

Calibration strategy of isotope ratio infrared spectroscopy (IRIS) for $\delta^{13}\text{C}$ of CO_2 monitoring

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Outlines

1. Introduction

2. Materials and methods

3. Results and Discussion

4. Conclusions

1. Introduction

[1] Important tracer, and traditional methods (IRMS), alternative method of IRIS

同位素组成 δ (isotopic composition)

$$\delta_{\text{sample}} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 10^3 \quad R = {}^{13}\text{CO}_2/{}^{12}\text{CO}_2$$

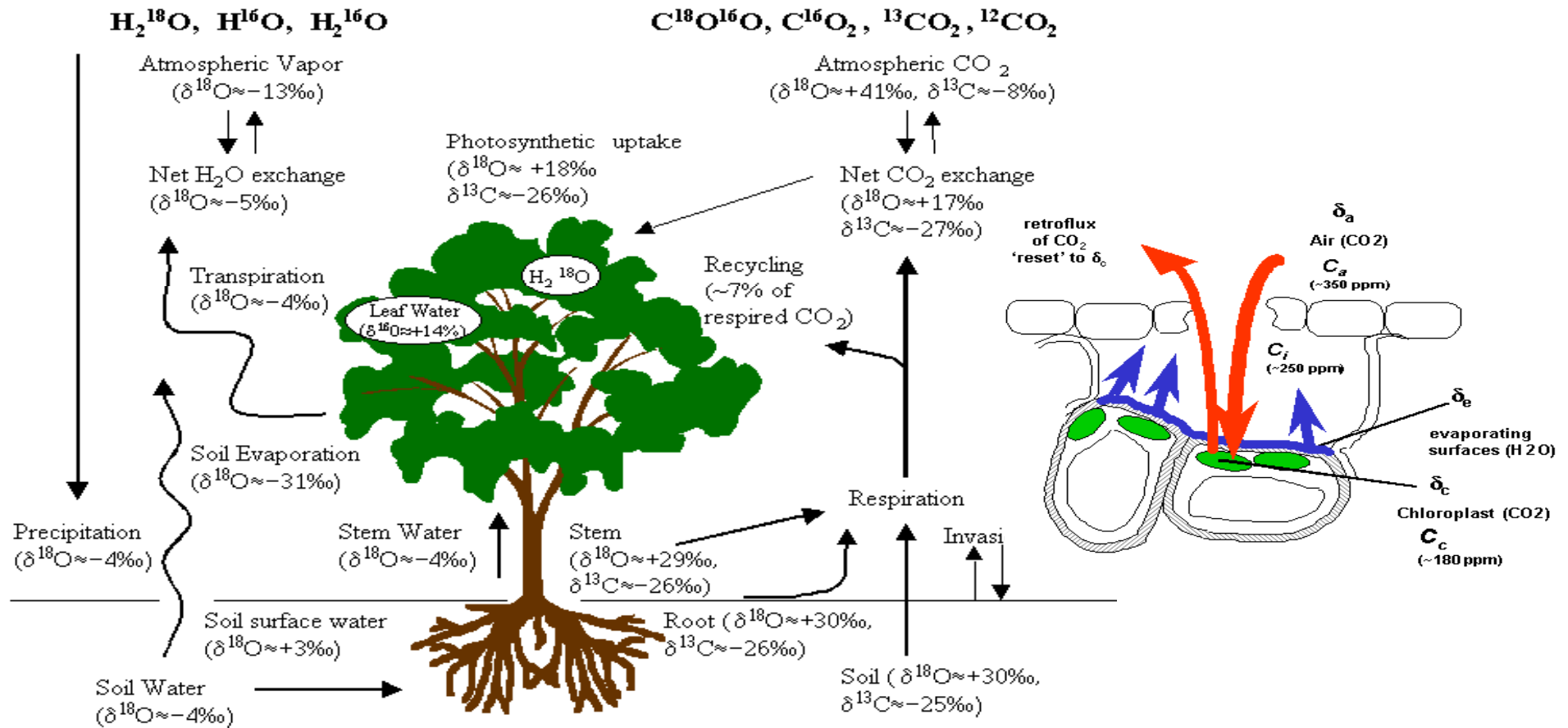
同位素判别 (isotopic discrimination Δ)

