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Transport and modeling of stratospheric inorganic chlorine

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Abstract

Correctly modeling stratospheric inorganic chlorine (Cl_y) is crucial for modeling the past and future evolution of stratospheric ozone. However, comparisons of the chemistry climate models used in the latest international assessment of stratospheric ozone depletion have shown large differences in the modeled Cl_y, with these differences explaining differences in the simulated evolution of ozone over the next century. Here in, we examine the role of transport in determining the simulated Cl_y using three simulations from the same off-line chemical transport model that have the same lower tropospheric boundary conditions and the same chemical solver, but differing resolution and/or meteorological fields. These simulations show that transport plays a key role in determining the Cl_y distribution, and that Cl_y depends on both the time scales and pathways of transport. The time air spends in the stratosphere (e.g., the mean age) is an important transport factor determining stratospheric Cl_y, but the relationship between mean age and Cl_y is not simple. Lower stratospheric Cl_y depends on the fraction of air that has been in the upper stratosphere, and transport differences between models having the same mean age can result in differences in the fraction of organic chlorine converted into Cl_y. Differences in transport pathways result in differences in vertical profiles of CFCs, and comparisons of observed and modeled CFC profiles provides a stringent test of transport pathways in models.

1 Introduction

The observed changes in ozone over the last two decades, as well as the expected future increases, are primarily the result of changes in the concentration of stratospheric inorganic chlorine (Cl_y) and bromine (Br_y). Therefore, correctly modeling stratospheric Cl_y and Br_y is crucial for modeling past and future stratospheric ozone levels. However, comparisons of the coupled chemistry climate models (CCMs) used in the latest international assessment of stratospheric ozone (WMO, 2007) have shown large dif-

ferences in the modeled Cl_y, both in terms of magnitude and the date that Cl_y returns to pre-1980 values (Eyring et al., 2006, 2007[1]). Furthermore, these differences appear to explain the differences in simulated ozone between the models, e.g. models with a later return of Cl_y to pre-1980 values also have later return of ozone. Given its importance for modeling ozone and the large differences between models, it is important to understand the causes of the differences in the simulations of Cl_y.

In the above CCM simulations the same time series of organic chlorine species (e.g., chlorofluorocarbons, CFCs) are specified in the lower troposphere and the same, or very similar, radiation schemes and chemical reactions are included in the models. This indicates that the differences in Cl_y are not due to differences in source gases, radiation, or stratospheric chemistry but are most likely due to differences in transport.

Here we explore this issue further by examining Cl_y from three simulations from the same off-line chemical transport model (CTM). The simulations use the same lower tropospheric concentration boundary conditions and the same chemical solver, but differing resolution and/or meteorological fields. As the boundary conditions and chemistry are exactly the same any differences in Cl_y are due to differences in the transport.

The model and simulations are described in the next section. In Sect. 3 we compare the Cl_y and mean age Γ from the CTM simulations, and also compare the simulated Cl_y with an estimate using the formulation used by Newman et at. (2006) to calculate EESC. These comparisons show that transport plays a key role in determining the distribution of Cl_y, and that Cl_y depends on both the time scales and pathways of transport.

[1]Eyring, V., Waugh, D. W., Bodeker, G. E., et al.: Multi-model projections of stratospheric ozone in the 21st century, J. Geophys. Res., 112, to appear, 2007.

2 Model description

The simulations examined are performed using the NASA Global Modeling Initiative (GMI) CTM (Douglass et at., 2004 and references therein). The CTM includes a full description of stratospheric chemistry, and can be driven by meteorological data from either a free-running general circulation model (GCM) or from a data assimilation system (DAS). We consider both cases here: Simulations are analyzed that used either the Goddard Earth Observing System (GEOS) DAS (Schubert et at., 1993) or the GEOS-4 GCM (Bloom et al., 2005).

As well as differing meteorological fields, the horizontal resolution and top of the CTM differs between some of the simulations. We consider three simulations:

1. GCM winds, 2° latitude × 2.5° longitude, top at 0.015 hPa with 33 levels ("GCM-HIGH").
2. GCM winds, 4° latitude × 5° longitude, top at 0.4 hPa with 28 levels ("GCM-LOW").
3. DAS winds, 4° latitude × 5° longitude, top at 0.4 hPa with 28 levels ("DAS-LOW").

The two "LOW" simulations are described in Considine et al. (2004), while the GCM-HIGH simulation is described in Douglass et at. (2006).

