *et al.* [1999] for the flux of heavy stratospheric CO<sub>2</sub> to the troposphere, we estimated the flux of heavy CH<sub>4</sub> using the observations of SUGA97 and calculated strat-trop mass fluxes. Box model results for relative δ<sup>13</sup>CH<sub>4</sub> changes between the scenarios agreed with the 2D model results to within ± 0.15‰.

## Model Scenario Descriptions

Five scenarios, differing in the magnitudes and/or location of the KIEs for CH<sub>4</sub> oxidation, were chosen to test the sensitivity of free tropospheric δ<sup>13</sup>CH<sub>4</sub> to 3 influences: realistic stratospheric chemistry and transport, tropospheric Cl chemistry, and use of the new KIEs for OH and O(<sup>1</sup>D) (Table 2). Scenario 1 incorporates the KIEs used in recent 2D model efforts, with BERG96 concentrating on the stratosphere only and GUPTA96 and Tyler *et al.* [1999] focusing on the troposphere. In scenario 2, we set the KIE for Cl to 1 in the stratosphere. The difference in free tropospheric δ<sup>13</sup>CH<sub>4</sub> at steady-state between scenarios 1 and 2 thus represents the influence of stratospheric Cl chemistry on tropospheric CH<sub>4</sub> in our model (see results below). The 2D model results of GUPTA96 showed that Cl in the troposphere may also influence free tropospheric δ<sup>13</sup>CH<sub>4</sub> (e.g., through Cl chemistry in the marine boundary layer (MBL)). To quantify this effect in our model, we set the KIE for Cl to 1 in scenario 3 in both



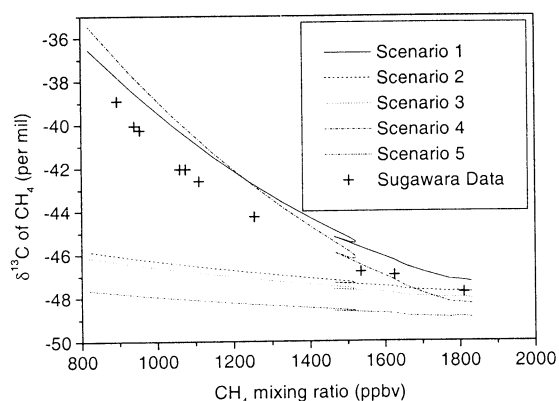
**Figure 2.**  $\delta^{13}\text{C}_4$  (‰) versus  $\text{CH}_4$  (ppmv) from model results (dotted line) and from high altitude balloon flights at  $38^\circ\text{N}$  in August 1993 (+) [Sugawara *et al.*, 1997], which are the only stratospheric observations available for  $\text{CH}_4 < 1.6$  ppmv. Shaded area represents the total range of monthly stratospheric variability for all model latitudes pole-to-pole.

the troposphere and the stratosphere. Importantly, scenario 3 also represents the set of KIEs used in inverse modeling efforts that pre-date the discovery of the large KIE for Cl [*e.g.*, FUNG91].

To investigate the significance of the recent changes in the KIEs for OH and  $\text{O}(^1\text{D})$ , scenario 4 was run. Comparison with scenario 1 yields the magnitude of their effects on predicted  $\delta^{13}\text{C}_4$ . In scenario 5, we set the KIEs of both Cl and  $\text{O}(^1\text{D})$  to 1 in the stratosphere. Thus, comparing free tropospheric  $\delta^{13}\text{C}_4$  from scenario 5 with that from scenario 4 yields the overall influence of stratospheric Cl and  $\text{O}(^1\text{D})$ . Finally, the difference in tropospheric  $\delta^{13}\text{C}_4$  between scenarios 5 and 4 compared to the difference between scenarios 2 and 1 gives the magnitude of the  $\text{O}(^1\text{D})$  KIE contribution to tropospheric  $\delta^{13}\text{C}_4$ , which in turn yields an estimate of the effect of the new OH KIE alone.