$$\Delta = (\delta_R - \delta_P) / (1 + \delta_P)$$

Characteristics of isotopes 同位素特性

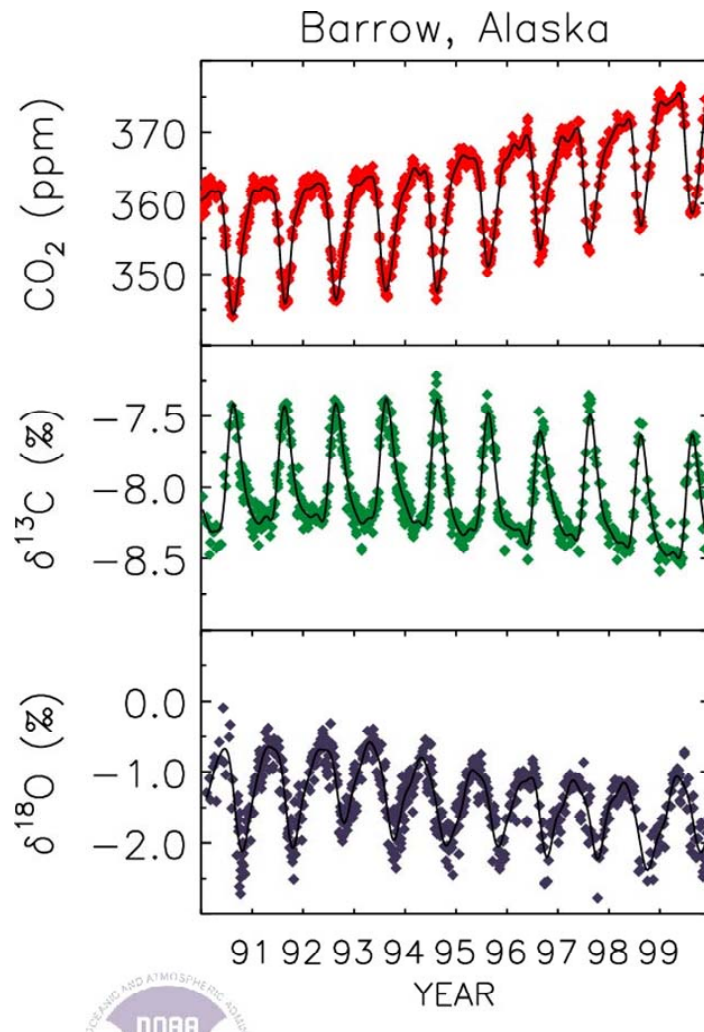
- 物理性质
- 同位素分馏作用
 - 平衡分馏效应 **Equilibrium isotope fractionation**
 - 动力学分馏效应 **kinetic isotope fractionation**
 - 扩散效应 **diffusive effects**
- 影响同位素分馏的主要因素
 - 化学组成
 - 晶体结构
 - 特殊效应

生态系统尺度

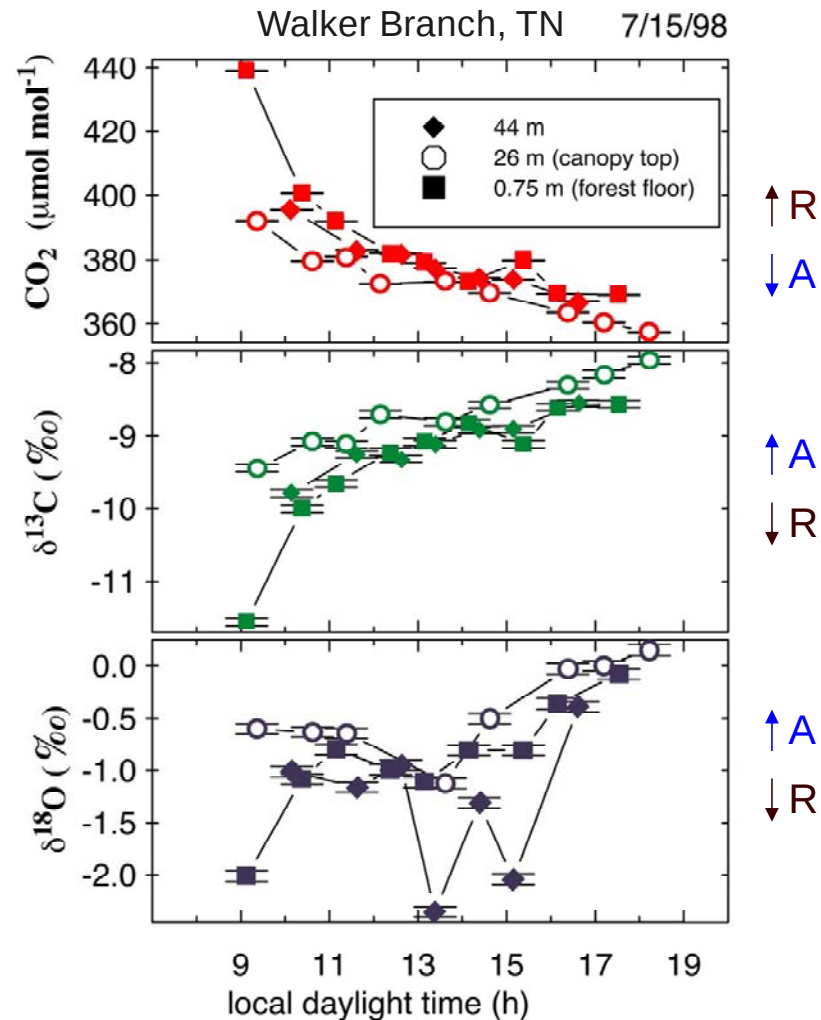


Major components for the use of stable isotopes in ecosystem gas exchange: The values are rough approximations and can greatly vary with geographical location and environmental conditions (given for demonstration purposes only and are based mostly on data from Israel). The main advantages of the isotopic approach lie in the unique labeling of flux components: Photosynthesis (depleted uptake) tend to enrich the atmosphere, while respiration (depleted release) tend to deplete the atmosphere in ^{18}O and ^{13}C ; leaf transpiration and soil evaporation are isotopically very different fluxes; root and soil respiration can have distinct ^{13}C labeling. (Values are on the SMOW and PDB scales for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values respectively).