All three simulations use the same chemical solver (see Douglass et at., 2004) and the concentration of halogens in the lower troposphere are specified as in table 4B-2 of WMO (2003). In each case a single year of meteorological fields is used in the CTM, but the source gas boundary conditions vary between years. In the GCM-HIGH simulation the boundary conditions start in 1974 and end in 2025. The "LOW" simulations were spun up for 5 years at 1995 source gas boundary conditions and then integrated through the year 2030. (Because 1995 boundary conditions were used rather than 1990 to 1994 conditions in the spin up of the "LOW" simulations the stratospheric chlorine is over-estimated in the early part of these simulations. However, the difference is much smaller than the inter-model differences discussed below.) For all simulations fields have been archived every 5 years.

Additional twenty year simulations of an age spectrum tracer (i.e. the mixing ratio of a conserved tracer was set to 1 for the first month and then set to 0 for the rest of the run, in the lowest two model levels) were also run. This tracer allows calculation of the mean age of air in the stratosphere as well as the full age spectra (Waugh and Hall, 2002).

3 Results

3.1 CTM simulations

We first consider the Cl_y distribution in the three simulations. As shown in Fig. 1(a–c; top panels) the general features of the Cl_y distributions are the same, e.g., there are values larger than 3 ppb in the upper stratosphere and lower values in the tropics than mid- and high latitudes. However, there are quantitative differences, especially in the wintertime (southern) polar regions. For example, the South Pole Cl_y at 20 km varies from less than 1.5 ppb to around 3 ppb. As the surface concentrations and the chemistry are the same in all three simulations, this confirms the CCM results (Eyring et at., 2006) that transport plays a key role in determining Cl_y.

As Cl_y is formed by conversion of organic chlorine into inorganic chlorine species within the stratosphere, the time spent in the stratosphere is expected to play an important role in determining Cl_y. We therefore next consider the distributions of the mean age Γ. (Γ is calculated from simulations of the age spectra, and represents the annual-mean Γ, see Waugh and Hall, 2002.) As shown in Fig. 1(d–f; bottom panels) the mean age differs among all three simulations. The largest differences are between DAS-LOW and the two GCM simulations, with much younger ages in DAS-LOW. There are also differences in age between GCM-LOW and GCM-HIGH, but these are small in the lower stratosphere (e.g., the South Pole mean age at 20km is around 4.7 yrs in both GCM simulations).

Comparison of the Cl_y and Γ distributions shows that Cl_y is, in general, larger for

older Γ. However, this comparison also suggests that differences in Γ do not explain all the differences in Cl_y. This is clearly seen in vertical profiles within the spring Antarctic vortex: Around 20 km Γ from the two GCM based simulations are the same but there is a large difference in Cl_y, see Fig. 2a, b. Conversely, above this altitude there are much larger differences in mean age than in Cl_y between these two simulations. Hence, there is not a simple relationship between differences in mean age and those in Cl_y.

To explore the differences in Cl_y in more detail we compare the time series of lower stratospheric Cl_y at two locations where Γ is similar in the two GCM based simulations, see Fig. 3. In mid-latitudes the two GCM simulations have very similar Cl_y (Fig. 3a), but at the polar location there is a large difference (Fig. 3b). At both locations Γ and Cl_y from the DAS simulation are smaller than from the GCM simulations.

The differences in Cl_y could be due to differences in the simulated total amount of chlorine Cl_{tot}(the sum of organic and inorganic chlorine) in the stratosphere. However, Cl_{tot} is very similar among all three simulations (dashed curves in Fig. 3). There is a slight time shift between the DAS and two GCM simulations, which is consistent with the approximately 2 year difference in the mean age. However, the magnitude of Cl_{tot} is very similar and differences in Cl_{tot} do not explain the differences in Cl_y. As well as the time shift in Cl_{tot} between the DAS and GCM simulations there are slight differences in the peak values, which are due to differences in the width of the age spectra. However these differences are insignificant compared to the differences in Cl_y.

The above shows that the time spent in the stratosphere is important but this is not the sole transport factor determining stratospheric Cl_y(and differences between the simulations). Hence, the paths taken to get to a particular location must also be important for determining Cl_y.

