Electronic Supplementary Material (ESI) for Analytical Methods.
This journal is © The Royal Society of Chemistry 2014

## Supporting material:

### 1. Methods

The content of organic carbon in geological samples was determined using a continuous-flow isotope ratio mass spectrometer (CF-IRMS). The CF-IRMS system consists of an EA (Flash 1112 series) coupled to a Finnigan MAT 253 mass spectrometer. The combustion temperature was set at 960°C, and the temperature of reduction tube was set at 680°C. Standard samples with known carbon contents (glycine: $C_{wt}$%= 32%) were used to calibrate the measurement and to monitor the working conditions.

The carbonate percentage of geological samples was measured using GasBench II coupled to a Finnigan MAT 253 isotope ratio mass spectrometer. The geological samples were firstly weighed, carbonate contained in those samples then reacted with 103% phosphoric acid at 70°C to generate $CO_2$ and the resulted $CO_2$ was finally introduced to isotope ratio mass spectrometer for measurement. The area of first peak of sample $CO_2$ (m/z=44) was compared with that of pure carbonate standard to calculate the percentage of carbonate in geological samples.

### 2. Figures

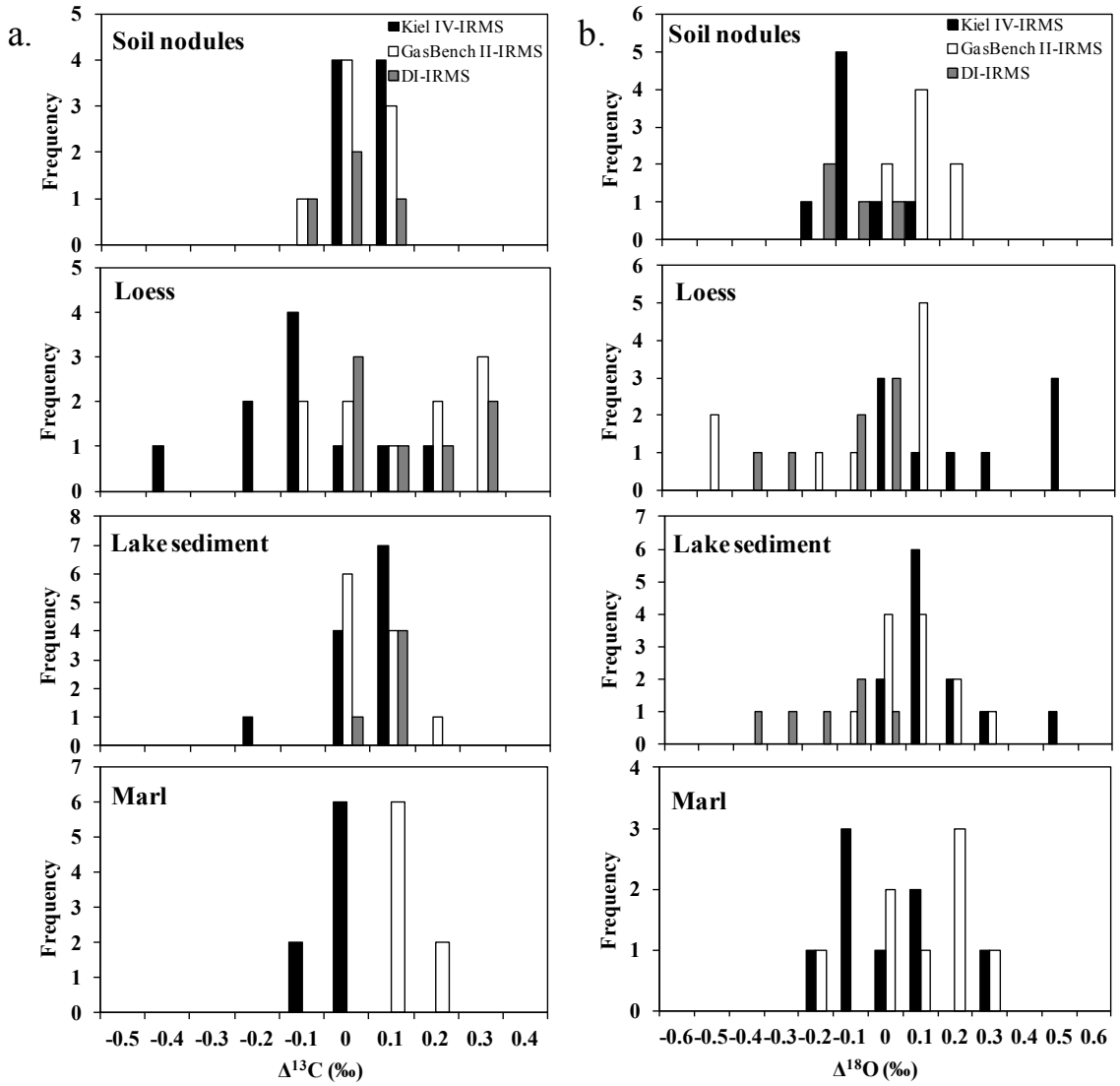


Fig. S1 A statistical diagram showing (a) differences in $\delta^{13}C$ values ($\Delta^{13}C$) and (b) differences in $\delta^{18}O$ values ($\Delta^{18}O$) measured using Kiel IV, GasBench II and dual inlet IRMS.

