The spatial and temporal variation of oxidant component in the Martian atmosphere observed by MEX/PFS

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Introduction ~CH_4~

- The current topic of Martian study

  ⇩

  Detection of CH_4

Table 1. The observation of the martian methane

Formisano et al., 2004	0-35 ppb (*variable)
Krasnopolsky et al., 2004	10.5 ppb
Mumma et al., 2009	0-45 ppb(*variable)

- “The methane mixing ration shows **variation**” ⇒ **Why**？

  (This question is the key of **origin** of methane !)

Mixing ratio (ppb)

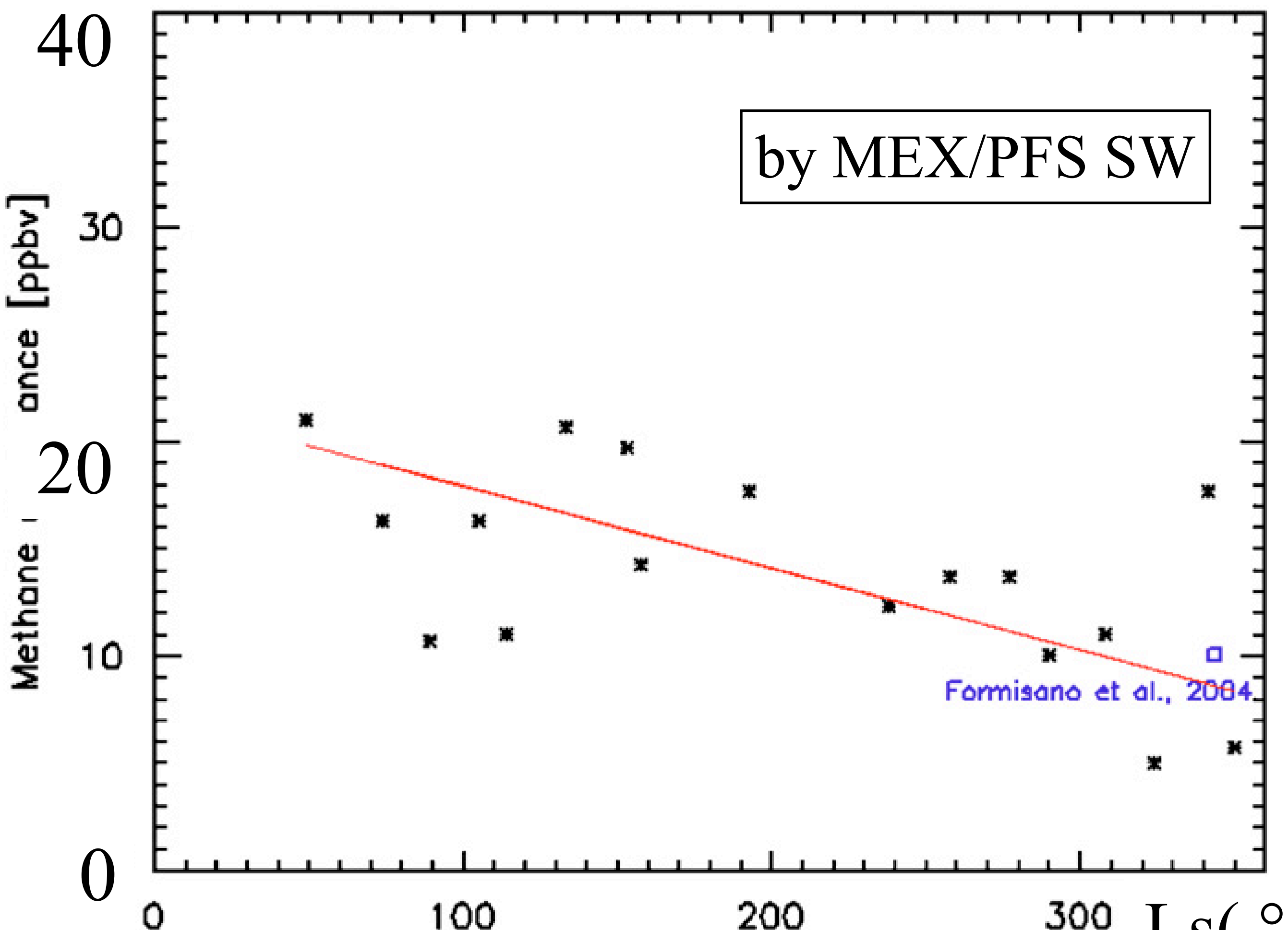


Fig 1. The Methane mixing ratio variation with Ls [Geminale et al, 2008]

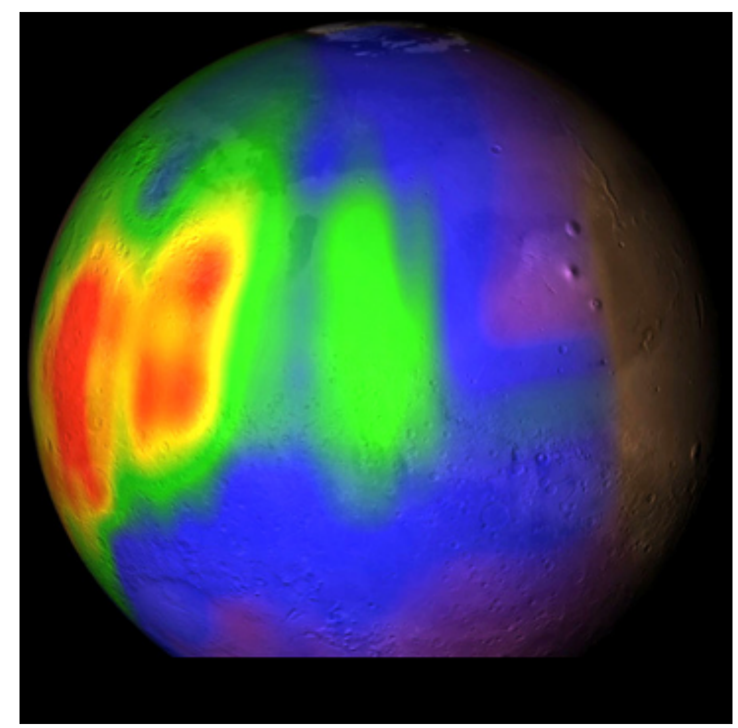


Fig 2. The geometrical distribution observed by IRTF/CSHELL [Mumma et al., 2009]

Introduction ~H2O2~

- <u>Vast quantities of H2O2 can be produced in the Martian dust storms and devils (simulation)</u> [Atreya et al., 2006]

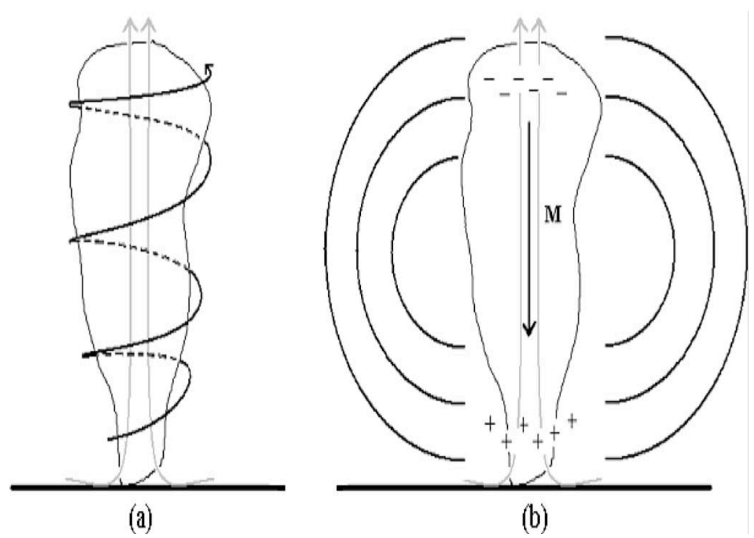


Fig3. structure of a dust devil [Jackson ,2006]

Triboelectric process
(in dust storm/devil)

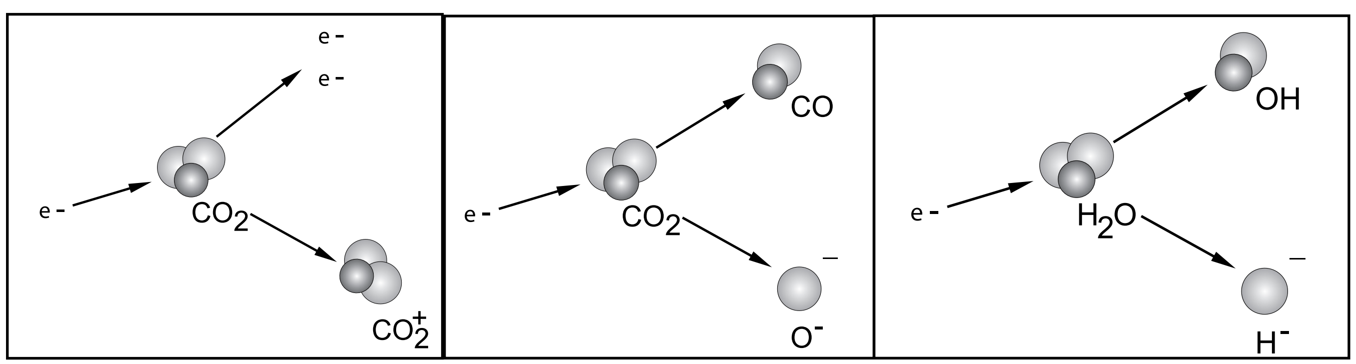


Fig 4. The interaction of electrons with CO2 and H2O [Delory et al., 2006]

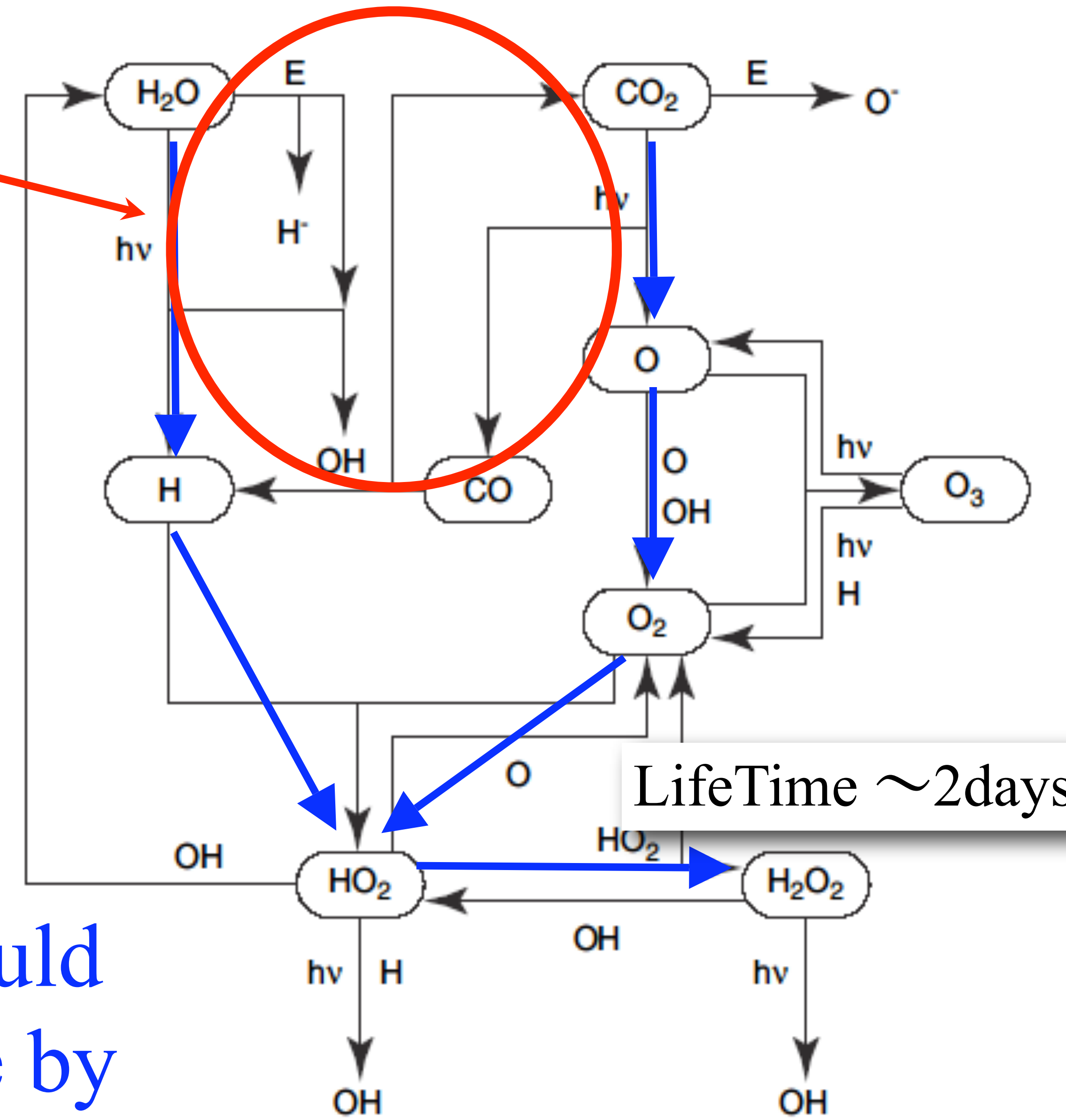


Fig 5. New mechanism for producing oxidant [Atreya et al., 2006]

The calculated abundance of H2O2 could reach **200** times (~ **4ppm**) that produce by photochemistry alone.

<u>Saturation</u>, <u>condensation</u> and <u>precipitation</u>?

Introduction ~CH4 & H2O2~

- <u>The loss process of CH4</u> [Atreya et al., 2007]

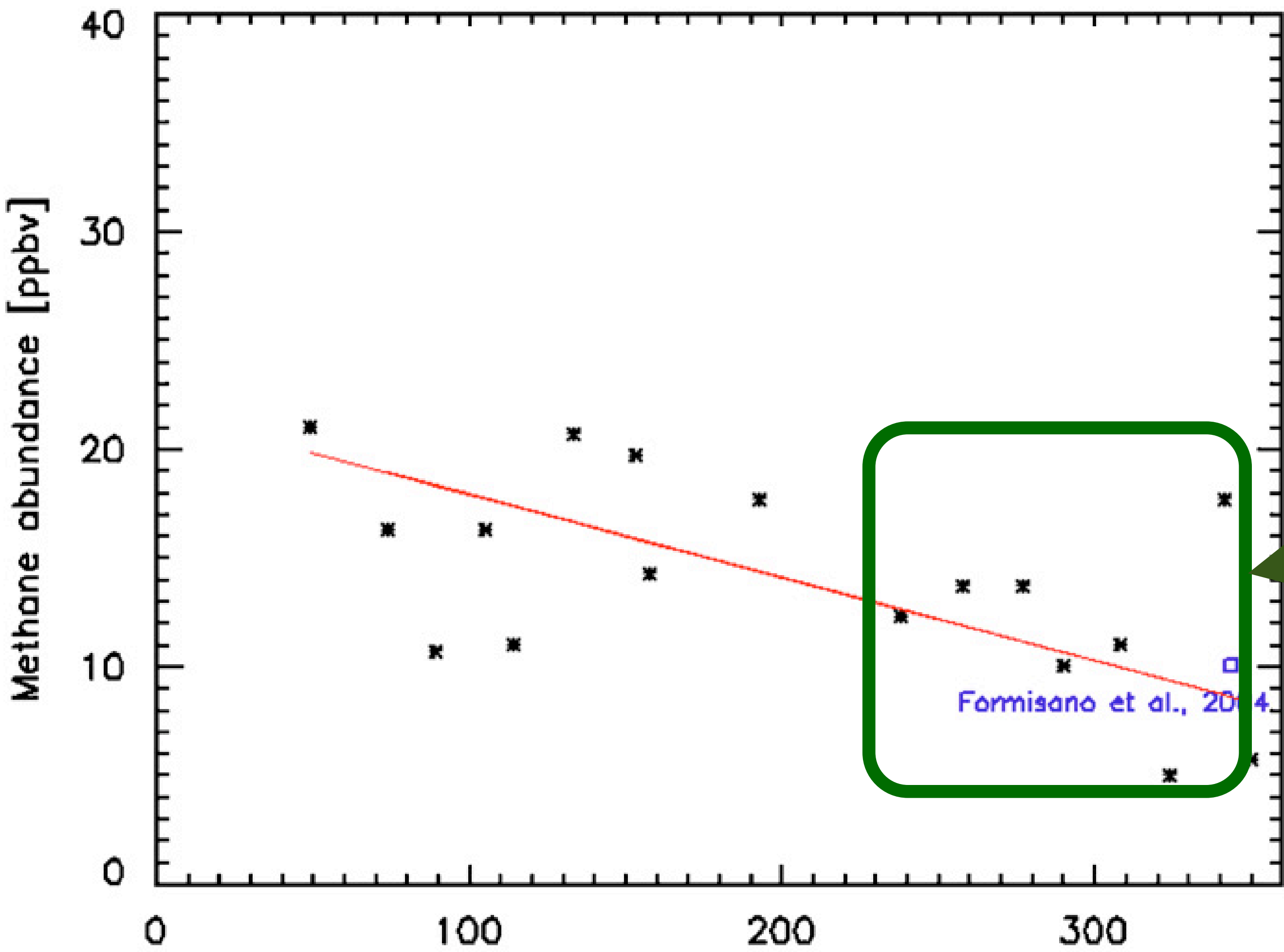
1.Photochemistry

Lifetime→300-600 years

2.Oxidation

Oxidation by string oxidant

Methane is destroyed by means of oxidation from H_2O_2 generated around dust grains?



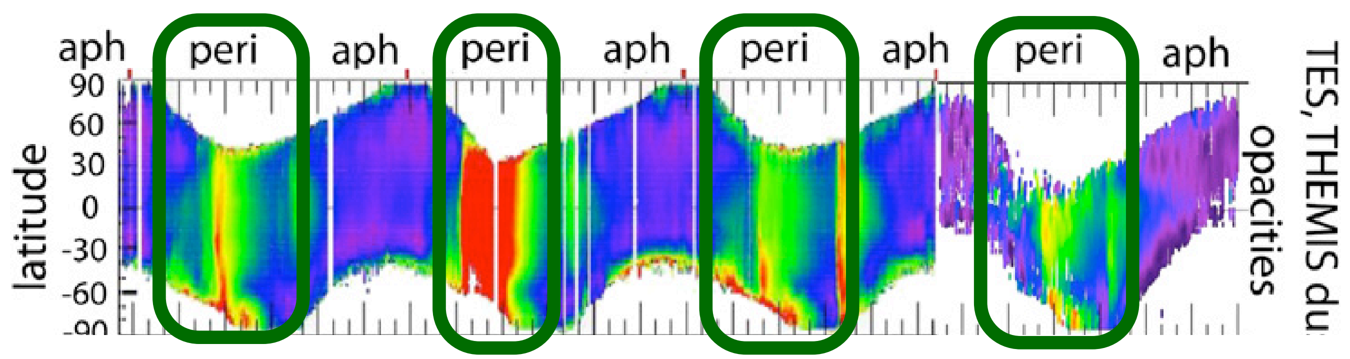


Fig 6. IR dust opacities as a function of time and latitude [Lillis et al., 2008]

Introduction ~H2O2~

Table 2. Previous H_2O_2 observations

Ref.	Ls	Instrument	Date	Wavelength ($\mu m/cm^{-1}$)	Mixing ratio
Krasnopolsky et al., 1997	222°	FTS @ Kitt peak (R=120000)	1988/6	8.08-8.14 1229-1237	upper limit (30ppb)
Encrenaz et al., 2002	112°	IRTF/TEXES (R=80000)	2001/2	8.05-8.10 1235-1243	upper limit (6ppb)
Clancy et al., 2004	254°	JCMT	2003/9	362.156 GHz	18±4ppb
Encrenaz et al., 2004	206°	IRTF/TEXES	2003/7	8.05-8.10 1235-1243	20-50ppb
Encrenaz et al., 2008	332°	IRTF/TEXES	2005/11/30-12/1	8.05-8.10 1235-1243	15±10ppb

We have not understood fully seasonal variation and global map.

Objective

1. The seasonal variation of the H2O2
2. The longitudinal and latitudinal variation of the H2O2
3. To compare the variation of H2O2 with that of CH4 using same data set.

MEX/PFS

Consecutive and high spectral resolution observation
→ Mars Express / Planetary Fourier Spectrometer

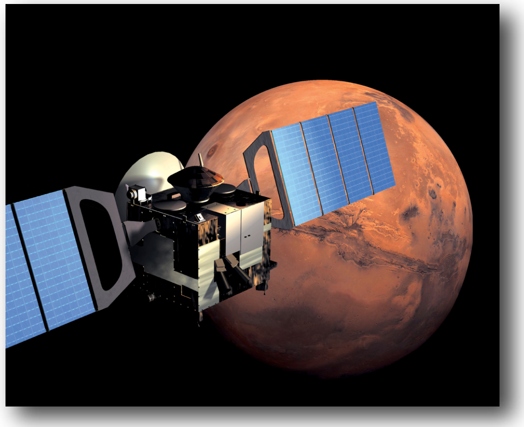


Table 3. PFS character

	Spectral range	Spectral resolution	FOV	NEB	Detector
SW	1.2-5.5μm	$1.3cm^{-1}$	1.7°	$4 \times 10^{-8} W cm^{-2} sr^{-1}$	Photoconductor
LW	5.5-45μm	$1.3cm^{-1}$	2.8°	$5 \times 10^{-9} W cm^{-2} sr^{-1}$	Pyroelectric

[Formisano et al., 2005]

Wave length : 300-400 cm-1 (25-33μm)

Related Presentation

V. Formisano et al., "Search for hydrogen peroxide in the Martian atmosphere." (Poster Presentation)

The example of PFS spectrum

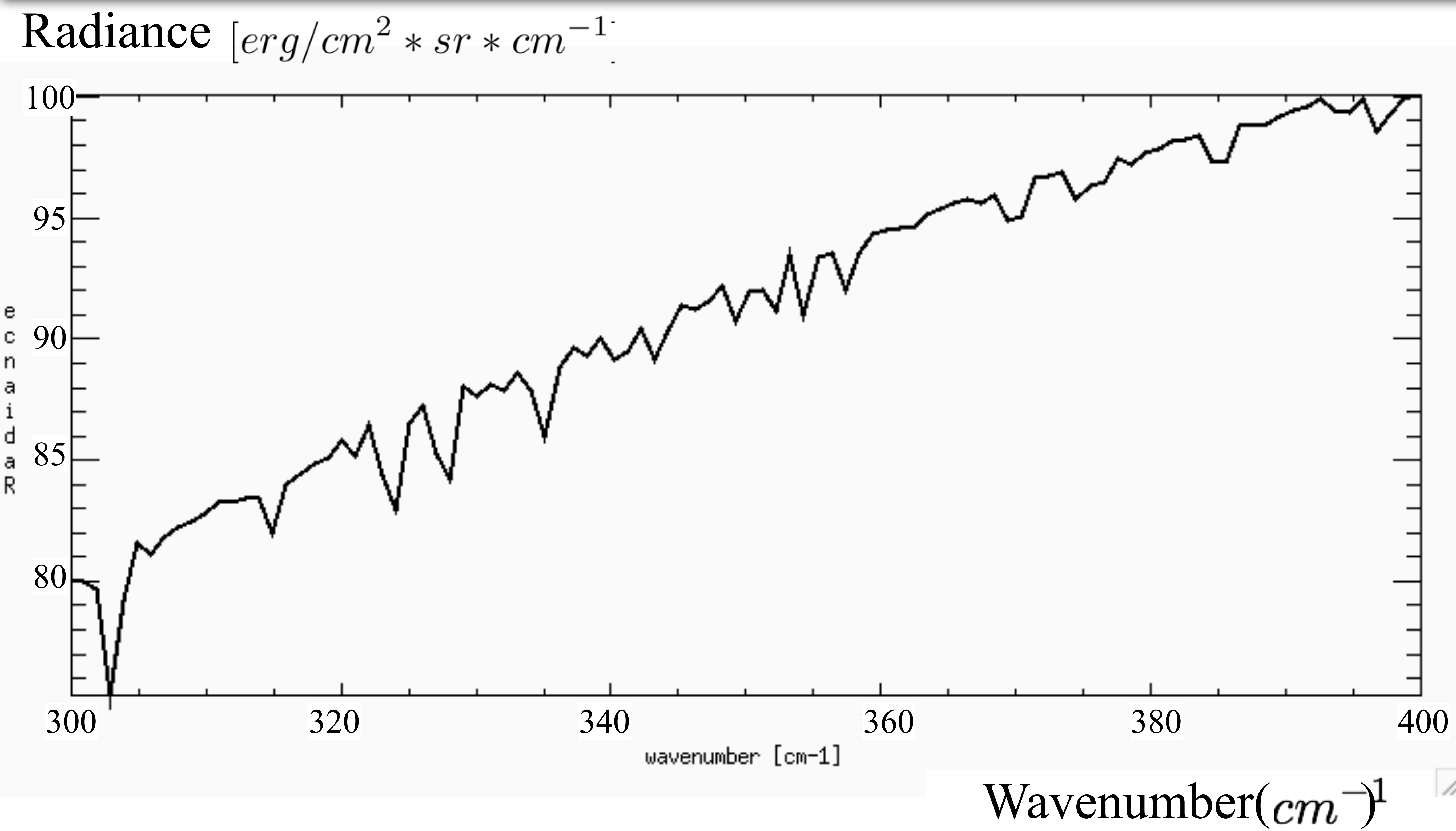


Fig 7. The example of spectrum observed by the PFS at 300-400cm-1 (average 2000 measurements)

Line strength in 300-400 cm-1

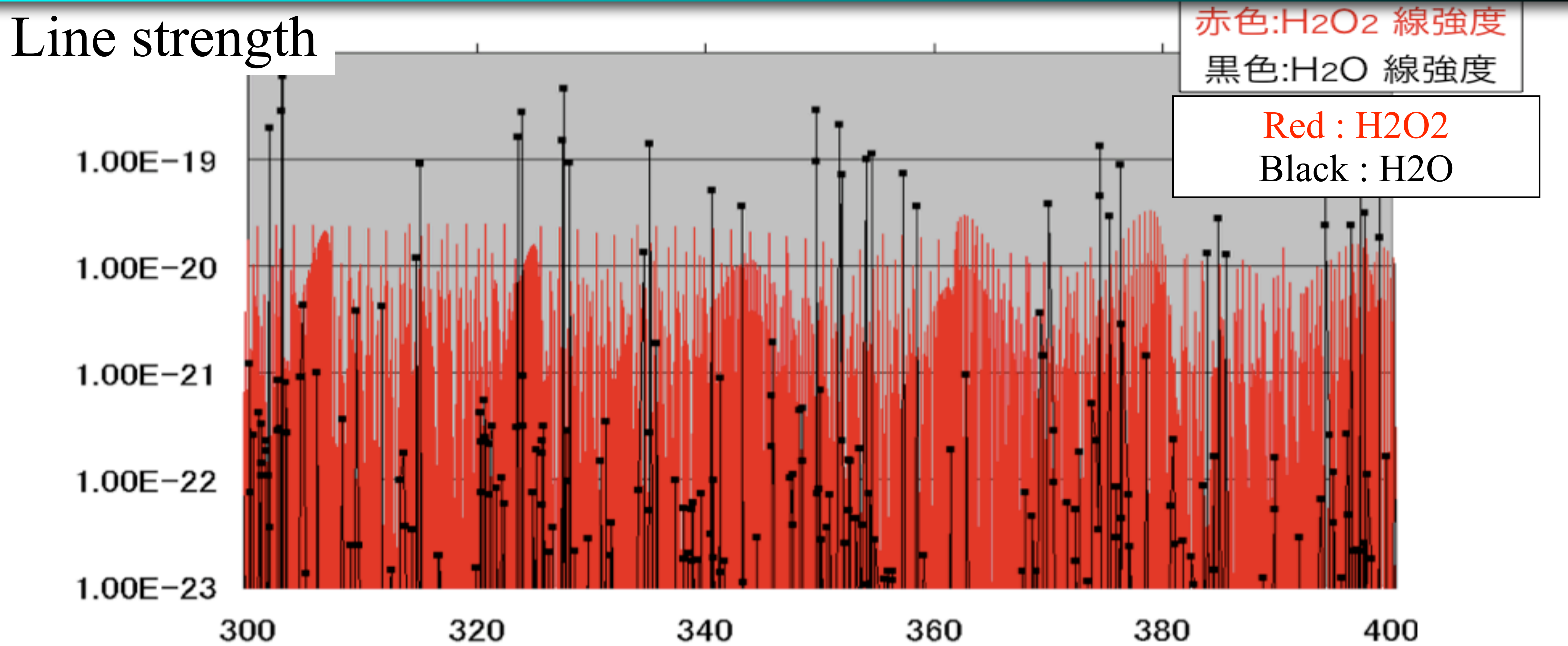


Fig 8. H2O2 and H2O line strength in 300-400 cm-1

Forward model

- **Radiative transfer** model using **line-by-line** model including gaseous absorption by **H2O** and **H2O2**
- On the assumption of a **plane-parallel geometry** and **clear sky**
- Parameters of absorption lines from **HITRAN04** database
- Pressure, temperature and H2O vertical profile from **Mars Climate Databasae**
- H2O2: **Constant** of mixing ratio in the range between 0 to 200 km
- Instrumental function is provide by MEX/PFS PI team.

The result of Forward model

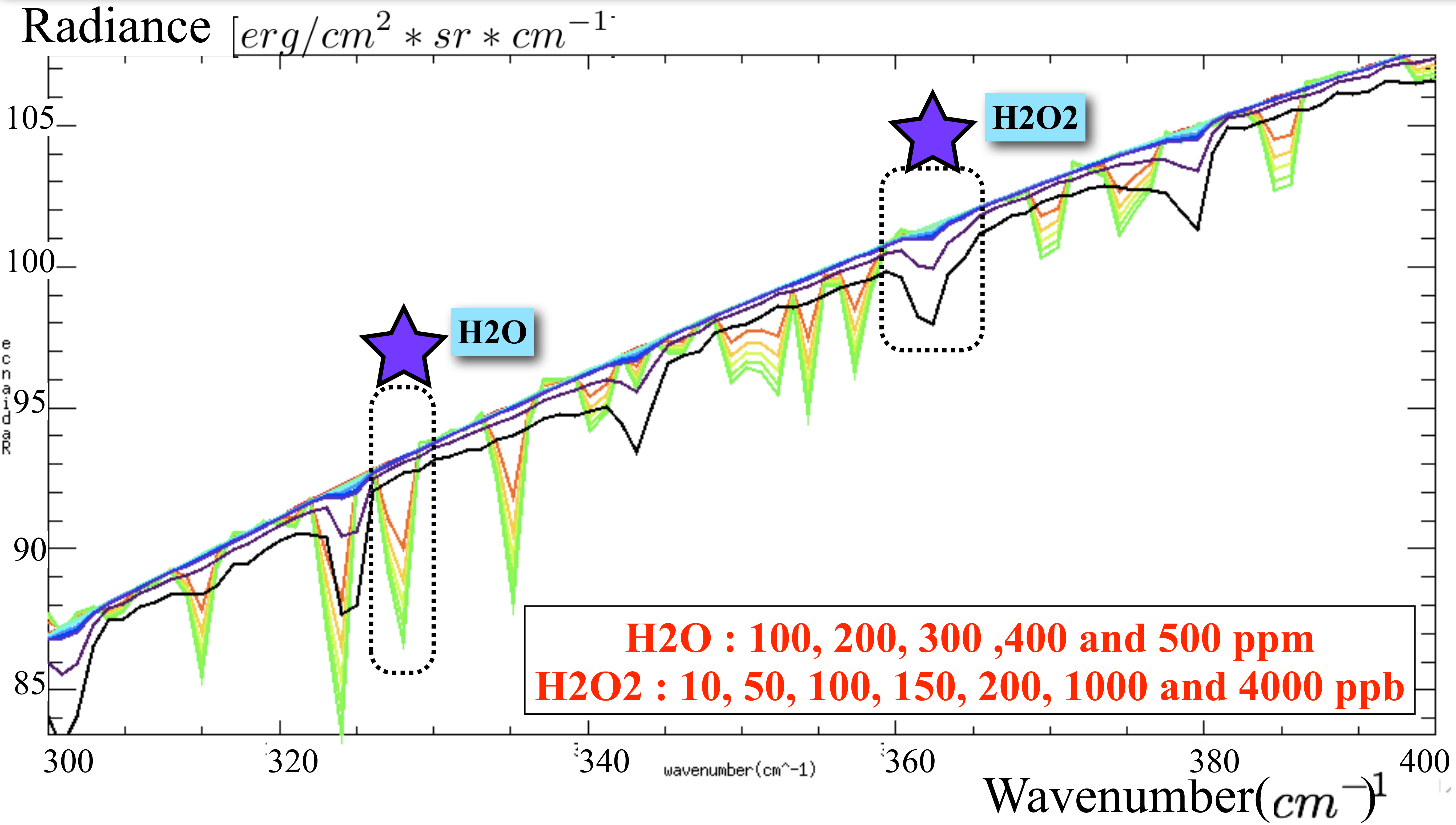


Fig 9. The expected observation by the PFS spectral resolution (300-400cm-1)

The result of Forward model

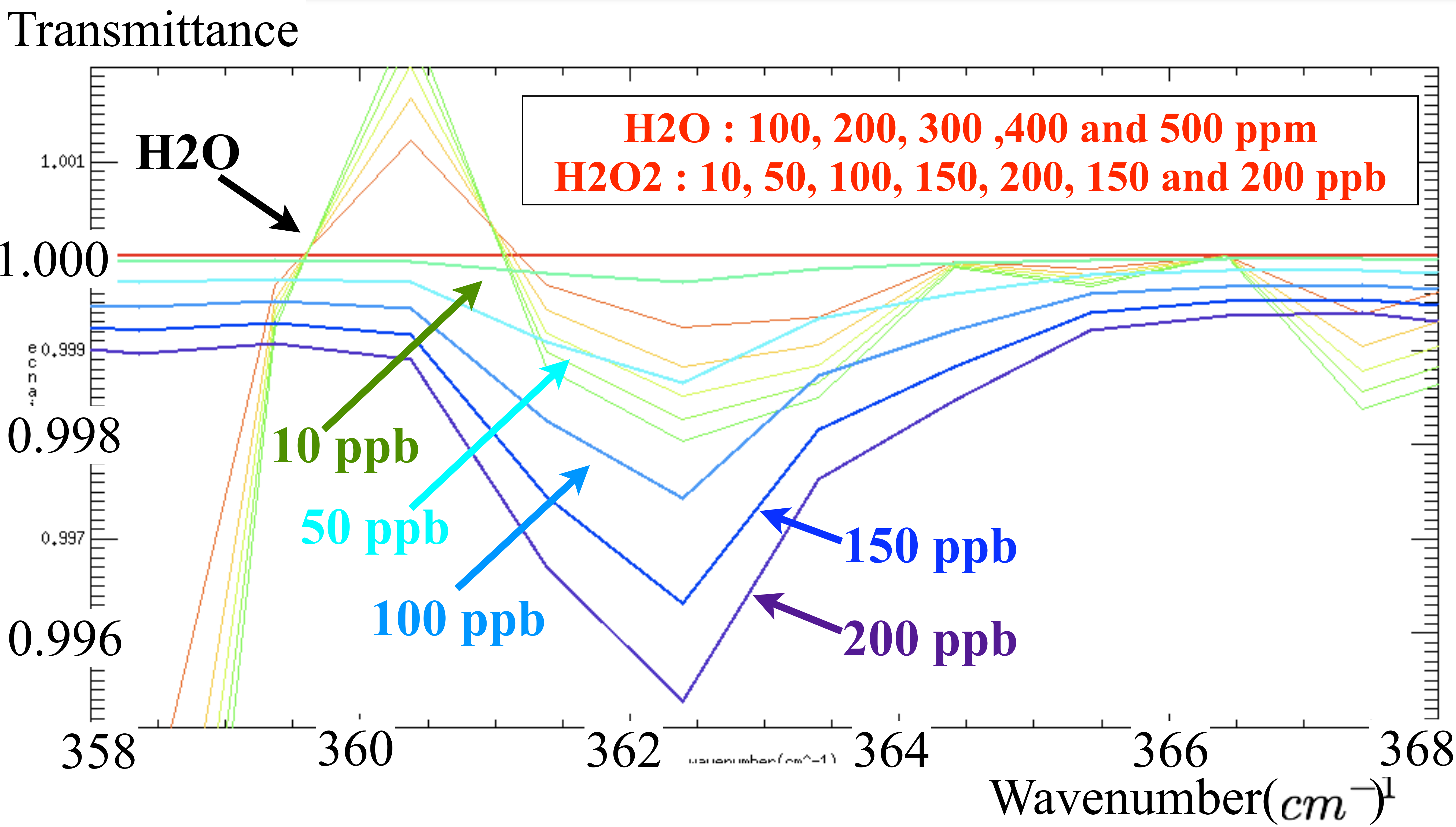


Fig 10. The expected observation by the PFS spectral resolution (358-368cm-1)

Data handling

Step1 Average of interferograms (Raw data)

Step2 FFT the averaged interferograms

*The noise equivalent radiance = ~1 [CGS] at 300 - 500 cm-1 [Giuranna et al., 2005]

*Average of **2000** measurements → noise level = ~0.02 [CGS] (= ~ 0.0004)

*The calculated line depth of **50ppb** of H2O2 at 362 cm-1 is ~ 0.05[CGS] (= ~ 0.001)

50ppb of H_2O_2 can be measured with SNR = 2.5

* Data set

Martian one year (year 2004 - 2005)

* Data selection

Low and middle latitude (-60°~60°)
Emission angle < 30°
Only nadir observation
Surface temperature > 200K

The method of fitting

Step1

<u>Retrieval the martian surface temperature and surface emissivity</u>

(using the least squares method)

Surface temperature is retrieved -->> at 1250 - 1350cm-1

Surface emissivity -->> at 312.9, 326.0, 330.1, 359.4, 365.4, 366.4, 389.6, 390.7, 391.7 and 392.7 cm-1

Step2

<u>Retrieval the H2O column abundance</u>

(using the Levenberg-Marquardt aloglism)

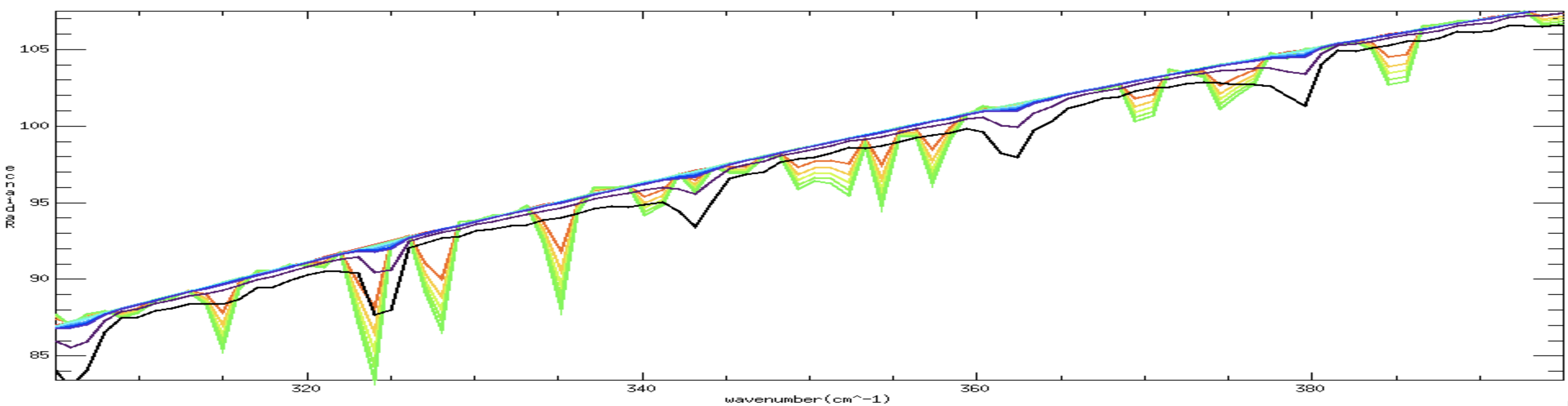
H2O -->> at 326 - 332 cm-1

Step3

<u>Retrieval the H2O2 column abundance</u>

(using the Levenberg-Marquardt aloglism)