3.2 Theory

To understand the differences in simulated Cl_y we estimate the Cl_y using the formulation of Newman et at. (2006, 2007). In this formulation Cl_y is estimated by summing the

contribution from each CFC, i.e.,

$$Cl_y^*(t) = \sum_i n_i F_i \hat{\rho}_i(t) \quad (1)$$

where n_i is the number of chlorine atoms in source gas i, $\hat{\rho}_i$ is the source gas mixing ratio if the gas was conserved in the stratosphere, and F_i the fraction of species dissociated while it has been in the stratosphere. The mixing ratio $\hat{\rho}_i$ depends on the tropospheric concentrations ($\rho_{i,\mathrm{trop}}$) and the troposphere to stratosphere transport time scales:

$$\hat{\rho}_i(t) = \int_{-\infty}^{t} \rho_{i,\mathrm{trop}}(t') G(t - t') dt'. \quad (2)$$

where $G(t)$ is the age spectrum. The fractional release is given by

$$F_i = (\hat{\rho}_i - \rho_i)/\hat{\rho}_i, \quad (3)$$

where ρ_i is the actual concentration of the source gas at given stratospheric location.

We focus here on lower stratospheric Cl_y and, as in Newman et at. (2006), assume that the fractional releases are solely a function of the mean age, i.e. $F_i = F_i(\Gamma)$. Although we assume a dependence only on the mean age it is important to know that the release rates also depend on pathways, and the functional relationships are not necessarily the same for all simulations. $F_i(\Gamma)$ are determined separately for the three simulations using the method of Schauffler et al. (2003) applied to the simulated fields for 2000.

We first compare Cl_y^* with the directly simulated Cl_y. In these calculations of Cl_y^* we use the age spectrum G(t) simulated within the CTMs (see Sect. 2), the $\rho_{i,\mathrm{trop}}$ used in the CTMs, and the above estimates of F_i. As shown in Fig. 4 the Cl_y^* estimated from G(t) and F matches the time evolution of Cl_y and the differences between the simulations. There are some differences between Cl_y^* and Cl_y for GCM-LOW, but these differences are much smaller than model-model differences, and Cl_y^* is a good representation of Cl_y at a few % level. (Note virtually the same Cl_y^* is obtained if the approximate age

spectrum used by Newman et al. (2006), an inverse Gaussian age spectra with width equal to half the mean age, is used rather than the true model age spectrum, see dashed curves in Fig. 4.)

Given this general agreement we can now explore the differences in the individual contributions to Cl_y^*. As $\rho_{i,\mathrm{trop}}$ is the same in all simulations and the differences in Cl_{tot} are small, differences in fractional release are the main cause for differences in Cl_y.

Fig. 5 shows the variation of lower stratospheric concentration (a, b; top panels) and fractional release F (c, d; bottom panels) with mean age Γ, for CFC-11 (left) and CFC-12 (right). Very similar results are found for other CFCs. Focusing first on the two GCM based simulations we see that the CFC concentrations and F are very similar for $\Gamma < 4$ years, but differences occur for older ages. For old ages (polar air) the CFC concentrations are lower for GCM-HIGH, which means that the fraction of CFC converted into Cl_y is larger (i.e. F is larger). Thus, differences in transport can result in differences in the fraction of organic chlorine converted into Cl_y, and hence differences in Cl_y, for air with the same mean age.

The fractional release rates for the DAS simulation differs from both the GCM simulations. The maximum values of both Γ and F are smaller in the DAS simulation (the smaller F is consistent with the smaller lower stratospheric Cl_y in the DAS simulation). For fixed Γ, F is larger from the DAS simulation than the GCM simulations. This is because comparing air with the same Γ in the DAS and a GCM simulation is not a comparison of air at the same location. A lower stratospheric location in DAS with the same Γ as in one of the GCM simulations will be at a higher latitude, e.g., air at 20 km with $\Gamma = 2.4$ yrs in the DAS simulation is at the South Pole, whereas $\Gamma = 2.4$ yrs is in the subtropics in both GCM simulations (Fig. 1). A higher latitude location generally has a higher percentage of air that has been in CFC loss regions, and so higher latitude air with the same age will have higher F. If comparisons between F are made at the same location then F is smaller in the DAS simulation than the GCM simulations, and as a result Cl_y is smaller.

