The Rayleigh model used in SI Section 1.4 (fractionation in gas/particle partitioning of nitrate):

```
clear all
%using the ice-core measured H+ concentrations, scaled to
%aerosol acidity
%not consider T change from the entire record, model the
%trend of d15N from 1772 to 2006



%data in
age=xlsread('acidity_T.xlsx', 'H1:H236'); %time period of the record
Hi=xlsread('acidity_T.xlsx', 'I1:I236'); %ice core H+ concentrations
%volcanic peaks/biomass burning valleys were replaced
%with average of before/after points;
Rd15N=xlsread('acidity_T.xlsx', 'K1:K236'); %Measured d15N,gaps were
%filled with averages of before/after
%Ta=xlsread('acidity_T.xlsx','M1:M236');%Temperature anomaly in
%Northern Hemisphere, turn on when testing the sensitive to T change;
H=10^(-4).*Hi; %scaling to aerosol acidity, acording to an aerosol pH
%of 4
T=298.15;%assuming standard temperature
%T=287.15+Ta;%varying temperature accoridng to Northern hemisphere
%temperature anomaly, turn on when necessary;
Wl=10^(-12); %liquid water content of aerosols, 10^-6 g m-3
%(10^-12 L/L air)

%Calculated the fraction of p-NO3- in total nitrate

Y=15.4*2.1*10^5.*exp(-8700*(1/298.15-1./T)).*exp(8700*(1./T-
1/298.15)); %Henry's law constant and HNO3 dissociation constant vary
%with T, here consider T constant
%[HNO3]=PHNO3/(R*T)+[NO3-]*Wl, total atmospheric nitrate concentration
%(mol/L air)equals to concentration in gas form (mol/L air) plus
%nitrate in
%particle form (mol/L water)
%f=Wl/(H/R*T*Y+Wl), fraction of particle nitrate in total nitrate
x=0.08206.*T;
X=x.*Y;
B=Wl+H./X;
f=Wl./B;%fraction of P-no3 in total nitrate

e=-0.021;% fractionation constant
d15N1=(1+0).*f.^e-1; % particle phase N15, starting material with
d15N=13.4 per mil, using the average of d15N before 1850
d15N2=(1+0).*(1-f.^(e+1))./(1-f)-1; %gas phase N15,starting material
with d15N=13.4 per mil, using the average of d15N before 1850
D_d15N=1000.*d15N2-1000.*d15N1; %difference between gas and particle
%phase
dif=D_d15N(1:end)-mean(D_d15N(1:80));%this gives the changes in d15N
%relative to pre-1850 values
C_d15N=dif+13.4;%13.4 is the measured average d15N before 1850; this
%forces the modeled result agree with the measured d15N before 1850;

%when e=-0.0085
```

```
e=-0.0085;% fractionation constant
d15N11=(1+0).*f.^e-1; % particle phase N15
d15N21=(1+0).*(1-f.^(e+1))./(1-f)-1; %gas phase N15
D_d15N1=1000.*d15N21-1000.*d15N11; %difference between gas and particle
%phase
dif1=D_d15N1(1:end)-mean(D_d15N1(1:80));% this gives the changes in
%d15N relative to pre-1850 values
C_d15N1=dif1+13.4; %this forces the modeled result agree with the
%measured d15N before 1850;



fig('units','inches','width',7,'height',5,'font','Helvetica','fontsize'
,16,'border','on');



title('Summit N15 trend')
xlabel('Age(calendar year)')
ylabel('\delta^{15}N(per mil)');
hold on;
plot(age,Rd15N,'r');
hold on
plot(age,C_d15N,'b');
hold on
plot(age,C_d15N1,'g');
hold on



hleg1=legend('measured','modeled e=-0.021','modeled e=-0.0085');
axis([1770 2010 -20 40]) ;
set(gca,'XTick',[1770:40:2010]);

% end;
```

The model used in S1.5 (fractionation in NO_x cycle):

```
% model is modified from the original box model developed by J. Jarvis
and E.