H2O2 -->> at 360.4, 361.4, 362.4, 363.4, 364.4 and 365.4 cm-1



The example of fitting result

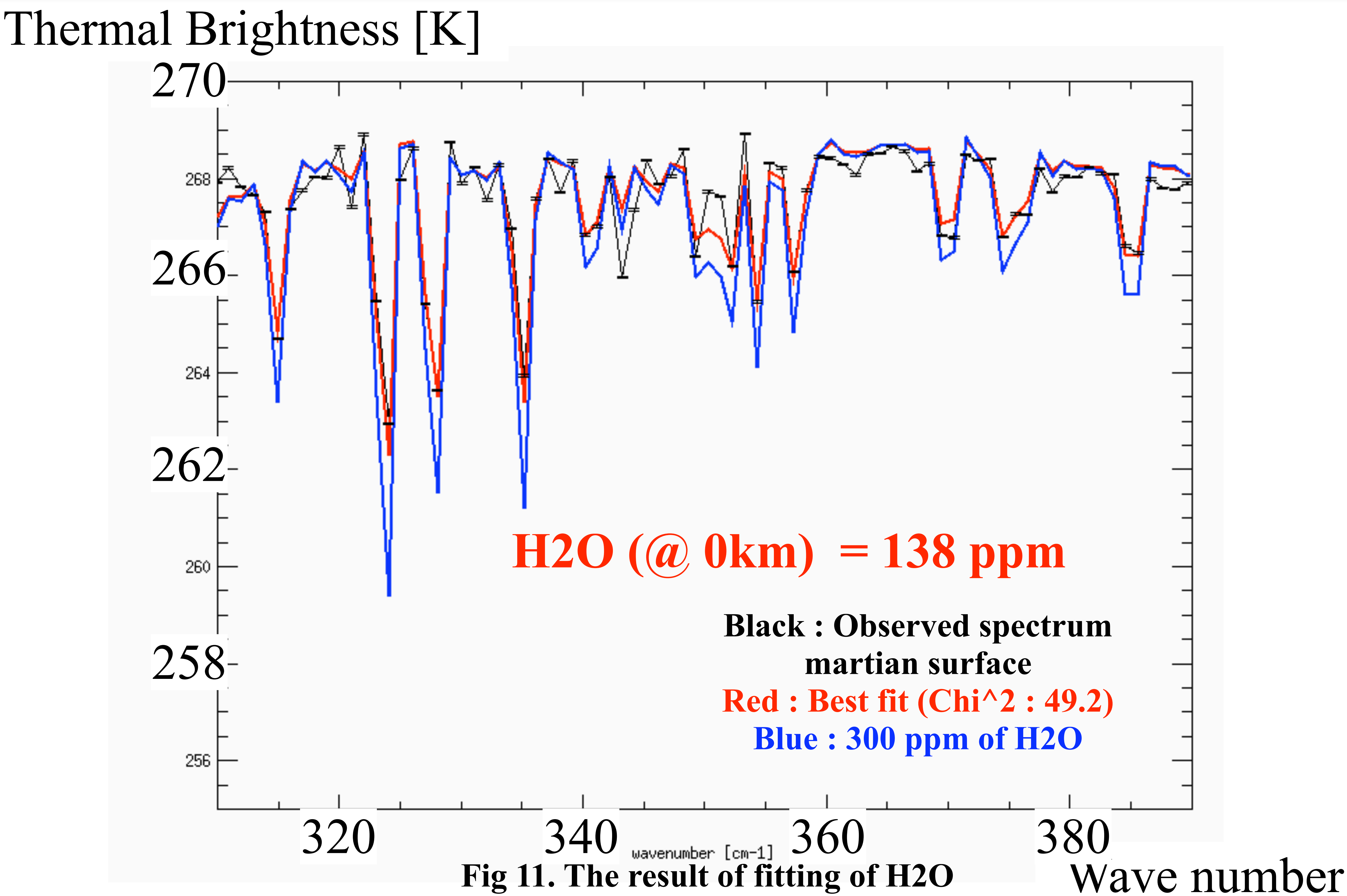


Fig 11. The result of fitting of H2O

The example of fitting result

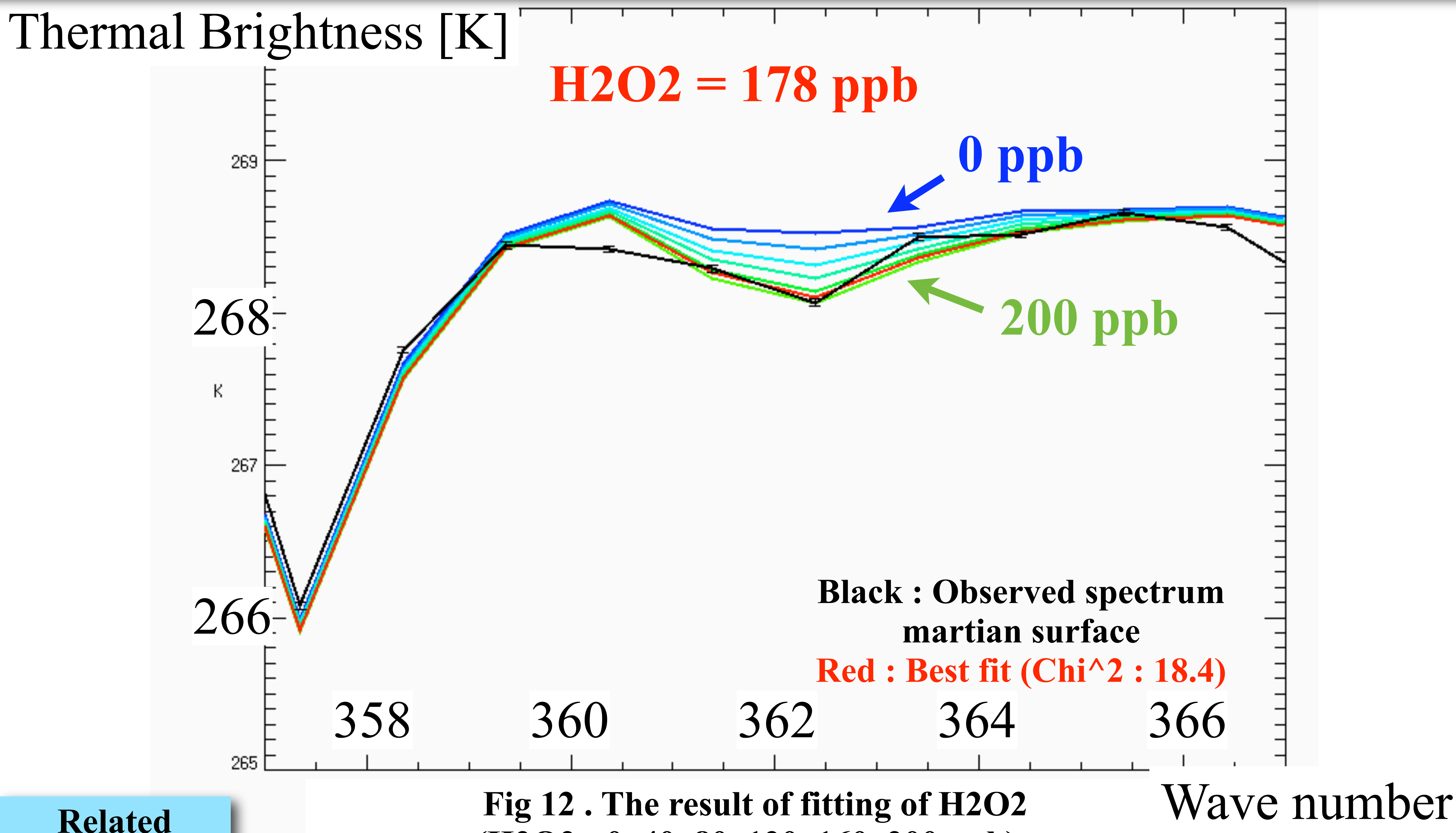


Fig 12 . The result of fitting of H2O2
(H2O2 : 0, 40, 80, 120, 160, 200 ppb)

Related Presentation

V. Formisano et al., "Search for hydrogen peroxide in the Martian atmosphere." (Poster Presentation)

Result of Seasonal variation

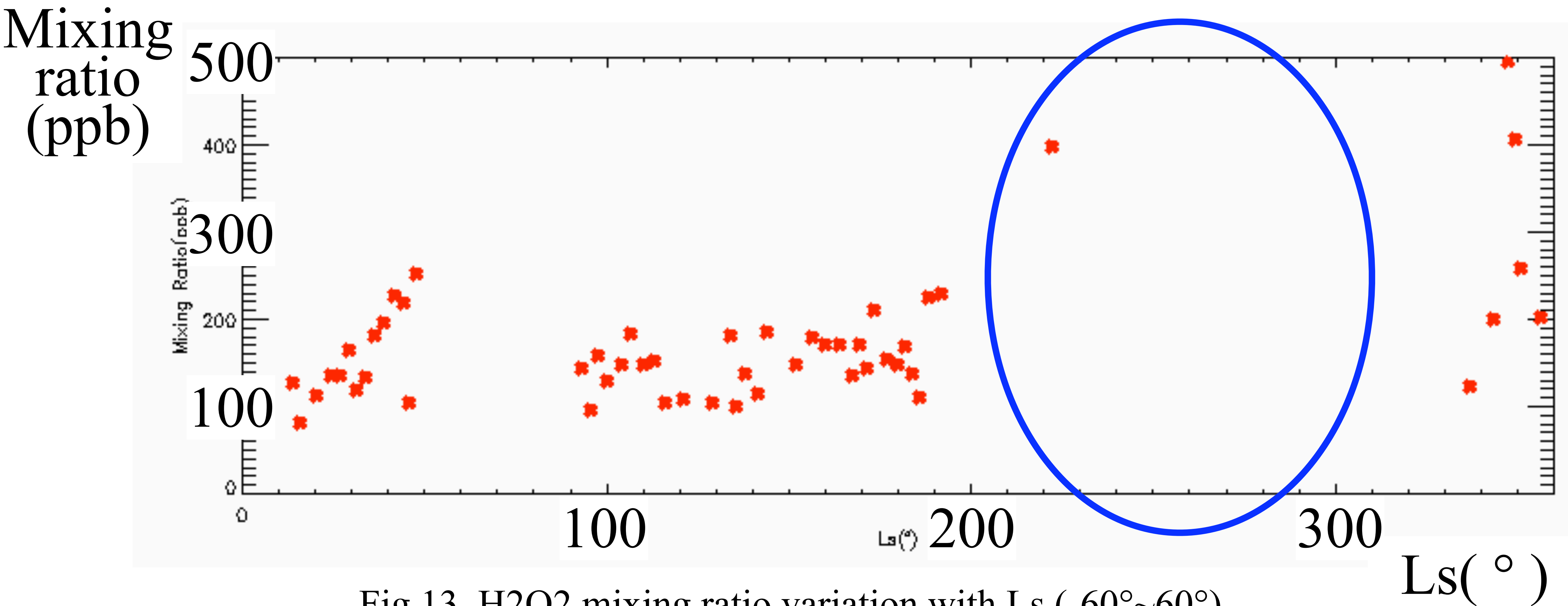


Fig 13. H2O2 mixing ratio variation with Ls.(-60°~60°)

The seasonal variation is suggested, but it is necessary to discuss whether the variation is meaningful or not because there are the period we have not analyzed yet. To derive the seasonal variation in another martian year is indispensable.

Future works

- ✓ To check the validity of analyzing method.
- ✓ To derive the seasonal variation in another martian year.
- ✓ To investigate whether there are the enhancement of H2O2 abundance in short time scale.
- ✓ To compare the variation of H2O2 with that of CH4 using same data set together with INAF-team.
- ✓ We plan to observe the martian H2O2 by APEX sub-millimeter telescope at the end of this November.

APEX proposal

A sensitive search for minor constituent related to possible sources and sinks of methane on Mars	
Altitude	5107 m, Latitude: 23°00'20.8" South, longitude: 67°45'33.0"
Antenna	12 m
Beam	18”@345GHz
Frequency	220-370 GHz, 1.25-1.39 THz
Receiver	APEX-2 [275-370 GHz] FFTS 8192 channels (122 kHz) Bandwidth : 1 GHz
Date(proposal)	17 Nov. 2009, UT7:00-9:30
Mars diameter	8.8”
Doppler	-9.78 km/s (12 MHz)
Line	SO2(358.2156 GHz), H2O2(362.156 GHz)
Total RMS=0.016K	Total : 1.563(SO2), 1.458(H2O2) Tsum : 5.00(SO2), 4.67(H2O2)

APEX proposal

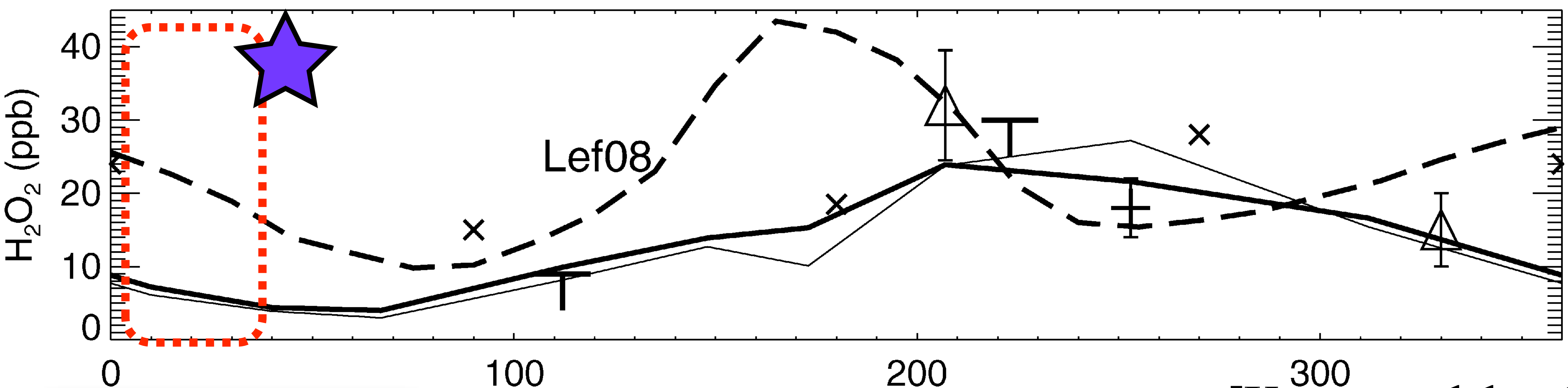
In this proposal, we search the minor elements related to the production and the loss processes in the expected methane cycle by the first-time simultaneous spectroscopic observation of SO2 and H2O2.

Purpose :

✓SO2 : Improvement of S/N and a search in the other seasonal phase than previous our observation -> conclude the contribution of crustal activities to the production of methane.

✓H2O2 : Establish the production and loss processes of the oxidizer and help to constrain between several models of seasonal variation.

✓The vertical profile of H2O2 : The relationship to water -ice clouds and dust storm E-fields



[Krasnopolsky, 2009]

Related Presentation

H.Nakagawa et al., "Search for SO2 in the Martian atmosphere by ground-based submilimeter observation." (Poster Presentation)

Summary

- ✓ The variation of H_2O_2 is the useful indicator to understand the variation of the oxidizer. It can constrain the variation of CH_4 because the oxidizer is a candidate of the sink of CH_4.

- ✓ The variation of H_2O_2 can be obtained by MEX/PFS. Though it is still preliminary, the seasonal variation is suggested in one martian year.

- ✓ Our sub-millimeter observation by APEX aims to obtain the vertical profile of H_2O_2. This observation helps to constrain Martian photochemical model.

To be continued ...

Appendix I

The example of fitting result

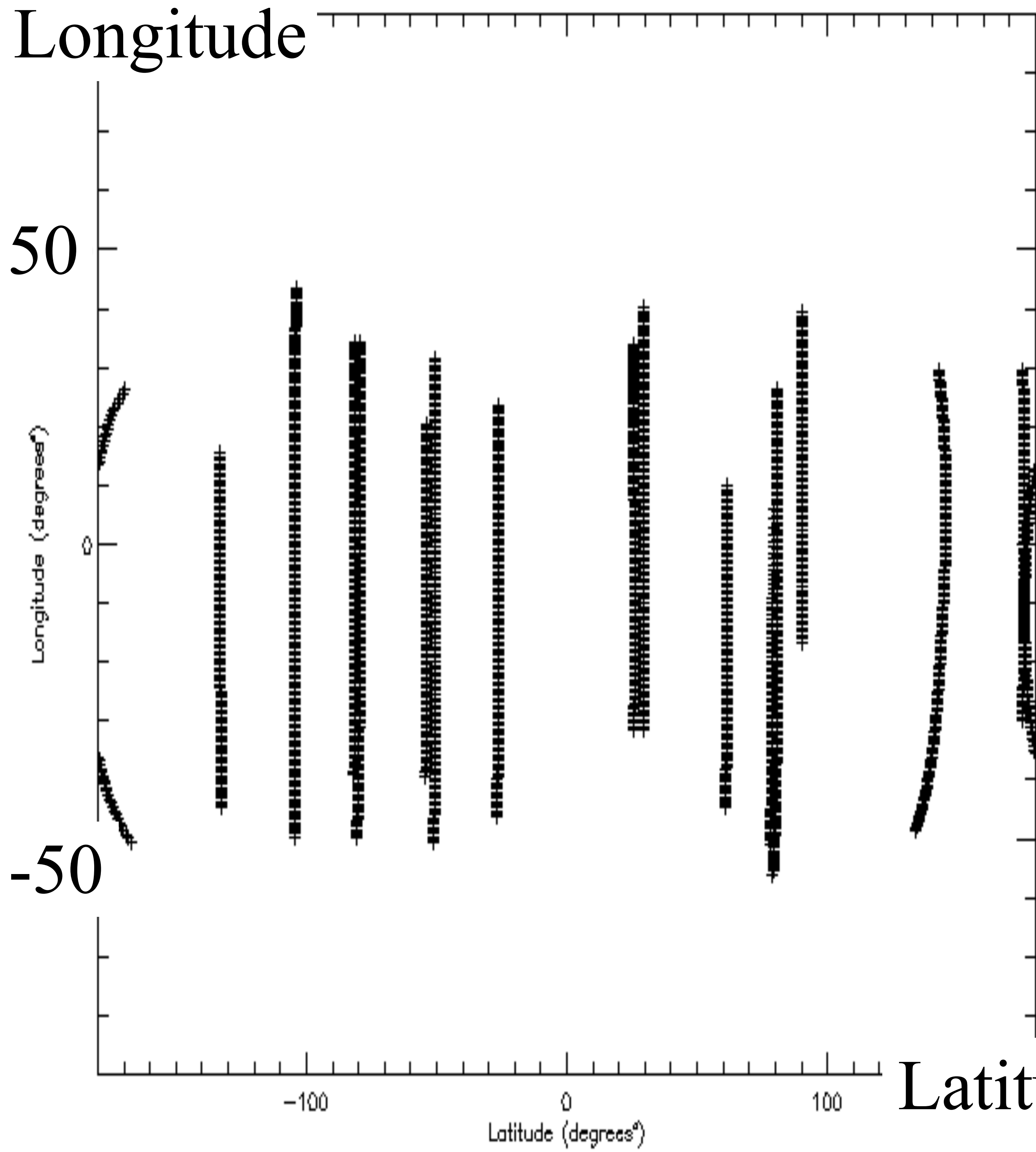


Fig 14. The geographical distribution used for Fig 7, 11 and 12

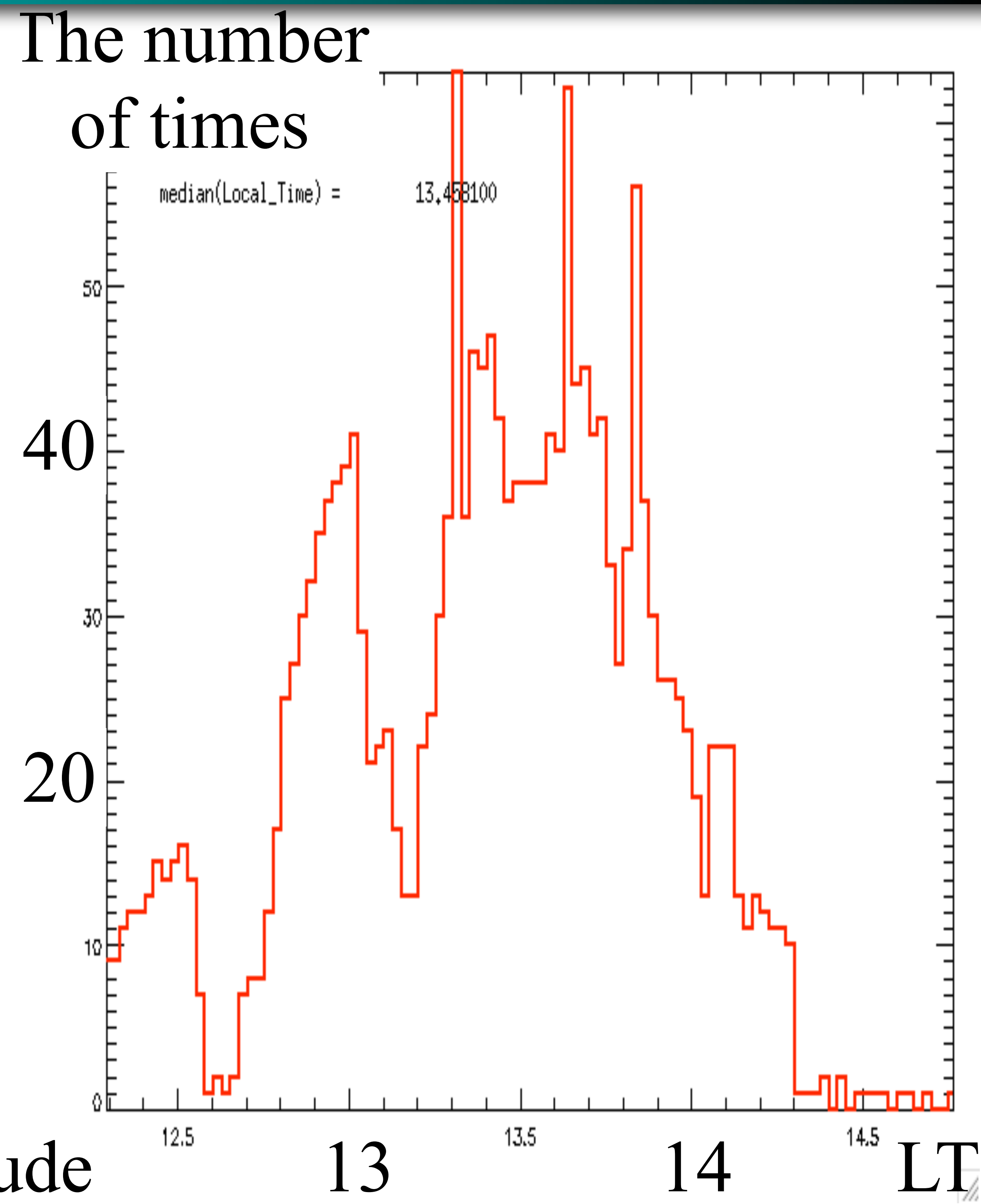


Fig 15. The histogram of LT used for Fig 7, 11 and 12

The example of fitting result

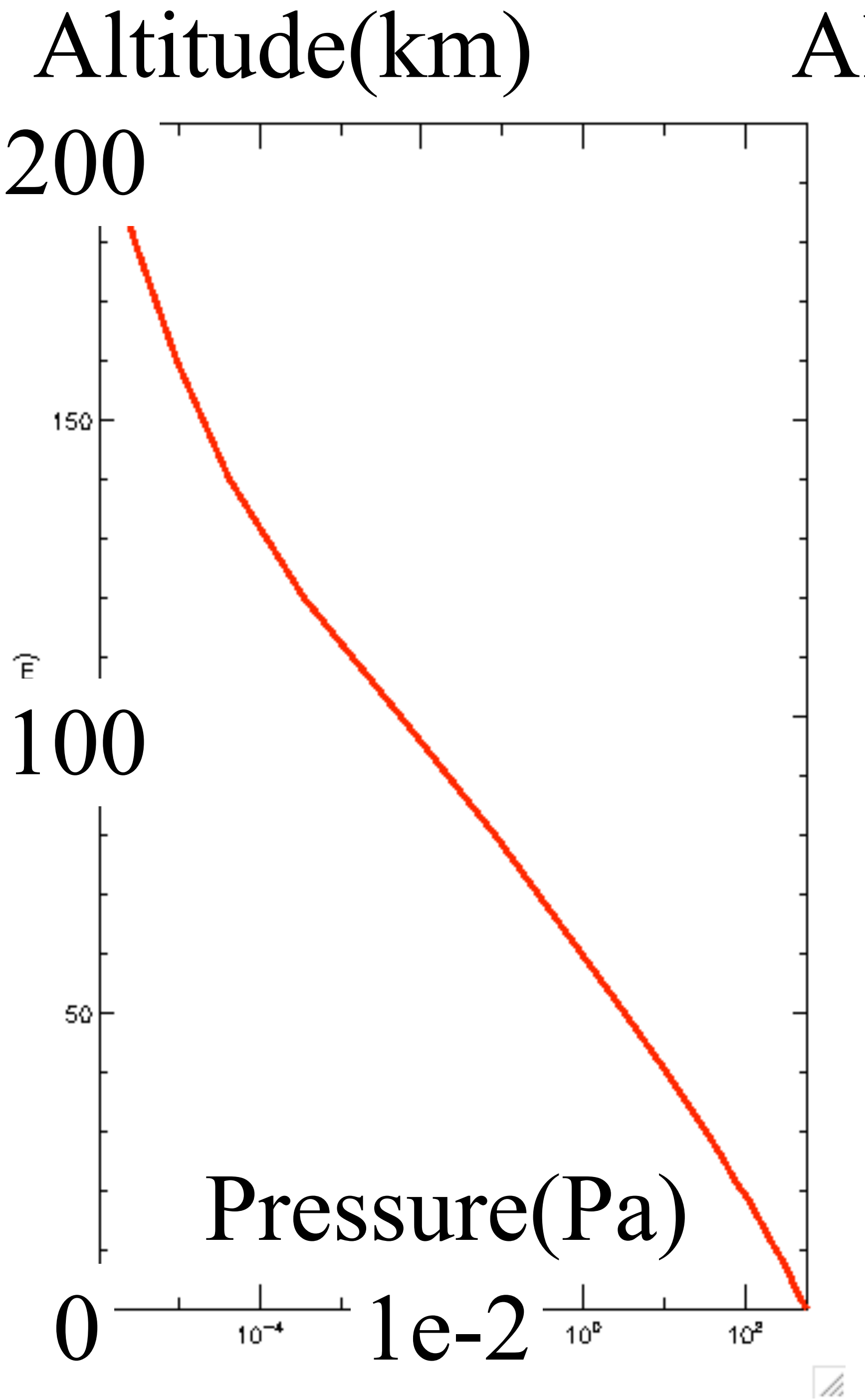


Fig 16. The vertical profile of pressure used for Fig 7, 11 and 12

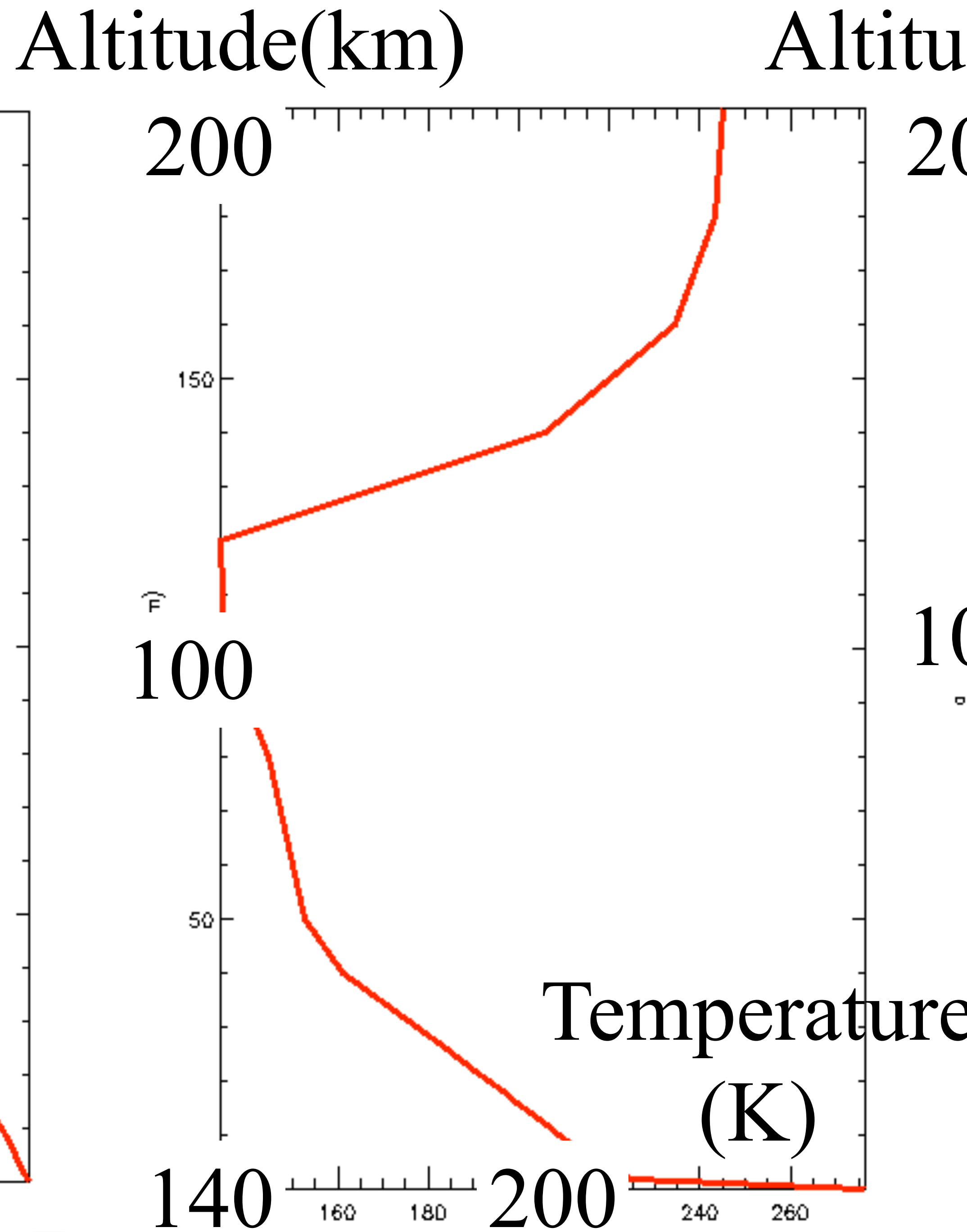


Fig 17. The vertical profile of temperature used for Fig 7, 11 and 12

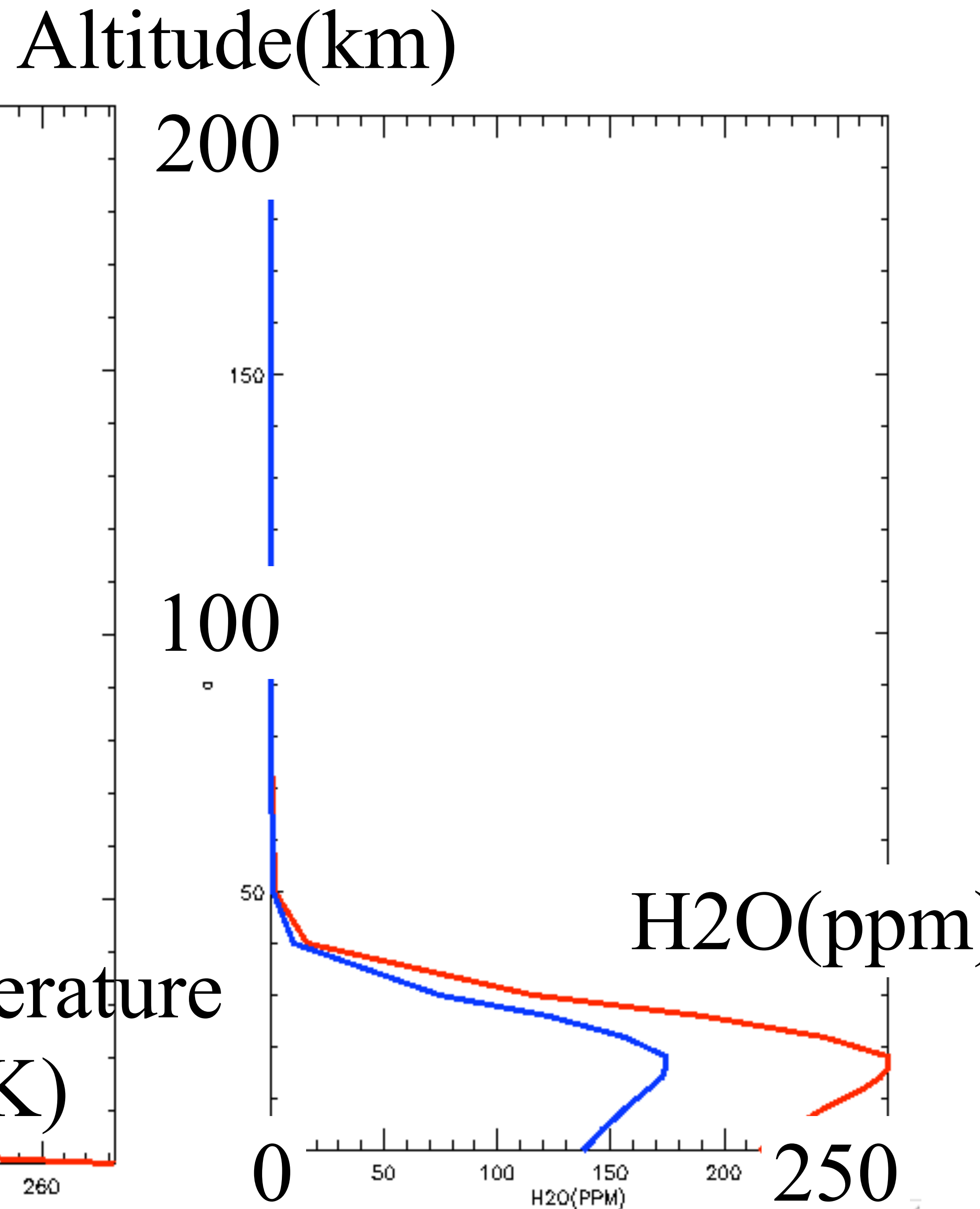


Fig 18. The vertical profile of H2O mixing ration used for Fig 7, 11 and 12 (Red : Initial profile, Blue: derived profile)

Radiative transfer model

$$I_\nu = I_\nu(0)e^{-\tau} + \int_{lower}^{upper} B(\tau)e^{-\int_\tau^{upper} d\tau'} d\tau$$

Non-scattering radiative transfer

$$\tau = \int \rho k(\nu) dz$$

k:absorption coefficient ρ:density

$$k(\nu) = \Sigma S(T) f(\nu - \nu_0)$$

S(T):line intensity f:line shape function

*Temperature correction of line intesisity

$$S(T) = S_0(T_0) \frac{exp(-\frac{hcE}{kT})}{exp(-\frac{hcE}{kT_0})} \frac{Q(T_0)}{Q(T)} \frac{1 - exp(-\frac{hc\nu_0}{kT})}{1 - exp(-\frac{hc\nu_0}{kT_o})}$$

S_0:line intensity at T_0=296[K] , E:Lower-state-energy (from HITRAN04)

*The method of calculation of Q(T) [Gamache et al., 2000]

$$Q(T) = A + BT + CT^2 + DT^3$$

A,B,C,D is constant
(depend on molecular species)

Radiative transfer model

The line shape function is Voigt function

$$f(\nu-\nu_0)=\frac{1}{\alpha_D\pi^{\frac{1}{2}}}Voigt(x,y) \qquad \left(x=\frac{\nu-\nu_0}{\alpha_D(T)} \quad , \quad y=\frac{\alpha_L(p,T)}{\alpha_D(T)} \right)$$

*The method calculation of α_L and α_D

$$\alpha_L(p,T)=\alpha_L(p_0T_0)\frac{p}{p_0}(\frac{T_0}{T})^T$$

The value of $\alpha_L(P_0,T_0)$ is from HITRAN04

$$\alpha_D(T)=\frac{\nu_0}{c}(\frac{2k_BT}{M_r})^{\frac{1}{2}}$$

Mr:molecular weight

Voigt function $$Voigt(x,y)=\frac{y}{\pi}\int\frac{exp(-t^2)}{y^2+(x-t)^2}dt \qquad \left(t=\frac{\nu-\nu'}{\alpha_D(T)} \right)$$

*The solution of Voigh function refers to [Drayson, 1976]

Radiative transfer model

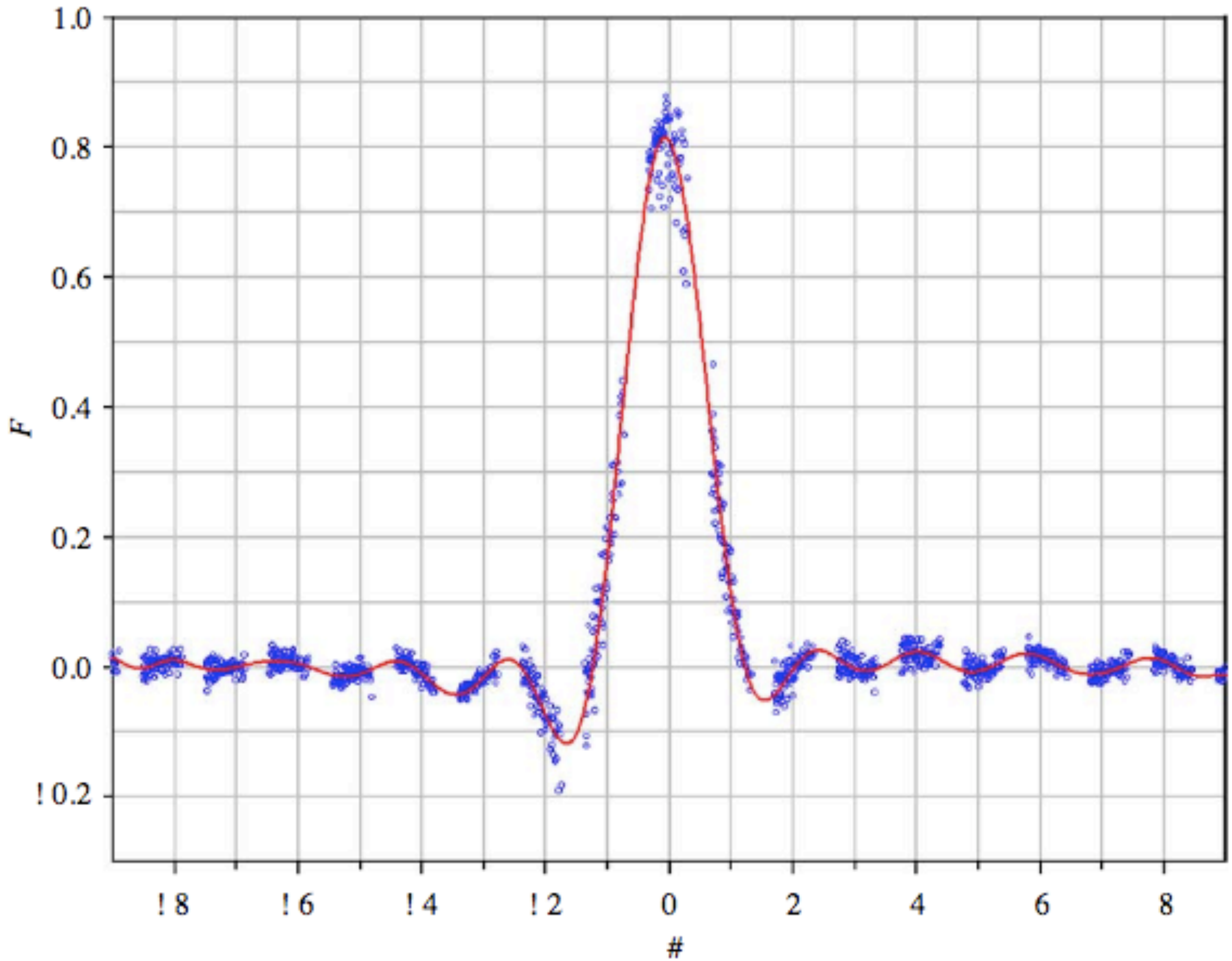
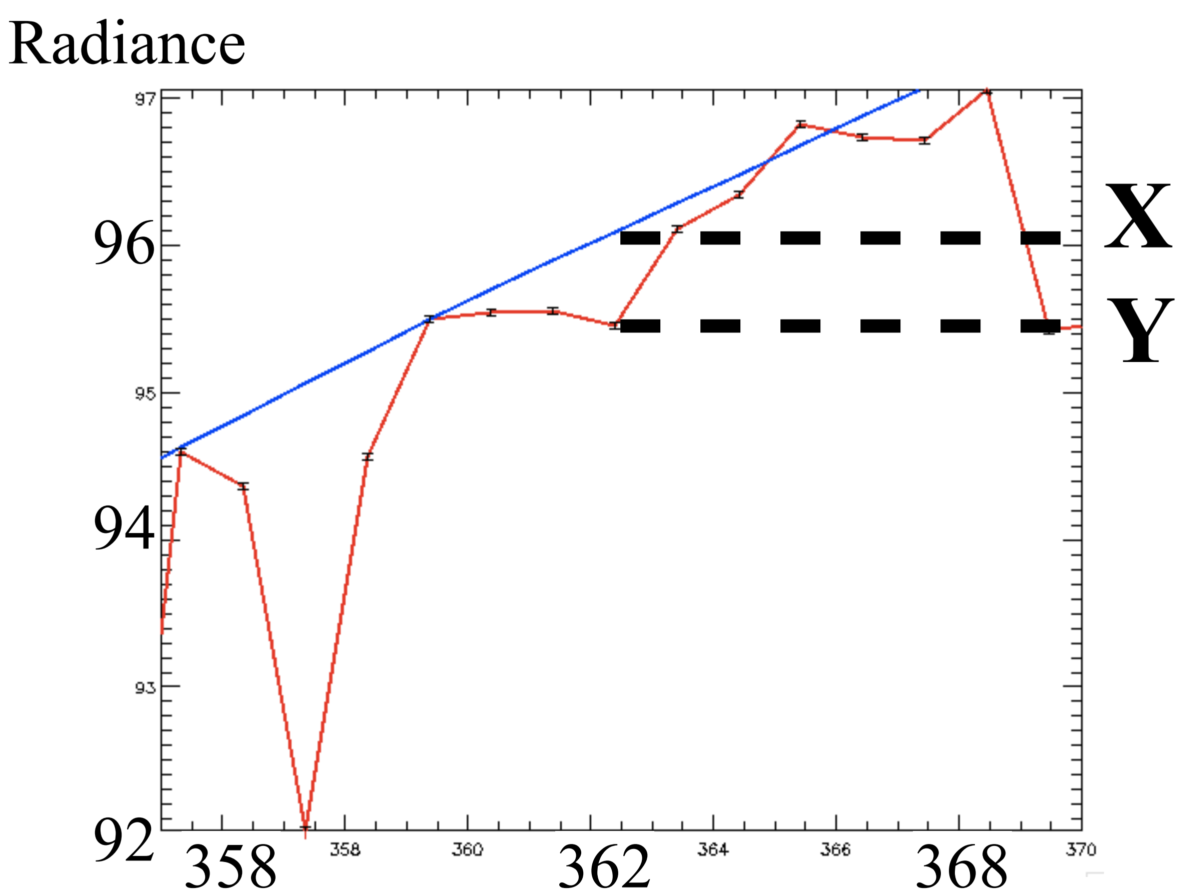