The differences in the fractional release of CFCs in the Antarctic vortex can be clearly seen in the vertical profiles of the CFCs, see Fig. 2c, d. One consequence of this is that observations of CFCs can probably be used to differentiate model simulations of Cl_y. For example, the solid circles in Fig. 2c, d show the monthly average CFCs near 80°S from the Atmospheric Chemistry Experiment (ACE) (Bernath et al., 2005) observations in September 2005. (The model and ACE CFCs are from September rather than October as ACE samples south of 79° S in early September but not later.) All three simulations overestimate the observed CFC abundances, with the best agreement for the GCM-HIGH simulation. This suggests that GCM-HIGH has the most realistic simulation of Cl_y.

Unfortunately, the corresponding profiles of Cl_y cannot be determined directly from ACE as Cl_2O_2 (which is a significant reservoir of Cl_y inside Antarctic lower stratospheric vortex in September) is not measured. However, measurements of HCl and ClO in October 2005 by Aura MLS indicate that at 20 km Cl_y is around 3.3 ppb (Figs. 4–8 of WMO, 2007). Consistent with the above CFC comparisons, the modeled Cl_y are too low, with GCM-HIGH the most realistic.

4 Discussion

Previous analysis of models has shown that Γ is very important for correctly estimating Cl_y. However, the above comparisons have shown that although the mean age in the polar lower stratosphere may be the same in two simulations, this does not mean that Cl_y will be the same. It is important to consider the pathways that the air has taken, which can be different even if Γ is the same. Even if two parcels have the same Γ one parcel could have lower CFC concentrations, higher fractional releases, and larger Cl_y if this parcel spent more time in regions with larger CFC photolysis. This is illustrated schematically in Fig. 6 which shows two parcels with same transit time from the tropopause but different pathways. As a result the two parcels have different photochemical exposure (Schoeberl et at., 2000) and Cl_y.

The larger CFC concentrations, and hence smaller Cl_y, in the GCM-LOW simulation could be explained by a smaller fraction of the polar air having been in the middle-upper stratosphere where CFCs are photolyzed. This is supported by the analysis of Strahan and Polansky (2006). They showed that with lower horizontal resolution there are leakier transport barriers (in subtropics and edges of polar vortices), which results in more rapid transport of young air to polar regions. The leakier barriers also allow more recirculation of air between the tropics and extratropics, allowing air to becomes old without spending time in the upper stratosphere. The greater influence of young air in the GCM-LOW simulation can also be seen in the age spectra, see Fig. 7 (see also Fig. 14 of Strahan and Polansky , 2006). In the GCM-LOW simulation there is a much higher percentage of young air (<2 years) than in the GCM-HIGH simulation. Also, air arrives continuously in GCM-LOW whereas the GCM-HIGH simulation shows an episodic annual injection of air into the polar region in the transport (Strahan and Polansky , 2006).

5 Conclusions

The CTM simulations presented here show that transport plays a key role in determining the distribution of Cl_y, and that large differences in Cl_y can occur in models using the same surface concentrations of source gases and same chemistry. The time air spends in the stratosphere (e.g., the mean age, Γ) is an important factor but this is not the sole transport factor determining stratospheric Cl_y. Stratospheric Cl_y also depends on where the air has been. Differences in transport pathways can result in differences in the fraction of air that has been in the upper stratosphere, where organic chlorine is converted into Cl_y, even for air with the same mean age. Thus there can be differences in Cl_y for air with the same Γ.

This analysis shows that to correctly model Cl_y it is necessary to correctly simulate both the time scales and pathways for stratospheric transport. The mean age provides a stringent test of the transport time scales, and can be inferred from observations.

A complementary test of transport pathways is also required. Hall (2000) introduced the "maximum path height" distribution which quantifies transport pathways and compliments the age spectrum. However, this quantity cannot be observed. We therefore have to rely on simulations of chemical species to assess the model transport. As shown above transport-induced differences in Cl_y can be clearly seen in profiles of CFCs, and observations of CFCs (e.g., Fig. 2c, d; bottom panels) are available to assess the reality of the transport pathways in models. Hence, comparison of simulated mean age and CFCs with observations provide complementary tests that assess the transport time scales and pathways in models. The complementary nature of tracers with different lifetimes for evaluating transport can also be seen in Schoeberl et at. (2005), where multiple tracers are used to constrain the age spectrum.