## Results and Discussion

Modeled  $\text{CH}_4$  and  $\delta^{13}\text{C}_4$  are shown in Figure 1 as a function of altitude and latitude. Mixing ratio contours in the stratosphere compare well with satellite observations [*e.g.*, Park *et al.*, 1999]. As expected,  $\delta^{13}\text{C}_4$  increases as  $\text{CH}_4$  is



**Figure 3.**  $\delta^{13}\text{C}_4$  (‰) versus  $\text{CH}_4$  mixing ratios (ppbv) in August for the 5 model scenarios in Table 2. Crosses are observations from Sugawara, *et al.* [1997] as in Figure 2.

**Table 3.** Relative differences (Row Scenario – Column Scenario) in free tropospheric  $\delta^{13}\text{C}_4$  in ‰

Scenario	1	2	3	4	5
1	NA	0.50	0.77	1.02	1.62
2		NA	0.27	0.52	1.12
3			NA	0.25	0.85
4				NA	0.60
5					NA

oxidized. The difference between tropospheric and stratospheric  $\delta^{13}\text{C}_4$  is large, ranging from 1‰ near the tropopause to 50‰ in the upper stratosphere. Due to the paucity of  $\delta^{13}\text{C}_4$  observations in the stratosphere, a comparison of model results with observations is most easily made by plotting  $\delta^{13}\text{C}_4$  versus  $\text{CH}_4$  at approximately the same latitude and time of year (Figure 2). The shape of the modeled relationship is similar to the observations, although there is an offset of  $\sim 1\%$ . Given the simple troposphere in our 2D model, making the average global source of  $\text{CH}_4$  lighter by 1‰ would bring closer agreement in absolute values. However, since it is the shape of the stratospheric  $\delta^{13}\text{C}_4:\text{CH}_4$  relationship that strongly depends on the relative oxidation rates by OH, Cl, and  $\text{O}(^1\text{D})$  and the associated KIEs (*e.g.*, Figure 3), and since our concern here is to compare the relative isotopic compositions between model scenarios and not their absolute values, we chose not to vary arbitrarily the global average source of  $-52.16\%$  simply to match the balloon data. In addition, systematic errors as large as 1.5‰ in the stratospheric measurements may exist [SUGA97].

From a comparison of the  $\delta^{13}\text{C}_4:\text{CH}_4$  relationships for the 5 scenarios (Figure 3), it is clear that only those with a large KIE for Cl in the stratosphere (1 and 4) capture the steep curvature of the observed  $\delta^{13}\text{C}_4:\text{CH}_4$  relationship, as shown previously [SUGA97; BERG96]. By comparing free tropospheric  $\delta^{13}\text{C}_4$  (*i.e.*, at  $\sim 1800$  ppbv  $\text{CH}_4$ ) from scenarios 2 and 1, we further conclude that transport of heavy  $\text{CH}_4$  from the stratosphere enriches tropospheric  $\text{CH}_4$  by 0.5‰ at steady-state (Table 3). Importantly, 0.5‰ is comparable to both the north-south gradient in  $\delta^{13}\text{C}_4$  (0.5‰) and the seasonal amplitude in  $\delta^{13}\text{C}_4$  at high northern latitudes (0.4‰) [Quay *et al.*, 1999]. The magnitudes of the latitude gradient and seasonal amplitudes serve as critical constraints for inverse models. Therefore, input of heavy  $\text{CH}_4$  from the stratosphere (or lack thereof) could alter deduced source strengths if not accurately modeled. While newer inverse models may contain a highly parameterized stratospheric input [HEIN97], the fact that transport from the stratosphere also exhibits a strong dependence on season and latitude [*e.g.*, Holton *et al.*, 1995] could serve to amplify (or, in some cases, dampen) the influence of stratospheric Cl chemistry on  $\delta^{13}\text{C}_4$  in the free troposphere. For example, taking the higher mass flux through the northern hemisphere (NH) stratosphere into account might exacerbate the deduced source strength differences between the NH and SH. Likewise, a larger flux of heavy  $\text{CH}_4$  from the NH stratosphere in March/April/June might amplify the underlying seasonal maximum in  $\delta^{13}\text{C}_4$  due to seasonal source strength variations. To further explore the potential influence of the seasonal and latitude dependence of stratospheric transport on  $\delta^{13}\text{C}_4$ , however, a 3D model of the troposphere and stratosphere is required.