区域/全球尺度



生态系统尺度

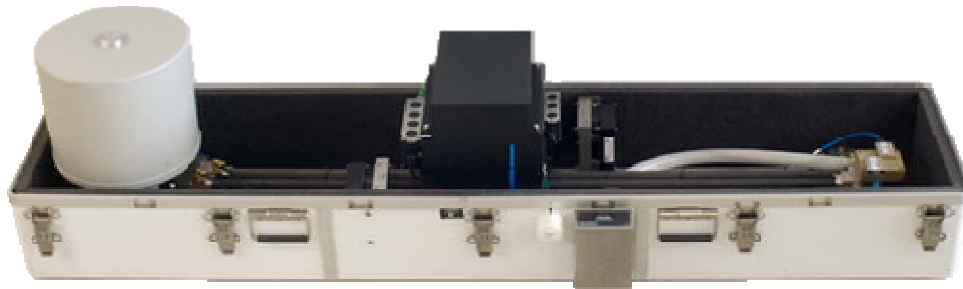


Isotope ratio mass spectrometry (IRMS), an accurate but expensive and high-maintenance analytical method;
Alternative method of IRIS, continuously

[2] **State of the art of IRIS**, and necessity of frequent calibration: stability and concentration dependence



Model TGA100/100A/200, Campbell Scientific Inc.



PICARRO

Models G1101i/2101i



Aerodyne Research



Model DLT-100



Because of instrumental drift and sensibility to changing environmental parameters, frequent calibration is necessary to ensure accurate measurements.

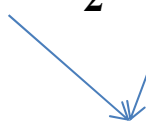
[3] State of the art of calibration methods

同位素组成 δ (isotopic composition)

$$\delta_{\text{sample}} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 10^3$$

 Methods 3 (delta gain and offset) and 4 (delta offset)

$$R = {}^{13}\text{CO}_2 / {}^{12}\text{CO}_2$$

 Methods 1 (mixing ratio gain and offset)

Methods 2, isotopic mixing ratio gain and offset

[4] Objectives of our study

Inter-comparison of different calibration methods for Los Gaots and Picarro measurement

2. Material and Methods

2.1. Analyzers, sampling and calibration systems

In brief, the analyzer was configured with **two three-way solenoid**, with three air sample or calibration gas intakes.



Model DLT-100



PICARRO

Models G1101i



2.2. Calibration procedure

Method 1: A two-point mixing ratio gain and offset calibration procedure (by Bowling et al.)

$$x_{a,t}^{12} = \frac{x_{2,t}^{12} - x_{1,t}^{12}}{x_{2,m}^{12} - x_{1,m}^{12}} (x_{a,m}^{12} - x_{1,t}^{12}) + x_{1,t}^{12}$$

$$x_{a,t}^{13} = \frac{x_{2,t}^{13} - x_{1,t}^{13}}{x_{2,m}^{13} - x_{1,m}^{13}} (x_{a,m}^{13} - x_{1,t}^{13}) + x_{1,t}^{13}$$

$$[\text{CO}_2] = [^{12}\text{CO}_2] + [^{13}\text{CO}_2] + f[\text{CO}_2]$$

$$R_a = [^{13}\text{C}]/[^{12}\text{C}] = [^{13}\text{CO}_2]/[^{12}\text{CO}_2] = R_{\text{VPDB}}(1 + \delta_a/1000)$$

$$[^{12}\text{CO}_2] = [\text{CO}_2](1 - f)/(1 + R_{\text{VPDB}}(1 + \delta_a/1000))$$

$$[^{13}\text{CO}_2] = [\text{CO}_2](1 - f) - [^{12}\text{CO}_2]$$

Method 2: A two-point isotopic mole mixing ratio calibration procedure (by Lee et al.)

$$\delta_{a,1} = (R_1 \frac{x_a^{13}}{x_1^{13}} \frac{x_1^{12}}{x_a^{12}} \frac{1}{R_{\text{VPDB}}} - 1) \times 1000$$

$$\delta_{a,2} = (R_2 \frac{x_a^{13}}{x_2^{13}} \frac{x_2^{12}}{x_a^{12}} \frac{1}{R_{\text{VPDB}}} - 1) \times 1000$$

$$\delta_a = \frac{(\delta_{a,2} - \delta_{a,1})}{(x_2^{12} - x_1^{12})} (x_a^{12} - x_1^{12}) + \delta_{a,1}$$

Method 3: A delta gain and offset calibration procedure

$$\delta_i^{13} \text{C}_{\text{VPDB}} = \delta_i^{13} \text{C}_{\text{raw}} \cdot m + b$$

