The Ozone Deficit in the Stratosphere and Mesosphere

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Abstract

Modifications were made to a photochemical model to try to correct its predictions of O3, OH, HO2 and ClO concentrations in the stratosphere and mesosphere. Both these regions of the atmosphere were examined to see if the modifications would improve the simulations in both areas. The rate of the reaction of HO2+O→OH+O2 was reduced by 40%. The reaction ClO+OH→HCl+O2 was added to the model at 0%, 4% and 6% branching ratios. A new rate constant for ClO+OH→products, k(T)=(8.9±2.6)×10^{-12} exp(295±90/T) (Kegley-Owen et al., 1999), was also examined. Although these significantly improved model results for concentrations of ClO, OH, HO2 and O3 in the stratosphere and mesosphere, they did not completely resolve discrepancies between the model predictions and measurements.

Introduction

There has been increased concern over the amount of O3 in the stratosphere ever since the ozone hole was discovered in the mid-1970’s (Collins, 1998). Anthropogenic releases of chemicals containing chlorine were determined to be responsible for the ozone hole and have been suggested as a cause of ozone depletion throughout the stratosphere (Molina and Rowland, 1974). Computer models have been used to predict the effects of such chemicals in the atmosphere. However, these models have consistently underestimated the concentration of ozone in the stratosphere and mesosphere. In the stratosphere, the models have under-predicted ozone production by 10-30% (Siskind et al., 1995). This problem has come to be known as the “ozone deficit”, which was first identified in 1983 (Solomon et al., 1983).

The mesosphere, the area of the atmosphere from about 50-85 km (Brasseur and Solomon, 1986), is sometimes called the “ignoro-sphere” (Pearce, 1999) due to the lack of scientific interest in it and the difficulty in obtaining measurements of chemicals in this region. It is too high for balloon based measurement and too low for satellite measurement. However, scientists are now becoming more aware of its importance. It may be showing some of the first consequences of increases in greenhouse gases. As greenhouse gases absorb more of the back-radiation from Earth, there is less radiation available to heat the mesosphere. Already, the mesosphere has cooled by up to one degree a year for the past thirty years (Pearce, 1999). In some places, the top of the mesosphere has dropped up to 8 km in altitude as it cools and therefore contracts (Pearce, 1999).

Another reason that the mesosphere must be considered in an analysis of the ozone deficit is that the chemistry of the mesosphere is thought to be relatively simpler. If the chemistry used in the mesospheric models is wrong, then models of the lower areas of the atmosphere are probably incorrect also (Pearce, 1999).

Photochemical models also inaccurately predict other chemicals. An HO2 deficit has also been noted in the stratosphere (Jucks et al., 1998), the area of the atmosphere from about 20 km to 50 km (Brasseur and Solomon, 1998), and in the mesosphere (Sandor and Clancy, 1998). An OH model over-prediction in the mesosphere has also been noticed (Sandor and Clancy, 1998). The discrepancies between measured and modeled results are most likely due to the
uncertainties within the models. There can be uncertainties of 20-40% (Jucks et al., 1996) in the rates of the reactions in the model. There can also be reactions that are not included in the model because they are not thought to be significant in the atmosphere. Uncertainties also propagate into the models through the uncertainties in the inputs. These various sources of uncertainties have been explored in order to correct the models.

Since it was first discovered, the mesospheric ozone deficit in models has been resolved through the 40% reduction of the rate of the reaction

\[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]  \hspace{1cm} (1)

(Sandor and Clancy, 1998). This also solved the HO\textsubscript{2} and OH discrepancies in the mesosphere. However, no OH surplus is evident in the stratosphere, and this change made model predictions of OH worse in the stratosphere (Jucks et al., 1998).