Fig 19.The instrumental function used for calculation the synthetic spectrum [Giuranna, et al., 2005]

100 average

* Average of 100 measurement

* Data set ;
* Data selection ; Only nadir observation
  ; Deribed surface temperature > 200K
* The method of analysis ; Simply, derive the transmittance at 362 cm-1



Transmittance = Y / X
Absorption = 1 - Y / X

H2O2 4ppm → Absorption ~ 0.03
H2O2 1ppm → Absorption ~ 0.01
H2O2 200ppb → Absorption ~ 0.005
H2O2 100ppb → Absorption ~ 0.002

To investigate whether there are the enhancement of H2O2 abundance in short time scale. (The limit of detection ~ 200ppb)

Result of 100 average

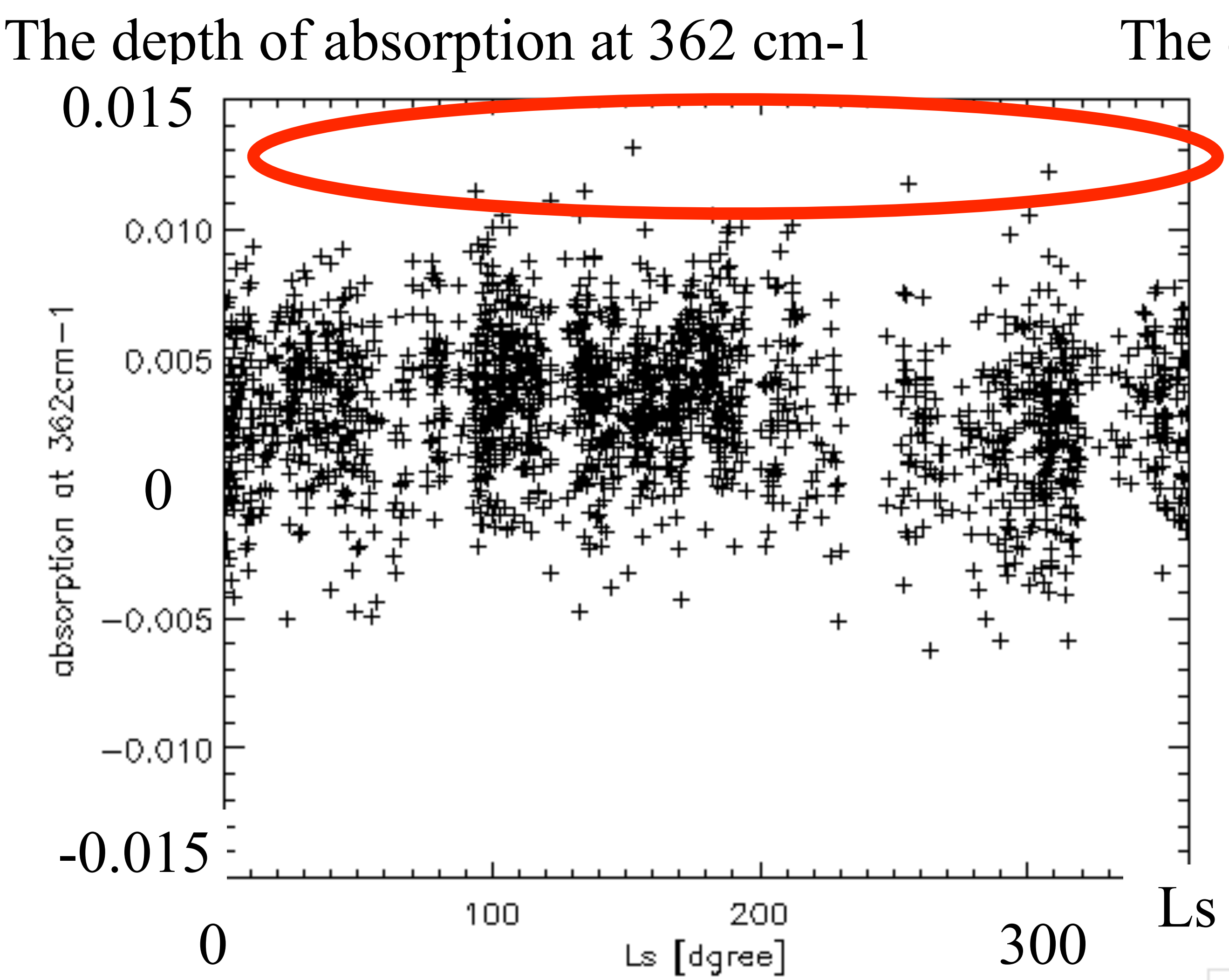


Fig 20. The depth of absorption at 362 cm-1 with Ls

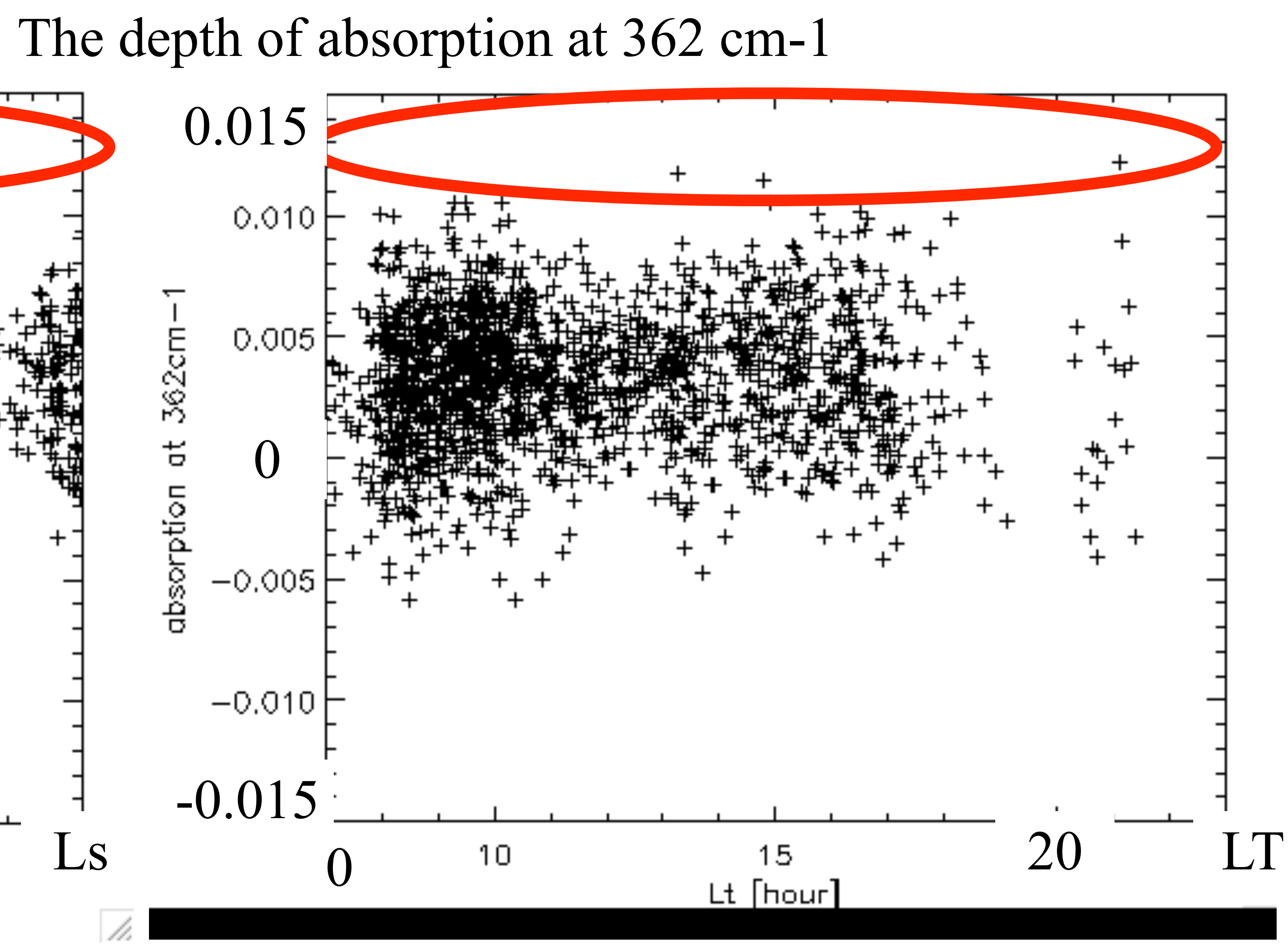


Fig 21. The depth of absorption at 362 cm-1 with Local time

Result of 100 average

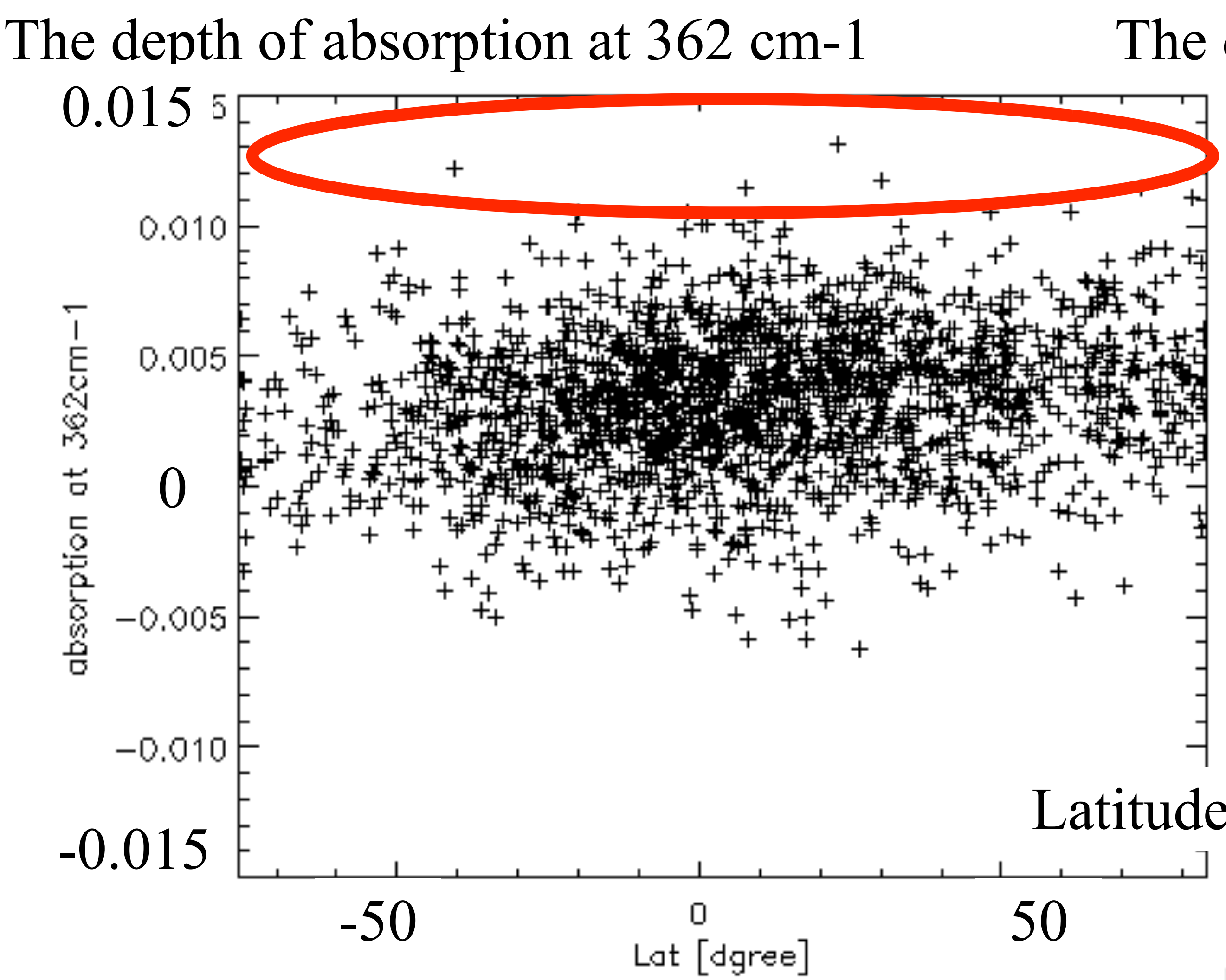


Fig 22. The depth of absorption at 362 cm-1 with Latitude

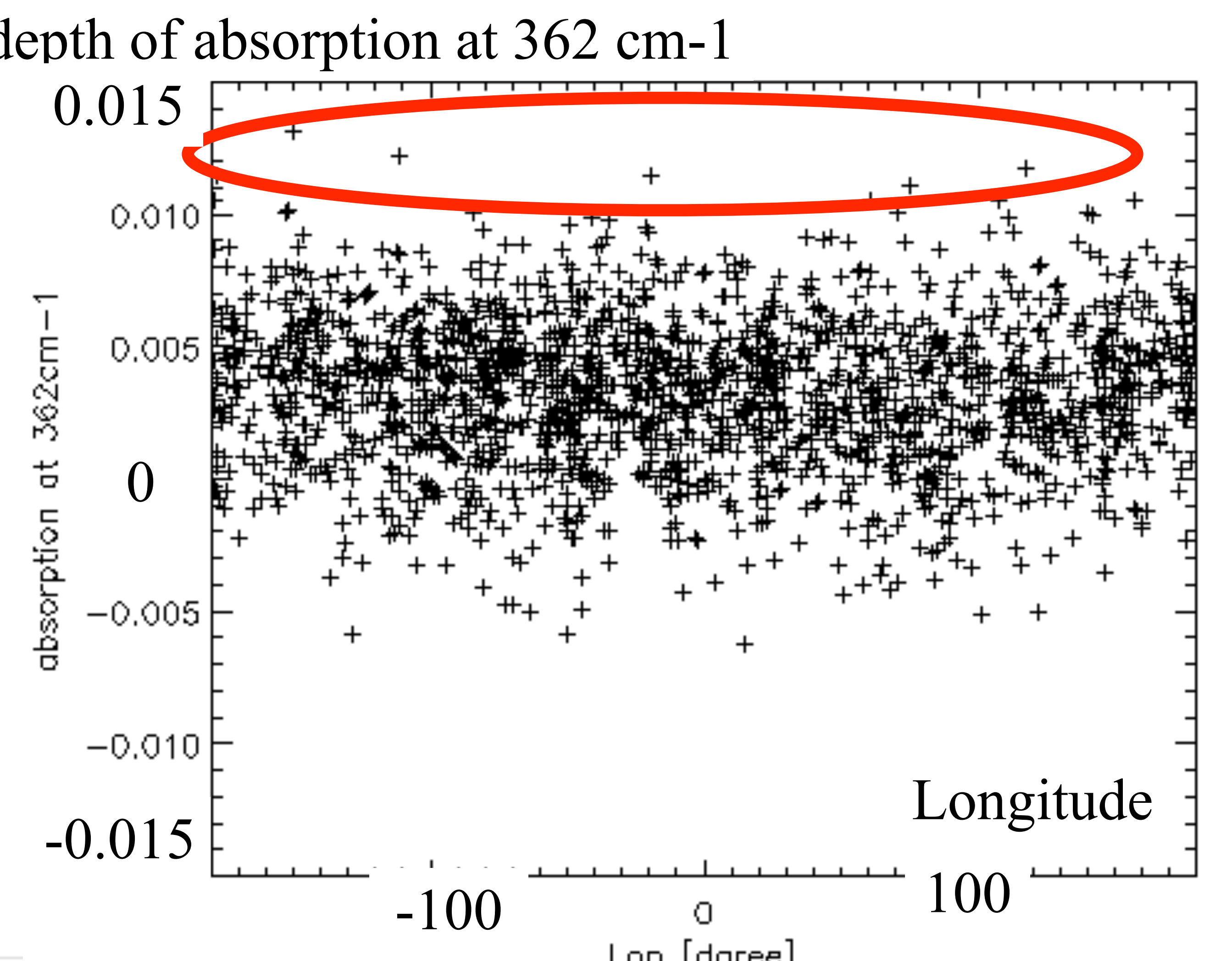


Fig 23. The depth of absorption at 362 cm-1 with Longitude

Result of 100 average

The depth of absorption at 362 cm-1

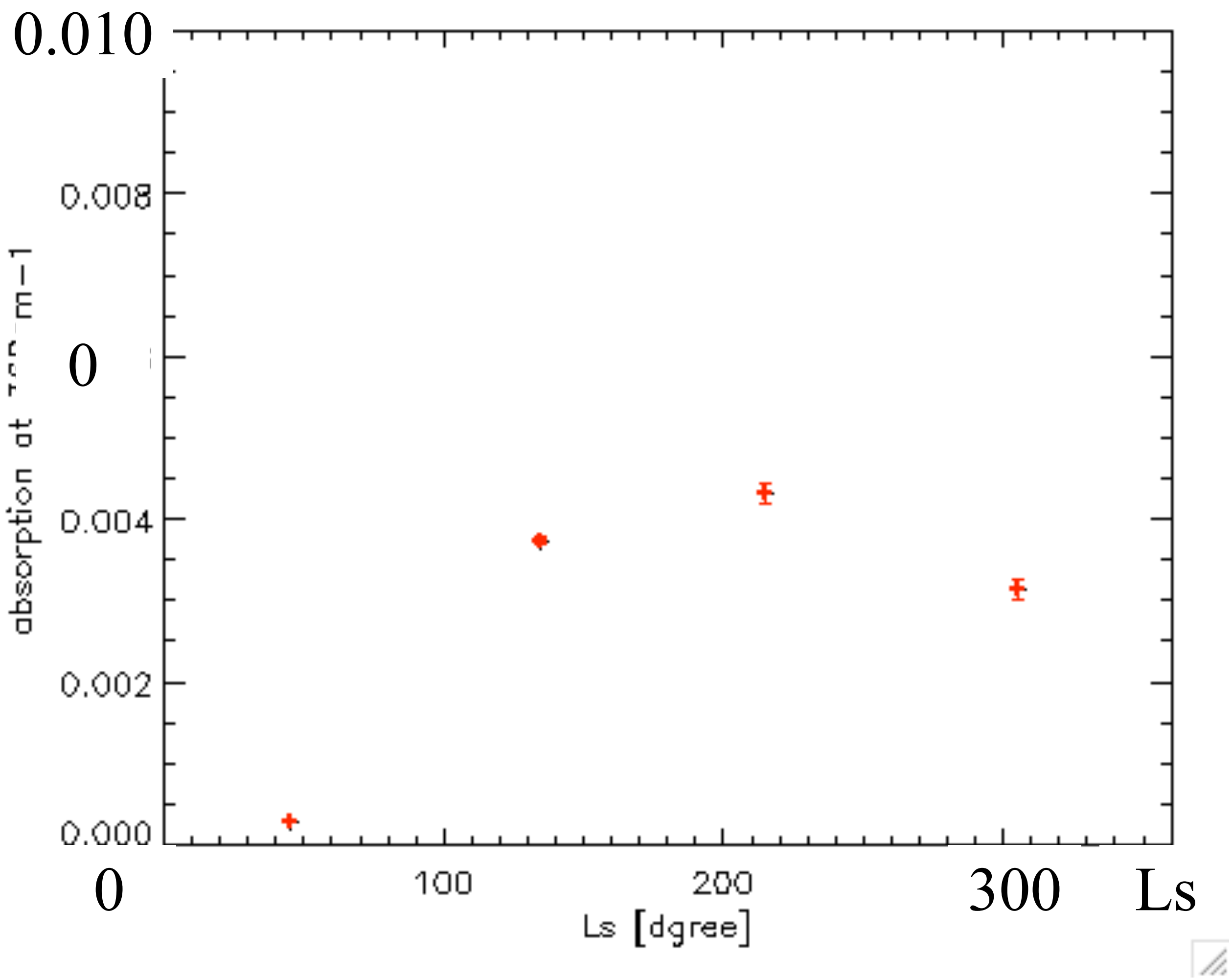


Fig 24. The average every 90° of Fig. 20

The depth of absorption at 362 cm-1

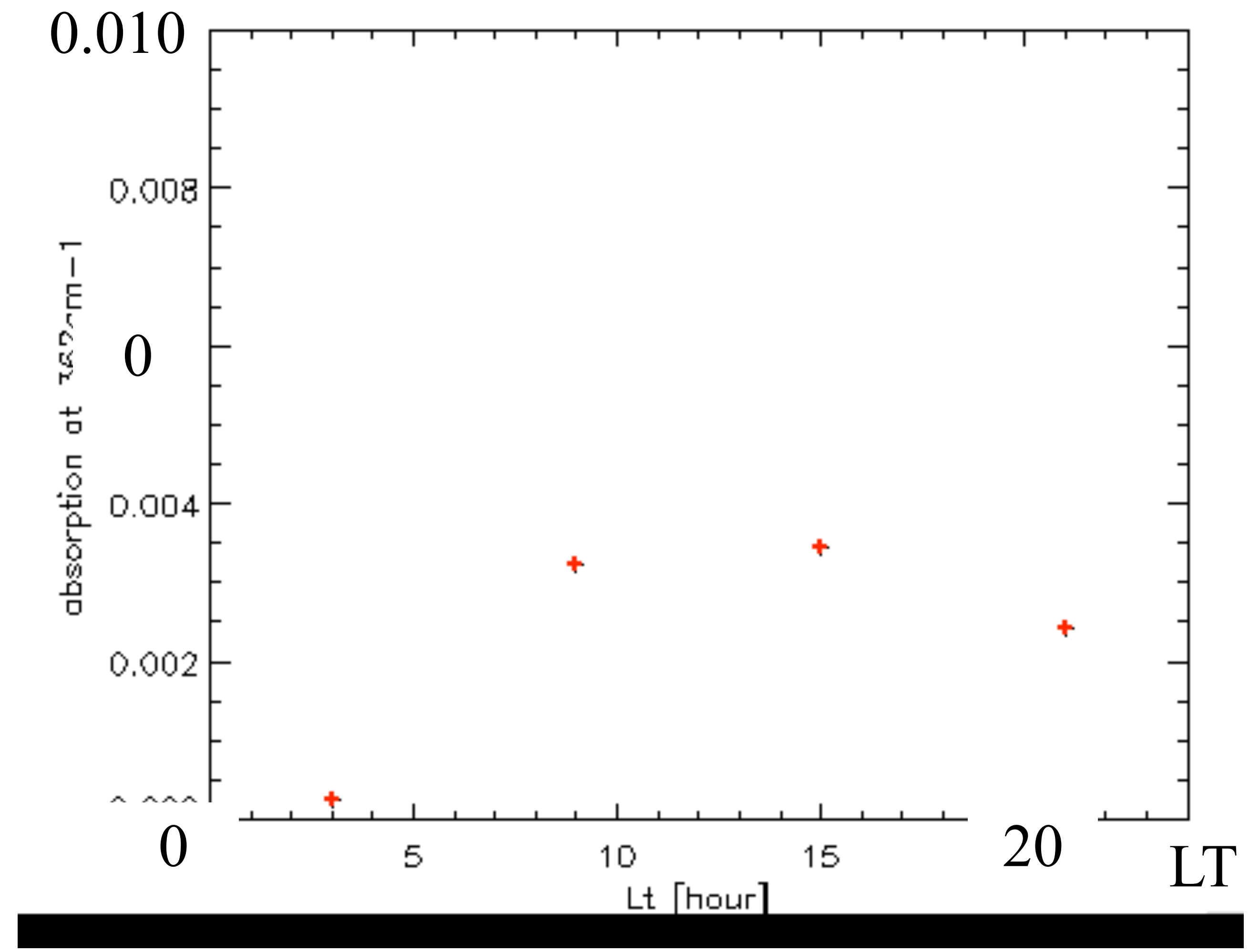
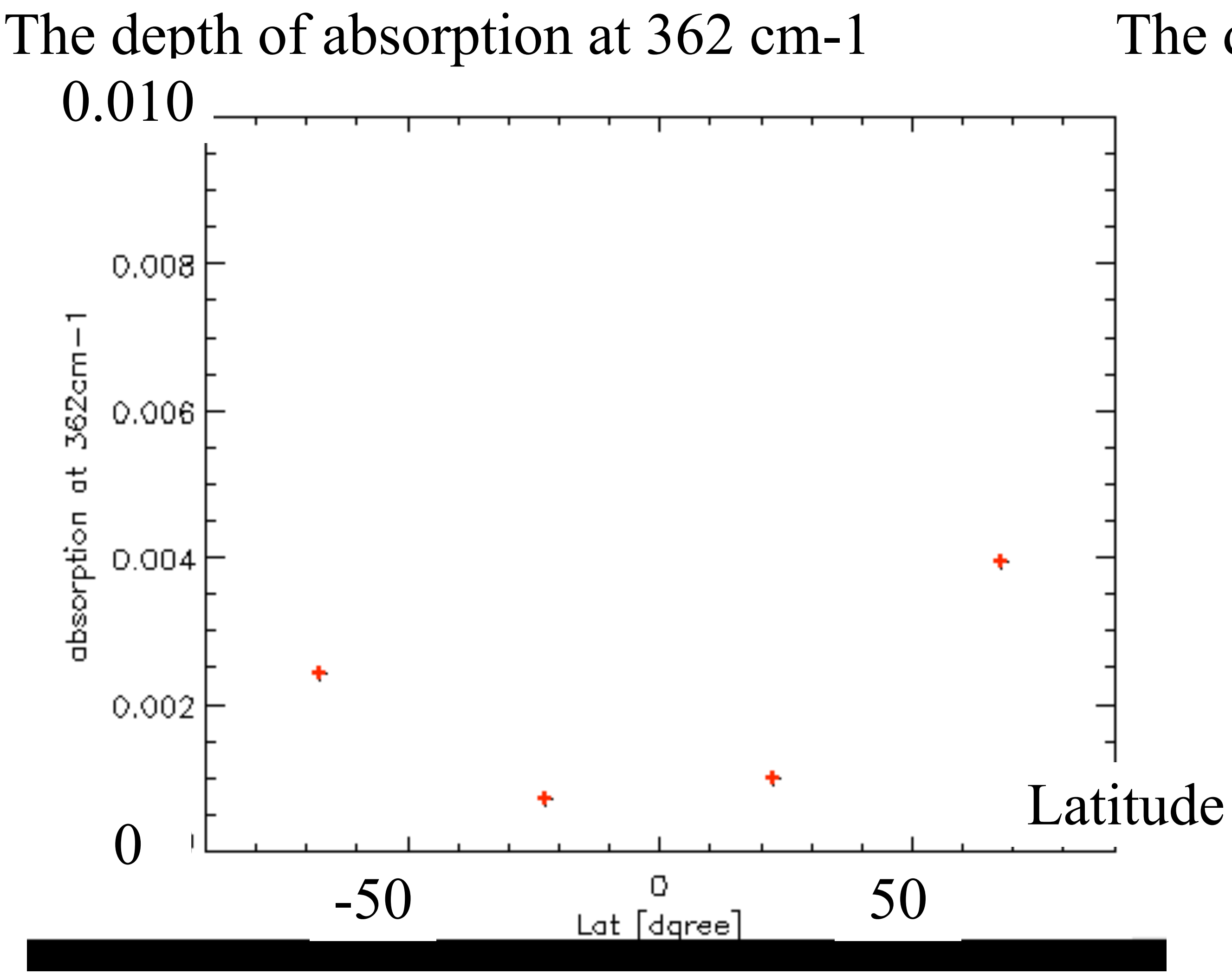


Fig 25. The average every 6 hours of Fig. 21

Result of 100 average



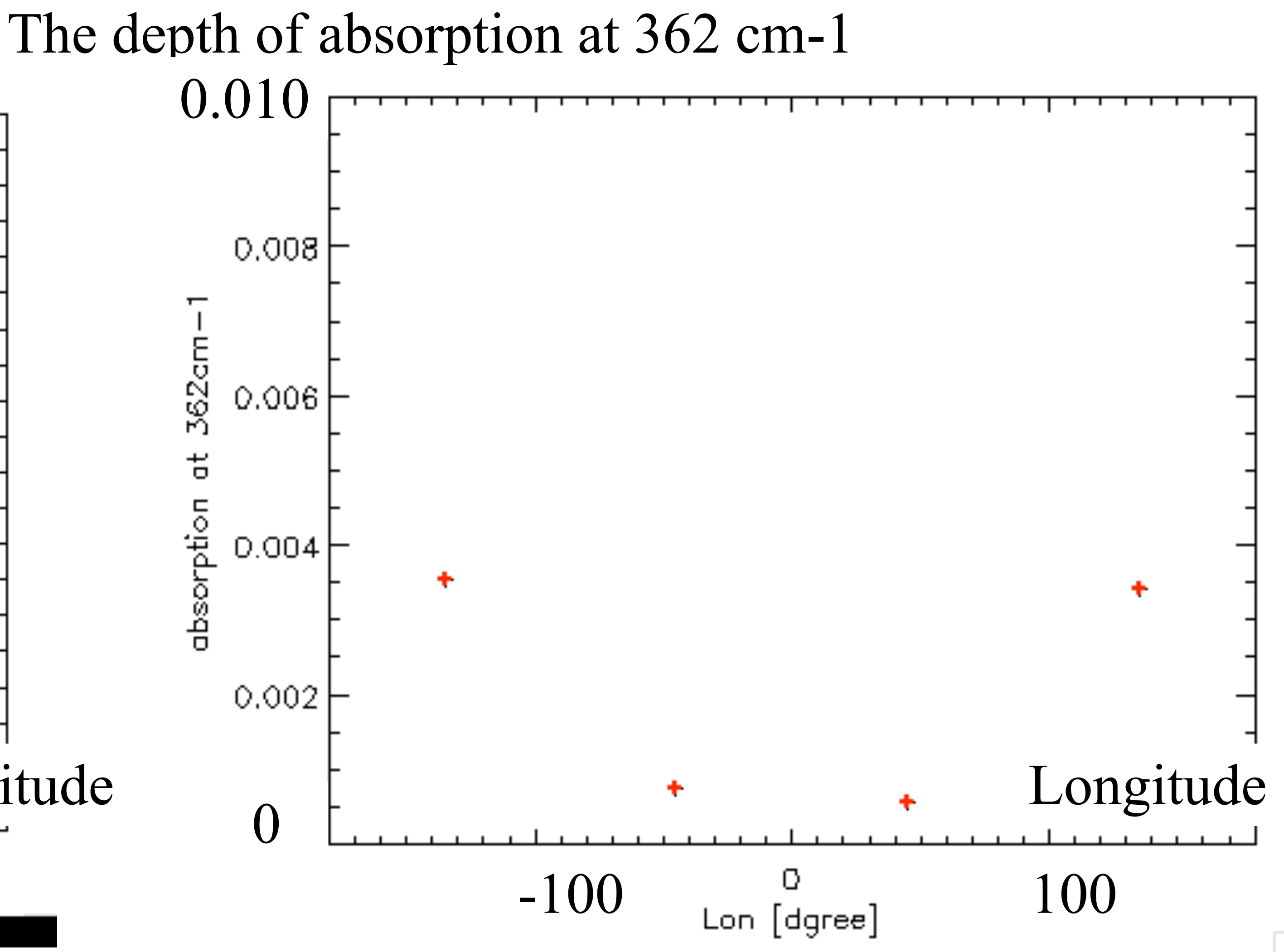


Fig 26. The average every 45° of Fig. 22

Fig 27. The average every 90° of Fig. 23

Simulation

Table. Recent simulation of variation of hydrogen peroxide

Ref.	概要	特徴
Krasnopolsky, 2006	GCM + 光化学過程 + Heterogeneous loss	Seasonal, spatial and LT variation
Moudden, 2007	GCM + 光化学過程	4 seasonal global maps
Lefever et al., 2008	GCM + 光化学過程 + Heterogeneous loss	Seasonal variation
Krasnopolsky, 2009	GCM + 光化学過程 + Heterogeneous loss	Krasnopolsky, 2006の改良版

*GCMと結合することで変動を予測

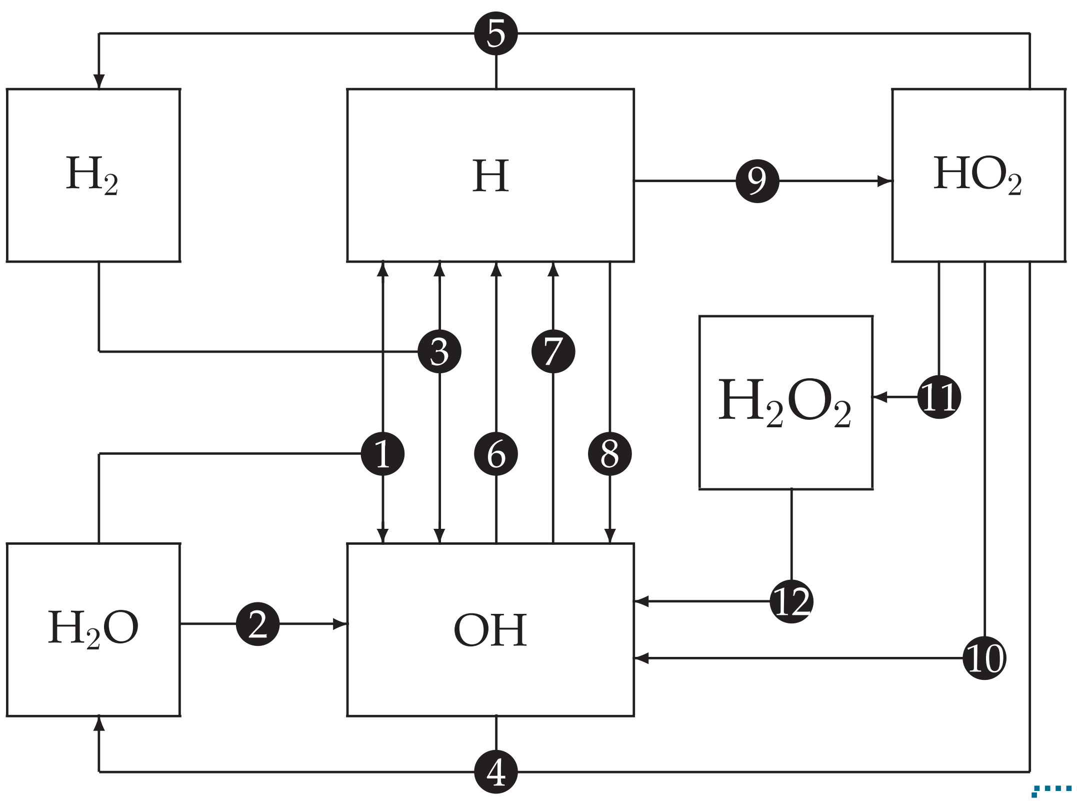


Fig. Production and loss of odd hydrogen
[Moudden, 2007]

1. H2O + hν → H + OH
2. O + H2O → 2OH
3. O + H2 → H + OH
4. OH + HO2 → H2O + O2
5. H + HO2 → H2 + O2
6. OH + CO → CO2 + H
7. O + OH → O2 + H
8. H + O3 → OH + O2
9. H + O2 + M → HO2 + M
10. O + HO2 → OH + O2
11. 2HO2 → H2O2 + O2
12. H2O2 + hν → 2OH

*Heterogeneous loss : H2O2 + H2O ice → uptake
(Ls = 30°~120° , 10°Sにおいて最も影響大)

Simulation ~Seasonal variation~

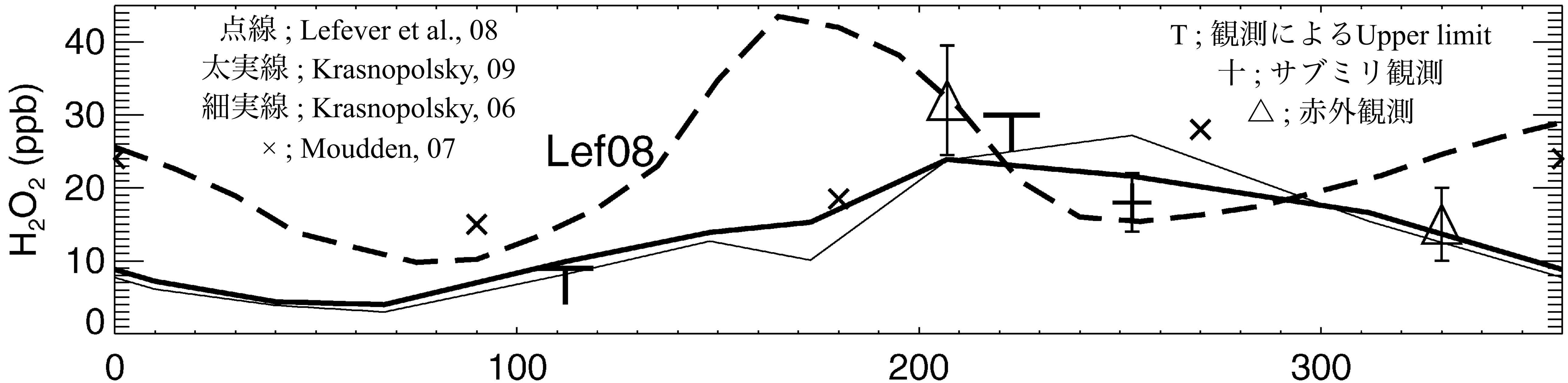


Fig. Simulated seasonal variation of hydrogen peroxide [Krasnopolsky, 2009]

- LefとKraはやや相違点がみられる。特に極大時期が違う。

⇒ 両モデルの差 (1)Heterogenous lossメカニズム

(2) 反応式⑪の反応係数

- Ls = 207°の観測はLef08を支持
- Ls =112°と330°の観測はKraを支持

  (Ls = 253°の観測は両方のモデルを支持)
- どちらのモデルがより現実を再現しているかは、将来の観測に期待される

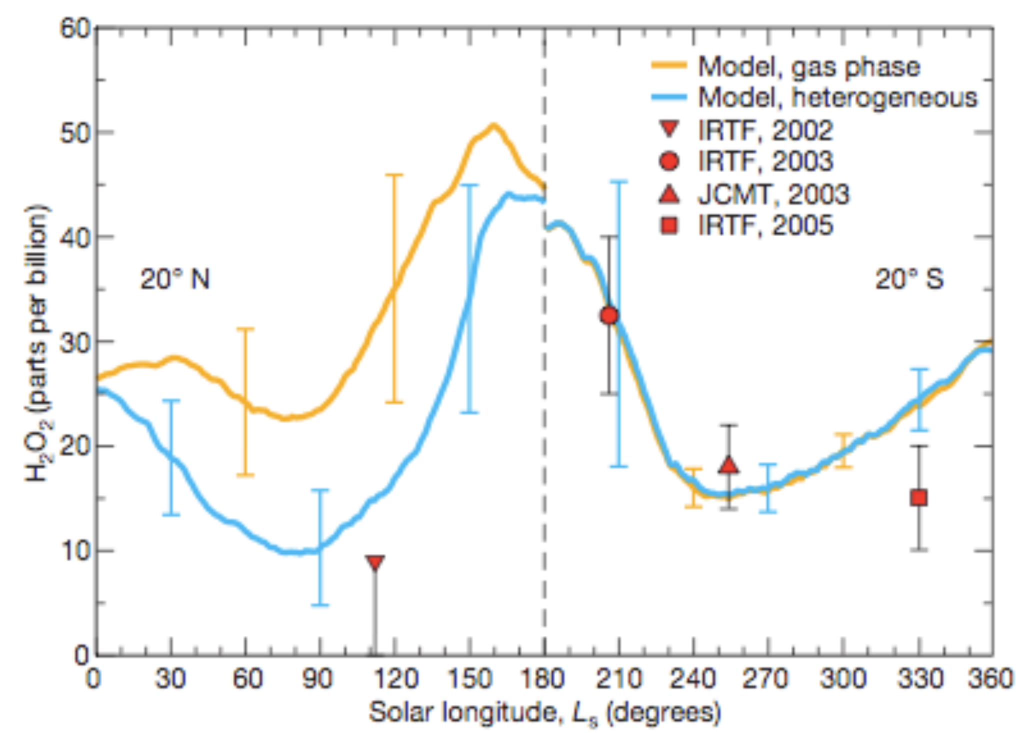


Fig. Simulated seasonal variation of hydrogen peroxide [Lefevre et al., 2008]