% Steig
% NOx concentration change from preindustrial period to the present day
% doesn't affect the final results, so NOx can be turned on or off;
% this model also calculate the d15N of Nitrate assuming no additional
% fractionation occurs from the conversion of NO2 to HNO3

clear all
% using GEOS-chem input concentrations for PI and PD, unit:
molecules/cc
O3 = [5.99079E+11   1.04574E+12];
NOx = [1163844358   8212086750];
% NOx = [1163844358 1163844358];
OH = [1054885.3  1328296.9];
T = [298 298]; %assuming no temperature change between PI and PD
% Reactions involved
```

```
% R1 NO + O3 --> O2 + NO2, this direction is dominated by O3 oxidation,
for
% simplification, ignor HO2/RO2
% R2 NO2 + hv --> O + NO
% R3 NO2 + OH --> HNO3     where rate = k3*NO2*OH
% R4 NO2 + O3 --> NO3 + O2 where rate = k4*NO2*O3
% R5 NO3 + NO2 --> N2O5    where rate = k5*NO3*NO2
% R6 N2O5 + H2O --> 2HNO3  where rate = k6*N2O5 (assume H2O is abundant
in
% troposphere)
k1 = 3.0E-12*exp(-1500./T);          %cm3/molecules/s; JPL 2003
k2 = 8e-3;  %s-1 at surface (8E-3 in Seinfeld and Pandis, p.144)
k3 = (2.4E-30).*((T/300).^(-3.1));    %cm3/molecules/s; Joel T. value
from JPL 2000
k4 = 1.2E-13.*exp(2450./T);           %cm3/molecules/s; JPL 2003
k5 = (2.2E-30).*((T/300).^(-3.9));    %cm3/molecules/s; Joel T. value
from JPL 2000
k6 = 2.0E-21;             %k6 at 298 is less than 2.0E-21;
cm3/molecules/s; JPL 2003

% Let Rstd reflect the natural abundance of 15N.
Rstd = 0.0036;
%Let M represent 15-N in general.
%Set d15N of bulk NOx to be 15 per mil lighter than the standard.
MOx = (Rstd-Rstd*15/1000).*NOx;
alpha1 = 1.018;
NO2 = NOx./(1+(k2./(k1.*O3))); % considering a steady state between NO
and NO2
NO = NOx - NO2;
MO = MOx./(1 + alpha1*NO2./NO);
MO2 = MOx - MO;

% Putting in delta notation gives us
d15NO =(MO./(NO-MO) - Rstd)/Rstd * 1000;
d15NO2 = (MO2./(NO2-MO2) - Rstd)/Rstd * 1000;

PI = d15NO2(1);
PD = d15NO2(2);
d15NO2_change = PD-PI;

% Figure Plot d15N of NO2 in PI and PD;
figure;
bar2(d15NO2); ylabel('\delta ^{15}N of NO2');
set(gca,'XTickLabel',{'PI';'PD'});

% calculating d15N in nitrate, assuming alpha = 1;

N2O5 = k4.*NO2.*O3./k6;
HNO3flux_fromN2O5path = k6.*N2O5;
HNO3flux_fromOHpath = k3.*NO2.*OH;
HNO3flux = HNO3flux_fromOHpath + HNO3flux_fromN2O5path;
alpha2 = 1;
HMO3flux = alpha2.*HNO3flux.*MO2./NO2;
d15HNO3 = (HMO3flux./HNO3flux - Rstd)/Rstd * 1000;
```

```
% Figure Plot d15N of NO2 in PI and PD;
figure;
bar2(d15HNO3); ylabel('\delta ^{15}N of HNO3');
set(gca,'XTickLabel',{'PI';'PD'});

%end
```

Database: (concentrations are in μeq L^{-1})

	$\delta^{15}N(NO_3^-)$	NO_3^-	SO_4^{2-}	H^+	HNO_3