ClO has also been overestimated by models which suggests a problem with ClO chemistry also (Khosravi et al., 1998). There are two pathways for the reaction ClO + OH:

\[ \text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2 \]  \hspace{1cm} (2)

\[ \text{ClO} + \text{OH} \rightarrow \text{HO}_2 + \text{Cl} \]  \hspace{1cm} (3)

At first it was thought that reaction (2) did not occur at all. However, more recent studies indicate that there is a small branching ratio of 5\pm2\% for reaction (2) (Lipson et al., 1995). Lipson et al. (1995) also suggests a 6\% branching ratio of reaction (2) at stratospheric temperatures. Adding reaction (2) in a small branching ratio reduces the ozone deficit in the stratosphere (Jucks et al., 1996), yet it has little effect on ozone in the mesosphere due to the lower concentrations of ClO in that area (Brasseur and Solomon, 1986). This is due mainly to the fact that in the mesosphere reactive HO\textsubscript{x} species are the dominant chemical species with respect to ozone loss whereas in the stratosphere, Cl\textsubscript{x}, or reactive chlorine becomes a more important sink for ozone destruction (Brasseur and Solomon, 1986).

Adding the branching ratio alone or reducing the rate of reaction (1) alone does not solve the model ozone deficit in both areas (Siskind et al., 1996). However, using both the 40\% reduction in reaction (1) and a 6\% branching ratio of reaction (2), Khosravi et al. (1998) were able to decrease the ozone deficit in the stratosphere and bring [ClO] (the brackets denote concentration of, e.g. the concentration of ClO) predictions into good agreement.

Kegley-Owen et al. (1999) reported a new rate constant for the reaction ClO+OH\rightarrow products of k(T)=(8.9\pm2.6) \times 10^{-12} \exp(295+90/T). In their study, the ClO concentration was determined by its absorption spectrum rather than by titration (Kegley-Owen et al., 1999). The previous rate constant recommended in DeMore et al. (1997), hereafter referred to as JPL-97, was k(T)=1.1 \times 10^{-11} \exp(120+150/T). A faster rate for ClO+OH\rightarrow products could give better results for predictions of the concentrations of the chemicals ClO, O\textsubscript{3}, HO\textsubscript{2} and OH. Since the rate of a reaction is equal to the rate constant times the concentrations of reactants, increasing the rate constant increases the rate of the reaction. The Kegley-Owen et al.
(1999) rate constant actually produces a faster rate over the temperature range involved due to the increased temperature dependency (Figure 1).

Methods

The model used was a time-dependent photochemical model (Siskind et al., 1995) developed by Rusch and Eckman (1985). It extends from 36-82 km with an altitude step of 2 km and contains 84 reactions. It is one dimensional, meaning it predicts chemicals at different altitudes at a certain latitude and longitude. The reaction rates were updated to those recommended in JPL-97 except for the experimental variations when one or two of the reaction rates were varied (Table 1). Since the model does not include horizontal transport, results for ozone are less accurate above 82 km and below 40 km since outside of these altitudes ozone has a long enough lifetime for transport to take affect.

Inputs to the model were [H$_2$O], [CH$_4$], [Cly], [NOx], latitude, longitude and the date. [H$_2$O] and [CH$_4$] must be input into the model because their lifetimes are long enough that horizontal transport, which the model does not include, must be taken into consideration for them. The model does include vertical transport. The total reactive odd nitrogen, which is defined in the model as [NOx]=([NO]+[NO$_2$]), was not varied for different model runs. This was set to a mixing ratio of 1.5 x 10$^5$. However, the set value of total reactive chlorine, or Cly, which was defined as [Cly]=[HCl]+[ClO]+[Cl], was changed due to the increase of Cly from anthropogenic sources over time. The values used for the [Cly] were the [HCl] values reported in Muller et al. (1999) on pg. 6.20 since HCl is the dominant component of Cly above 55 km (Muller et al., 1999).

The model predictions were compared to [O$_3$], [OH], and [HO$_2$] measurements presented in Jucks et al. (1998), [OH] measurements presented in Summers et al. (1997a), [O$_3$] and [ClO] measurements presented in Hartman et al. (1996), and [ClO] measurements presented in Michelsen et al. (1996). The altitude uncertainty for the measurements in Hartman et al. (1996) of ozone was estimated to be ±0.3 km and the altitude uncertainty in the Summers et al. (1997a) article was also estimated to be ±0.3 km. The altitude uncertainties in all the other measurements were the uncertainties reported in the articles.