Simulation ~Dependence on LT~

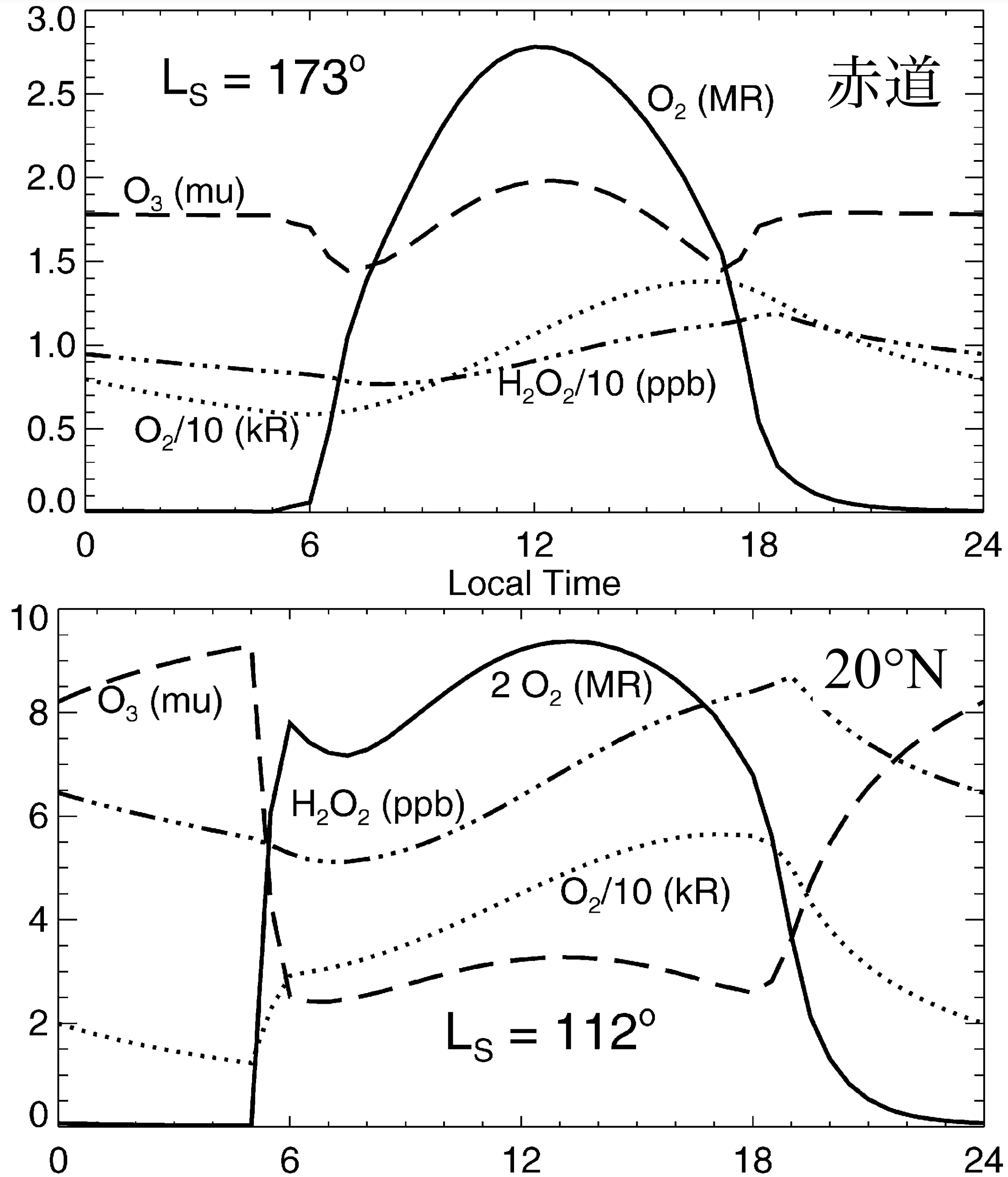


Fig. Diurnal variations of photochemical products. [krasnopolsky, 2006]

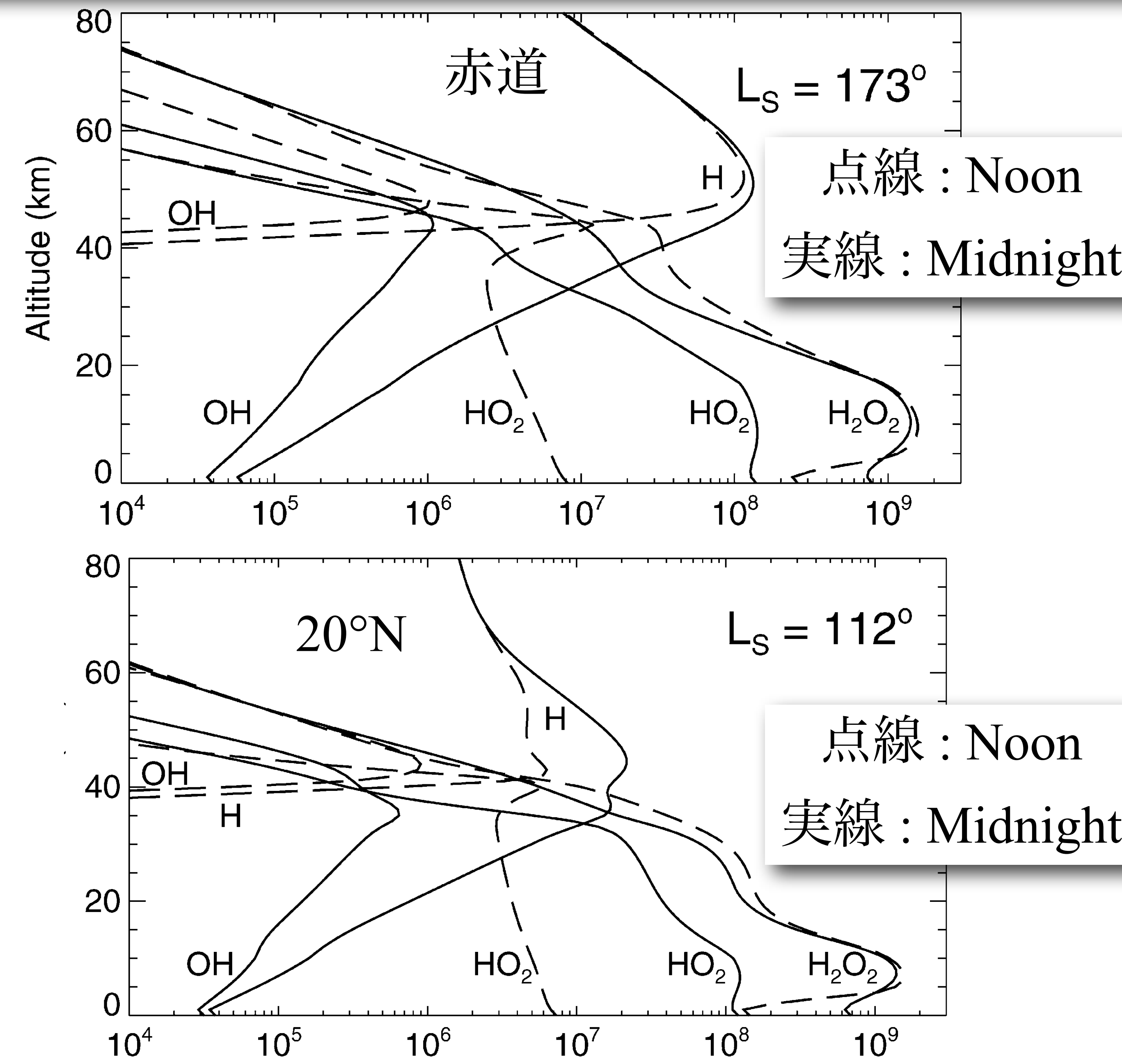
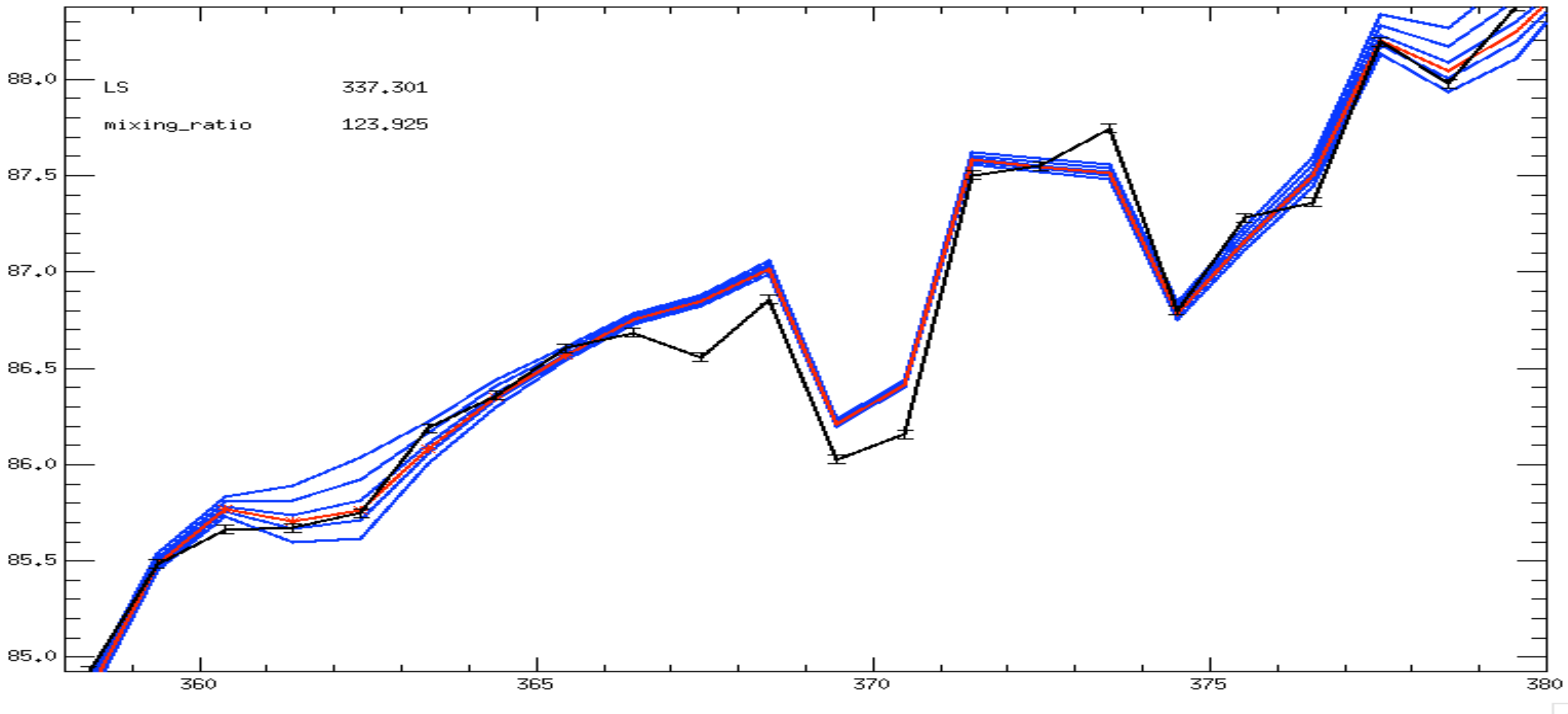


Fig. Odd hydrogen density profile at noon and midnight. [Krasnopolsky, 2006]

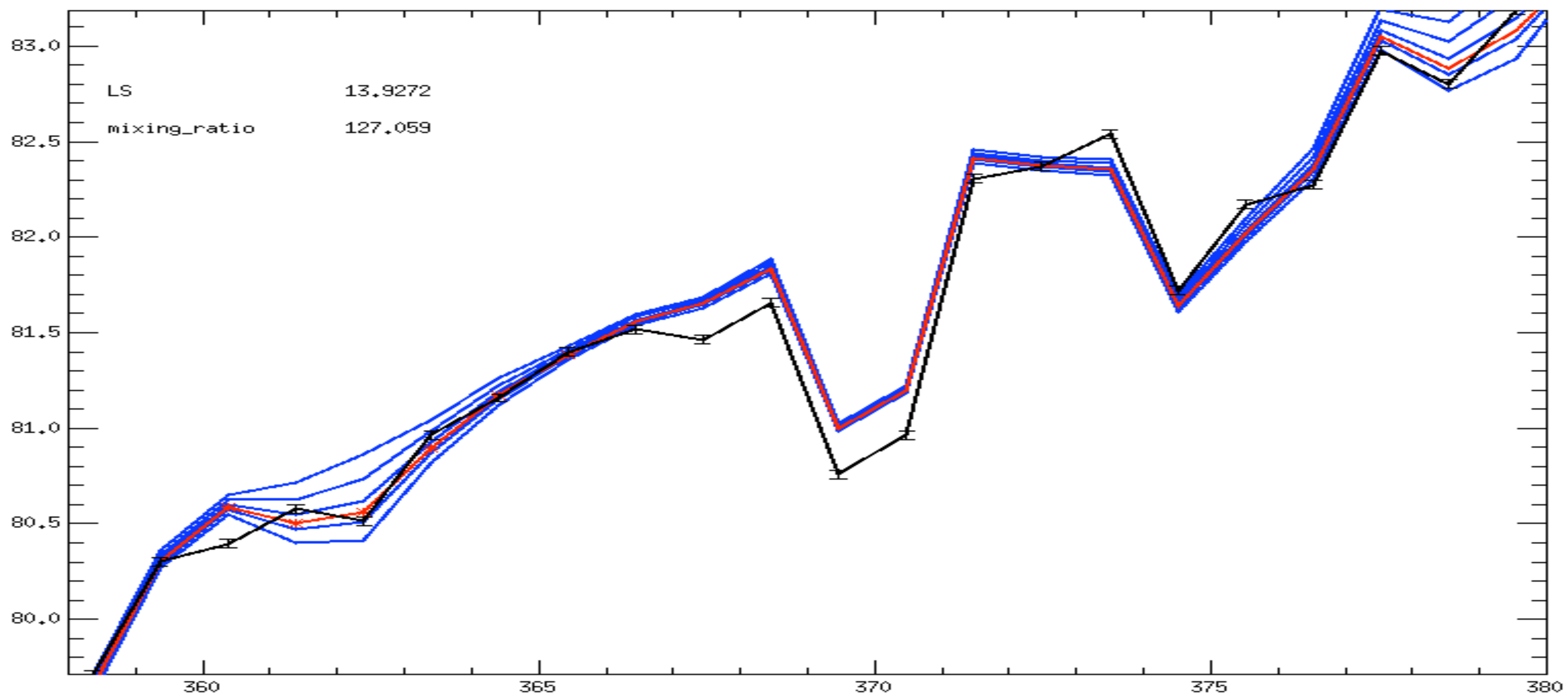
LT依存性はなし

他のOdd hydrogenはすぐにH2O2に変化 (H2O2は良い指標となる)

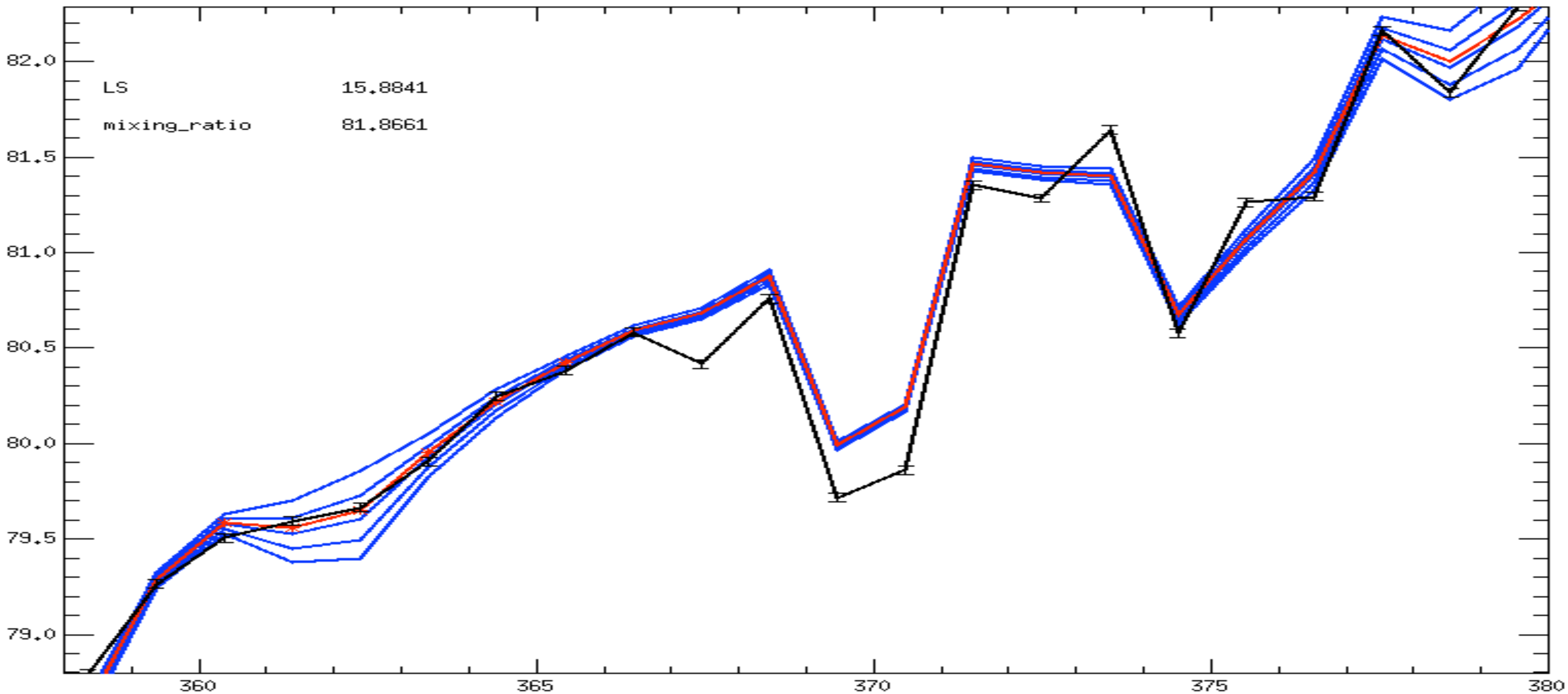
Appendix II



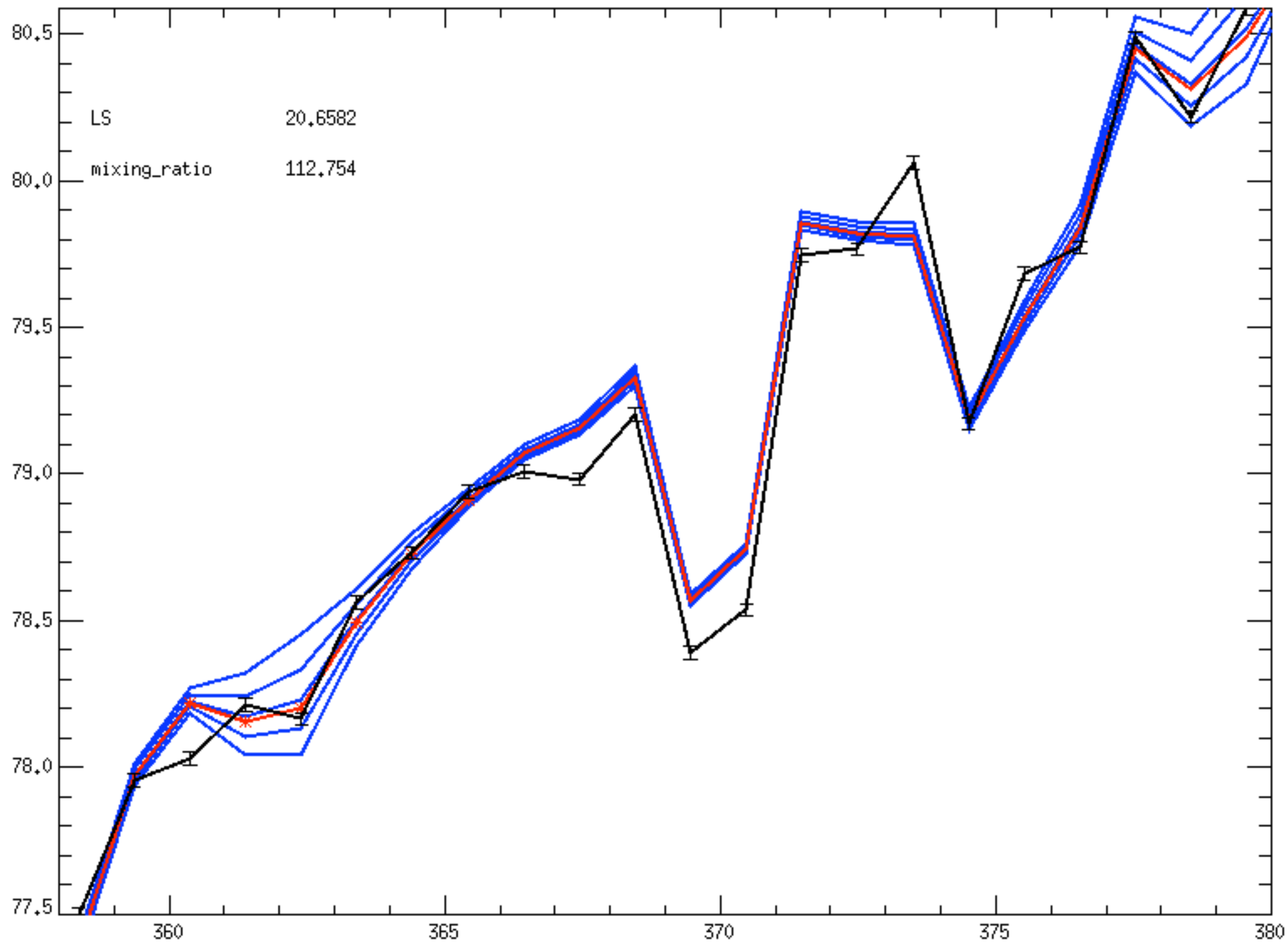
LS 337.301
mixing_ratio 123.925
88.0
87.5
87.0
86.5
86.0
85.5
85.0
360
365
370
375
380



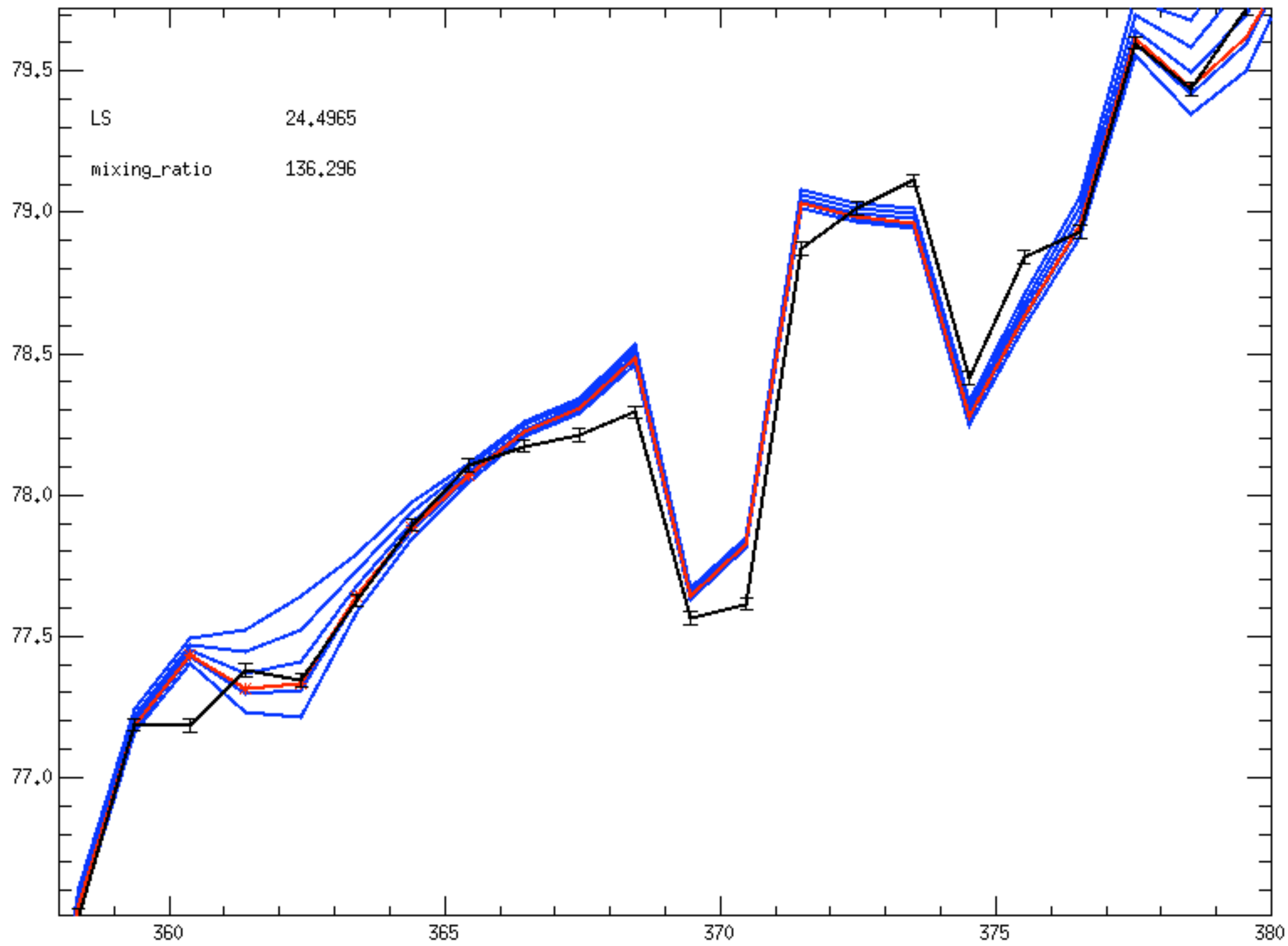
LS 13.9272
mixing_ratio 127.059
83.0
82.5
82.0
81.5
81.0
80.5
80.0
360
365
370
375
380

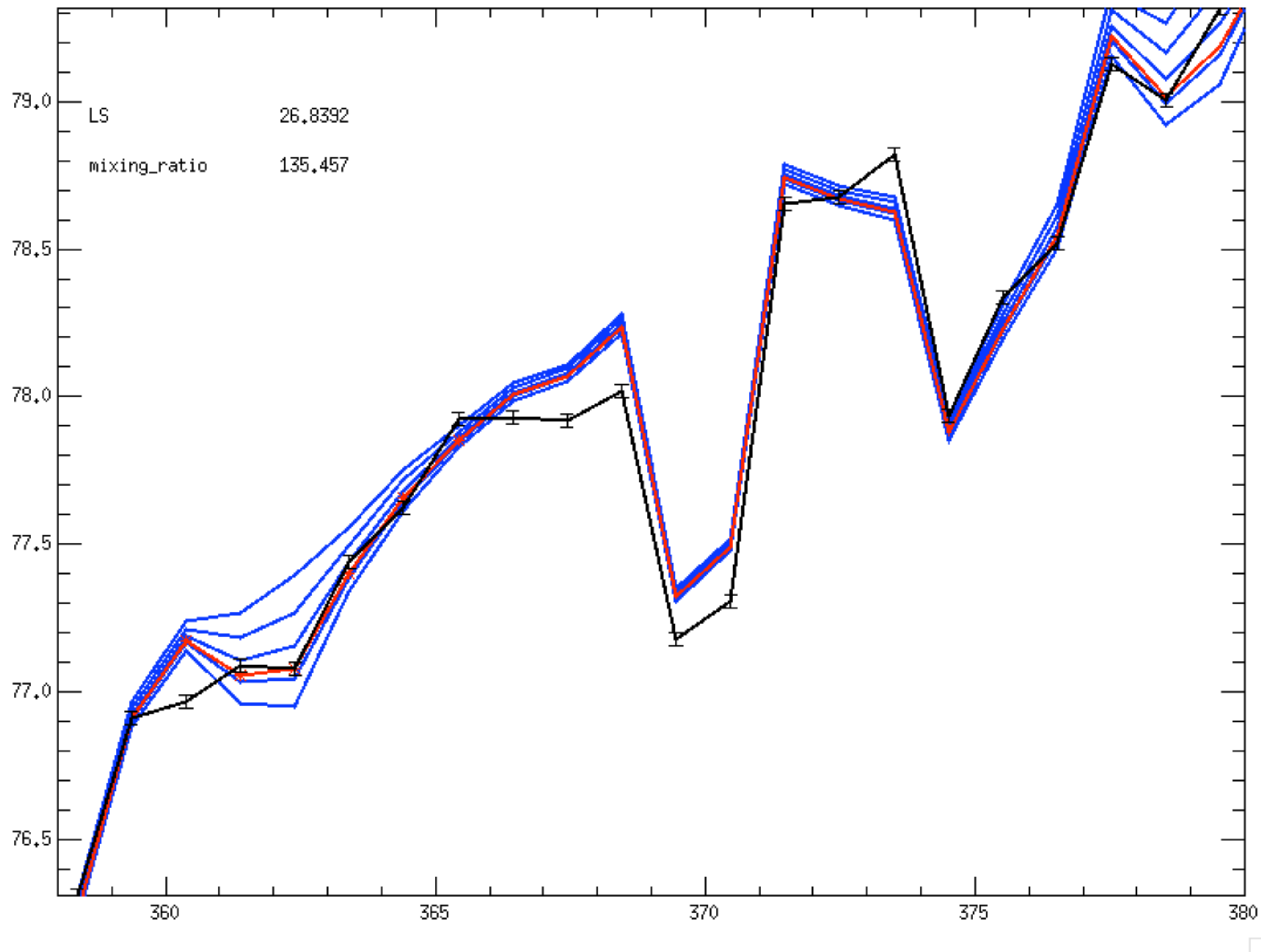


82.0
81.5
81.0
80.5
80.0
79.5
79.0
LS 15.8841
mixing_ratio 81.8661
360
365
370
375
380

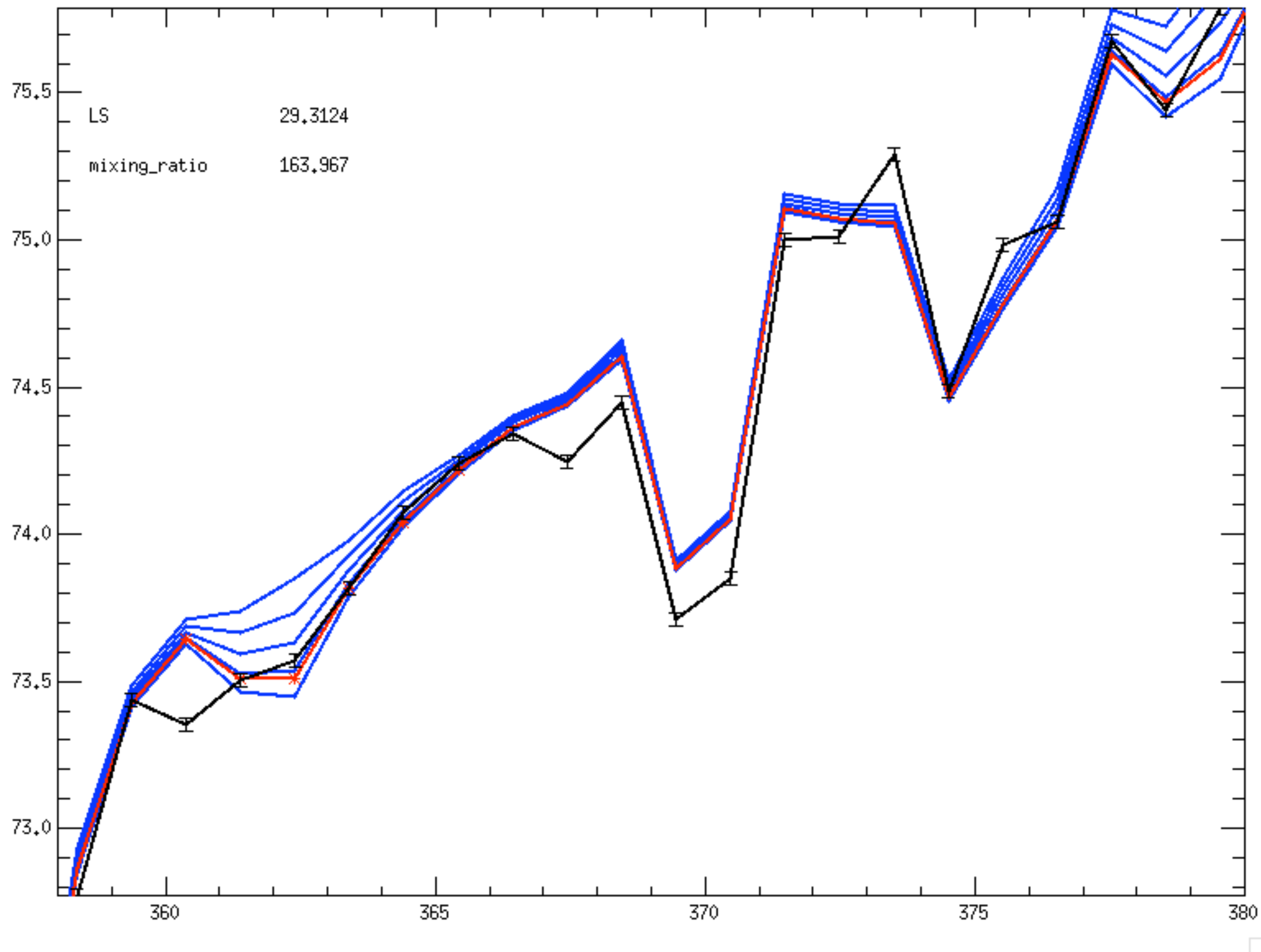


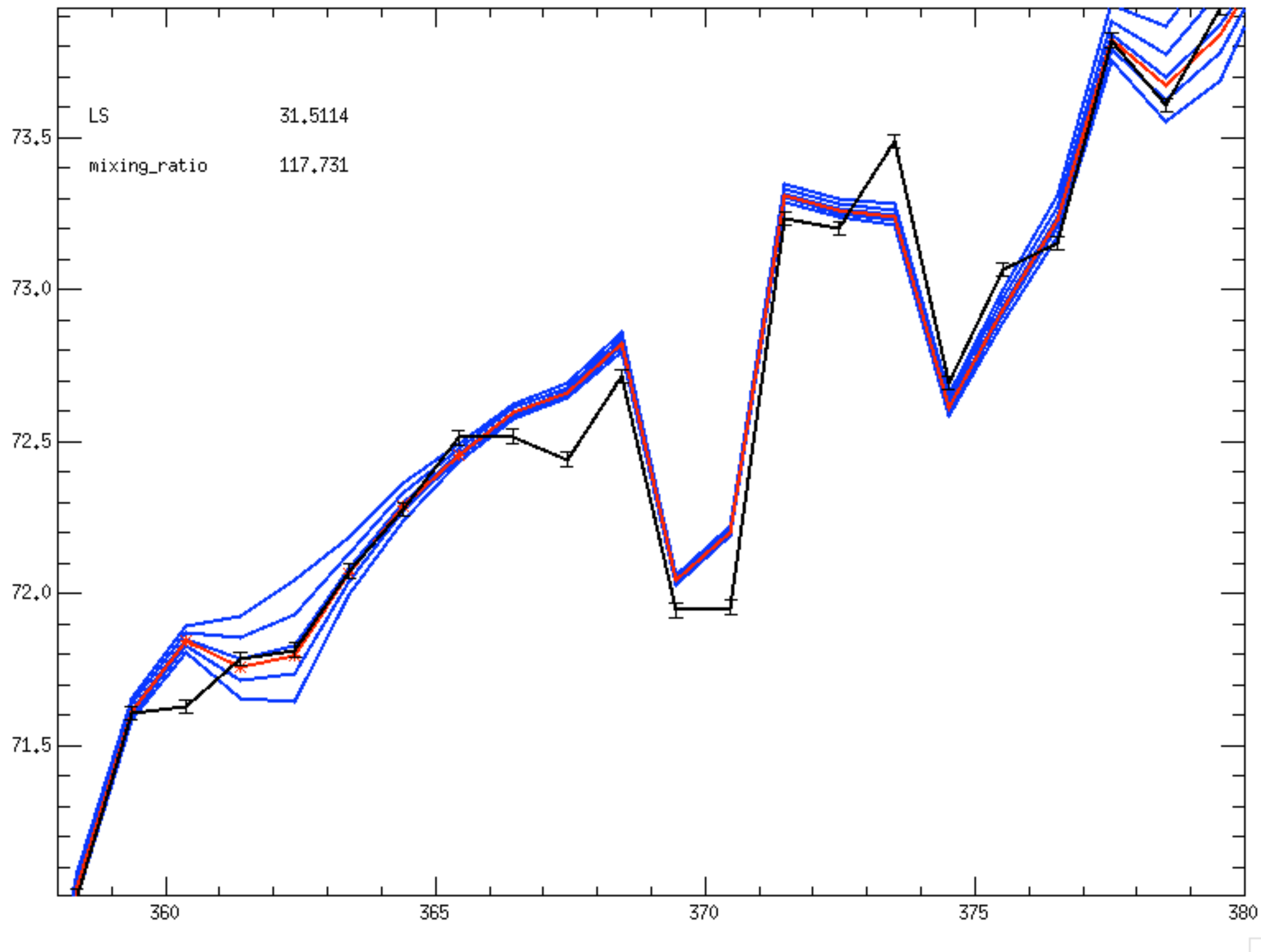
LS 20.6582
mixing_ratio 112.754
80.5
80.0
79.5
79.0
78.5
78.0
77.5
360
365
370
375
380

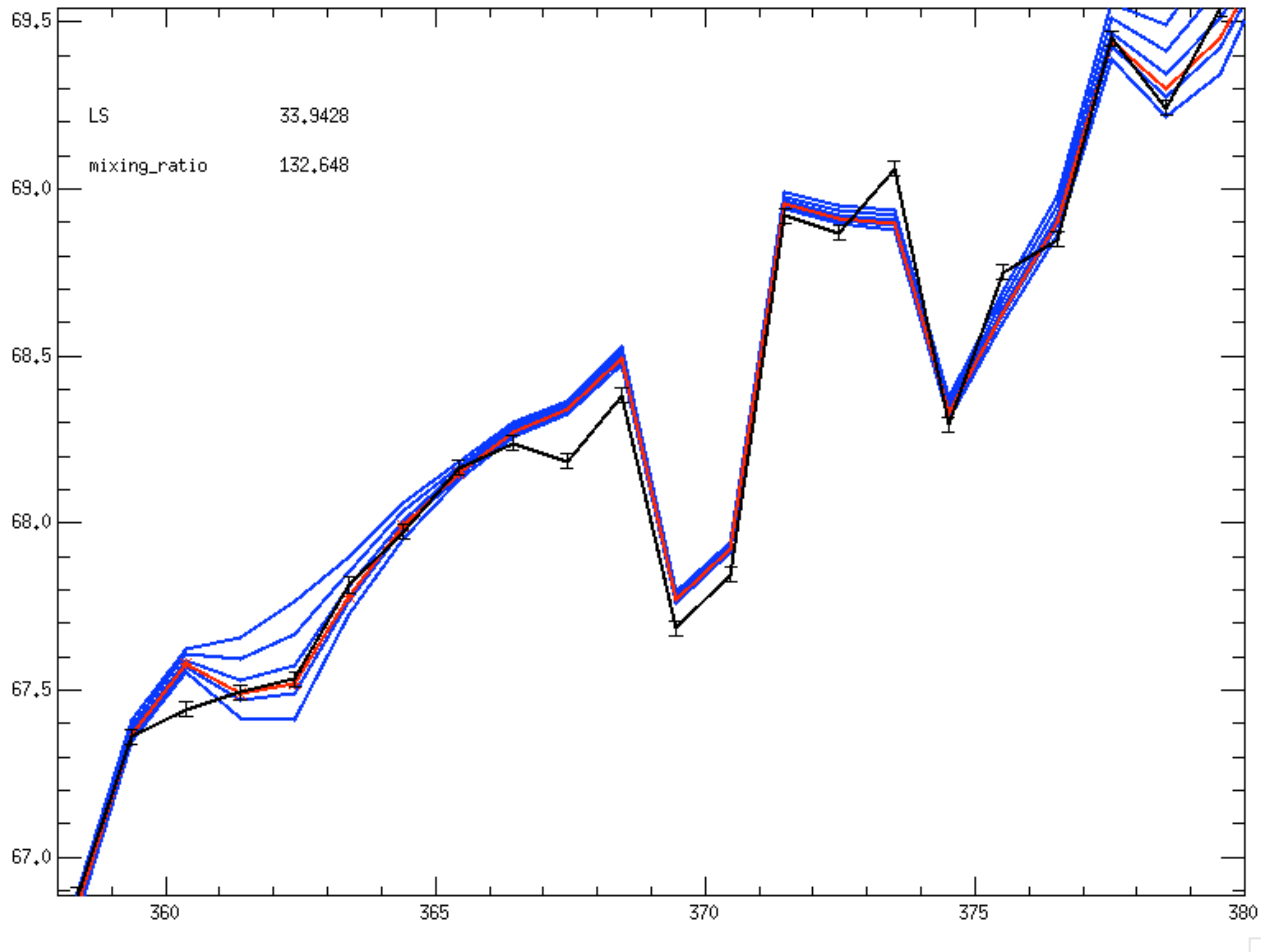

LS 24.4965
mixing_ratio 136.296
79.5
79.0
78.5
78.0
77.5
77.0
360
365
370
375
380