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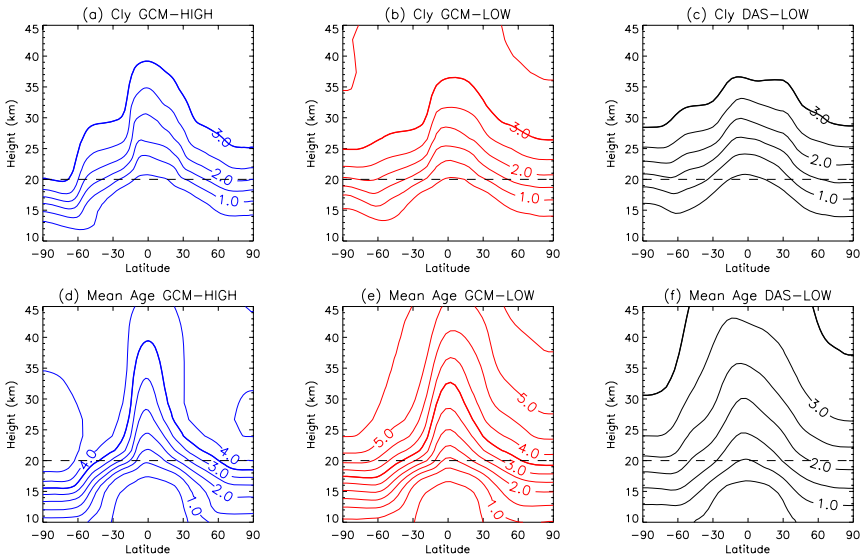

Fig. 1. Contour plots of (**a**–**c**; top panels) October-mean Cl_y, and (**d**–**f**; lower panels) annual-mean mean age for 2000, from three CTM simulations. In (a–c) the contour interval is 0.5 ppb, with the 3.0 ppb contour bold, while in (d–**e**) the contour interval is 0.5 years with 3.5 yr contour bold.

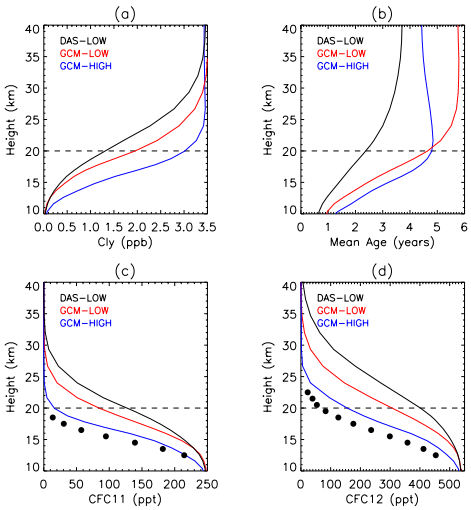

Fig. 2. Vertical profiles of **(a)** Cl_y, **(b)** mean age, **(c)** CFC11, and **(d)** CFC12 at 82S. Profiles for Cl_y are mean values for October 2000, mean age are annual mean values, and CFCs are for September 2005. The solid circles show ACE observations.

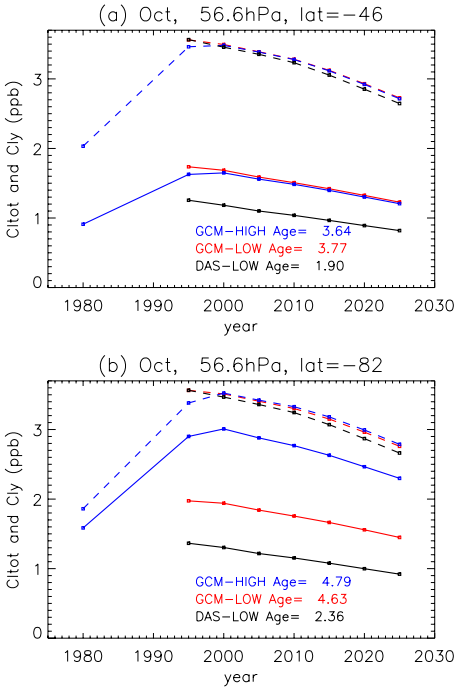

Fig. 3. Time series of October-mean Cl_y (solid) and Cl_{tot} (dashed) for **(a)** mid-latitude (46° S) and **(b)** polar (82° S) regions.