The water profile for the models in Figure 8 was from the [H$_2$O] measurements presented in Summers et al. (1997a) between 52-76 km and from Jucks et al. (1998) for 24-50 km (inputs are at 2 km intervals from 24-82 km). Above 76 km the water profile was a log extrapolation. The methane profile was interpolated from Summers et al. (1997b) from 24-70 km and 72-82 km was a log extrapolation. The water profile for the models in Figures 7, 9 and 10 was from Jucks et al. (1998) for 24-50 km, and Summers et al. (1997b) for 52-76 km and from 78-82 km was a log extrapolation. The methane profile for Figures 7, 9 and 10 was interpolated from Summers et al. (1997b) between 24-70 km and a log extrapolation from 72-82 km. For the models in Figure 11, the methane profile was from Abbas et al. (1996a) from 24-34 km and Abbas et al. (1996b) for 36-66 km and a log extrapolation between 68-82 km. The water profile was from Abbas et al. (1996b) from 24-66 km and from Summers et al. (1997b) for 68-78 km. From 80-82 km it was a log extrapolation. The water profile for Figures 6 and 12 was from Hartman et al.
(1996) between 24 and 80 km and a log extrapolation at 82 km. The methane profile for the models in Figures 6 and 12 was from Abbas et al. (1996a) for 24-34 km and Abbas et al. (1996b) for 36-66 km and for 68-82 km was a log extrapolation.

The log extrapolations do not have a great effect on the results of this study since the water profiles from measurements all extended up into the areas being compared. Above the height being compared, the water does not have a great effect on the results. Any comparisons made above the height of the log extrapolations have an additional uncertainty associated with them. The methane log extrapolations also do not have a great effect even though they occur slightly lower down due to the small effect of methane in the areas being studied.

The model runs were done at the same latitude and date, or a latitude and date well within the domain of the measurements, as the measurements being compared to. Longitude was not changed since this does not have a big effect on the model results. The time of day the results were plotted at correspond to the time of day of the measurements, or the results were plotted as daytime averages if the measurements were reported as such. Figures 6 and 12 are from models using March 24, 1992 as the input date. However, the measurements in these figures are averages for between these the dates March 24, 1992 and April 2, 1992 (Hartman et al., 1996).

A date in the middle of these dates would normally be used. However due to an error in calculating the date, March 24, 1992 was used instead. This does not have a great effect on the results due to the fact that, as said before, the measurements were the average over all of the days and the predictions of the model do not change greatly over the course of a few days.

For each set of measurements, a model using the rates recommended in JPL-97 was run. A model with the rate of reaction (1) reduced 40% was made, then a model including the 6% branching ratio as recommended by Khosravi et al. (1998). The rate constant of the reaction \( \text{ClO} + \text{OH} \rightarrow \text{products} \) was then changed to the Kegley-Owen et al. (1999) reported value and model runs were done at a 0%, 4%, and 6% branching ratio of reaction (2). Except for the standard model, all models used a 40% reduced rate for reaction (1) (Table 1).

**Results**

Figures 2, 3, 4 and 5 show comparisons of the standard model used in this study with the standard models presented in the Jucks et al. (1998), Summers et al. (1997a), Jucks et al. (1998) and Michelsen et al. (1996) respectively. They show that the model used in the study closely resembles other chemical models. Some discrepancy is expected since the models have varying inputs. Also, the model used in Michelsen et al. (1996) obviously could not contain the updated JPL-97 reaction rates.

**Ozone**

Figure 6 shows that the standard model under-predicts \( [O_3] \) by 26% at 40 km and 11% at 46 km. The other models resolve the deficit up to 42 km with model E only 4% off from the measurement and within the uncertainty of the measurement at 40 km. Although model E under-predicts \( [O_3] \) by only 13% at 46 km, this is still a significant reduction in the \( [O_3] \) deficit.
However, the models clearly over-predict [O\textsubscript{3}] in the mesosphere. Although this maybe due to the transport of water, which affects the input file, it may also indicate that there are problems with the model.

However, Figure 7 does not show this problem with [O\textsubscript{3}] in the mesosphere from another set of measurements. It shows that all the models predict [O\textsubscript{3}] within the uncertainty of the measurements. However, at 50 km the standard model produces a 27% [O\textsubscript{3}] deficit, which rises to a 36% deficit at 40 km. The other models are much closer to the values of [O\textsubscript{3}] and model E produces only a 19% deficit at 40 km.