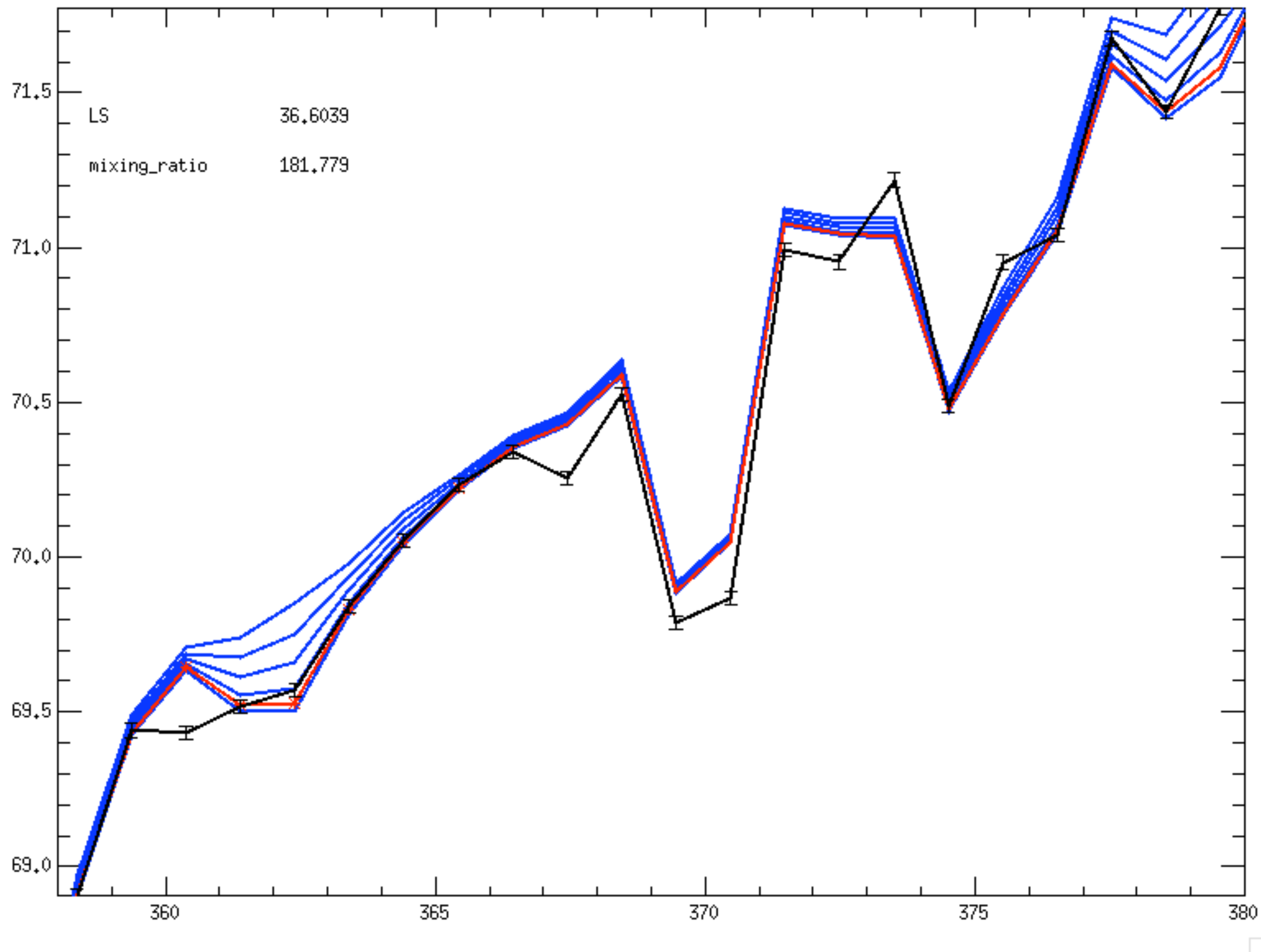
LS 26.8392
mixing_ratio 135.457
79.0
78.5
78.0
77.5
77.0
76.5
360
365
370
375
380


LS 29.3124
mixing_ratio 163.967
75.5
75.0
74.5
74.0
73.5
73.0
360
365
370
375
380

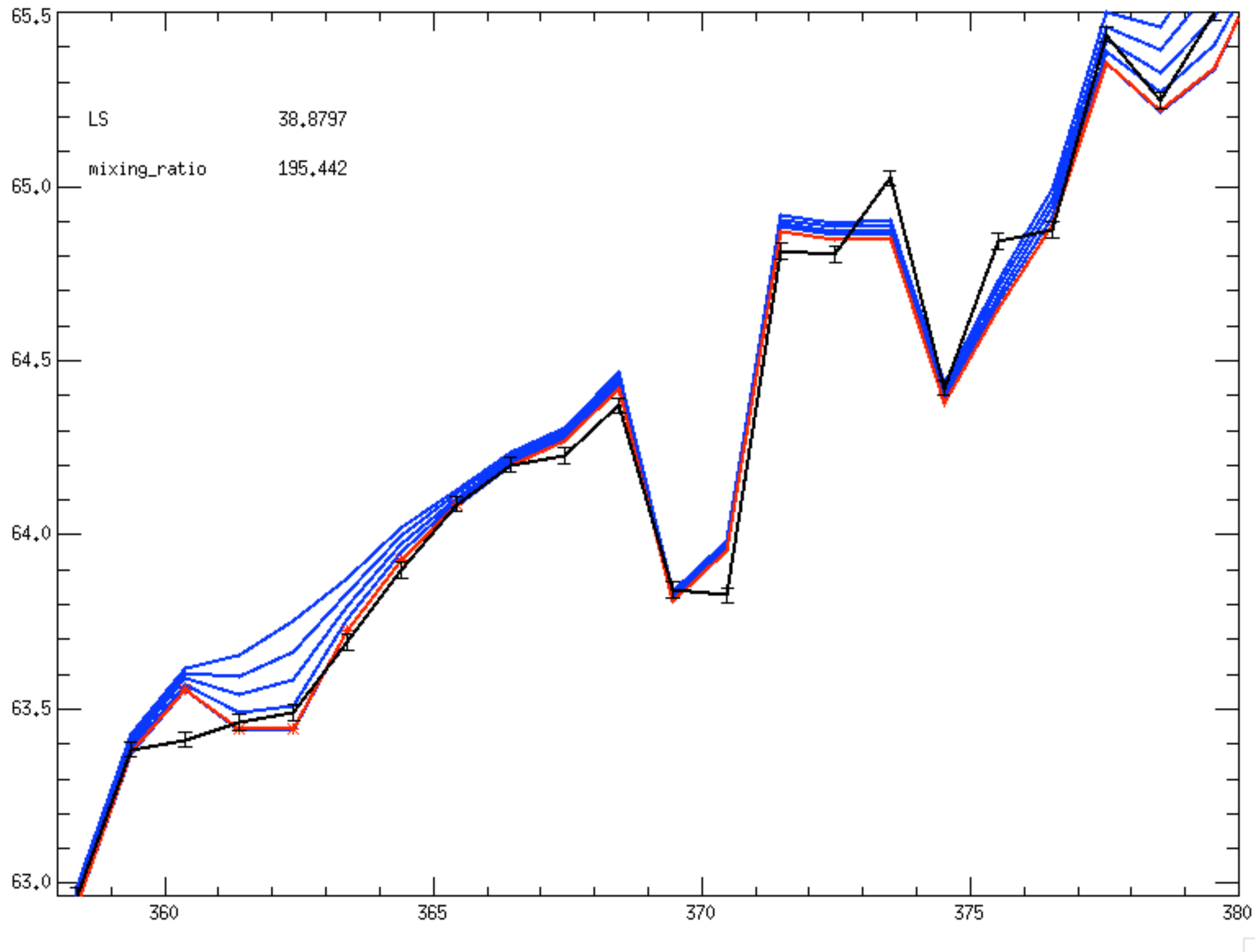

LS 31.5114
mixing_ratio 117.731
73.5
73.0
72.5
72.0
71.5
360
365
370
375
380



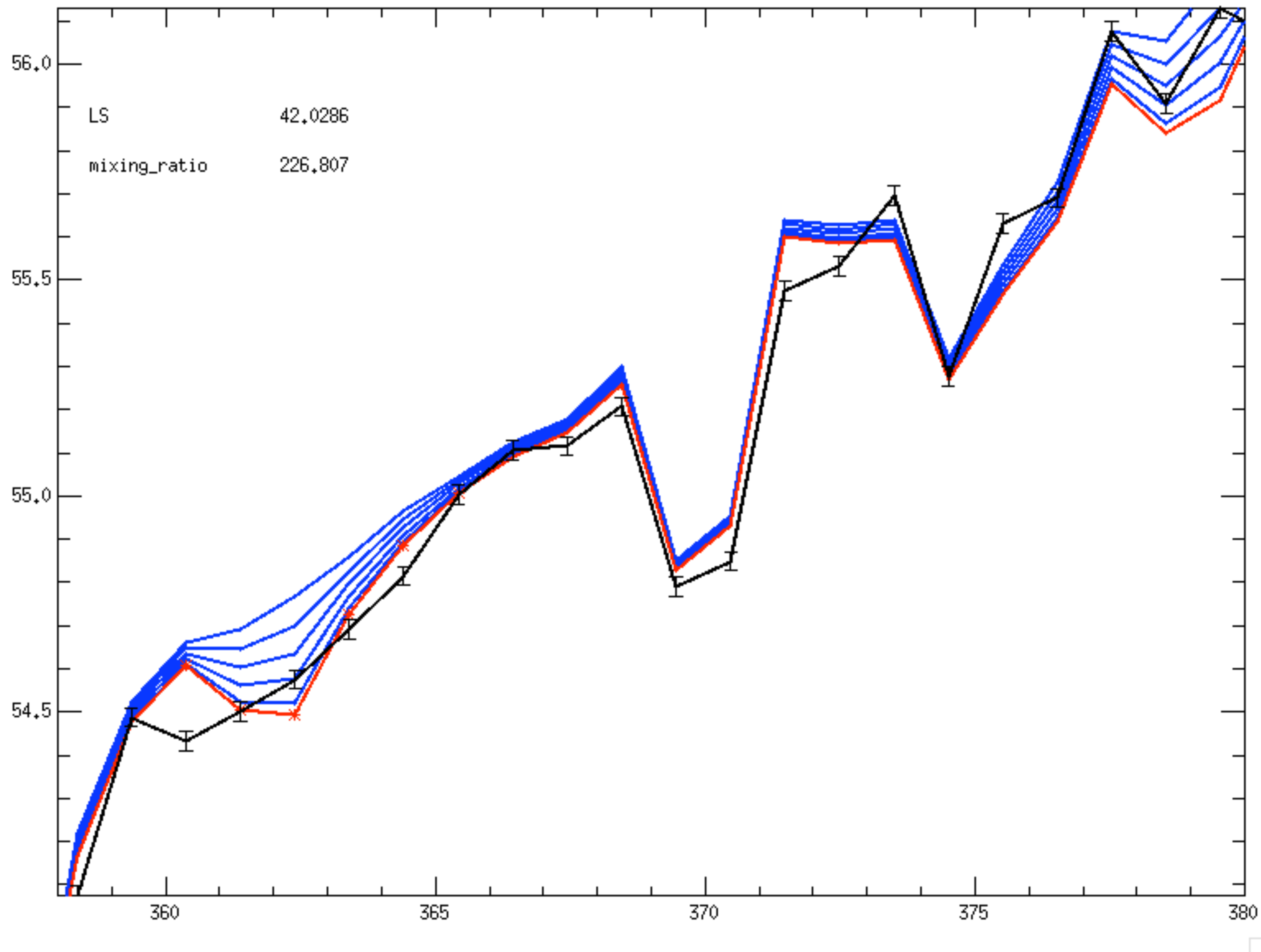
LS 33.9428
mixing_ratio 132.648
69.5
69.0
68.5
68.0
67.5
67.0
360
365
370
375
380



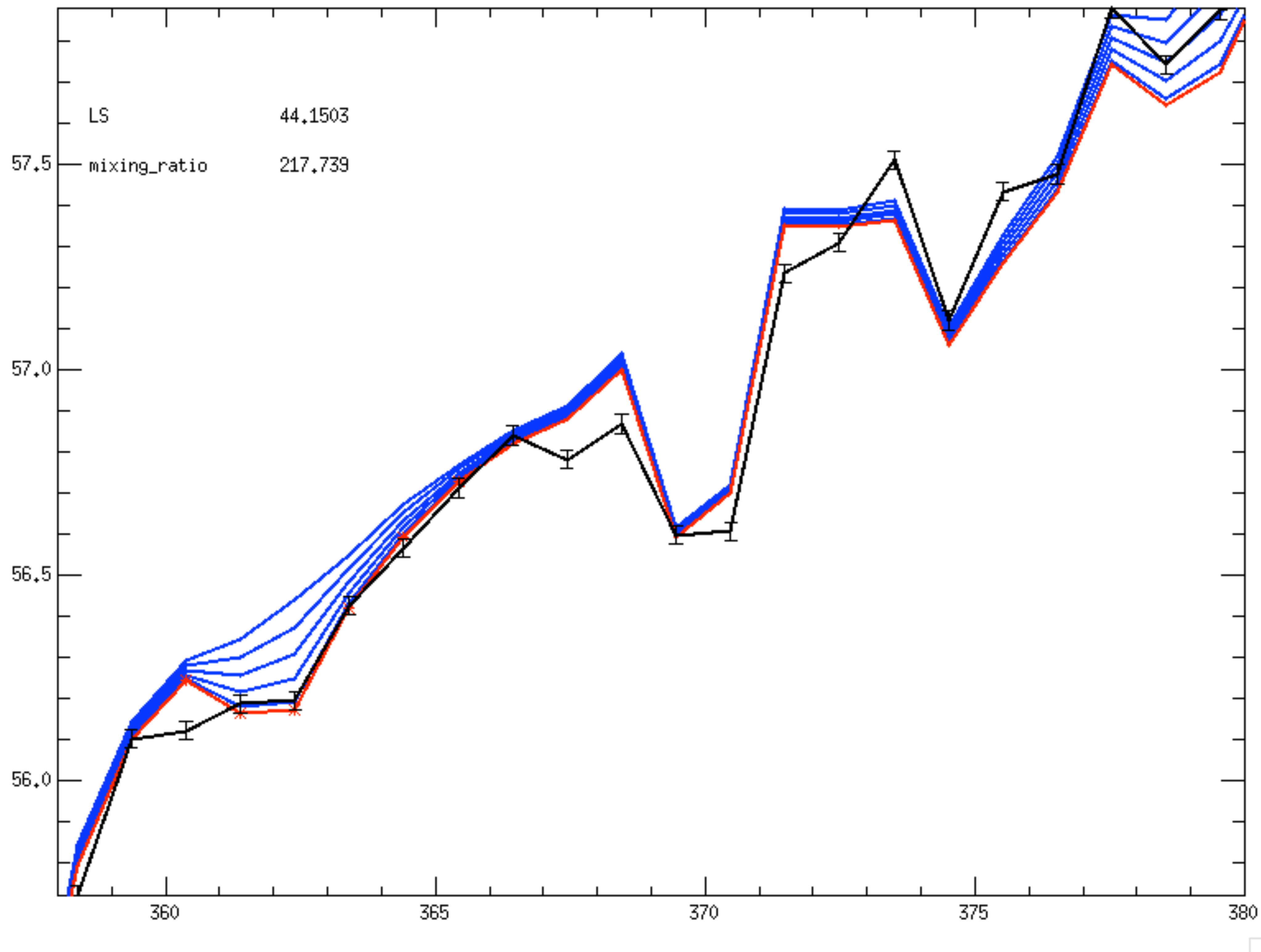
71.5
71.0
70.5
70.0
69.5
69.0
LS 36.6039
mixing_ratio 181.779
360
365
370
375
380

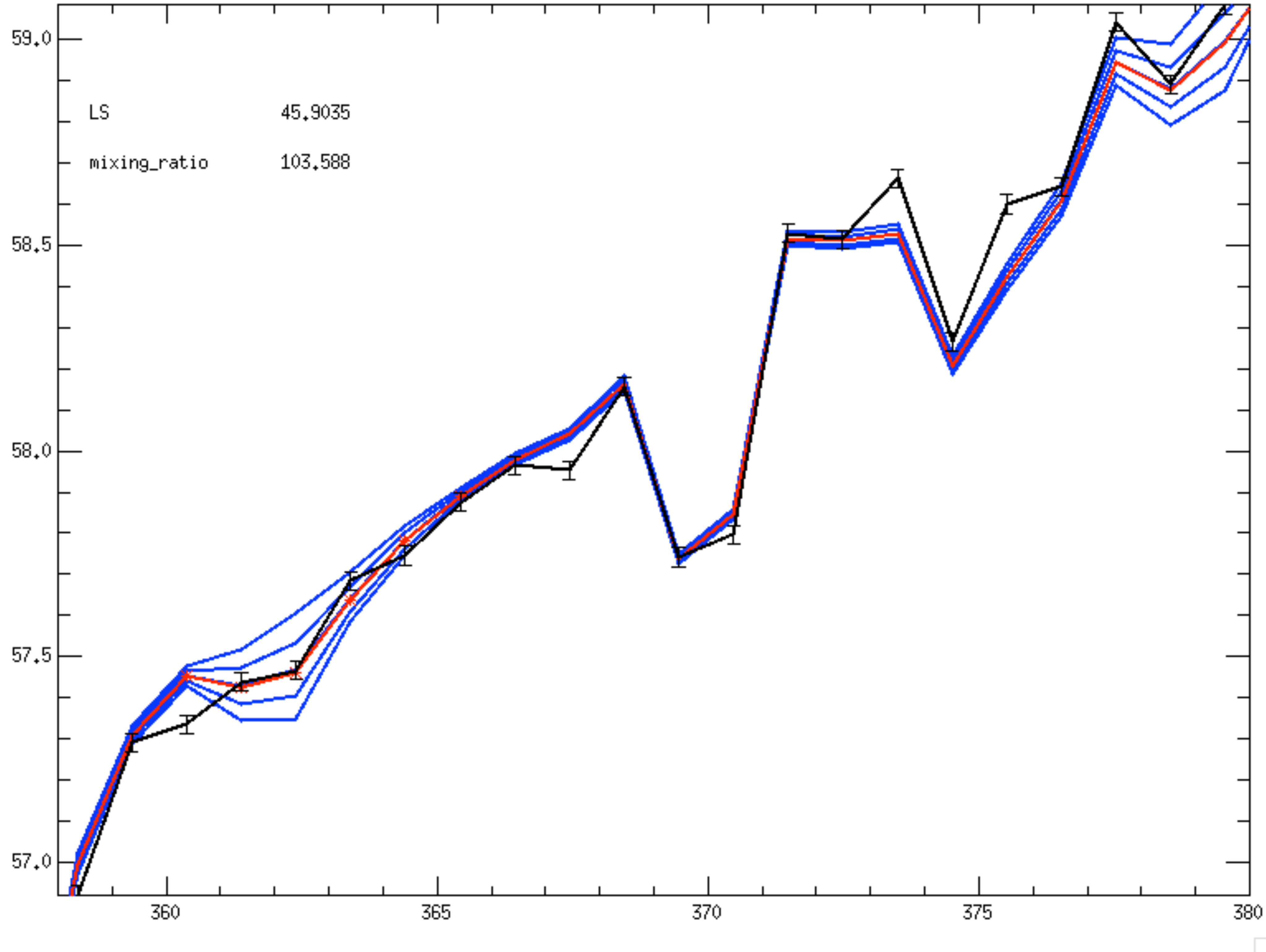


LS 38.8797
mixing_ratio 195.442
65.5
65.0
64.5
64.0
63.5
63.0
360
365
370
375
380

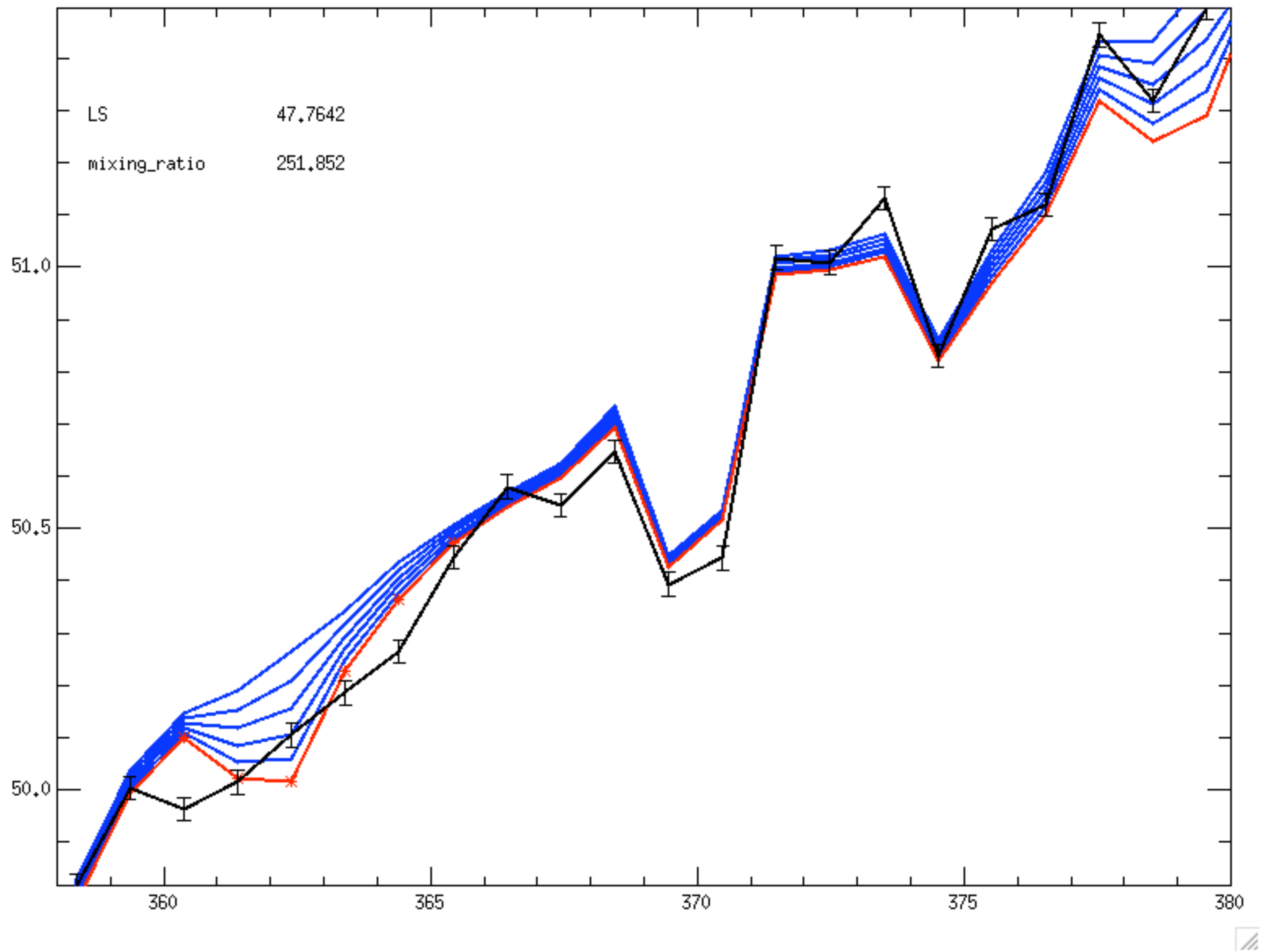


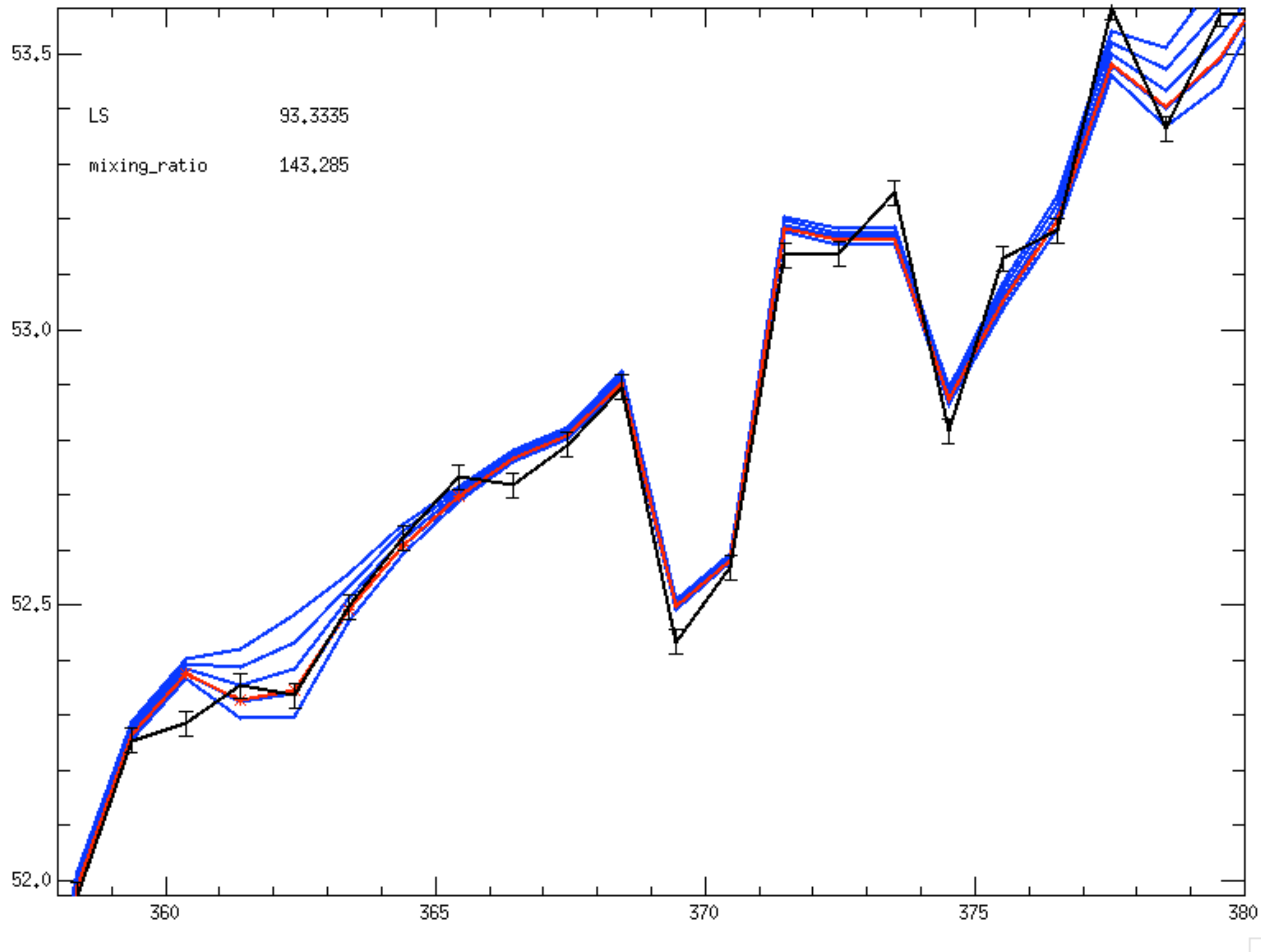
LS 42.0286
mixing_ratio 226.807
56.0
55.5
55.0
54.5
360
365
370
375
380


LS 44.1503
mixing_ratio 217.739
57.5
57.0
56.5
56.0
360
365
370
375
380

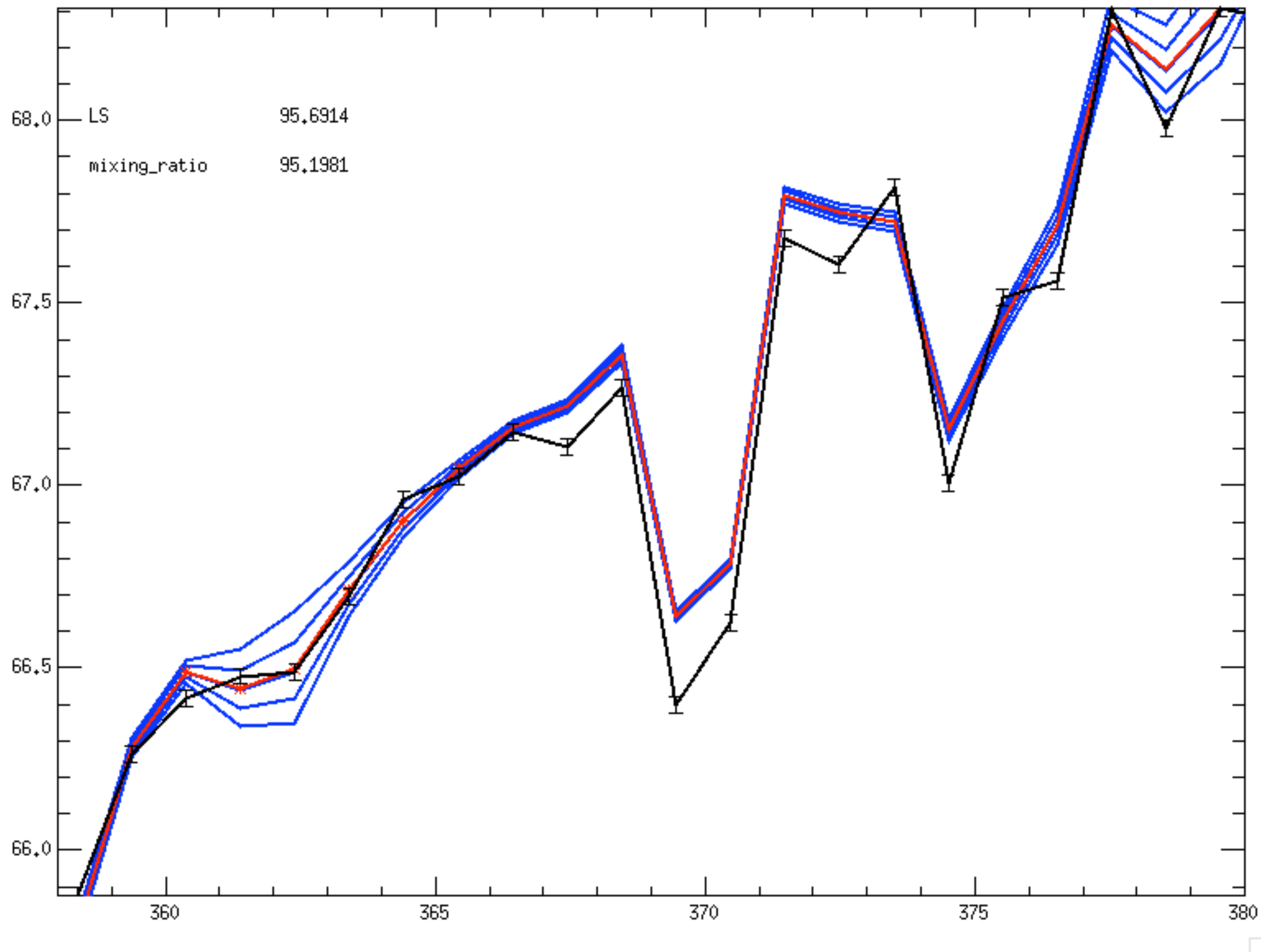


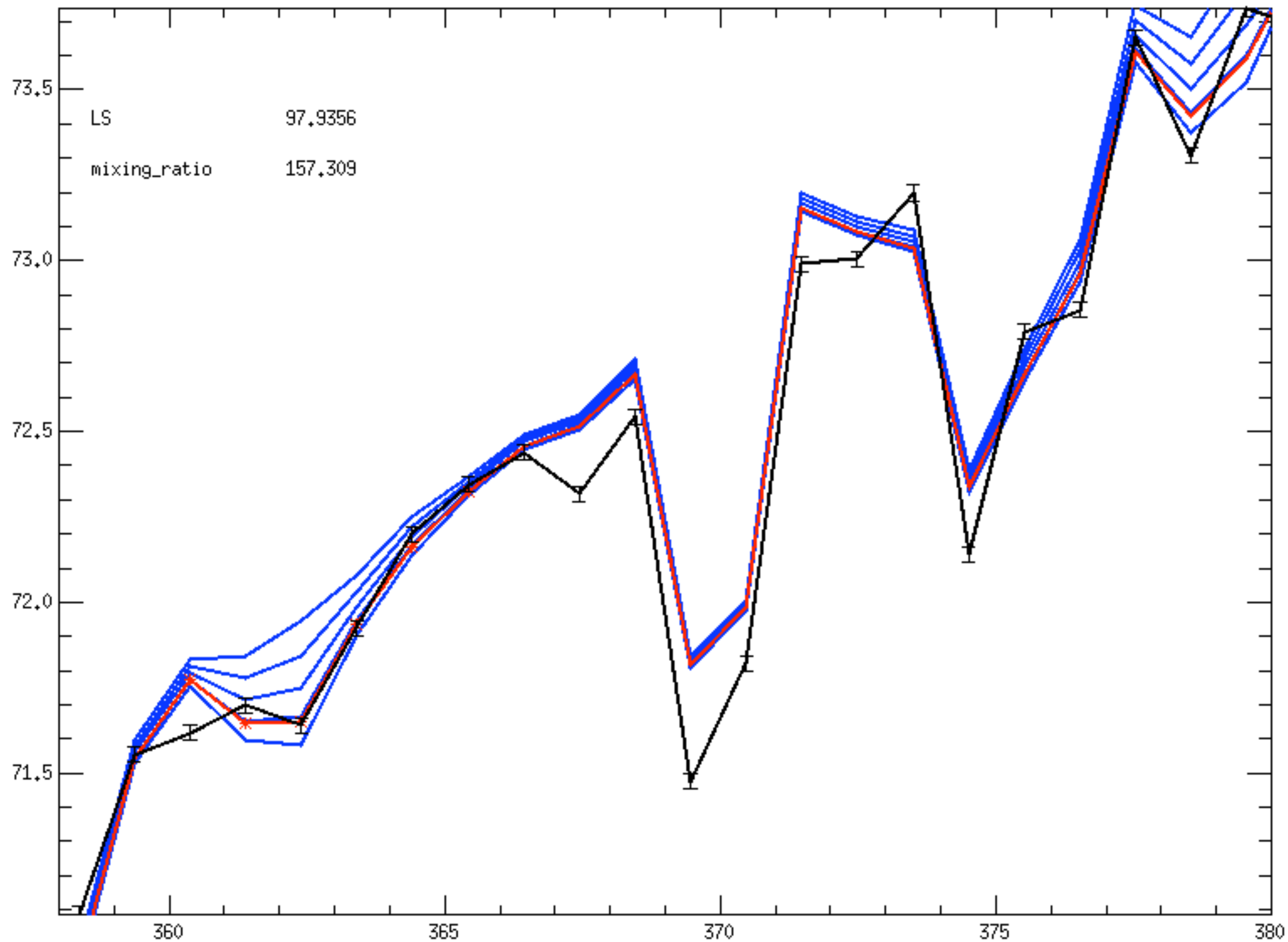
LS 45.9035
mixing_ratio 103.588
59.0
58.5
58.0
57.5
57.0
360
365
370
375
380


LS 47.7642
mixing_ratio 251.852
51.0
50.5
50.0
360
365
370
375
380

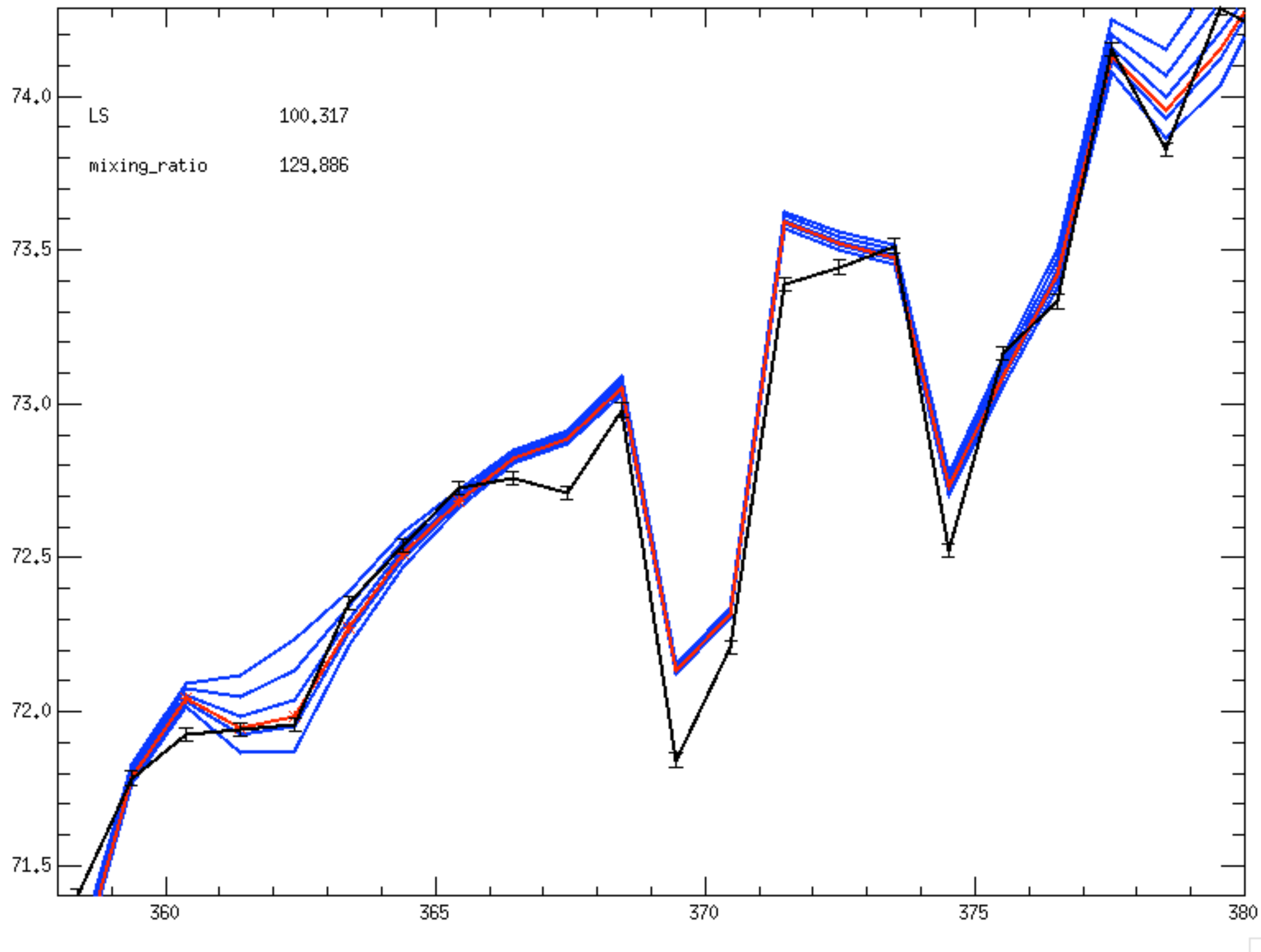


53.5
53.0
52.5
52.0
360
365
370
375
380
LS 93.3335
mixing_ratio 143.285

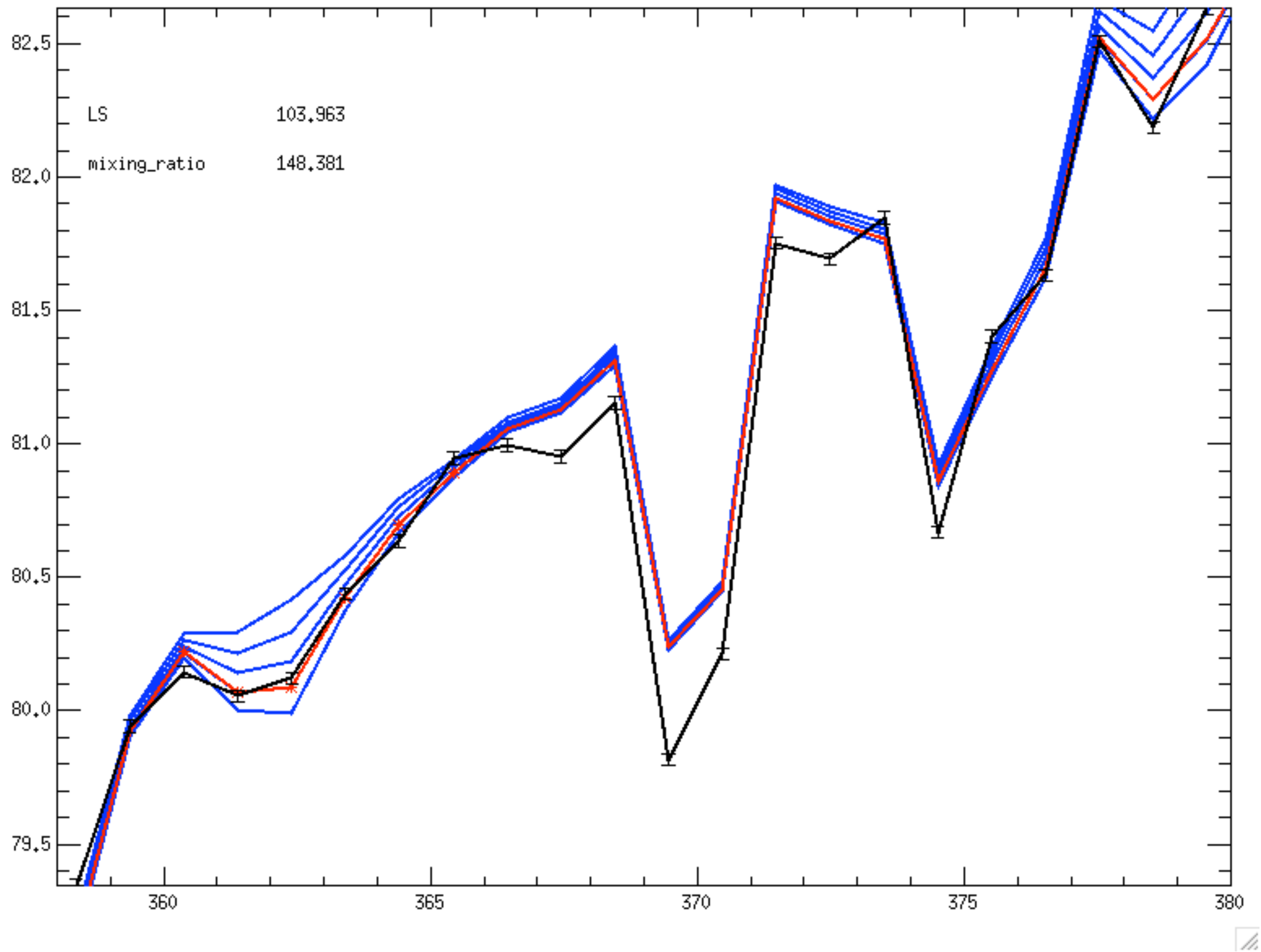

LS 95.6914
mixing_ratio 95.1981
68.0
67.5
67.0
66.5
66.0
360
365
370
375
380



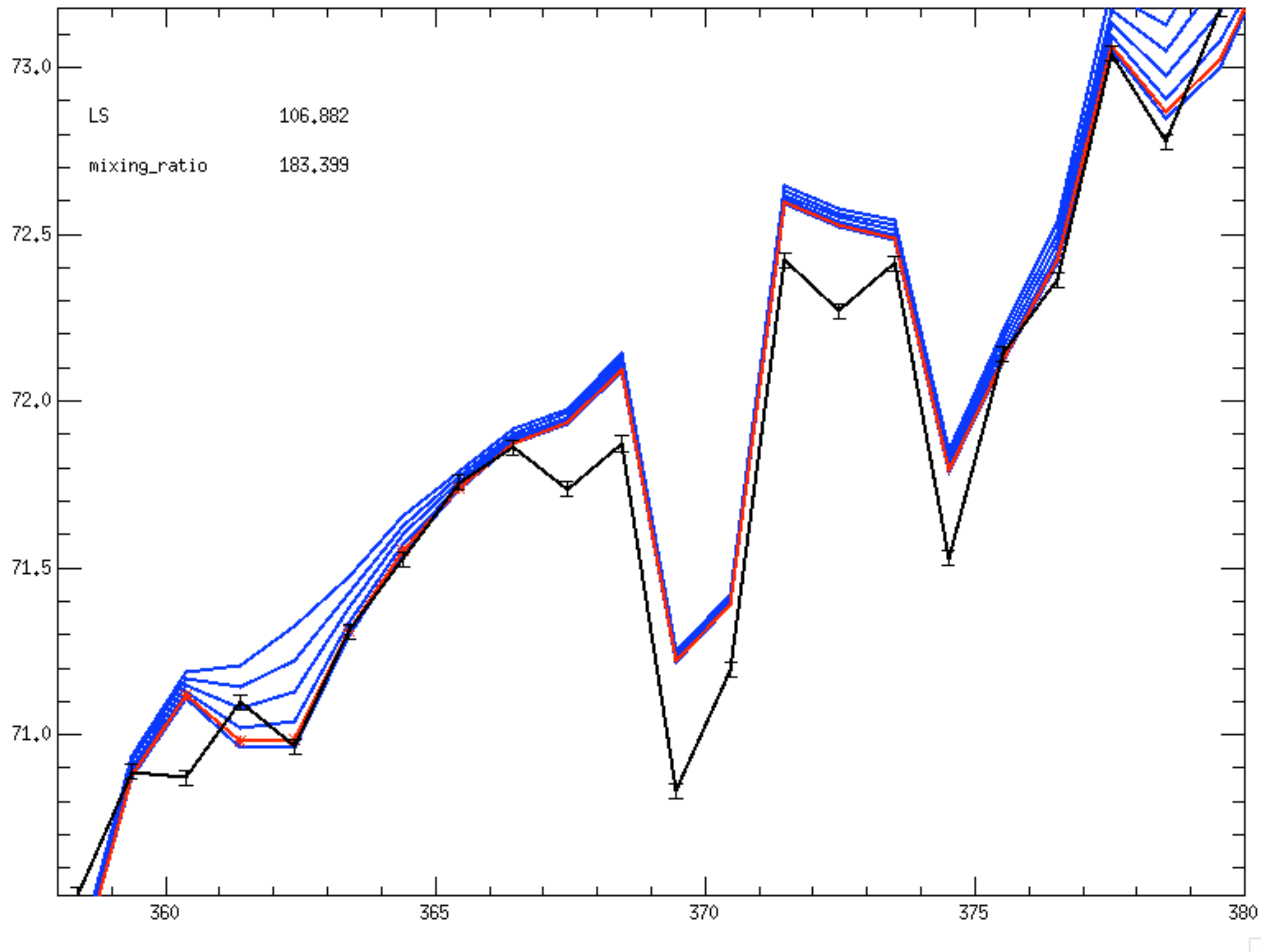
LS 97.9356
mixing_ratio 157.309
73.5
73.0
72.5
72.0
71.5
360
365
370
375
380