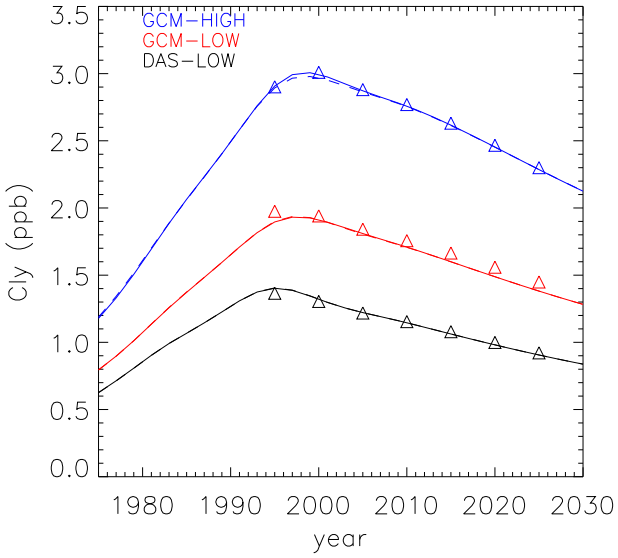

Fig. 4. Comparison of directly simulated Cl_y at 56.6 hPa and 82° S (symbols) and reconstruction using Newman et al. method (curves), for the three simulations.

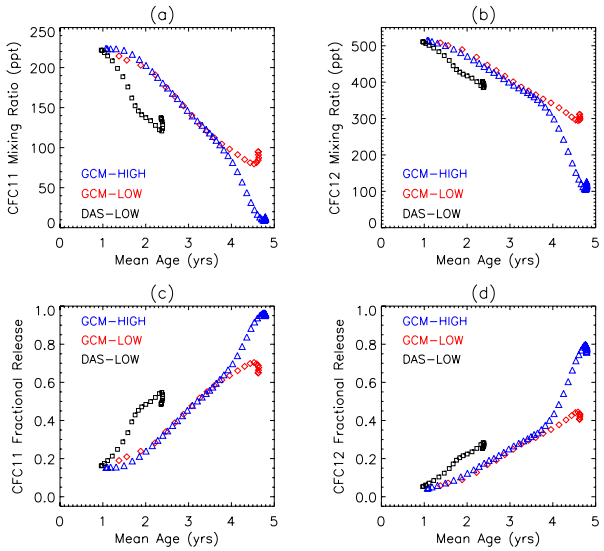

Fig. 5. Variation of **(a)** CFC11 concentration, **(b)** CFC12 concentration, **(c)** F_{CFC11}, and **(d)** F_{CFC12} with mean age Γ, for the three simulations.

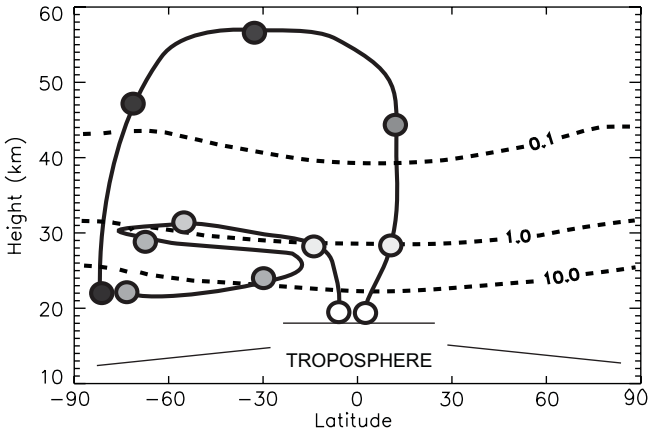

Fig. 6. Schematic diagram showing path of two irreducible parcels to sample point in polar lower stratosphere. The circles show the parcels locations at yearly intervals, with shading of the parcels indicating the Cl_y of the parcel (darker color represents a higher amount). The dashed contours show local photochemical lifetime of CFC-12, in years.

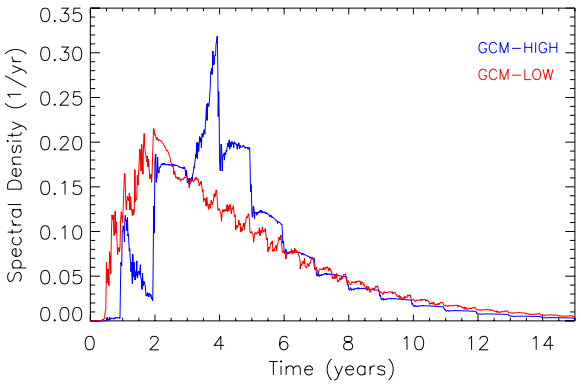

Fig. 7. Age spectrum at 56.6 hPa and 82° S from GCM-HIGH (blue) and GCM-LOW (red) simulations.