Method 4: A delta offset calibration procedure

$$\delta_a = \delta_{a,m} + (\delta_{r,t} - \delta_{r,m})$$

2.3.3 Calibration crosschecks and atmospheric measurement

1. Precision and stability

Compressed air tank: -9.8‰; 420ppm, 24hr

2. Calibration crosschecks

Compressed air tank A: **-8.909‰; 361.25ppm**

Compressed air tank B: **-8.652‰; 398.76ppm**

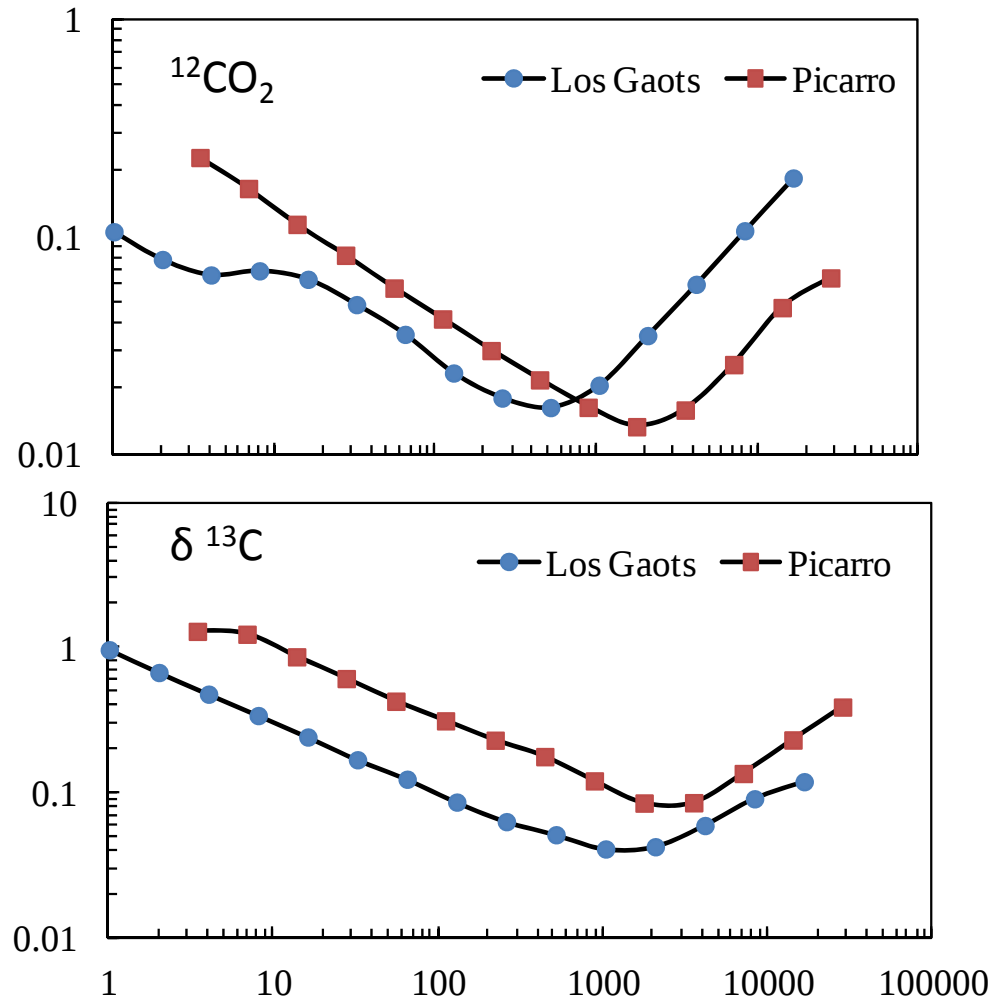
Compressed air tank C: **-10.134‰; 436.41ppm**

3. Atmospheric measurement, and keeling plot

Day of year: 103~109

3. Results and Discussions

3.1. Allan variance



Tank: -9.8‰, 420ppm—24hr

Allan deviation (square root of the Allan variance) expresses the measurement precision as a function of the averaging time.

Figure 1 Allan deviation as a function of averaging time, for both $^{12}\text{CO}_2$ concentration and $\delta^{13}\text{C}$

3.2. Comparison among different calibration methods

Table 1 Crosschecks of different calibration methods

	Concentration	Delta	Measured values	Method 1	Method 2	Method 3	Method 4
PIC	361.25	-8.909	-10.69 ± 0.54	-0.03 ± 0.65	0.02 ± 0.59	-0.25 ± 0.34	0.42 ± 0.39
	398.76	-8.652	-10.66 ± 0.56	0.01 ± 0.29	-0.01 ± 0.29	0.18 ± 0.32	0.20 ± 0.33
	436.41	-10.134	-12.34 ± 0.53	-0.02 ± 0.53	0.02 ± 0.59	-	-
LG R	361.25	-8.909	-13.35 ± 1.18	-0.05 ± 0.26	0.11 ± 0.23	-0.60 ± 0.10	1.37 ± 0.11
	398.76	-8.652	-13.84 ± 1.11	0.02 ± 0.11	-0.06 ± 0.11	0.49 ± 0.06	0.62 ± 0.12
	436.41	-10.134	-15.94 ± 1.19	-0.03 ± 0.21	0.11 ± 0.23	-	-

Concentration error sensitivity of method 1 (neglected, only in the text)