2006.00	1.44	1.95	0.91	1.99	1.49
2005.00	4.33	1.69	0.60	1.74	1.45
2004.00	-1.86	2.03	0.97	2.20	1.82
2003.00	0.86	2.52	0.86	2.55	2.16
2002.00	-7.78	1.96	0.60	2.01	1.71
2001.00	-0.77	1.98	0.80	2.30	1.74
2000.00	1.18	2.39	0.89	2.81	2.16
1999.00	-0.54	1.36	0.50	1.68	1.28
1998.00	-0.50	1.93	0.92	2.29	1.65
1997.00	-3.75	2.11	0.81	2.99	2.37
1996.00	-1.72	1.99	0.85	2.73	2.00
1995.00	-6.08	2.39	1.10	2.88	2.25
1994.00	-1.36	2.22	1.28	2.70	1.97
1993.00	-2.09	2.23	1.39	3.17	1.97
1992.00	-0.04	2.42	2.67	3.11	2.27
1991.00	-0.19	1.97	1.29	3.06	1.96
1990.00	-2.26	2.02	1.28	2.92	1.96
1989.00	-1.84	2.00	1.78	3.19	1.76
1988.00	2.62	1.96	1.59	2.99	1.74
1987.00	0.99	2.07	1.53	3.23	1.96
1986.00	-0.63	1.63	1.60	3.14	1.68
1985.00	0.68	1.69	1.86	3.18	1.53
1984.00	-0.42	1.64	1.70	3.06	1.51
1983.00	0.56	1.31	1.65	2.53	1.05
1982.00	-0.72	1.91	2.63	3.80	1.59
1981.00	0.76	1.85	2.08	3.02	1.58
1980.00	2.82	2.01	2.89	4.27	1.82
1979.00	-1.49	1.61	1.73	2.60	1.17
1978.00	-5.39	1.85	1.47	2.70	1.43
1977.00	-3.84	1.88	2.00	3.41	1.63
1976.00	-4.59	2.31	2.07	3.97	2.14

1975.00	1.71	1.79	2.82	4.29	1.73
1974.00	1.93	1.63	2.19	3.57	1.55
1973.00	3.02	1.92	2.27	3.74	1.70
1972.00	-2.80	2.06	2.41	4.08	1.85
1971.00	1.77	2.09	2.94	4.77	2.03
1970.00	1.85	1.58	2.57	3.94	1.52
1969.00	-3.71	1.89	2.51	4.22	1.84
1968.00	-3.63	1.77	1.92	3.49	1.67
1967.00	-0.42	1.44	1.88	3.17	1.41
1966.00	-0.97	1.32	2.57	3.61	1.20
1965.00	3.76	1.82	2.67	4.26	1.75
1964.00	3.73	1.59	1.90	2.39	1.45
1963.00	5.84	1.23	1.50	2.59	1.15
1962.00	6.00	1.51	1.85	3.14	1.40
1961.00	7.07	1.33	1.68	1.78	1.14
1960.00	5.02	1.41	1.99	3.13	1.30
1959.00	4.71	1.49	2.13	3.27	1.36
1958.00	3.42	1.25	1.89	2.73	1.02
1957.00	4.29	1.67	1.75	3.08	1.50
1956.00	6.68	1.32	1.92	2.85	1.11
1955.00	2.71	1.35	2.15	3.04	1.07
1954.00	5.84	1.42	2.17	2.86	0.97
1953.00	3.77	1.19	1.51	2.15	0.87
1952.00	4.25	1.08	1.33	1.72	0.62
1951.00	7.56	1.19	1.92	2.36	0.71
1950.00	5.10	1.63	2.77	3.01	1.08
1949.00	4.27	1.31	1.64	2.75	1.17
1948.00	8.72	1.10	1.64	2.33	0.86
1947.00	10.10	1.01	1.40	1.71	0.50
1946.00	7.11	1.01	1.56	2.36	0.85
1945.00	7.89	0.99	1.16	1.89	0.81
1944.00	7.39	1.34	2.02	2.76	0.95
1943.00	6.46	0.98	2.24	2.88	0.87
1942.00	6.56	1.13	1.67	2.19	1.02
1941.00	4.01	0.95	1.09	1.70	0.73
1940.00	9.42	0.81	1.01	1.38	0.66
1939.00	6.94	0.77	1.27	1.74	0.66
1938.00	5.88	0.81	1.11	1.58	0.59
1937.00	9.77	0.78	1.12	1.42	0.47
1936.00	9.96	1.33	1.04	1.65	0.99
1935.00	7.32	1.05	1.51	1.69	0.37
1934.00	6.85	1.16	1.26	1.64	0.76
1933.00	8.34	0.90	1.14	1.59	0.66

1932.00	7.73	1.20	0.91	1.36	0.86
1931.00	8.74	0.89	1.01	1.27	0.52
1930.00	8.33	1.00	1.53	1.63	0.31
1929.00	9.20	1.36	1.67	1.87	1.10
1928.00	8.99	1.04	1.14	1.39	0.59