OH

All of the models over-predict [OH] at altitudes above 48 km (Figure 8). The measurements used in the Figures 8 and 9 are from Jucks et al. (1998) up to 38 km. The measurements at 49 km and above are from Summers et al. (1997a). Between this area are measurements estimated from Conway et al. (1999). These sets were merged to create a profile of [OH] across the stratospause. The model runs correspond to the time of the Summers et al. (1997a) measurements.

The Conway et al. (1999) measurements bear some discussion. The measurements reported in Jucks et al. (1998) were made by a balloon borne instrument that took the measurements at an altitude of 38 km. The measurements made by the instrument above this altitude were fitted to the shape of an [OH] profile, which was later determined to be incorrect (Conway et al., 1999). The measured values of [OH] in Figure 5 between 40 and 48 km are those then estimated from the profile shape recommended in Conway et al. (1999) with the error being the same size as the other measurements from the balloon measurement.

Above 50 km, models A, B, C, D, and E become indistinguishable (figure 8). However, they all predict [OH] more accurately than the standard model. This shows that a 40% reduction in reaction (1) gives better predictions of [OH] in the mesosphere. It also shows that adding reaction (2) will not affect [OH] in this area. At 68 km, the standard model over-predicts OH density by 68%, while model E only over-predicts it by 34%. In the stratosphere, these models also predict [OH] within the measured uncertainty up to 40 km with model E matching the measurements and the standard model is off by 26% at this altitude. However, from 44 km to 54 km the standard model gives the best values for [OH], only being 4% off from the measurements whereas model E is 26% low.

Figure 9 is for models run at the same date, latitude and time as the Jucks et al. (1998) measurements. It again shows that the standard model over-predicts [OH] by 56% at 68 km while model E is only 23% high. The standard model is off by 47% at 54 km, and model E is again only 23% high. However, at lower altitudes, the standard model becomes better. However, at 40 km it is 12% higher than the measurement while model E is only 10% low.
HO₂

The standard model under-predicted [HO₂] in the mesosphere (Figure 10) as consistent with Jacks et al. (1998). Although the standard model was within the uncertainty of the measurement at 36 km, above this altitude it under-predicted [HO₂] by about 25% while model E was within the uncertainty of the measurements and never off by more than 5%. Reducing the rate of reaction (1) by 40% brought the models into agreement with the measurements. This shows that changing the rate of reactions (2) and (3) and changing the branching ratio of these pathways in addition to reducing the rate of reaction (1) will still provide accurate predictions of [HO₂].

ClO

The standard model also over-predicts [ClO] as consistent with Michelsen et al (1996) (Figure 11). It over-predicts [ClO] by 44% at 44 km and 57% at 40 km. Figure 11 shows that reducing reaction (1) alone does not resolve the problem. Adding the HCl+O₂ channel, however, does bring the measured and modeled results into much better agreement. Model E falls into the uncertainty within all but one of the measurements and is 10% high at 44 km. Model B only falls within the uncertainty of the measurements above 43 km as does model D. This shows that model E provides the best predictions of [ClO].

The measurements in Hartman et al. (1996) had large uncertainties so that all of the models fell within it at 45 km with models A and B providing the best match (Figure 12). The standard model was 16% high at 45 km while model E was 21% low. However, at 39 km model E provides the best match between modeled and measured results being only 10% high and within the uncertainty of the measurement. This shows that reducing the rate of reaction (1) by 40% brings [ClO] into better agreement with measurements. Considering both sets of measurements, model E provides the best [ClO] predictions.

Discussion

Reducing the rate of reaction (1) increased the amount of ozone by decreasing the rate of atomic oxygen loss (Figures 6 and 7). Since atomic oxygen rapidly converts to ozone via the reaction O+O₂+M→O₃+M (JPL-97), increasing atomic oxygen increases ozone. Increasing the rate of ClO+OH→products did not have an affect on ozone when there was a 0% branching ratio for reaction (2) (Figure 7). However, when the branching ratio was increased, the faster rate did increases ozone concentrations. Ozone concentrations increases due to there being less ClOₓ, ozone destroying chlorine which is [ClOₓ]=[Cl]+[ClO], available to destroy ozone via the reactions:

\[ \text{Cl}+\text{O}_3 \rightarrow \text{ClO}+\text{O}_2 \]  \hspace{1cm} (4)

\[ \text{ClO}+\text{O} \rightarrow \text{Cl}+\text{O}_2 \]  \hspace{1cm} (5)

When the branching ratio was at 0%, the total amount of reactive chlorine did not change when the rate of ClO+OH→products was changed, it simply changed what form the reactive chlorine
was in. However, increasing the rate of ClO+OH→products when the branching ratio is present increases the rate at which reactive chlorine is converted to inactive chlorine and thus increases ozone concentrations even further.