	Concentra tion	Delta	Bowling- error- +1%(436.41)	Bowling-error- -1%(436.41)	Bowling- error- +1%(361.25)	Bowling- error- +1%(361.25)
PIC	361.25	-8.909	-0.26 ± 0.70	0.20 ± 0.57	-	-
	398.76	-8.652	0.06 ± 0.31	-0.04 ± 0.28	-0.04 ± 0.28	0.06 ± 0.31
	436.41	-10.134	-	-	0.14 ± 0.48	-0.17 ± 0.58
LGR	361.25	-8.909	-0.28 ± 0.29	0.18 ± 0.22	-	-
	398.76	-8.652	0.07 ± 0.12	-0.03 ± 0.11	-0.03 ± 0.11	0.07 ± 0.12
	436.41	-10.134	-	-	0.13 ± 0.19	-0.18 ± 0.22

3.3 . Atmospheric measurement

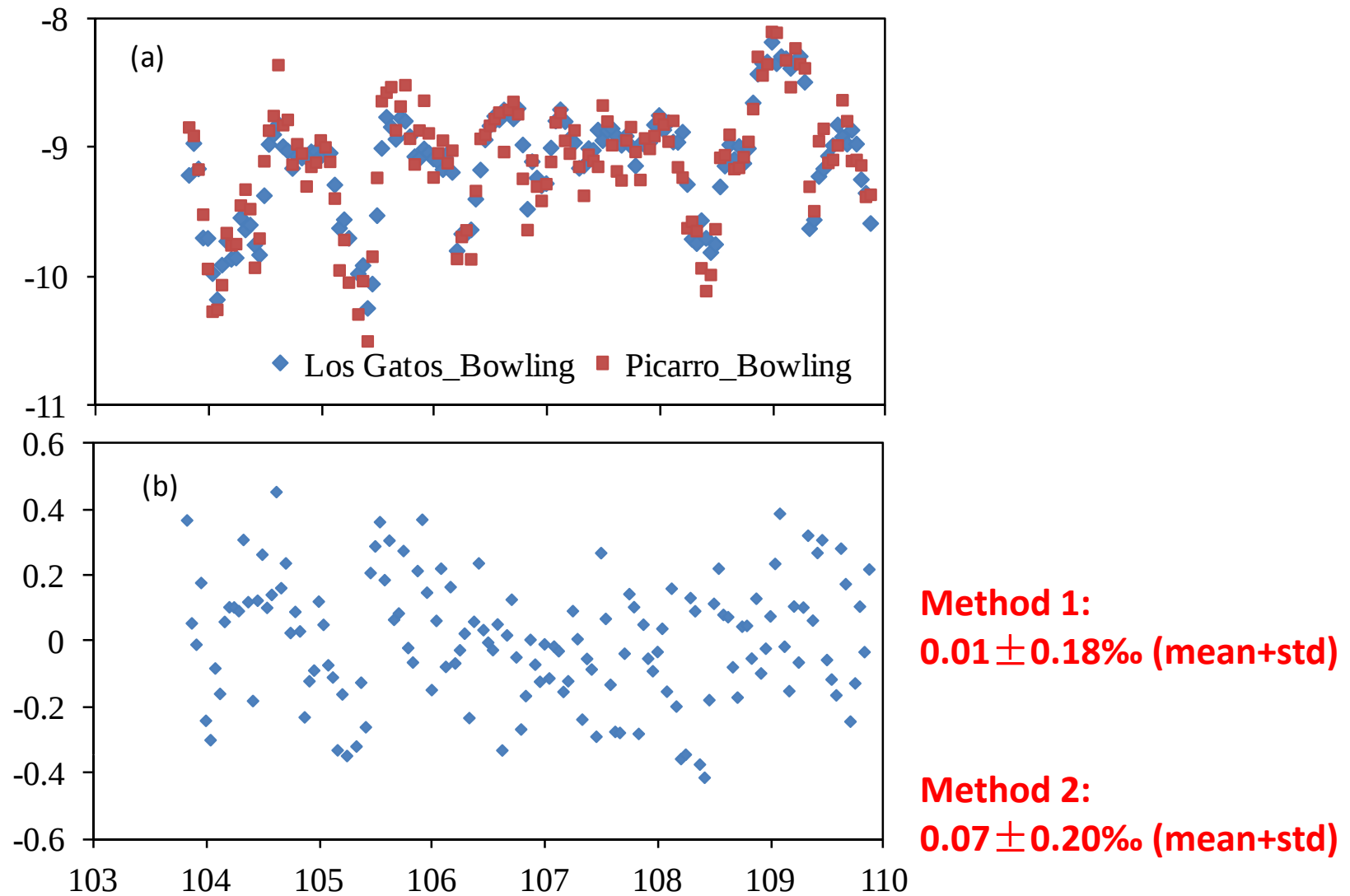
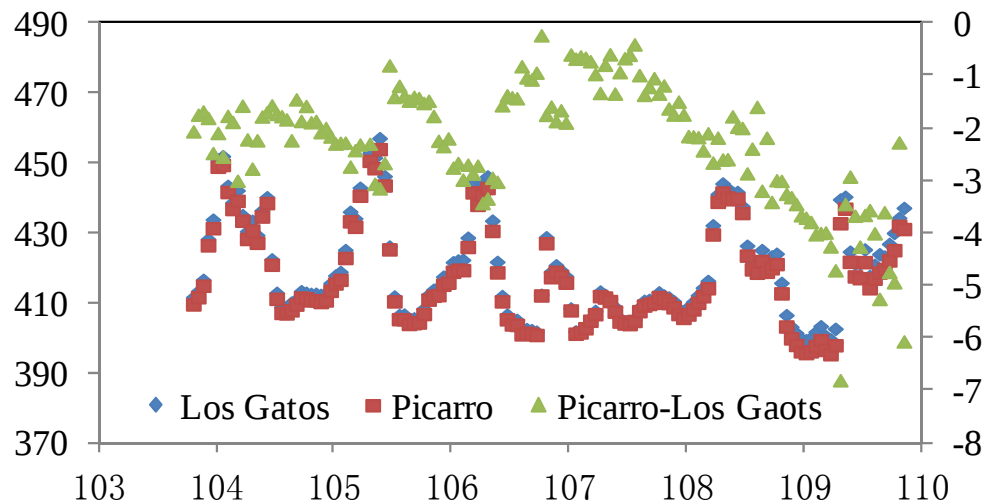