1927.00	9.69	1.34	1.21	1.68	0.84
1926.00	11.23	1.05	1.61	2.09	0.73
1925.00	8.89	1.02	1.52	2.00	0.86
1924.00	12.29	0.99	1.89	2.06	0.45
1923.00	10.55	1.50	1.60	2.34	1.21
1922.00	9.97	0.84	1.15	1.67	0.70
1921.00	10.10	1.11	1.24	1.52	0.55
1920.00	10.95	0.97	1.02	1.37	0.59
1919.00	8.80	1.39	1.69	1.50	0.72
1918.00	8.61	1.06	1.67	1.29	0.34
1917.00	8.10	1.03	1.64	1.61	0.15
1916.00	7.54	1.08	1.24	2.08	0.91
1915.00	8.28	0.96	1.00	1.80	0.98
1914.00	11.94	1.05	1.50	2.25	0.85
1913.00	10.85	1.20	1.90	2.97	1.18
1912.00	11.09	0.99	2.92	2.17	1.00
1911.00	11.10	0.90	1.00	1.36	0.61
1910.00	9.01	0.81	0.95	1.42	0.58
1909.00	9.42	1.07	0.88	1.60	0.98
1908.00	10.83	0.91	1.06	1.86	0.62
1907.00	12.70	0.88	1.41	2.12	0.77
1906.00	11.00	1.24	1.47	2.25	1.01
1905.00	9.58	1.05	0.91	1.79	1.00
1904.00	10.67	0.99	1.32	1.98	0.83
1903.00	12.04	0.95	1.47	2.01	0.78
1902.00	9.33	0.81	0.60	1.26	0.70
1901.00	11.77	1.02	0.87	1.70	0.97
1900.00	15.52	1.01	0.50	1.43	1.00
1899.00	10.05	1.10	0.80	1.63	1.06
1898.00	8.95	0.94	0.87	1.32	0.60
1897.00	9.50	1.02	0.71	1.23	0.77
1896.00	11.31	1.01	0.63	0.79	0.85
1895.00	9.49	0.81	0.56	0.97	0.69
1894.00	12.77	0.75	0.58	0.80	0.47
1893.00	17.87	1.16	0.87	0.64	0.80
1892.00	17.92	1.25	0.82	1.28	0.85
1891.00	12.18	0.91	0.82	1.28	0.65
1890.00	11.93	0.79	0.66	0.90	0.41

1889.00	11.79	0.93	0.62	1.18	0.68
1888.00	10.41	1.01	0.59	1.12	0.47
1887.00	8.13	0.74	0.74	1.06	0.44
1886.00	10.60	0.77	0.56	0.98	0.56
1885.00	11.13	1.00	0.86	0.44	0.52
1884.00	12.92	1.20	1.28	1.64	0.67
1883.00	10.50	1.43	2.00	1.31	0.98
1882.00	10.29	0.76	0.65	0.97	0.56
1881.00	12.21	1.04	0.67	1.24	0.71
1880.00	13.75	0.86	0.51	0.91	0.65
1879.00	10.41	1.05	0.51	1.33	0.95
1878.00	9.04	0.79	0.64	0.64	0.22
1877.00	9.88	0.90	0.71	1.05	0.45
1876.00	8.70	1.11	0.55	1.32	0.82
1875.00	12.65	0.80	0.46	0.71	0.32
1874.00	12.20	0.99	1.10	1.35	0.32
1873.00	9.83	0.78	0.73	0.93	0.36
1872.00	10.58	0.98	0.89	1.32	0.53
1871.00	12.03	0.91	1.16	1.67	0.64
1870.00	7.87	1.09	0.64	1.15	0.78
1869.00	9.51	1.00	0.90	0.51	0.20
1868.00	13.33	0.97	0.56	0.62	0.34
1867.00	7.59	1.52	0.72	0.73	1.01
1866.00	9.60	0.89	0.47	0.81	0.46
1865.00	13.54	1.05	0.50	0.94	0.63
1864.00	14.31	0.66	0.51	0.43	0.26
1863.00	14.76	1.15	0.73	0.78	0.59
1862.00	9.67	1.16	0.96	0.80	1.76
1861.00	15.02	0.88	0.77	0.82	0.38
1860.00	12.53	0.91	0.68	0.84	0.42
1859.00	14.13	0.78	0.73	0.86	0.35
1858.00	11.76	0.96	0.83	0.94	0.38
1857.00	11.26	0.78	0.57	0.54	0.11
1856.00	13.77	1.12	0.95	1.04	0.39
1855.00	12.33	0.80	1.16	1.38	0.35
1854.00	12.70	0.82	0.46	0.67	0.34
1853.00	9.93	1.14	0.75	0.66	0.38
1852.00	10.68	0.88	0.57	0.58	0.32
1851.00	8.35	0.73	0.61	0.57	0.15
1850.00	10.51	0.82	0.54	0.51	0.26
1849.00	14.19	0.68	0.47	0.34	-0.01