Figures 8 and 9 show [OH] decreases when the rate of reaction (1) is reduced by 40% since its rate of production via this reaction is decreased, which is expected. Increasing the rate of the reaction ClO+OH→products increased [OH] very slightly, also as expected. It was unexpected, however, that increasing the branching ratio of reaction (2) would increase OH density. This is probably due to the fact that although reaction (2) produces a loss of HOx, [HOx]=([OH]+[HO2]), it also destroys ClOx. ClOx destroys HOx via the reactions:

\[
\text{HO}_2+\text{Cl} \rightarrow \text{HCl}+\text{O}_2
\]

\[
\text{HO}_2+\text{ClO} \rightarrow \text{HOCI}+\text{O}_2
\]

The loss of ClOx and corresponding decreased rate of destruction of HOx actually leads to increased amounts of OH in the region between about 50 and 40 km. It was hoped that the addition of the HCl+O2 channel would increase model [OH] in the stratosphere. Although it increased [OH] by approximately 2% (Figures 8 and 9), this was clearly not enough to completely resolve the discrepancy. Below 40 km, the effect of decreased [ClOx] is overwhelmed by the increased OH production and model E predicts lower [OH] than the standard model (Figures 8 and 9).

The increase of [HO2] with the reduction in reaction (1) was expected since this decreases the rate at which it is lost. Increasing the rate of ClO+OH→products increased it probably by decreasing the amount of OH available to destroy HO2 via the reaction OH+HO2→H2O+O2. Increasing the branching ratio of reaction (2) also increased [HO2] for the same reason as the OH increase: less reactive chlorine available to destroy HOx.

The increase in [ClO] from the reduction in the rate of reaction [1] is most likely from the reduction of [OH] (Figures 11 and 12). Reducing the amount of OH reduces the rate of the reaction HCl+OH→Cl+H2O (Khosravi et al., 1998). The reduced amount of Cl then reduces the amount of ClO produced through reaction (4). Increasing the rate of the ClO+OH→products reactions also decreases [ClO] due to it being lost at a faster rate. Adding the branching ratio also decreases [ClO] by converting reactive chlorine into inactive HCl. This reduces the amount of ClO being produced by reaction (4).

Although the 40% reduction in reaction (1) is supported by this study and others of the stratosphere and mesosphere (Sandor and Clancy, 1998, and Khosravi et al., 1998), most laboratory studies of the rate of reaction (1) do not support such a low rate (JPL-97). Even though there are large uncertainties in the reactions given in JPL-97, the 40% reduction in reaction (1) is still outside of the uncertainty of the JPL-97 recommendation (Sandor and Clancy, 1998). However the recommendation in JPL-97 is based on five studies done at room temperature and temperatures in the stratosphere and mesosphere are much lower (Brasseur and Solomon, 1986). A study done by Hack et al. (1979) was not considered for the JPL-97 recommendation due to an incorrect rate for OH+H2O2→H2O+HO2 (Sandor and Clancy, 1998).
However, when this rate is corrected this study supports the 40% reduction of the rate of reaction (1) (Sandor and Clancy, 1998).

The new rate for reactions (2) and (3) was tried at a 4% branching ratio, which corresponds well to the JPL-97 rate at a 6% branching ratio for all of the species in the study (Orlando and Tyndall, personal communication, 1999) (Figures 6-12). A branching ratio of 6% is consistent with reports by Lipson et al. (1995) of a branching ratio of 5±2%. It is also within the uncertainty for the branching ratio of 0-14% given in JPL-97. However, the value for the branching ratio depends on the method with which it is measured. If the branching ratio was determined by fitting the measured products of the reaction to a certain reaction rate, than the branching ratio depends upon the rate used. In this case, the branching ratio that should be used with the Kegley-Owen et al. (1999) value for the rate would be 4% even though a branching ratio of 6% gives a better correlation between modeled and measured results (Figures 6-12).