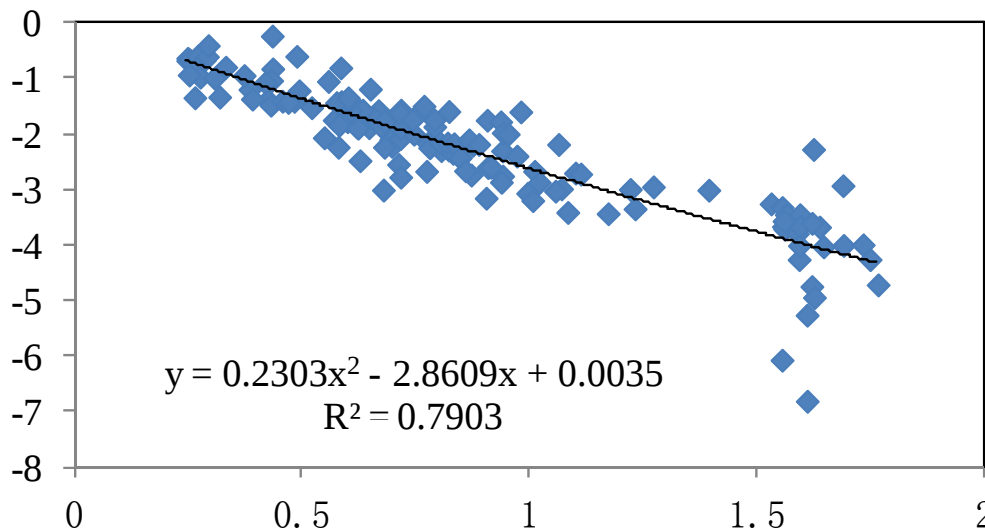
Figure 2 Daily variation of (a) $\delta^{13}\text{C}$ and by **method 1** and (b) residual error between Los Gatos and Picarro measurement



The diluted and dry-gas mole fractions are related by the following expression:

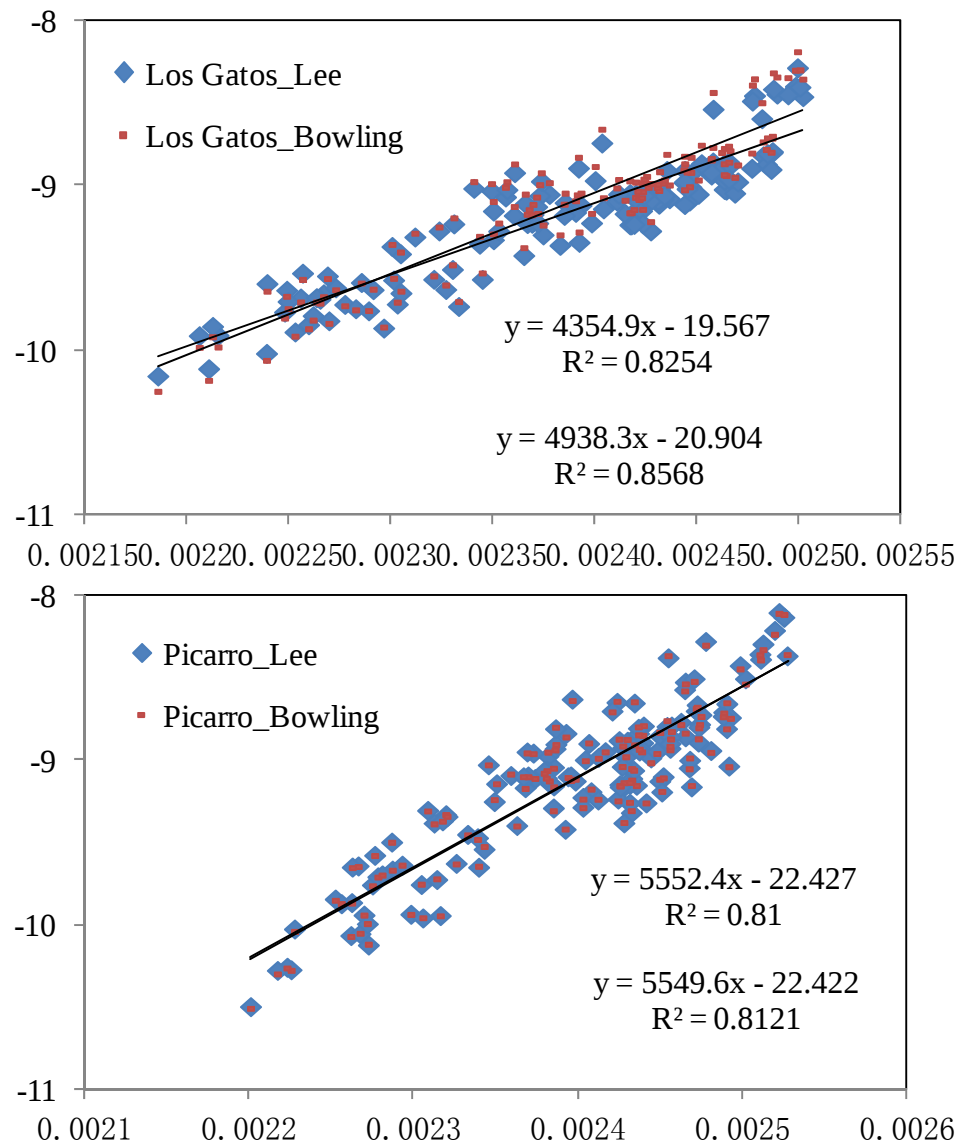
$$\frac{C_{\text{dilution}}}{C_{\text{dry}}} = 1 - 0.01H_{\text{act}}$$