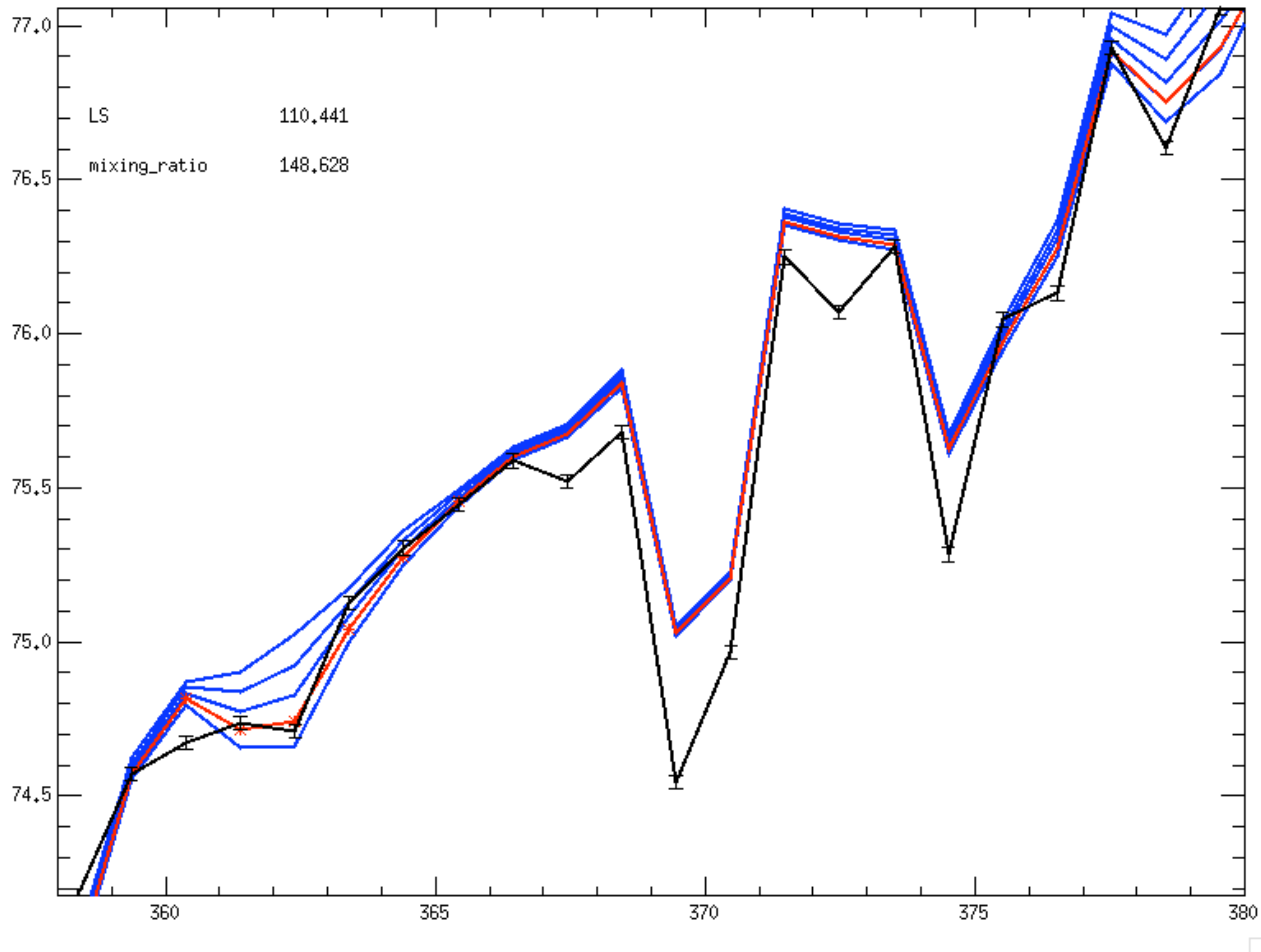


74.0
73.5
73.0
72.5
72.0
71.5
LS 100.317
mixing_ratio 129.886
360
365
370
375
380

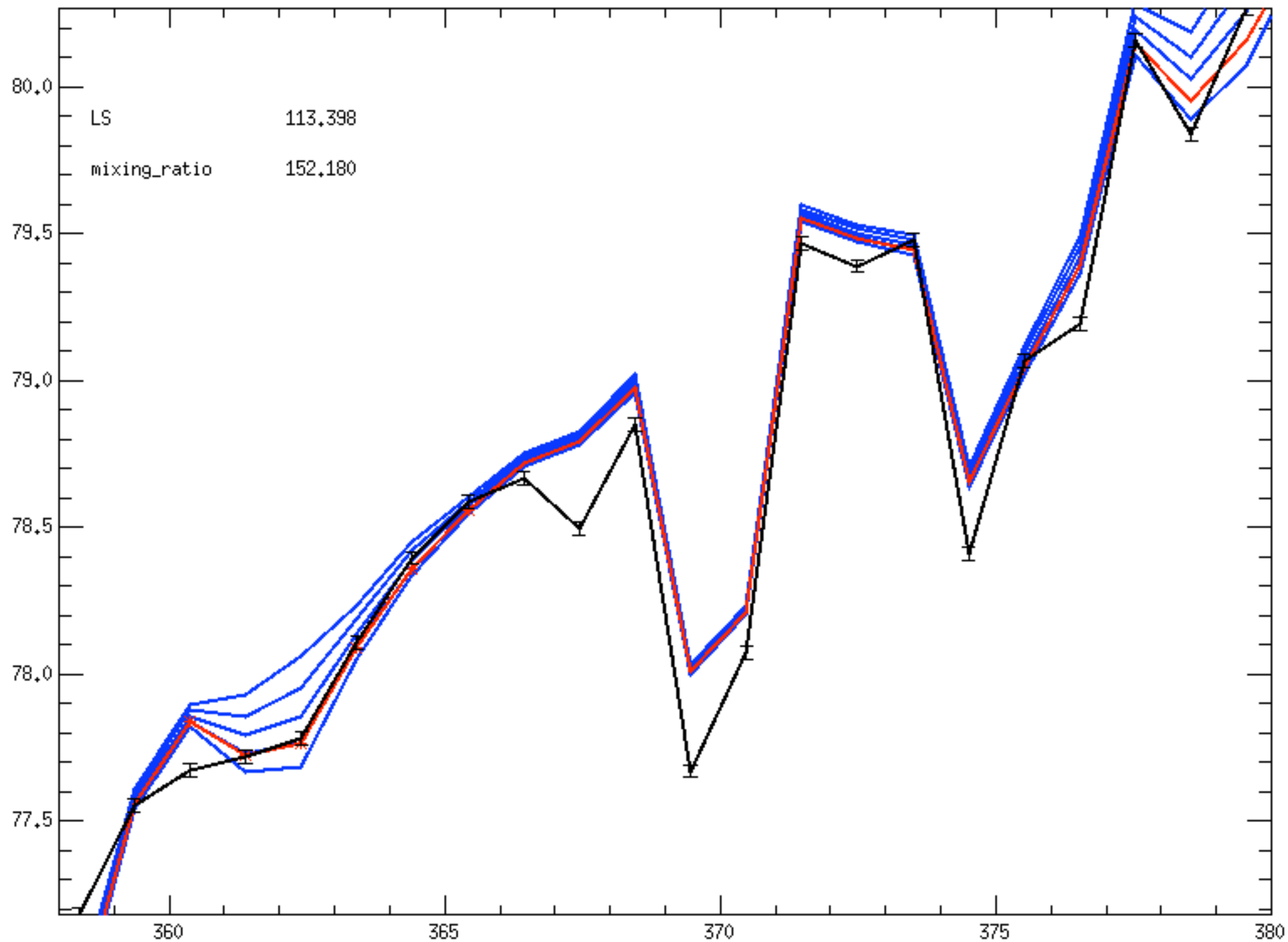


82.5
82.0
81.5
81.0
80.5
80.0
79.5
LS 103.963
mixing_ratio 148.381
360
365
370
375
380

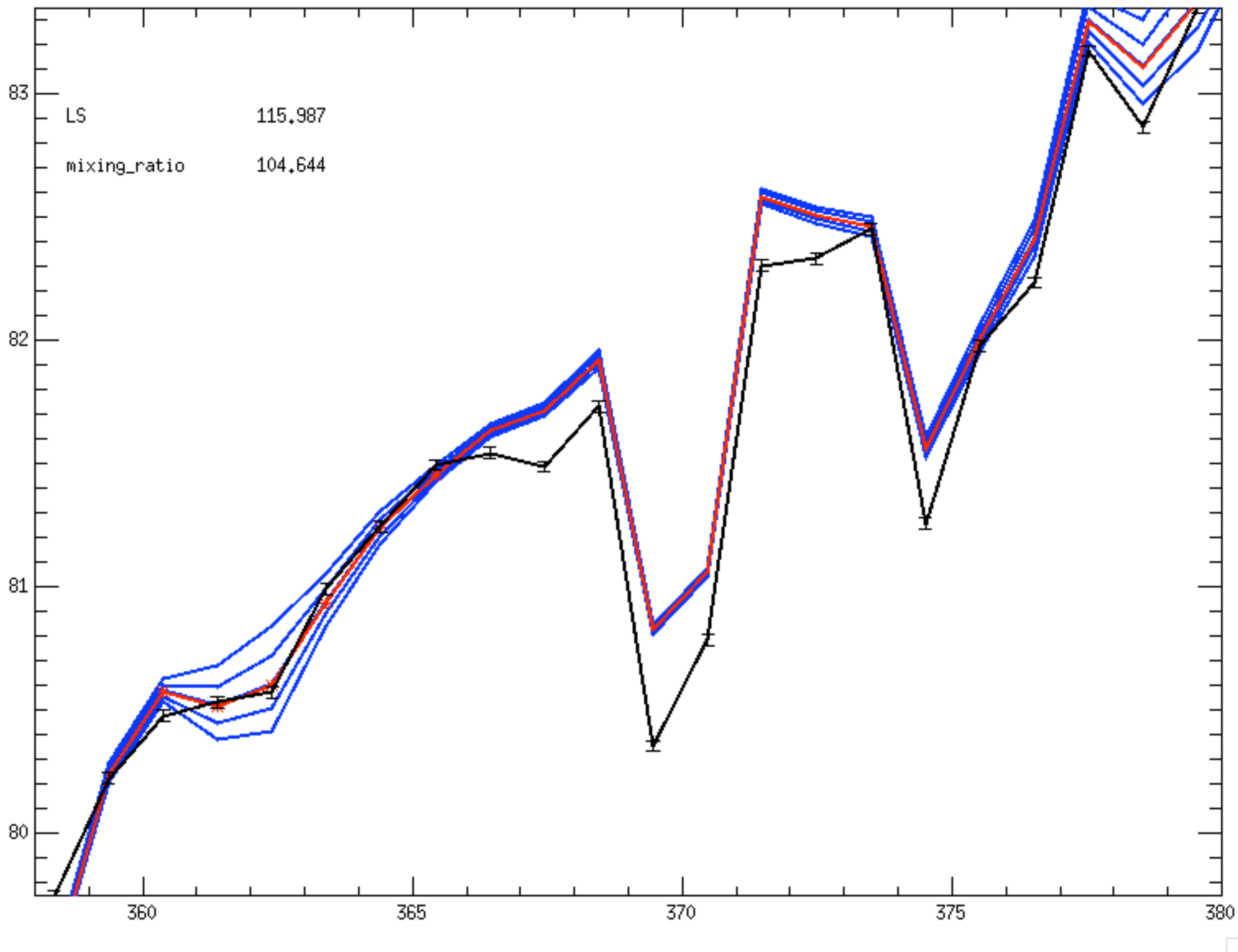

73.0
72.5
72.0
71.5
71.0
LS 106.882
mixing_ratio 183.399
360
365
370
375
380



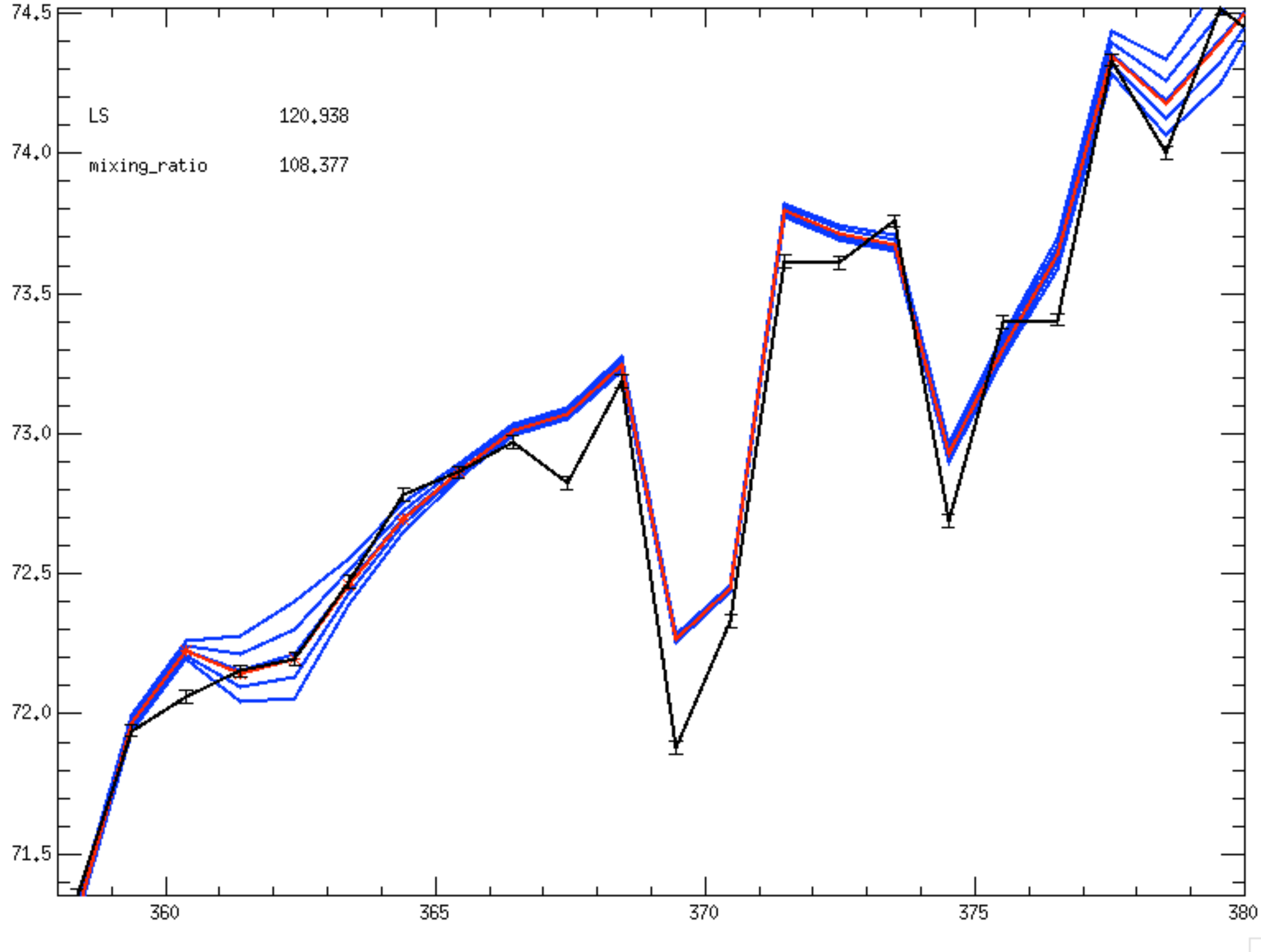
LS 110.441
mixing_ratio 148.628
77.0
76.5
76.0
75.5
75.0
74.5
360
365
370
375
380

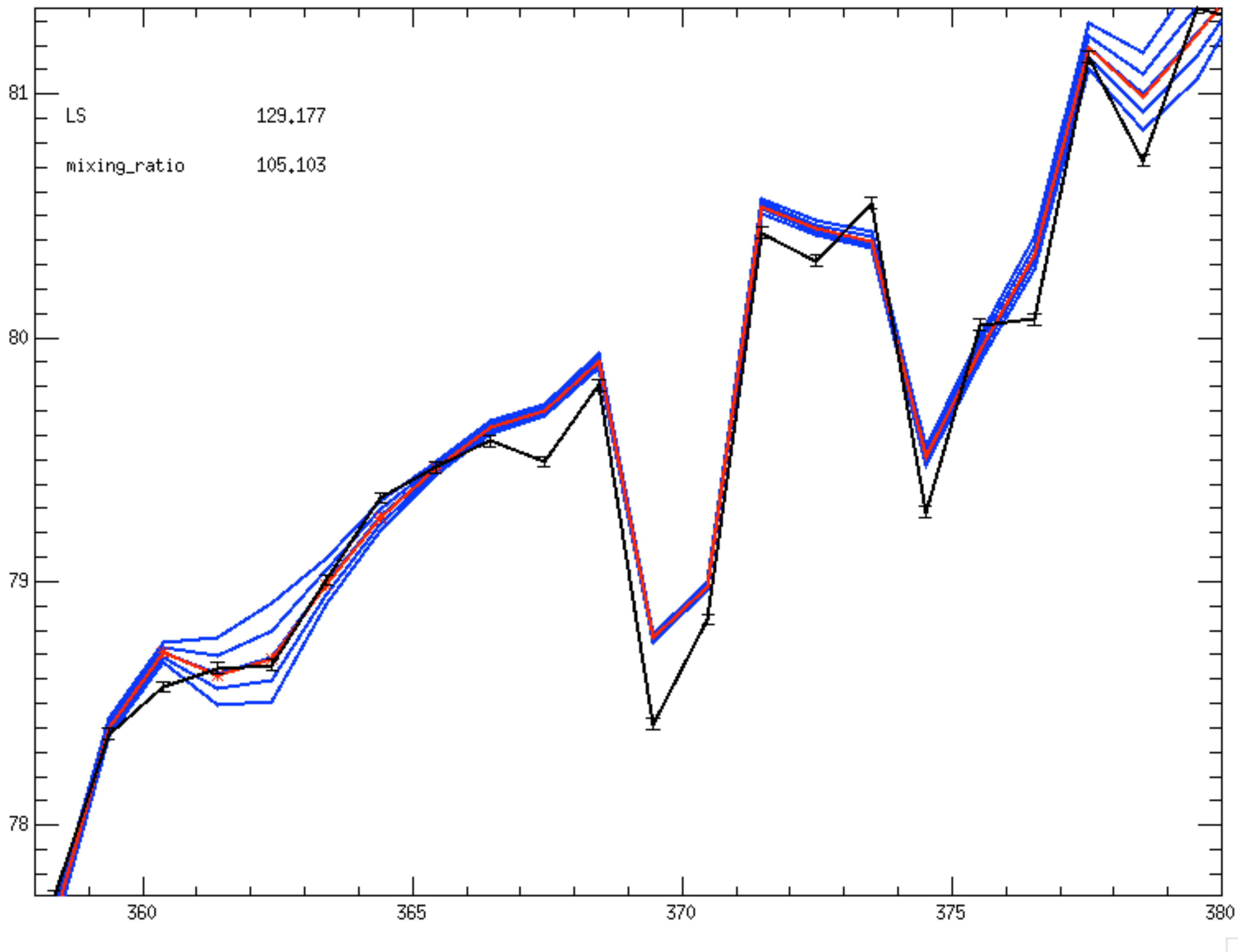


LS 113.398
mixing_ratio 152.180
80.0
79.5
79.0
78.5
78.0
77.5
360
365
370
375
380

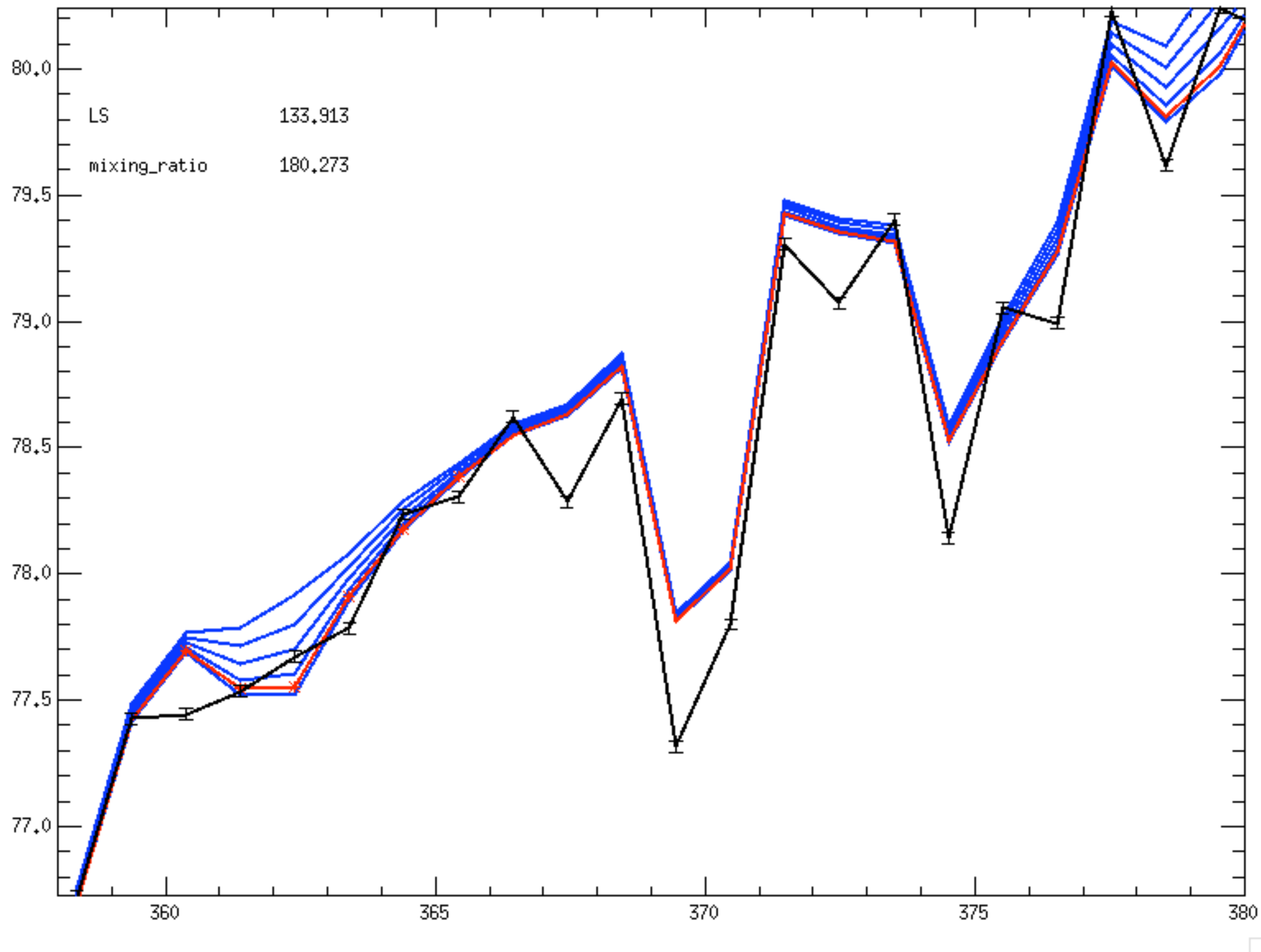


LS 115.987
mixing_ratio 104.644
83
82
81
80
360
365
370
375
380

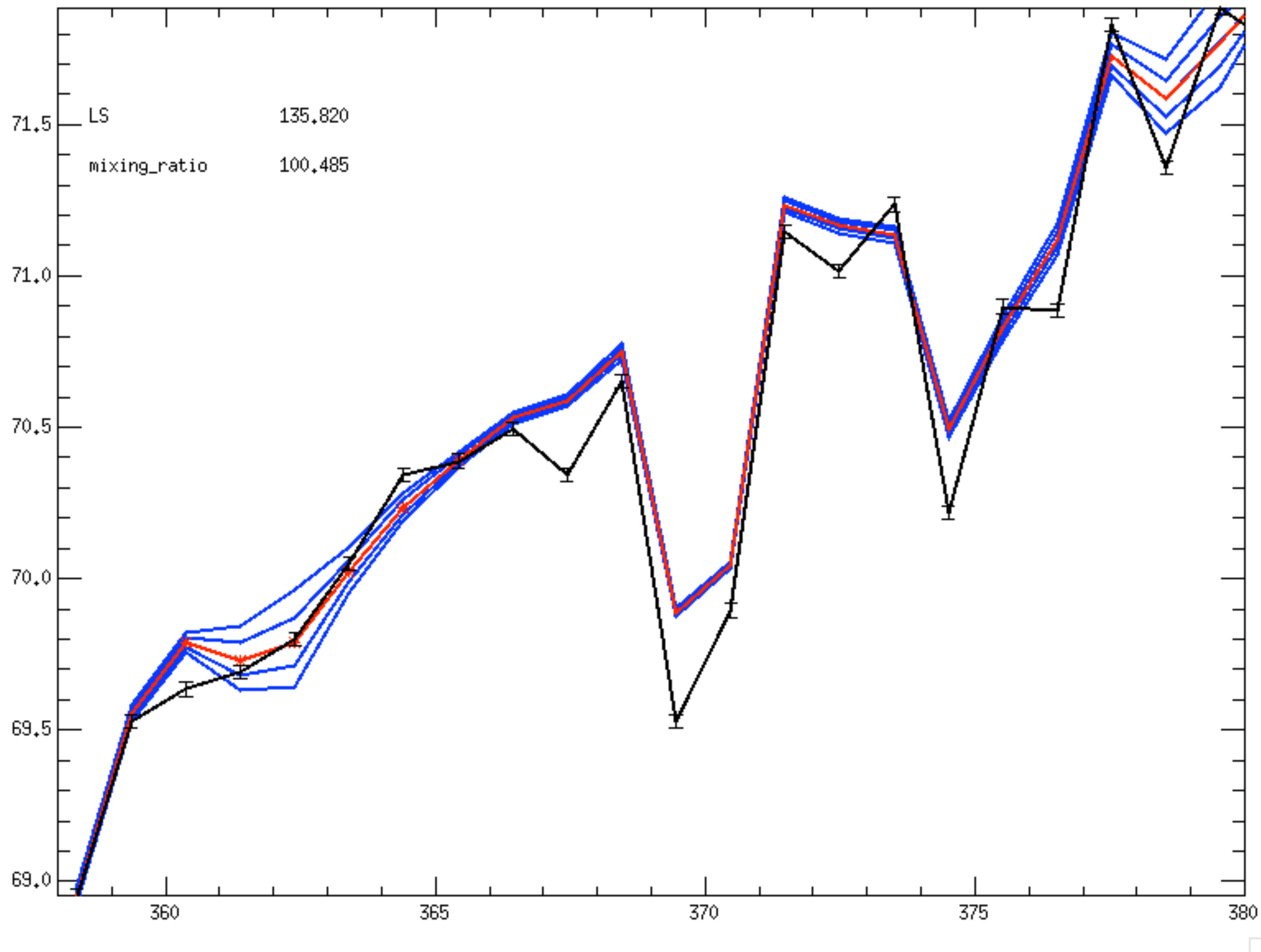

LS 120.938
mixing_ratio 108.377
74.5
74.0
73.5
73.0
72.5
72.0
71.5
360
365
370
375
380



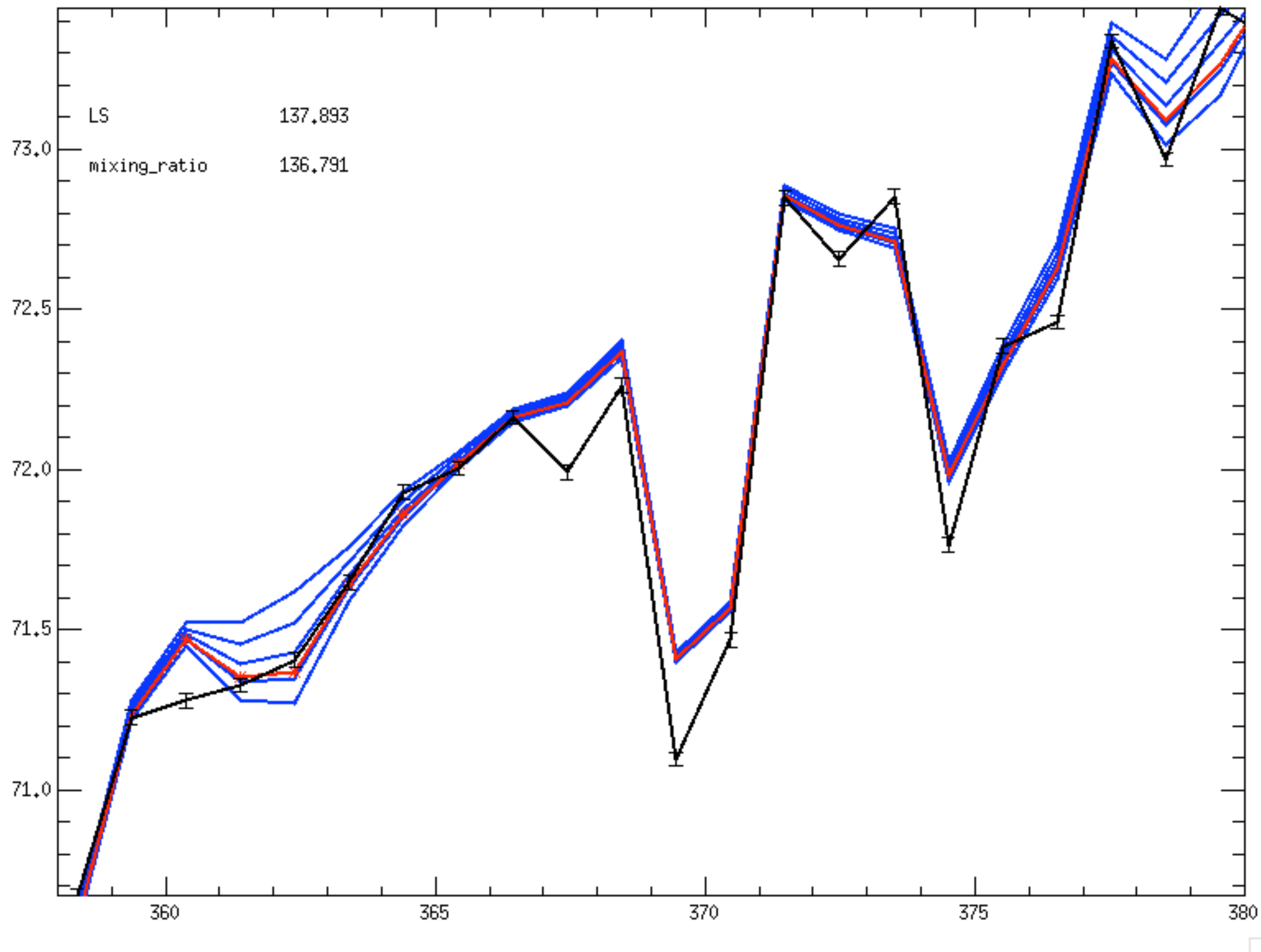
LS 129.177
mixing_ratio 105.103
81
80
79
78
360
365
370
375
380



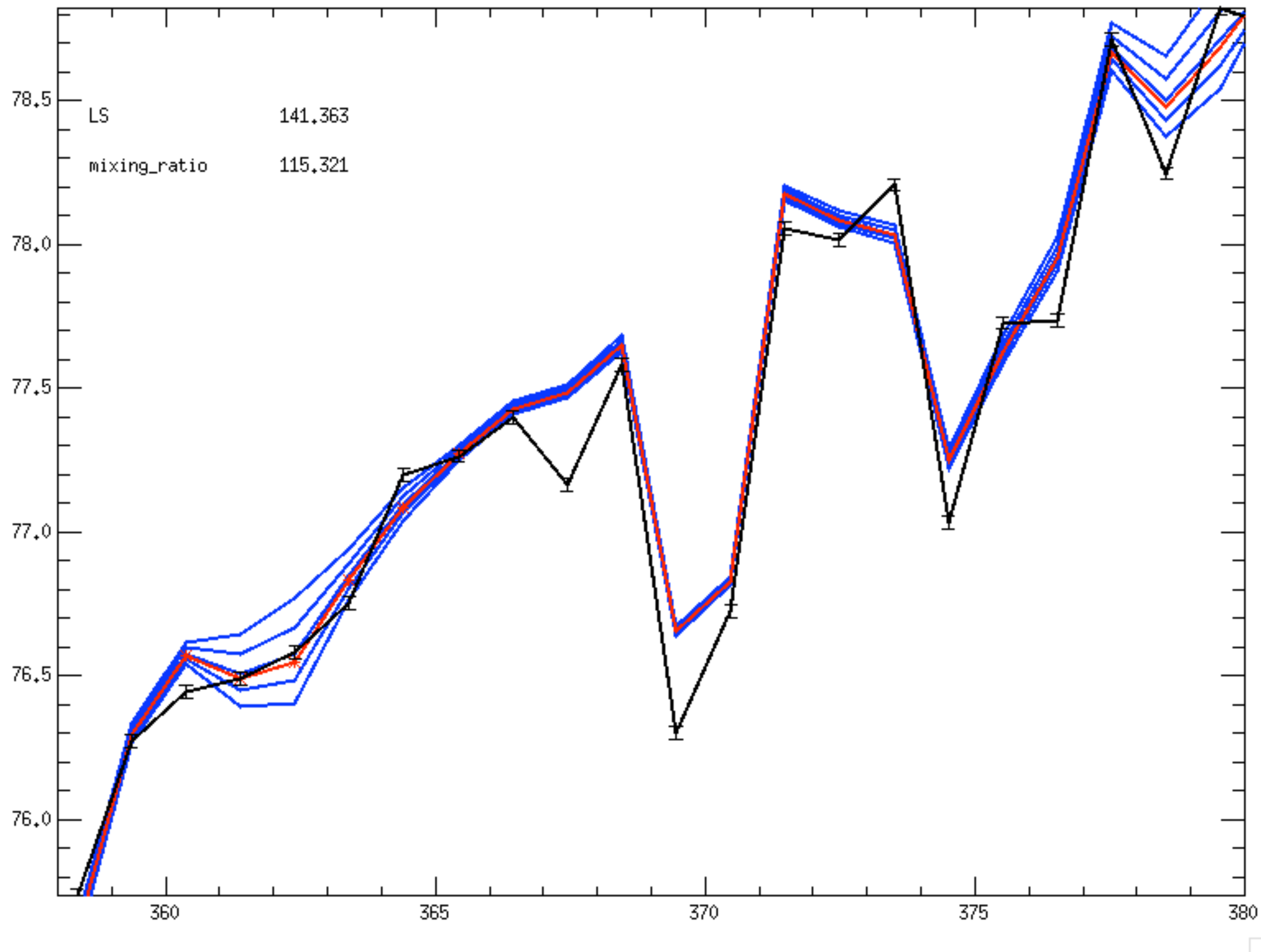
80.0
79.5
79.0
78.5
78.0
77.5
77.0
360
365
370
375
380
LS 133.913
mixing_ratio 180.273