Model E provided good predictions of [ClO]. [ClO] might have even better agreement with the addition of a minor ClO+HO2→HCl +O3 channel as suggested in (Chance et al, 1996). A 7% branching ratio, which is the limit reported by Lipson et al. (1995), might also bring better results. The model did not use into the temperature at which the measurements were taken, which has an impact on the concentrations of chemicals measured, as an input. This could be a source of the further discrepancies. Although the modifications resolved the [HO2] discrepancy in the stratosphere (Figure 10), they did not resolve the [OH] and [O3] differences between the model and measurements (Figures 6-9). This suggests that another reaction involving HOx and/or ozone is more likely to be the cause of the further discrepancy. Possibilities might be vibrationally excited O2 which would be effective only below 55 km (Siskind et al., 1995) with the ozone deficit resolved at 40 km (Muller et al., 1999), the area where results of [O3], [OH], and [HO2] are farthest from the measurements.

Conclusion

Overall, model E, with the rate of the reaction HO2+O→O2+OH reduced 40% from the JPL-97 value, a 6% branching ratio for the HCl+O2 channel and the Kegley-Owen 1999 et al. (1999) rate constant for ClO+OH→products, provided the best correlation between measured and model results for [O3], [HO2], [OH] and [ClO]. However, it did not always bring them within the uncertainties of the measured values (Figures 6-12). The modifications brought measured [ClO] and [HO2] into agreement. However, they did not bring [O3] and [OH] into agreement although it did improve the agreement between the model predictions and the measurements. This study shows a need for the continuation of studies of the ozone deficit in order to resolve it. It also demonstrates the need to examine both the mesosphere and the stratosphere due to the fact that "solving" the deficit in one area does not necessarily account for it in the other.
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References


Orlando, John, and Geoff Tyndall, personal communication, July 1, 1999.

Pearce, Fred, Chill in the air, New Scientist, 28-32, 1 May 1999.


<table>
<thead>
<tr>
<th>Model</th>
<th>Rate ( \text{HO}_2+\text{O} \rightarrow \text{OH} + \text{O}_2 )</th>
<th>Rate constant ( \text{ClO}+\text{OH} \rightarrow \text{products} )</th>
<th>Branching ratio ( \text{HCl}+\text{O}_2 )</th>
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<td>( 3.0 \times 10^{-11} e^{(200 \pm 100/T)} )</td>
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<td>model C</td>
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<td>6%</td>
</tr>
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Table 1

Rates are from JPL-97 except for ClO+OH \( \rightarrow \) products for models C-E is from Kegley-Owen et al. (1999).
Rate Constant of ClO+OH→products

JPL–97

Kegley–Owen et al. (1999)

Figure 1
[OH] at 9:15 am April, 30 1997 at 69 N

- standard model
- Jucks et al. (1998)
- standard model to 50 km and
- Summers et al. (1997a) standard model above 52 km

Figure 2
[OH] at 11 am Nov. 5, 1994 at 35 N

- standard model
- Jucks et al. (1998) standard model to 50 km and Summers et al. (1997a) standard model above 52 km

Figure 3
[HO2] at 9:15 am April 30, 1997 at 69 N

- Standard model
- Jucks et al. (1998)

Altitude (km)

[HO2] (10^6 cm^-3)

Figure 4
CIO Mixing Ratio at 11 am Nov. 5, 1994 at 44 N

- **standard model**
- Michelsen et al. (1996)

Altitude (km)

[CIO] (ppmv)

Figure 5
Ozone Daytime Average Mixing Ratio March 24, 1992 at 40 N

Figure 6  Bars represent ozone measurements from Hartman et al. (1996).
Figure 7: Bars represent measurements from Jucks et al. (1998).
Figure 8: Bars up to 38 km represent measurements from Jucks et al. (1998), 40 to 48 km are from Conway et al. (1996) and 50 km and above are Summers et al. (1997a).
Figure 9
Bars up to 38 km represent measurements from Jucks et al. (1998), 40 to 48 km are from Conway et al. (1996) and 50 km and above are Summers et al. (1997a).
Figure 12: Bars represent measurements from Hartman et al. (1996).