The presence of water vapour in the sample generates an underestimation of the CO₂ and CH₄ concentrations due to **dilution** and **spectral line broadening** effects.



-2.2 ± 1.1ppm (mean+std)

Figure 3 (a) Daily variation of CO₂ concentration for Los Gatos and Picarro measurement and (b) Dependence of CO₂ difference between Los Gatos and Picarro on the H₂O concentration



Geometric Mean Regression
(Reduced Major Axis Regression),
95% confident level)

Figure 4 keeling plot of $\delta^{13}\text{C}$ by method 1 (Bowling) and 2 (Lee, neglected) vs $1/\text{co}_2$ for (a) Los Gaots and (b) Picarro measurement

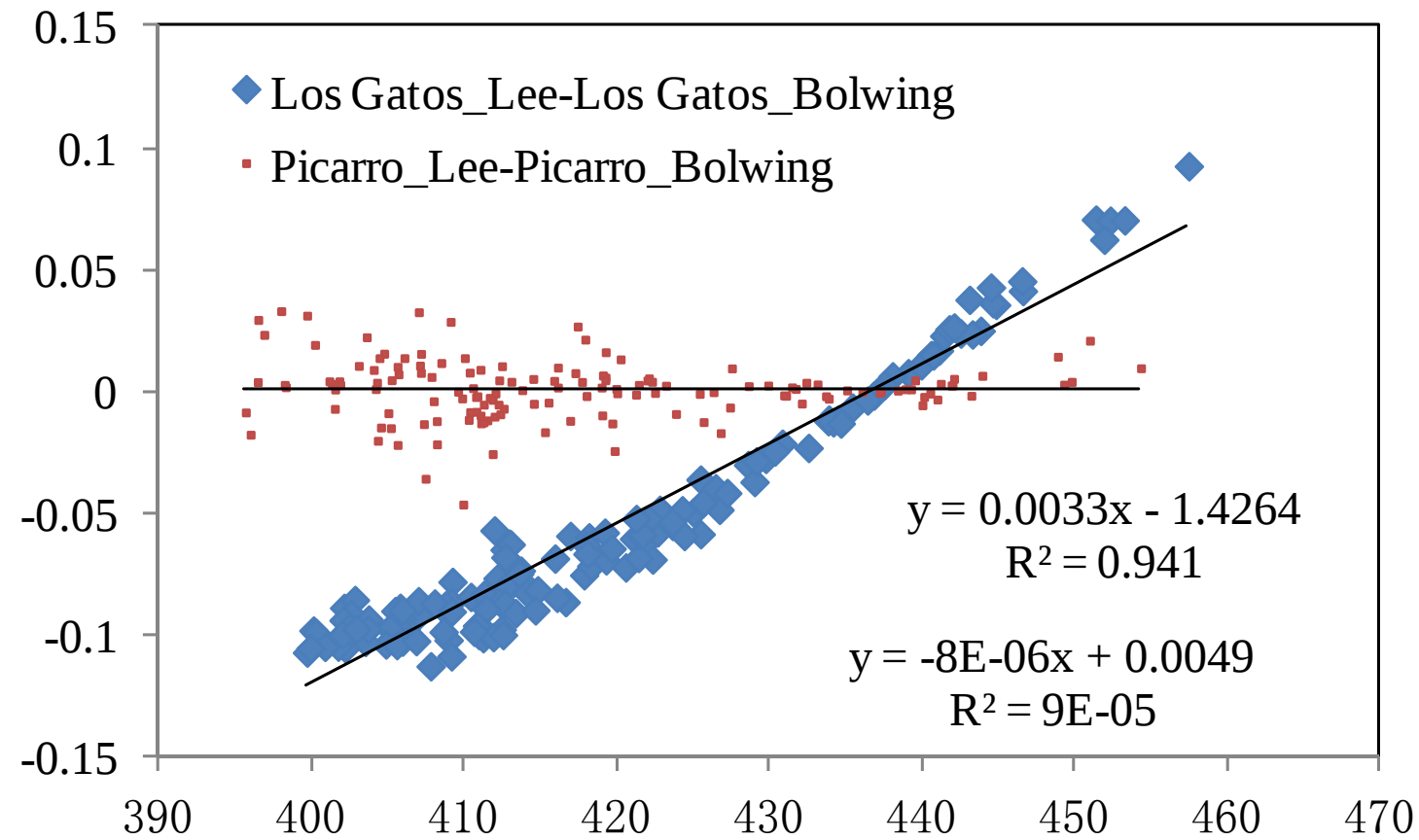