1848.00	13.35	0.80	0.47	0.57	0.39
1847.00	10.31	0.75	0.39	0.38	0.23

1846.00	13.39	0.96	0.64	0.30	0.17
1845.00	13.92	0.79	0.69	0.33	0.22
1844.00	11.40	0.79	0.97	0.61	0.17
1843.00	10.00	1.10	0.60	0.31	0.36
1842.00	11.81	0.90	0.65	0.29	-0.17
1841.00	13.85	0.81	0.56	0.35	0.10
1840.00	12.47	0.90	0.46	0.39	0.19
1839.00	16.06	0.79	0.44	0.47	0.25
1838.00	11.66	1.04	0.55	0.63	0.41
1837.00	14.99	0.71	0.72	0.67	0.38
1836.00	8.28	0.84	1.99	1.10	0.52
1835.00	13.12	0.87	1.19	1.54	0.47
1834.00	13.22	0.84	0.43	0.87	0.57
1833.00	10.19	0.92	0.72	1.05	0.40
1832.00	15.33	0.89	2.49	1.34	0.39
1831.00	11.80	0.91	0.99	1.64	0.72
1830.00	17.36	0.93	0.67	1.18	0.60
1829.00	14.89	0.80	0.68	0.96	0.40
1828.00	11.40	0.92	0.53	0.90	0.53
1827.00	16.84	1.07	0.39	1.01	0.70
1826.00	13.74	1.00	0.38	0.89	0.68
1825.00	16.30	0.92	0.37	0.91	0.74
1824.00	15.00	0.94	0.59	1.05	0.62
1823.00	15.70	1.03	0.70	1.09	0.54
1822.00	19.97	1.00	0.60	0.82	0.56
1821.00	16.79	1.20	0.56	0.43	0.74
1820.00	18.00	1.01	0.47	0.75	0.66
1819.00	17.72	1.14	0.58	0.49	0.65
1818.00	12.15	1.35	0.79	0.93	0.73
1817.00	12.15	1.32	1.21	1.55	0.71
1816.00	12.15	1.08	4.07	1.56	0.40
1815.00	16.65	1.23	1.44	1.56	0.69
1814.00	16.65	0.91	0.93	0.43	0.25
1813.00	16.17	1.05	0.81	0.55	-0.44
1812.00	14.39	0.91	0.68	0.67	0.35
1811.00	14.95	1.05	0.88	0.76	0.29
1810.00	12.15	1.31	2.75	1.47	-0.67
1809.00	12.15	0.99	1.29	0.18	-0.45
1808.00	12.15	0.82	0.45	0.61	0.13
1807.00	13.41	0.87	0.37	0.82	0.45
1806.00	13.41	0.79	0.47	1.03	0.72
1805.00	14.22	1.26	0.53	1.51	1.18
1804.00	12.02	1.09	0.54	0.94	0.72

1803.00	13.43	0.82	0.45	1.00	0.64
1802.00	11.40	0.97	0.47	0.97	0.73
1801.00	16.77	0.80	0.40	0.61	0.30
1800.00	15.80	0.93	0.55	0.71	0.58
1799.00	13.49	0.83	0.39	0.69	0.61
1798.00	15.83	0.86	0.49	0.87	0.51
1797.00	21.85	0.81	0.58	0.98	0.55
1796.00	16.71	0.78	0.57	0.71	0.44
1795.00	11.73	1.08	0.49	1.06	0.73
1794.00	10.21	1.37	0.48	0.20	1.02
1793.00	11.26	1.06	0.52	0.69	0.58
1792.00	14.73	0.93	0.57	0.33	0.38
1791.00	13.63	0.94	0.42	0.90	0.61
1790.00	13.18	0.97	0.58	0.74	0.43
1789.00	12.72	0.76	0.50	0.64	0.38
1788.00	11.99	0.97	0.46	0.98	0.71
1787.00	10.28	1.12	0.69	1.34	0.90
1786.00	12.15	0.85	0.53	0.70	0.35
1785.00	12.15	1.01	0.54	0.48	0.43
1784.00	12.15	1.24	8.56	1.40	1.04
1783.00	12.15	0.98	1.96	1.12	0.57
1782.00	11.52	0.77	0.43	0.84	0.63
1781.00	11.52	0.85	0.59	1.09	0.72
1780.00	10.49	0.64	0.52	0.87	0.46
1779.00	11.77	0.83	0.92	1.30	0.60
1778.00	13.04	1.67	0.55	1.48	1.20
1777.00	13.80	1.11	0.62	1.26	0.86
1776.00	12.15	0.76	0.43	0.82	0.58
1775.00	10.49	0.82	0.39	0.67	0.46
1774.00	11.56	1.05	0.53	0.77	0.44
1773.00	12.62	1.18	0.52	0.87	0.66
1772.00	12.75	0.98	0.48	0.67	0.58