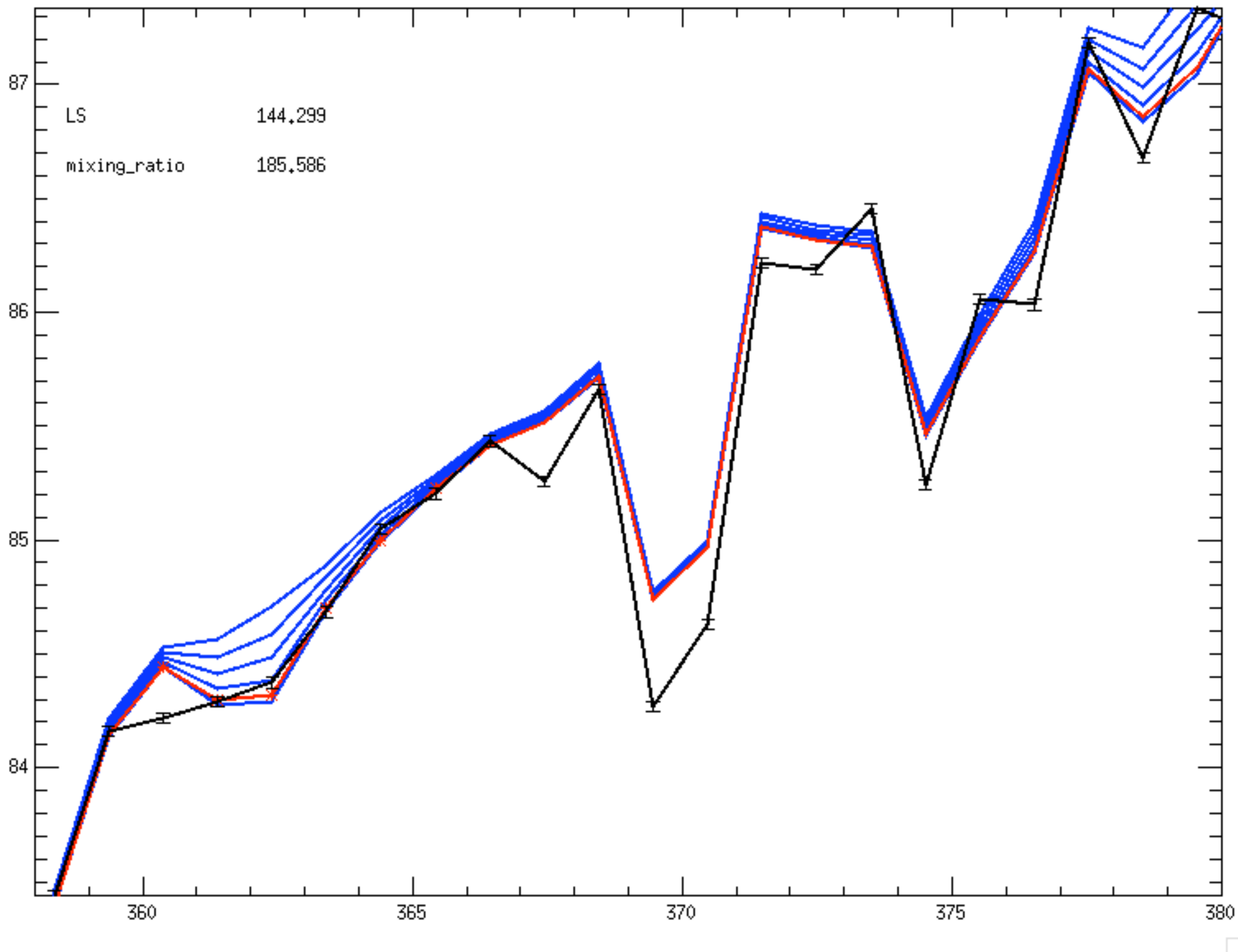
LS 135.820
mixing_ratio 100.485
71.5
71.0
70.5
70.0
69.5
69.0
360
365
370
375
380

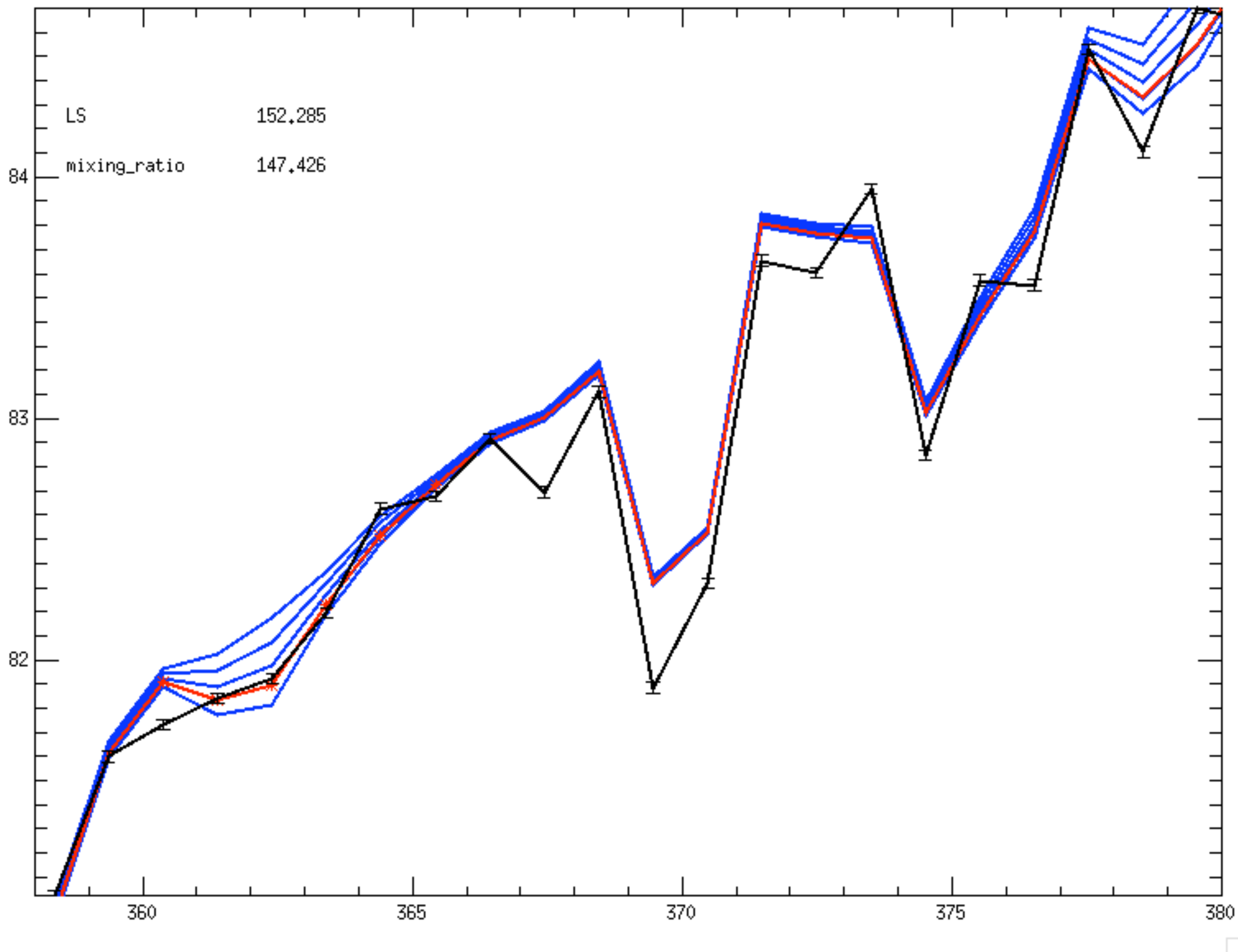


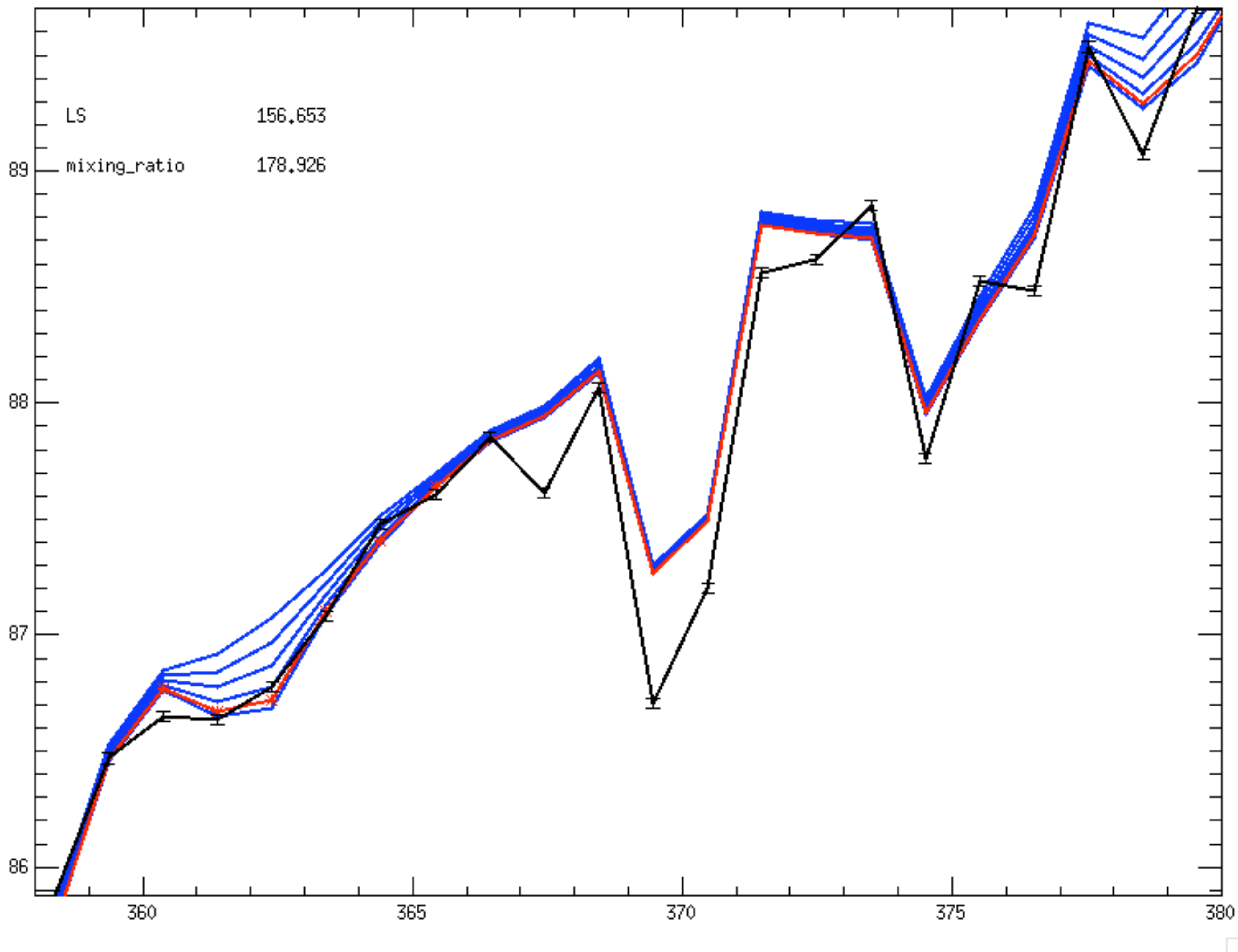
LS 137.893
mixing_ratio 136.791
73.0
72.5
72.0
71.5
71.0
360
365
370
375
380



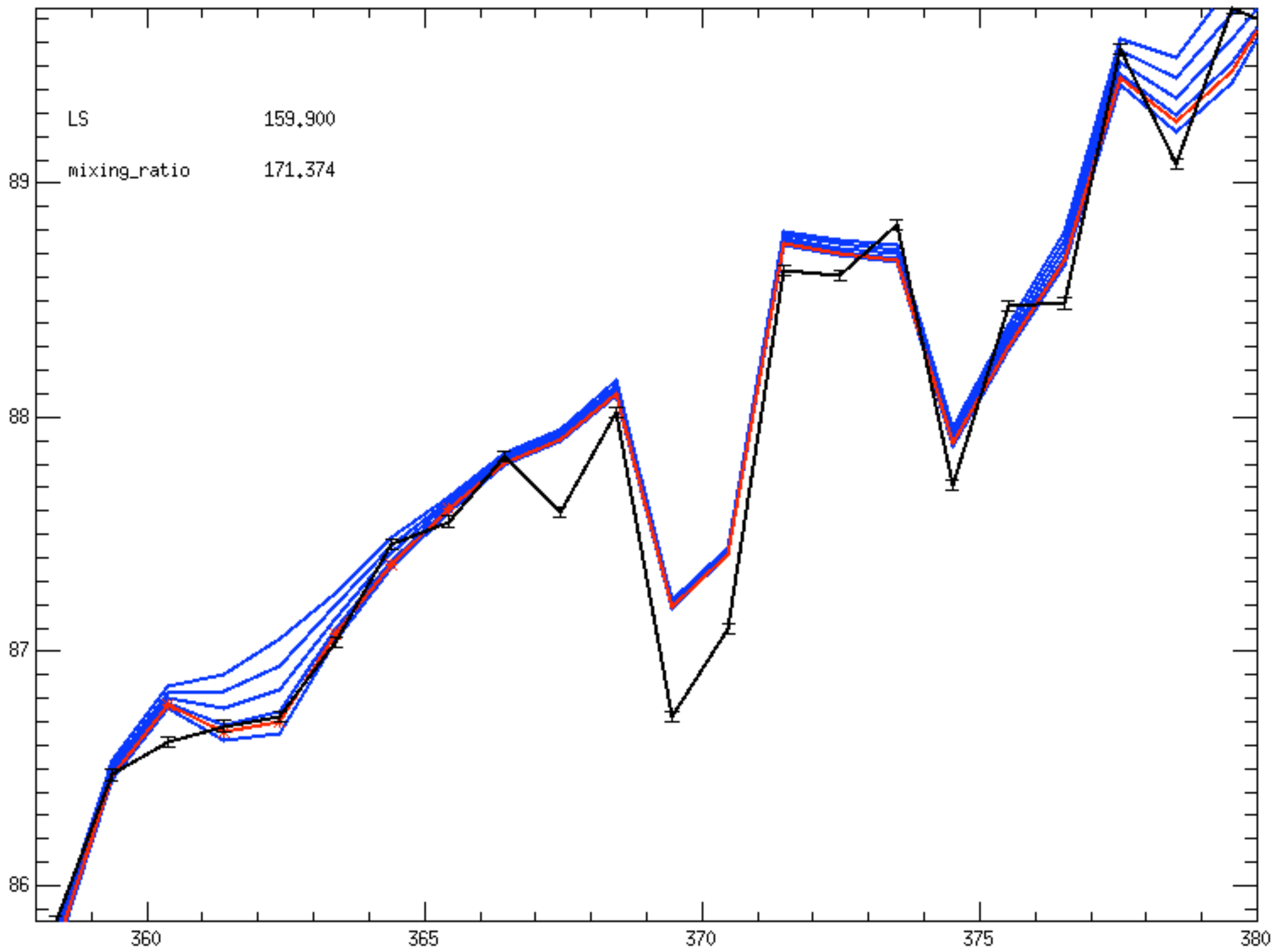
LS 141.363
mixing_ratio 115.321
78.5
78.0
77.5
77.0
76.5
76.0
360
365
370
375
380

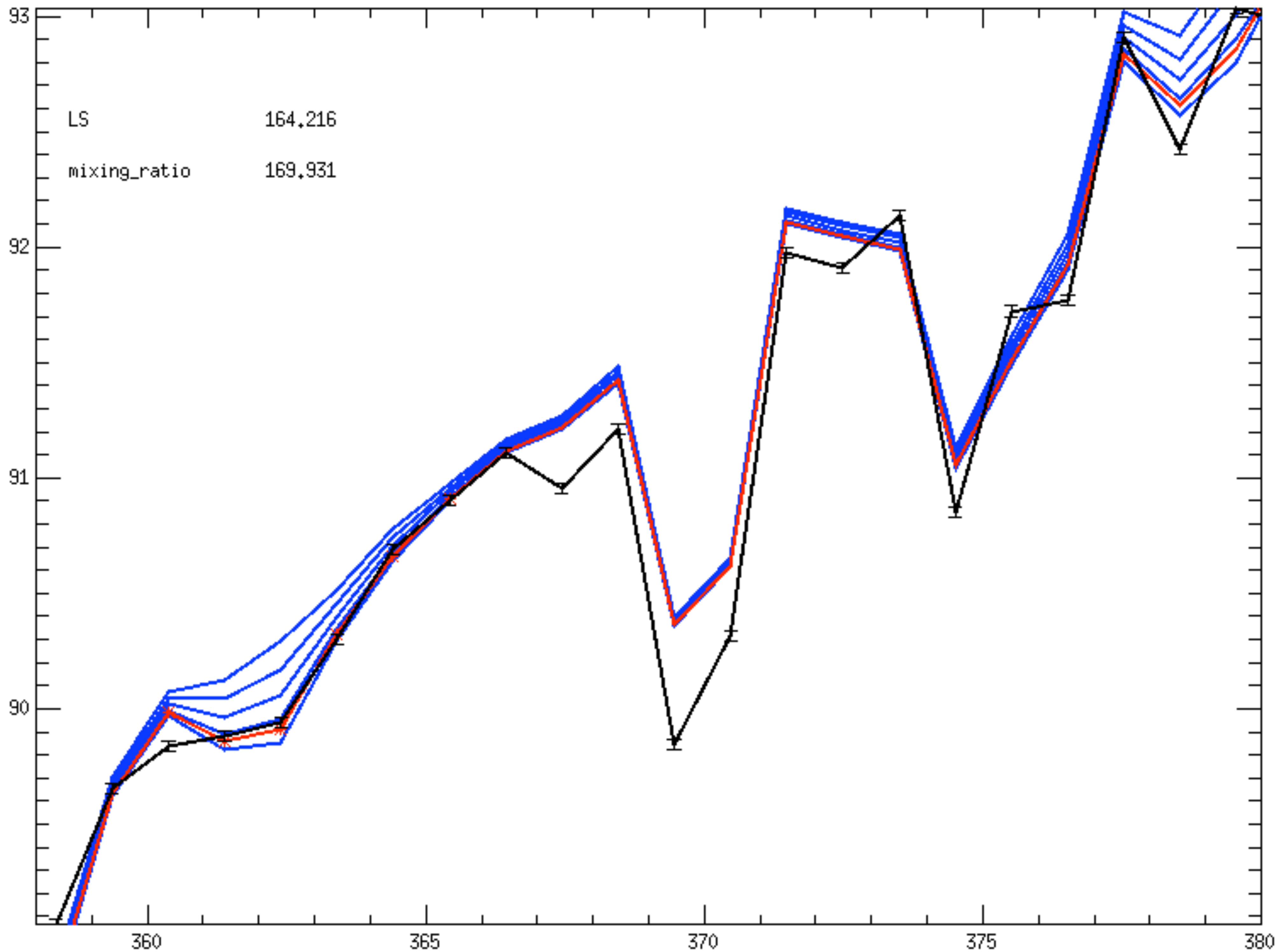

LS 144.299
mixing_ratio 185.586
87
86
85
84
360
365
370
375
380


LS 152.285
mixing_ratio 147.426
84
83
82
360
365
370
375
380

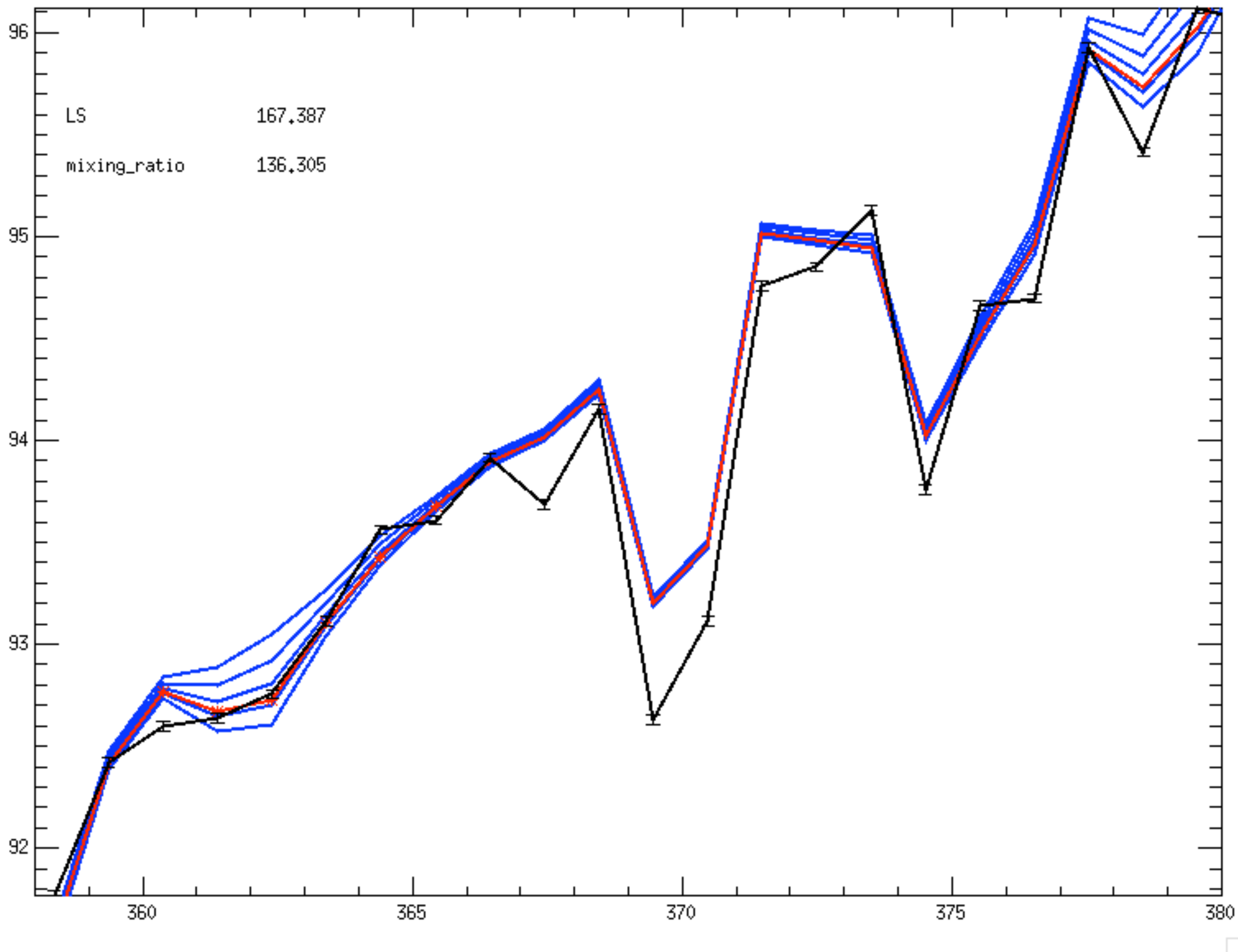


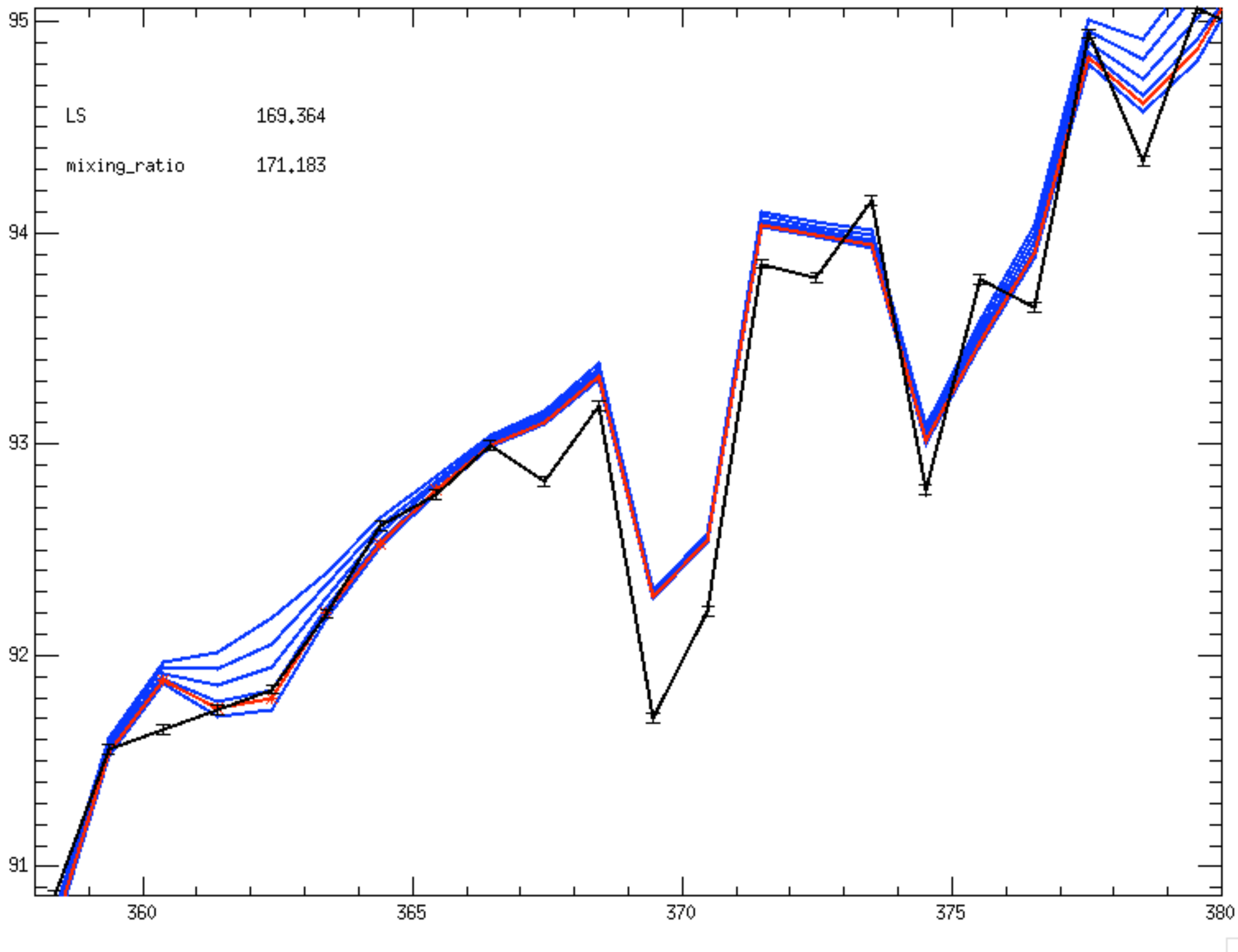
LS 156.653
mixing_ratio 178.926
89
88
87
86
360
365
370
375
380

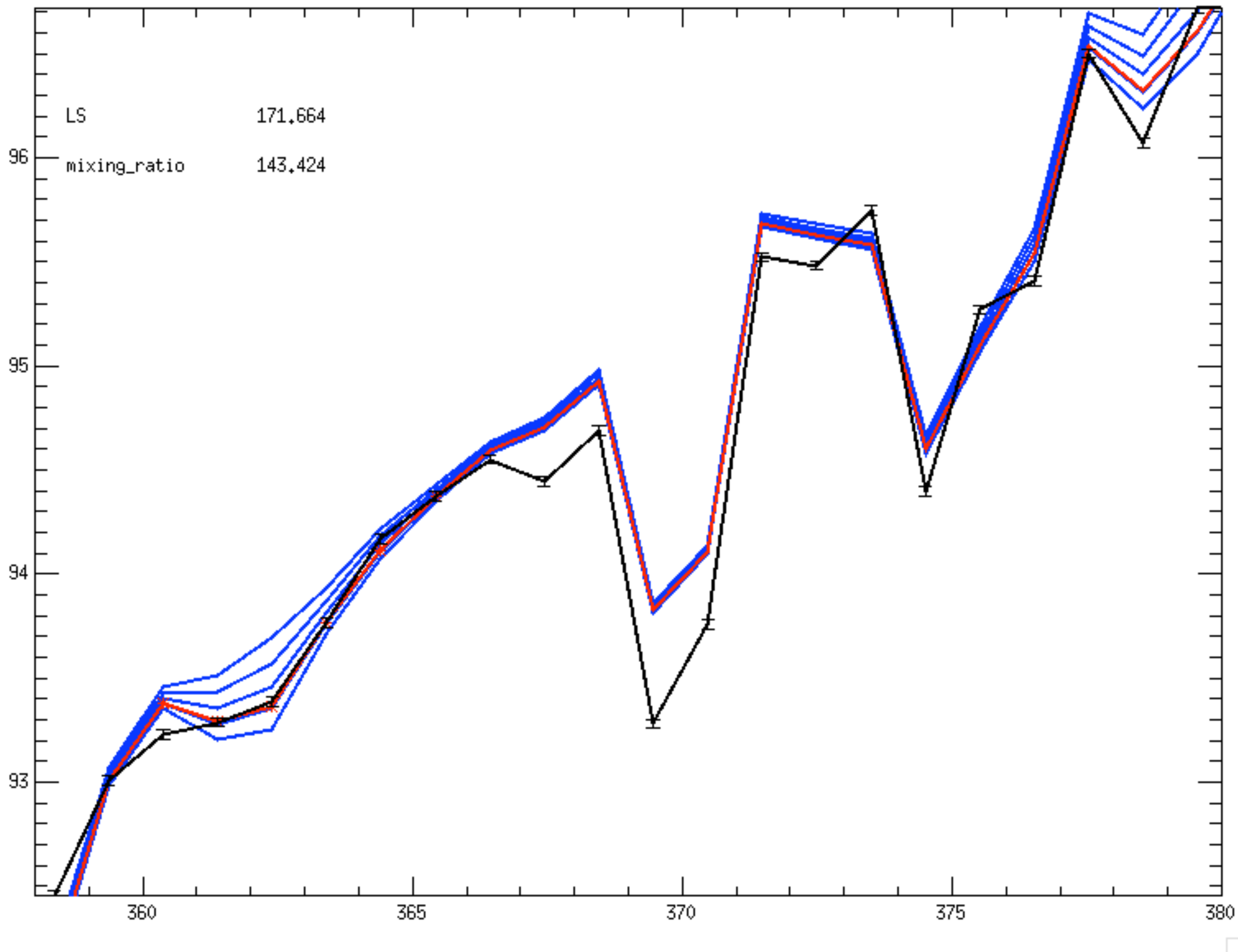

LS 159.900
mixing_ratio 171.374
89
88
87
86
360
365
370
375
380

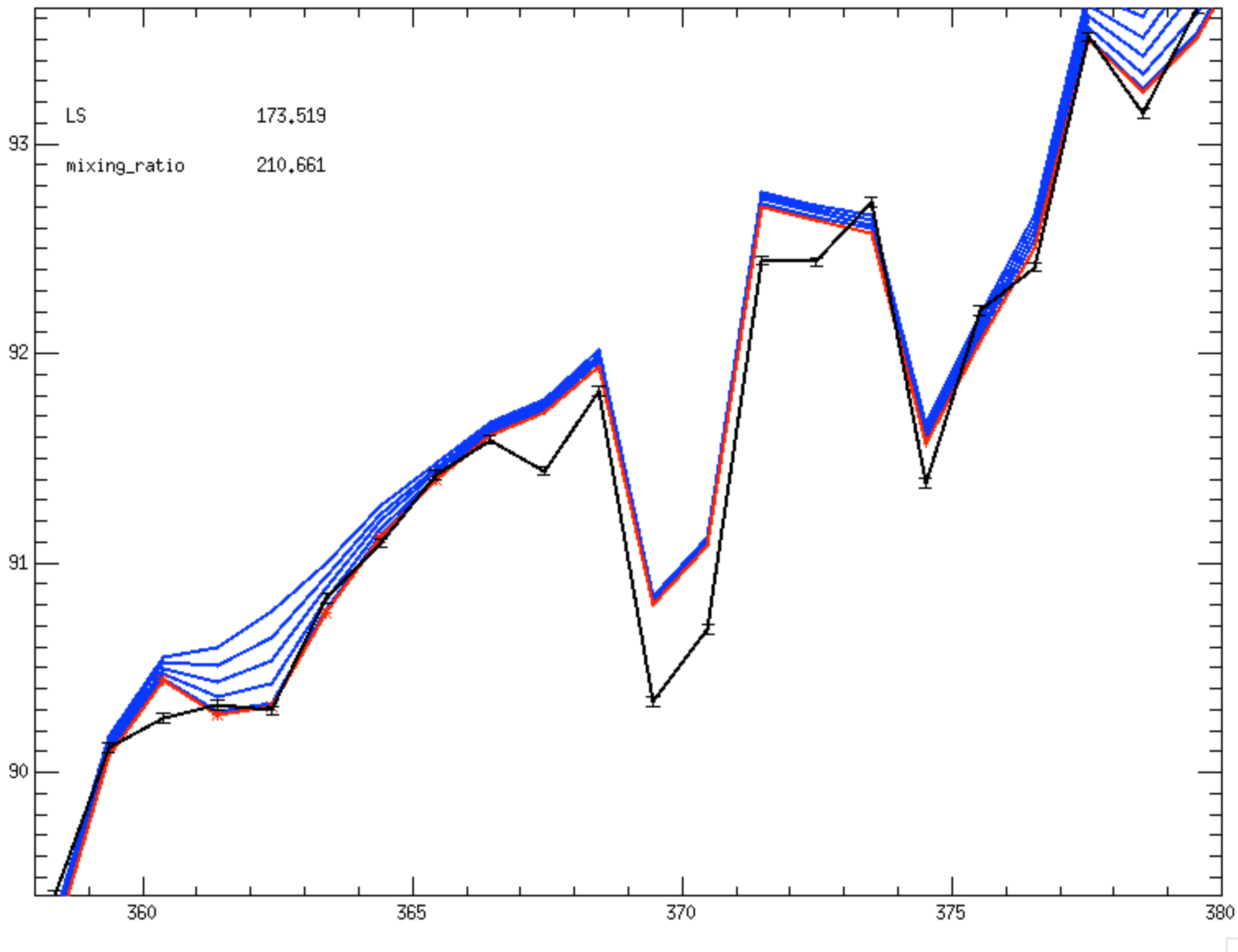


LS 164.216
mixing_ratio 169.931
93
92
91
90
360
365
370
375
380

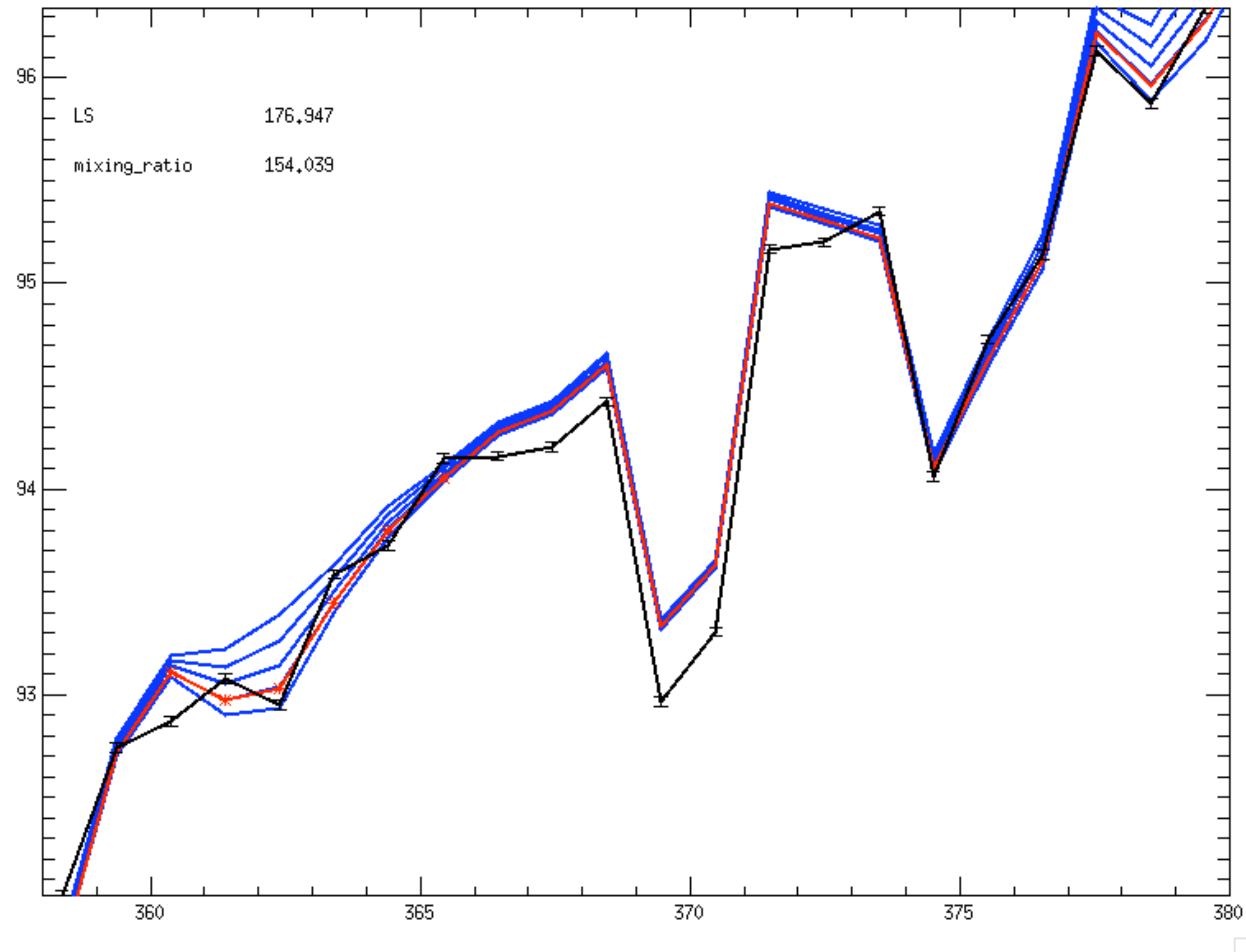

LS 167.387
mixing_ratio 136.305
96
95
94
93
92
360
365
370
375
380

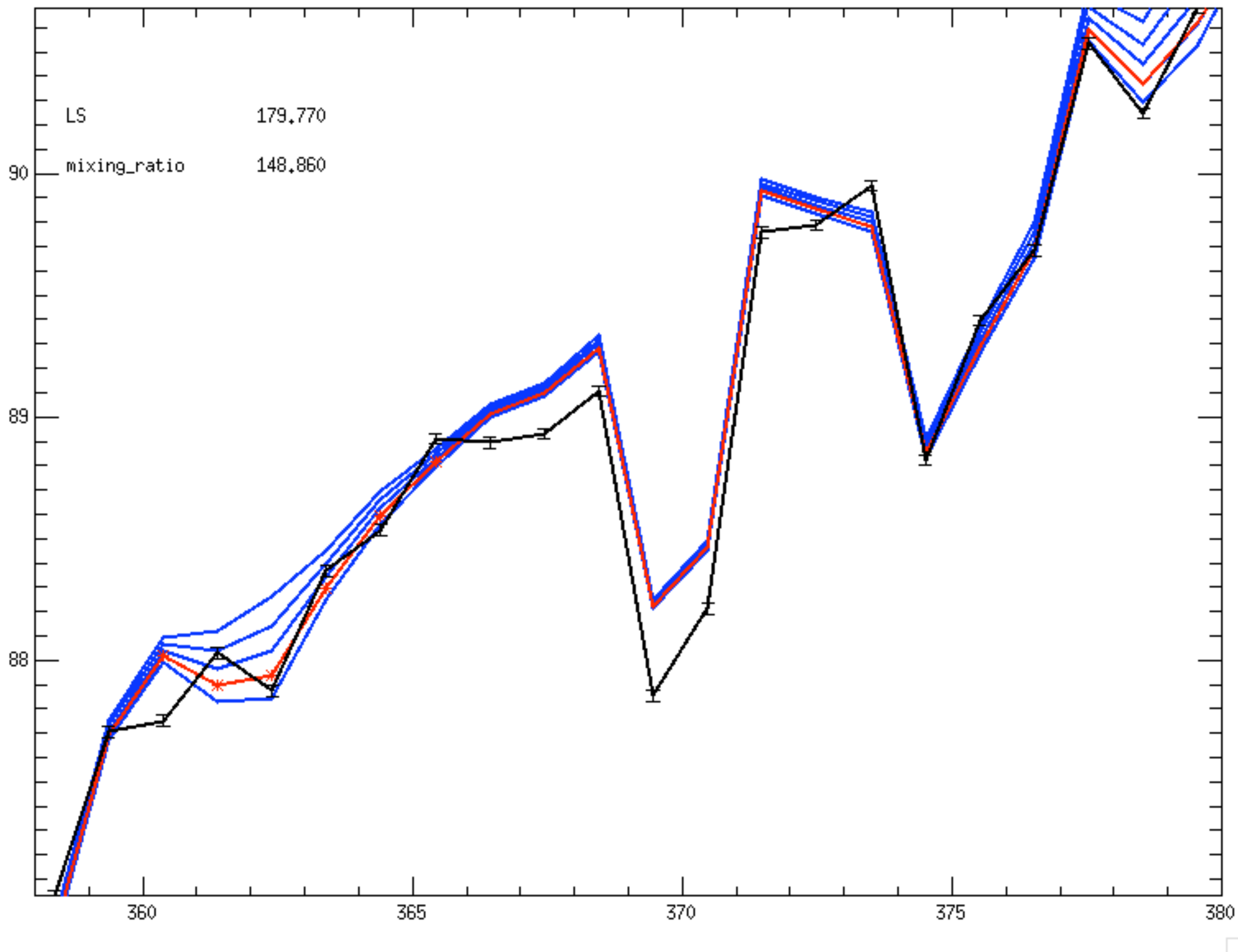

LS 169.364
mixing_ratio 171.183
95
94
93
92
91
360
365
370
375
380

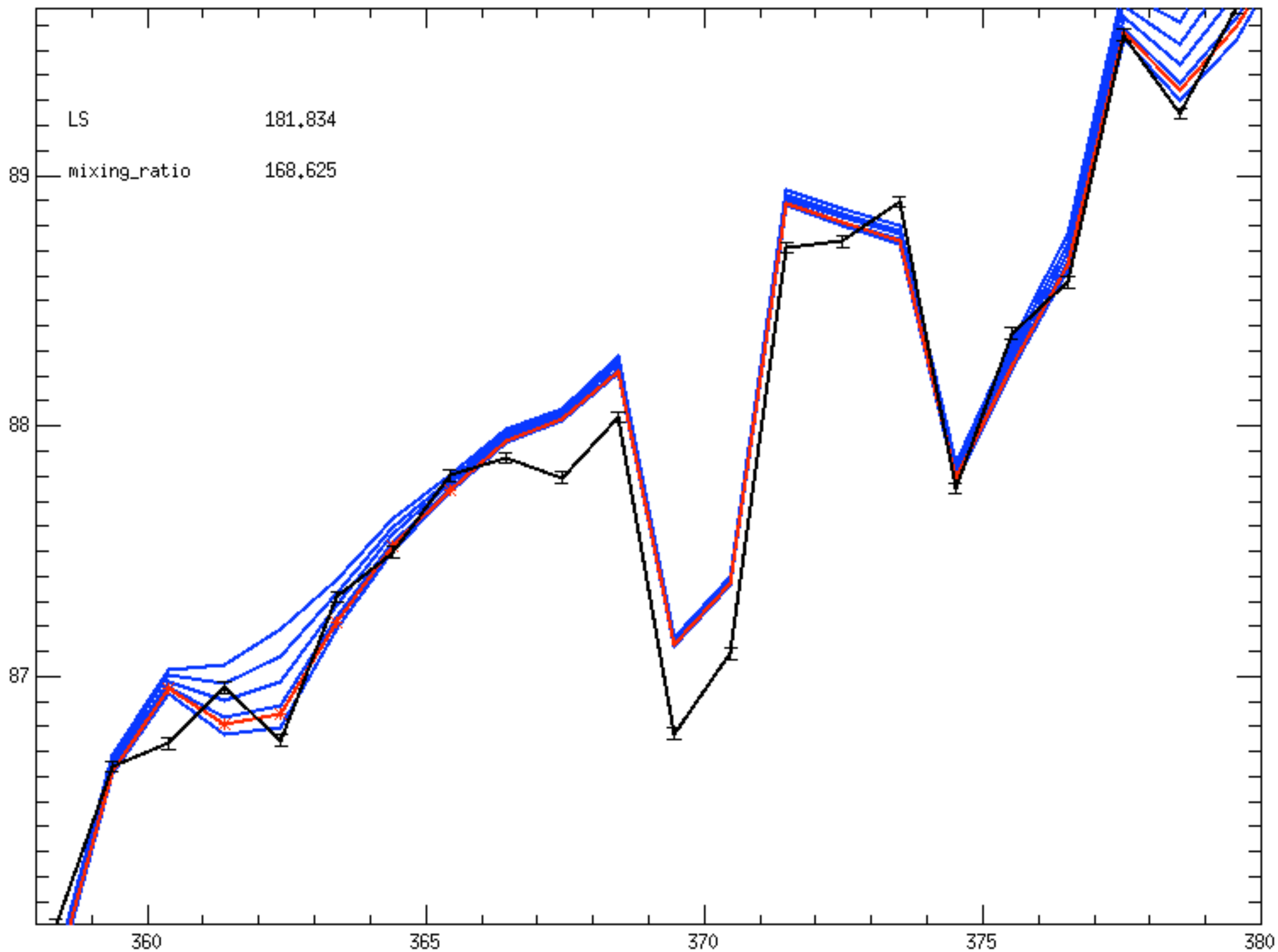

LS 171.664
mixing_ratio 143.424
96
95
94
93
360
365
370
375
380



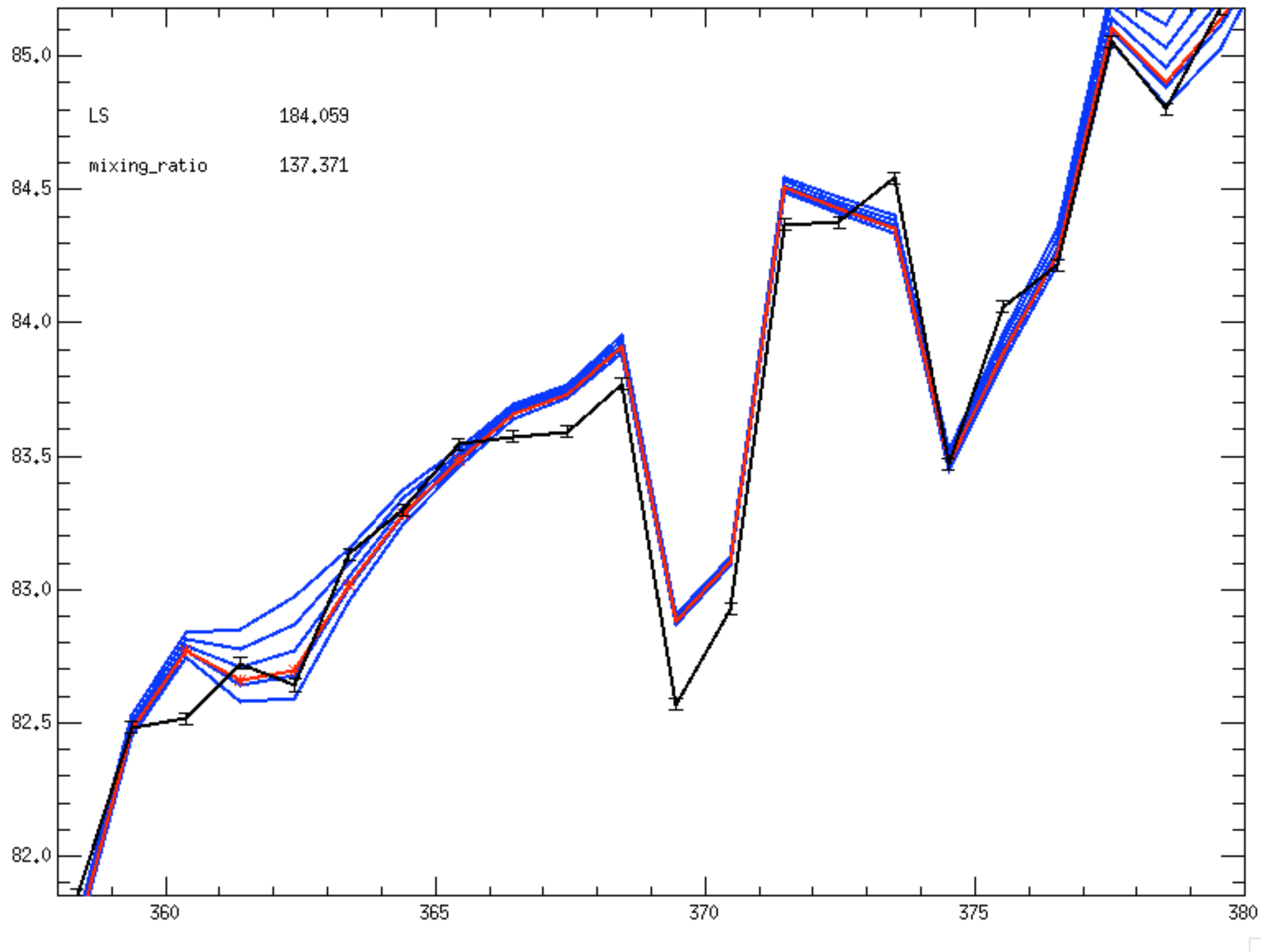
LS 173.519
mixing_ratio 210.661
93
92
91
90
360
365
370
375
380