The effect of tropospheric Cl on  $\delta^{13}\text{C}_4$  can be isolated in our model by comparing scenarios 2 and 3:  $\text{CH}_4$  in the troposphere is heavier at steady-state by 0.27‰, a value

similar to that calculated by GUPTA96. Our result is an estimate based solely on gas phase chemistry. Recently, measurements in the marine boundary layer (MBL) and at the air-snow interface have implicated heterogeneous chemistry in creating large atomic Cl concentrations which are both highly uncertain and highly variable in time and space, with estimates ranging from  $\sim 10^2$  to  $10^5$  atoms/cm<sup>3</sup> [Wingenter *et al.*, 1999; Spicer *et al.*, 1998; Impey *et al.*, 1997]. These values are comparable to or much larger than those in our model. Modeling heterogeneous Cl chemistry in the troposphere on a global scale will clearly be a challenge, yet it is clear that even Cl concentrations orders of magnitude smaller than OH can significantly fractionate tropospheric CH<sub>4</sub> on a global scale.

While including the large KIE for Cl in both the stratosphere and troposphere enriches tropospheric  $\delta^{13}\text{C}$  by  $\sim 0.8\%$ , the new, smaller KIE for OH will make predicted  $\delta^{13}\text{C}$  values lighter. Comparison of scenario 4 with 1 shows that the new OH and O(<sup>1</sup>D) KIEs deplete predicted steady-state  $\delta^{13}\text{C}$  by 1.02 ‰. A comparison of scenarios 4 and 5 reveals that the recent O(<sup>1</sup>D) KIE of 1.011, while affecting upper stratospheric  $\delta^{13}\text{C}$  significantly, enriches tropospheric  $\delta^{13}\text{C}$  by only 0.1‰. Thus, the effect of the new OH KIE is to decrease modeled tropospheric  $\delta^{13}\text{C}$  by 1.1‰. A global isotopic shift this large in modeled  $\delta^{13}\text{C}$  in the free troposphere has the potential to result in a significant alteration of the deduced CH<sub>4</sub> sources in inverse models that use observations of  $\delta^{13}\text{C}$  to constrain these sources and their distribution. Reducing the experimental uncertainty in the OH KIE is therefore critical to reducing uncertainties in the methane budget.

## Conclusions

Results from the incorporation of carbon KIEs for the oxidation of CH<sub>4</sub> by Cl, OH, and O(<sup>1</sup>D) into the LLNL 2D model indicate that chlorine chemistry in both the stratosphere and troposphere, as well as a small decrease in the KIE for OH+CH<sub>4</sub>, can significantly alter the predicted isotopic composition of free tropospheric CH<sub>4</sub>. These effects, in turn, may alter the magnitudes and/or distributions of CH<sub>4</sub> sources deduced from inverse modeling studies that do not include them. Including the large KIE for Cl in the troposphere and stratosphere enriches modeled  $\delta^{13}\text{C}$  in the free troposphere by  $\sim 0.8\%$ , using the new O(<sup>1</sup>D) KIE enriches it by 0.1‰, while using the new KIE for OH depletes it by 1.1‰. By chance, earlier inverse models that pre-date knowledge of both the Cl KIE and the potential new OH KIE [e.g., FUNG91] may be less in error (at steady-state) than more recent models that include Cl chemistry [e.g., HEIN97] but for the wrong reasons. Moreover, temporal trends in Cl and OH levels will affect  $\delta^{13}\text{C}$  differently if long time series of measurements (e.g., firn air or ice core data) are examined. Clearly, given the magnitude of our model results, inverse model studies should use, to the extent possible, as complete a description of chlorine chemistry and the most accurate KIEs as they become available in order to decrease uncertainties in deduced CH<sub>4</sub> source strengths and their distribution.

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