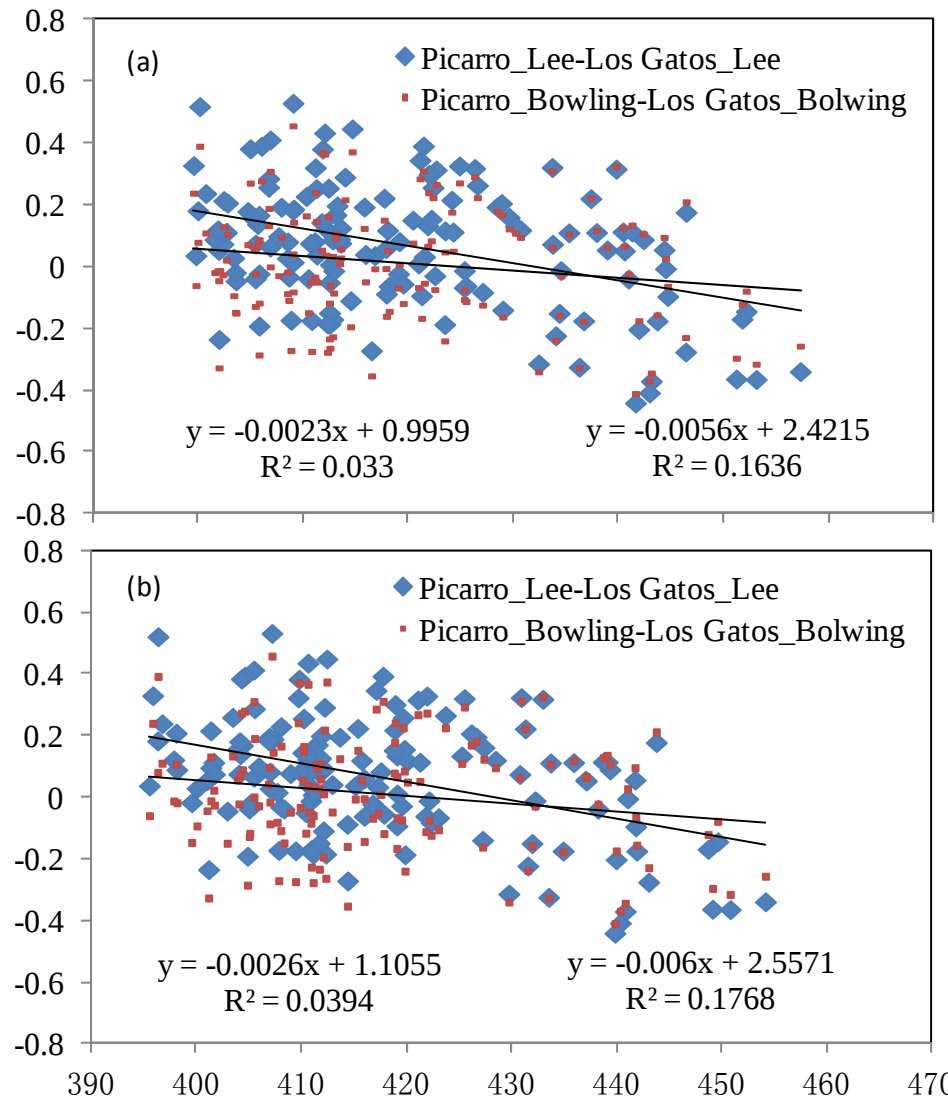


Figure 5 Dependence of delta difference between **method 1 (Bowling)** and 2 (Lee) on the co2 concentration for Los gatos and picarro measurement



Concentration dependence

Figure 6. Dependence of delta difference between Los gatos and picarro measurement on the(a) Los Gatos co2 concentration and (b) Picarro co2 concentration for **method 1 (Bowling)** and 2 (Lee, neglected)

4. Conclusion

- Method 1 and 2 were appropriate calibration methods
- Concentration dependence affect the intercept of keeling plot significantly
- Moisture correction should be taken care on the measurement of concentration and isotopic ratio of CO_2