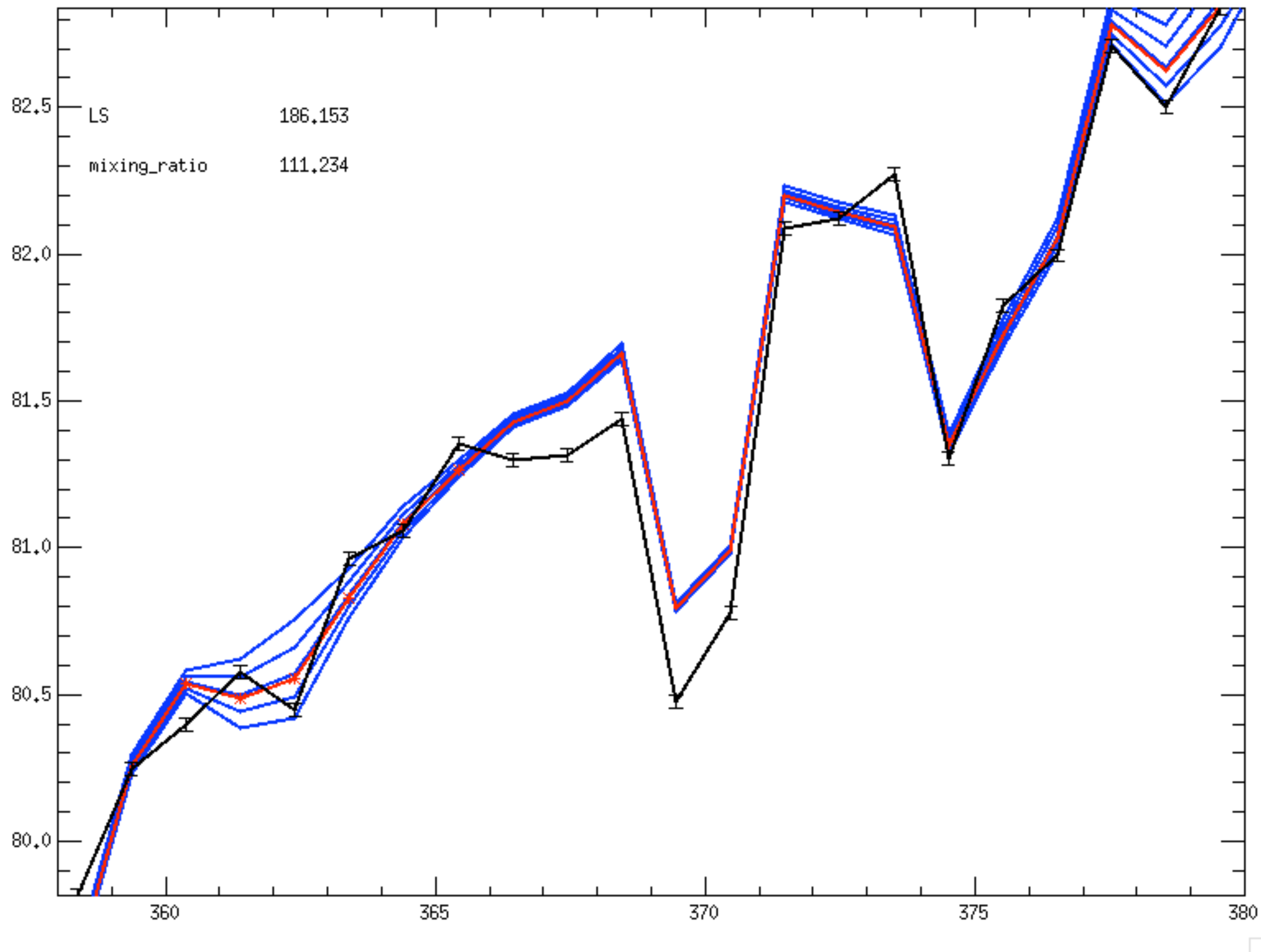

96
95
94
93
LS 176.947
mixing_ratio 154.039
360
365
370
375
380

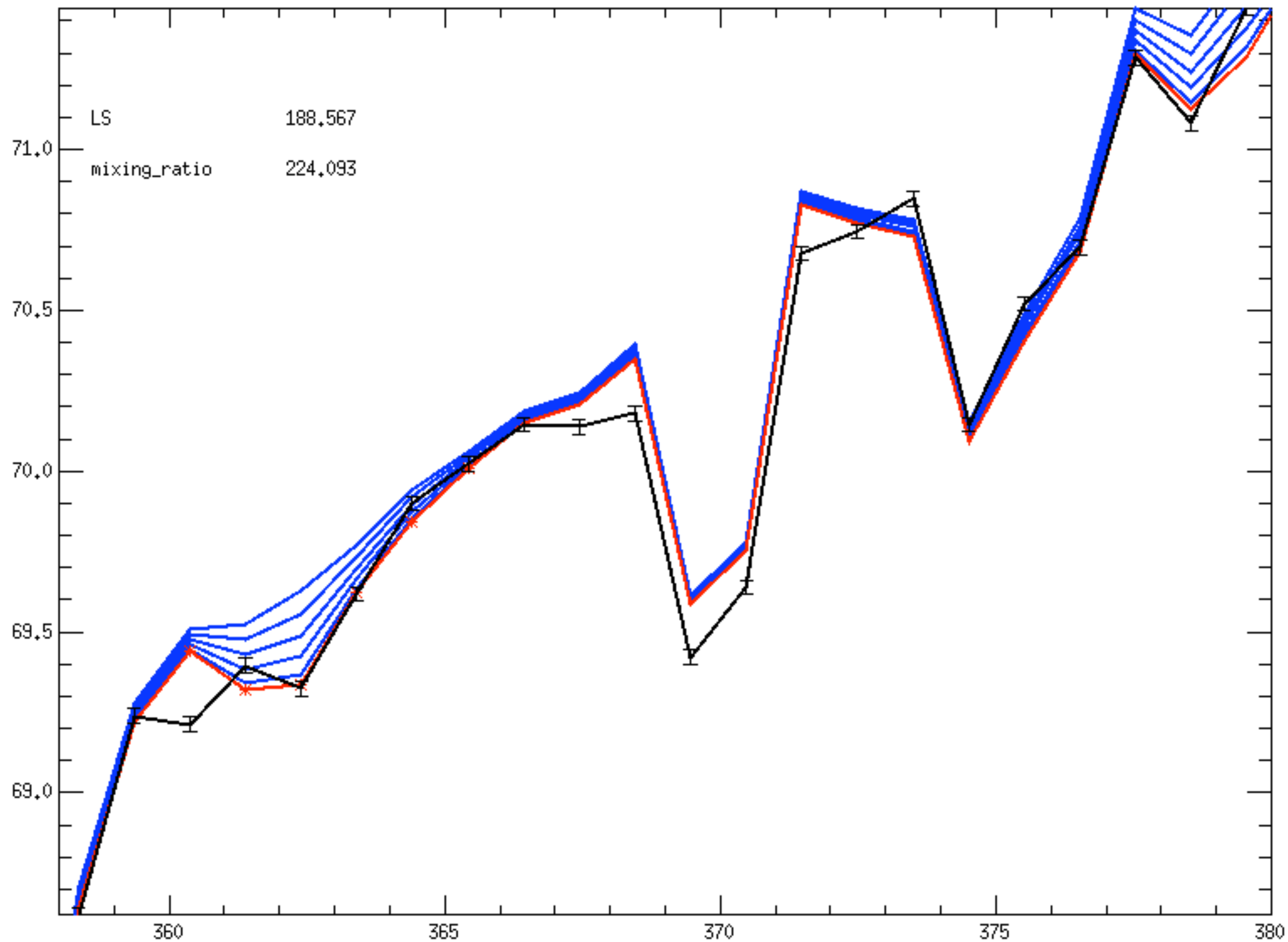

LS 179.770
mixing_ratio 148.860
90
89
88
360
365
370
375
380

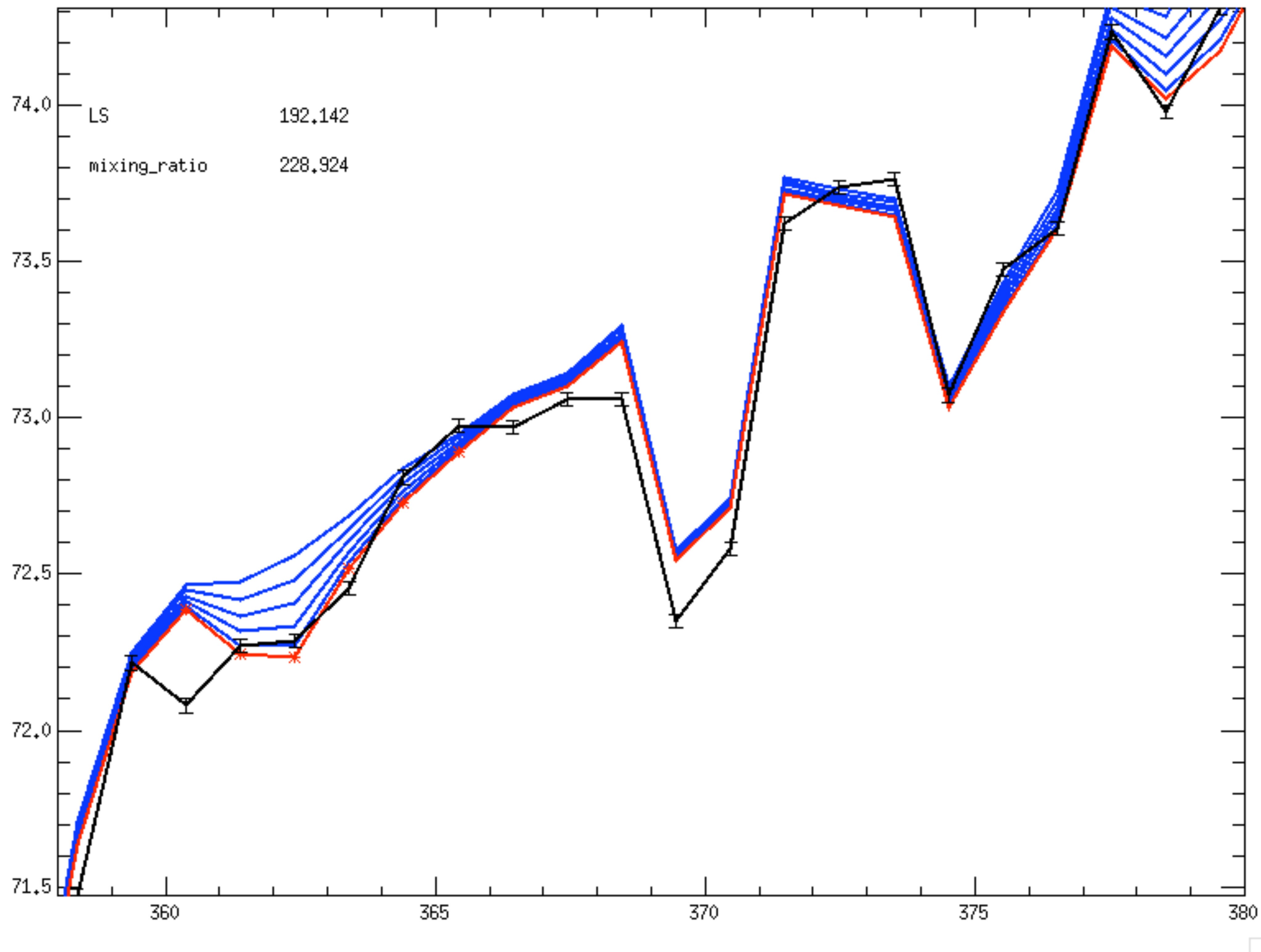


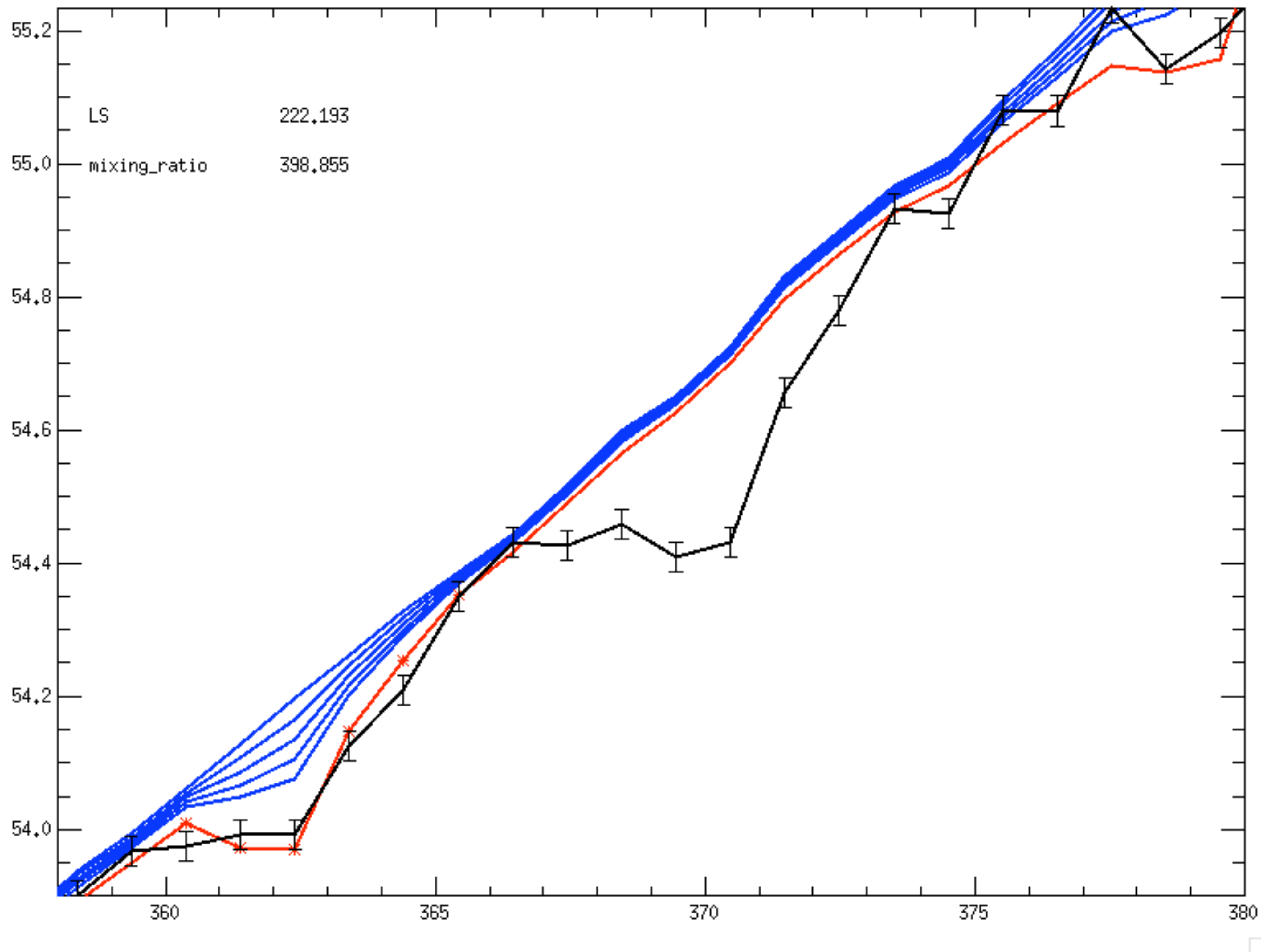
LS 181.834
mixing_ratio 168.625
89
88
87
360
365
370
375
380


85.0
84.5
84.0
83.5
83.0
82.5
82.0
LS 184.059
mixing_ratio 137.371
360
365
370
375
380

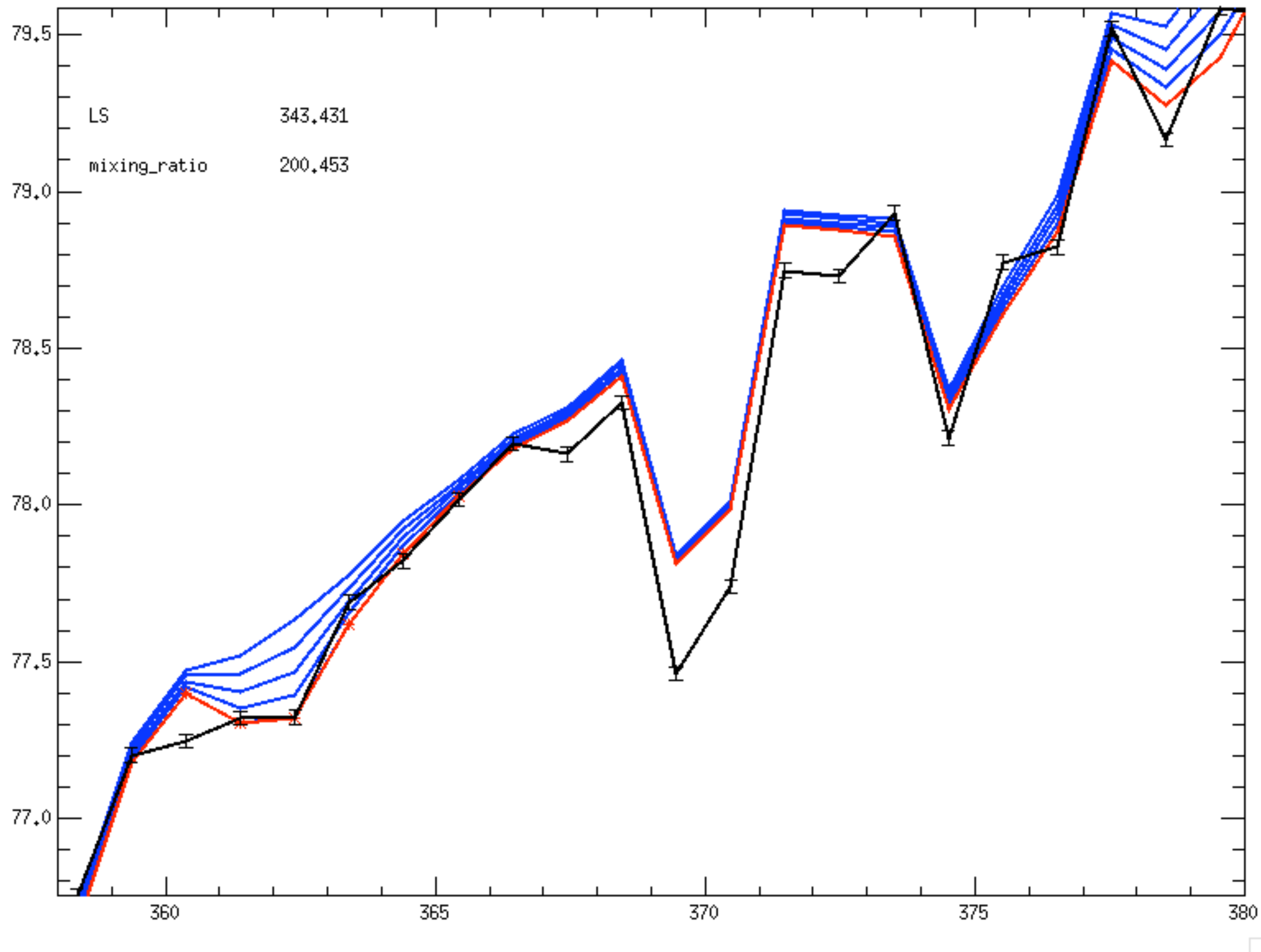

LS 186.153
mixing_ratio 111.234
82.5
82.0
81.5
81.0
80.5
80.0
360
365
370
375
380


LS 188.567
mixing_ratio 224.093
71.0
70.5
70.0
69.5
69.0
360
365
370
375
380

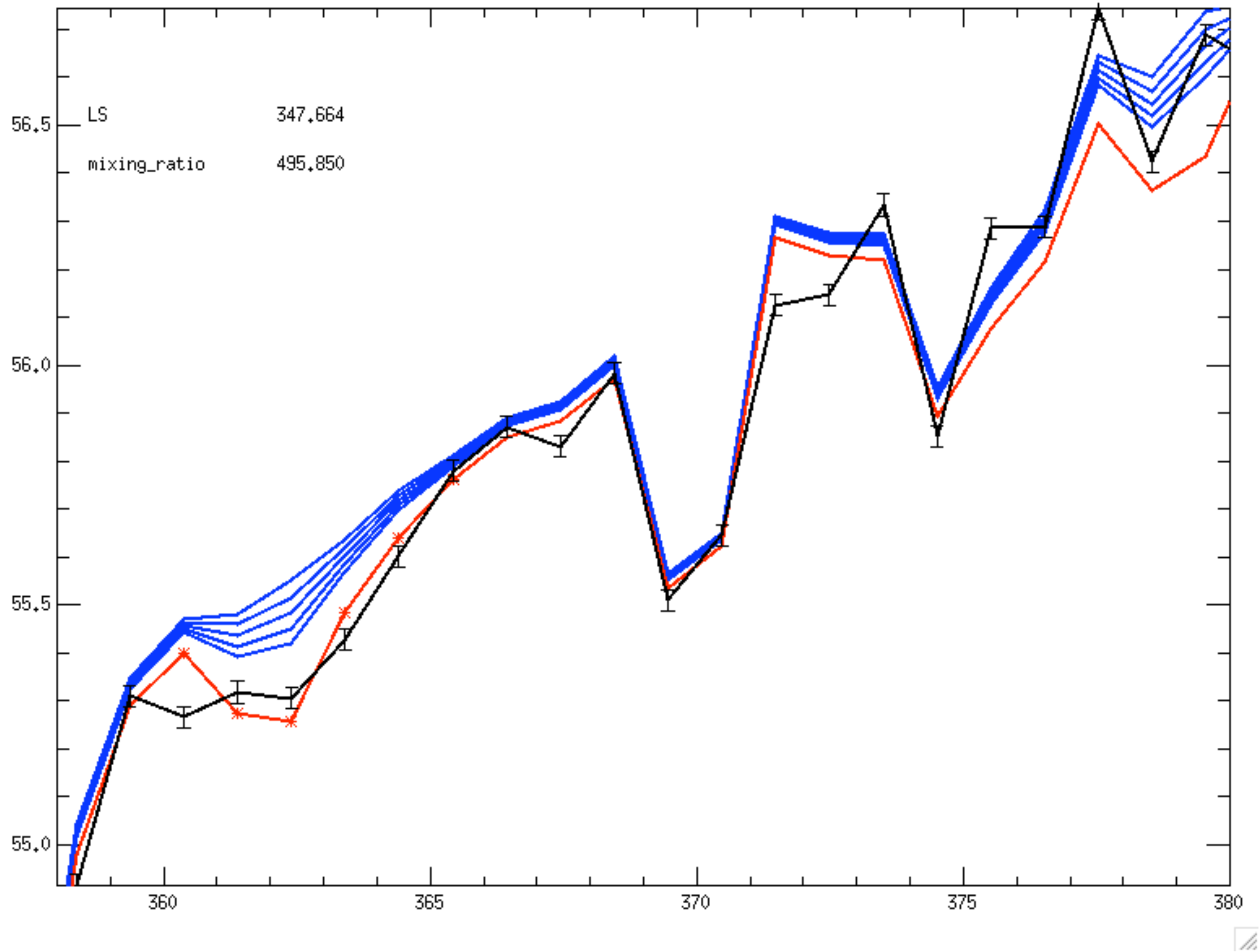

LS 192.142
mixing_ratio 228.924
74.0
73.5
73.0
72.5
72.0
71.5
360
365
370
375
380

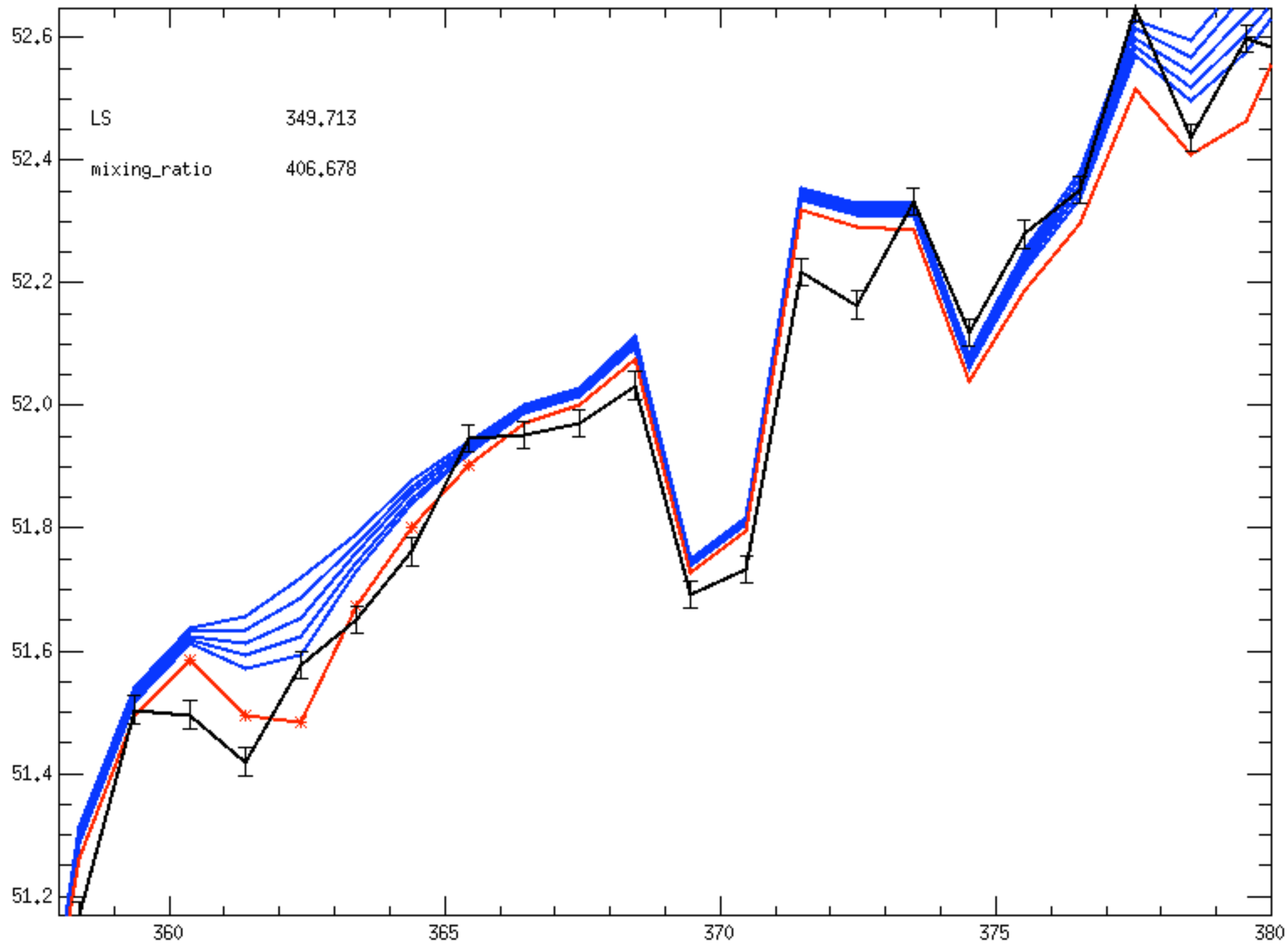


55.2
55.0
54.8
54.6
54.4
54.2
54.0
LS 222.193
mixing_ratio 398.855
360
365
370
375
380



LS 343.431
mixing_ratio 200.453
79.5
79.0
78.5
78.0
77.5
77.0
360
365
370
375
380


LS 347.664
mixing_ratio 495.850
56.5
56.0
55.5
55.0
360
365
370
375
380



LS 349.713
mixing_ratio 406.678
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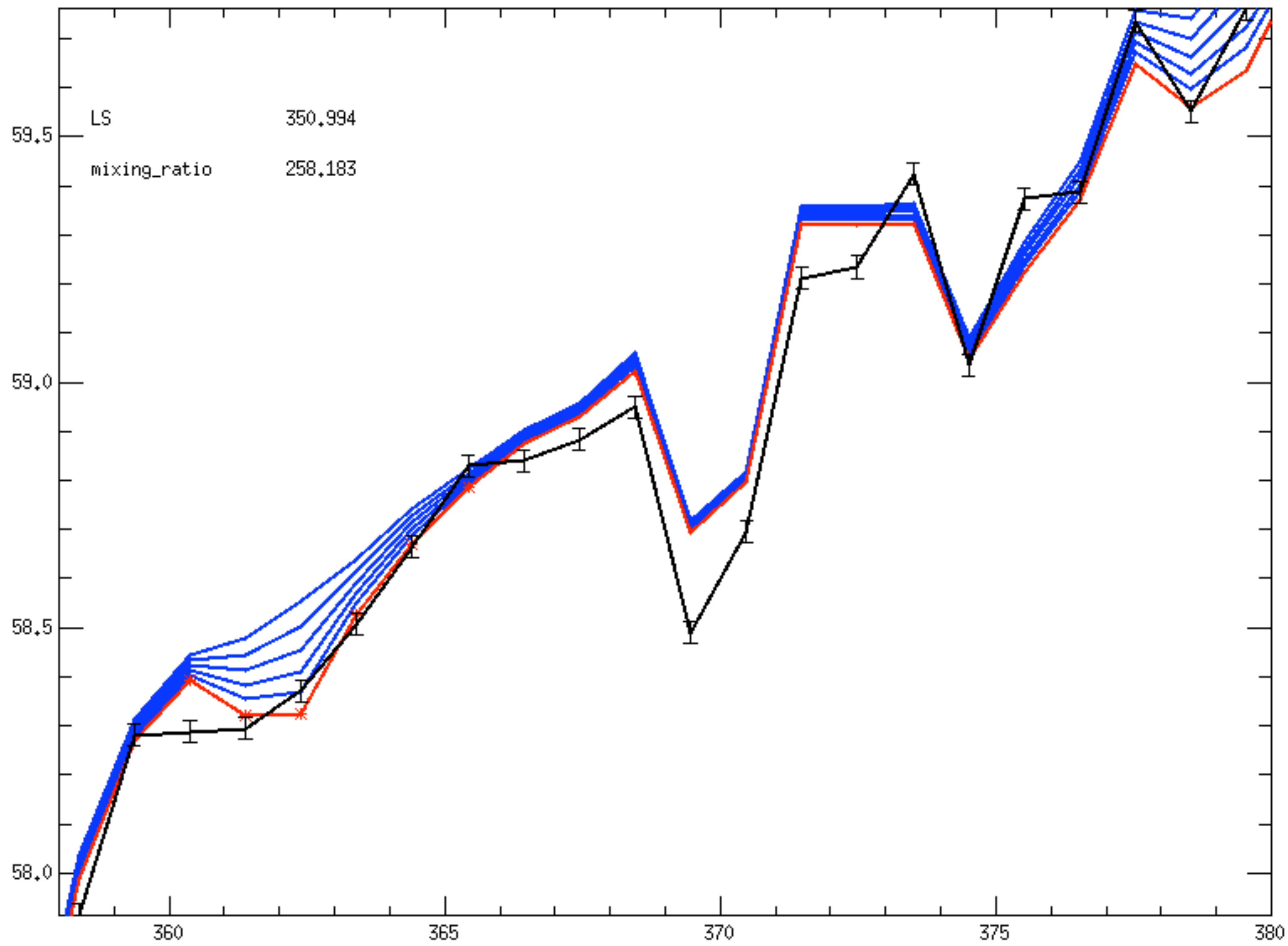
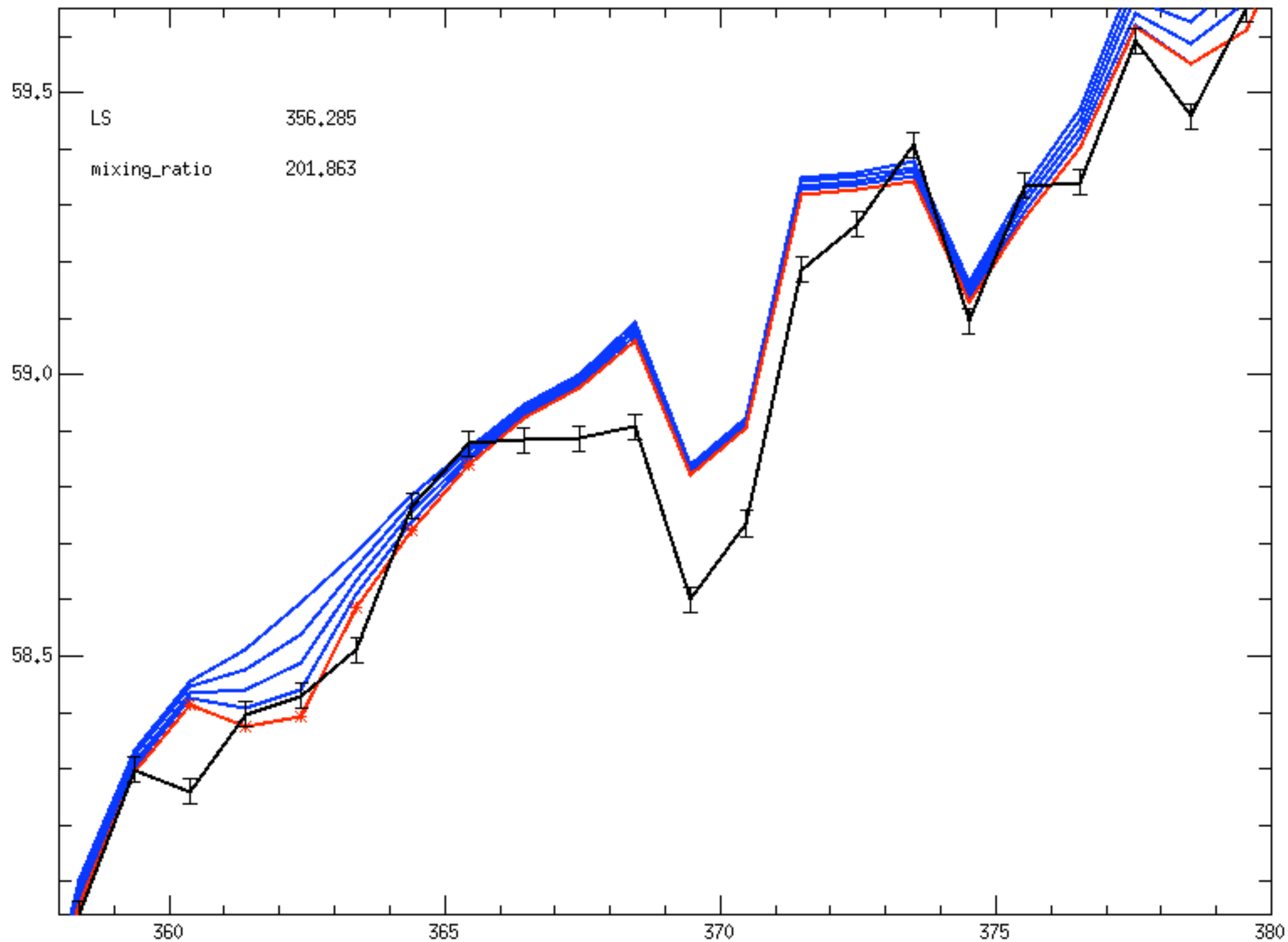
52.4
52.2
52.0
51.8
51.6
51.4
51.2
360
365
370
375
380



LS 350.994
mixing_ratio 258.183
59.5
59.0
58.5
58.0
360
365
370
375
380


LS 356.285
mixing_ratio 201.863
59.5
59.0
58.5
360
365
370
375
380