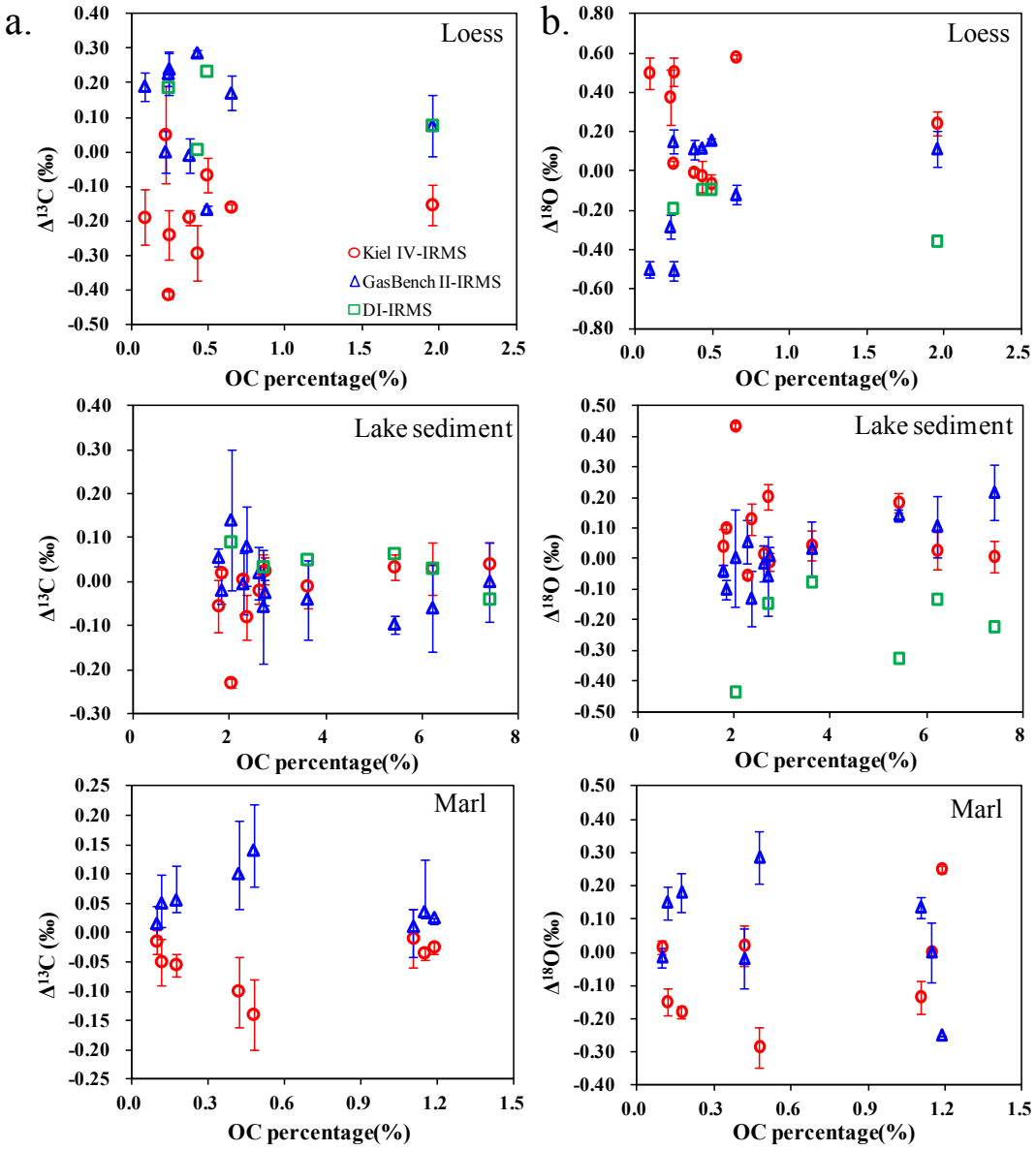


Fig. S2 Changes in $\Delta^{13}C$ and $\Delta^{18}O$ values of loess, lake sediment and marl along with organic carbon (OC) content.

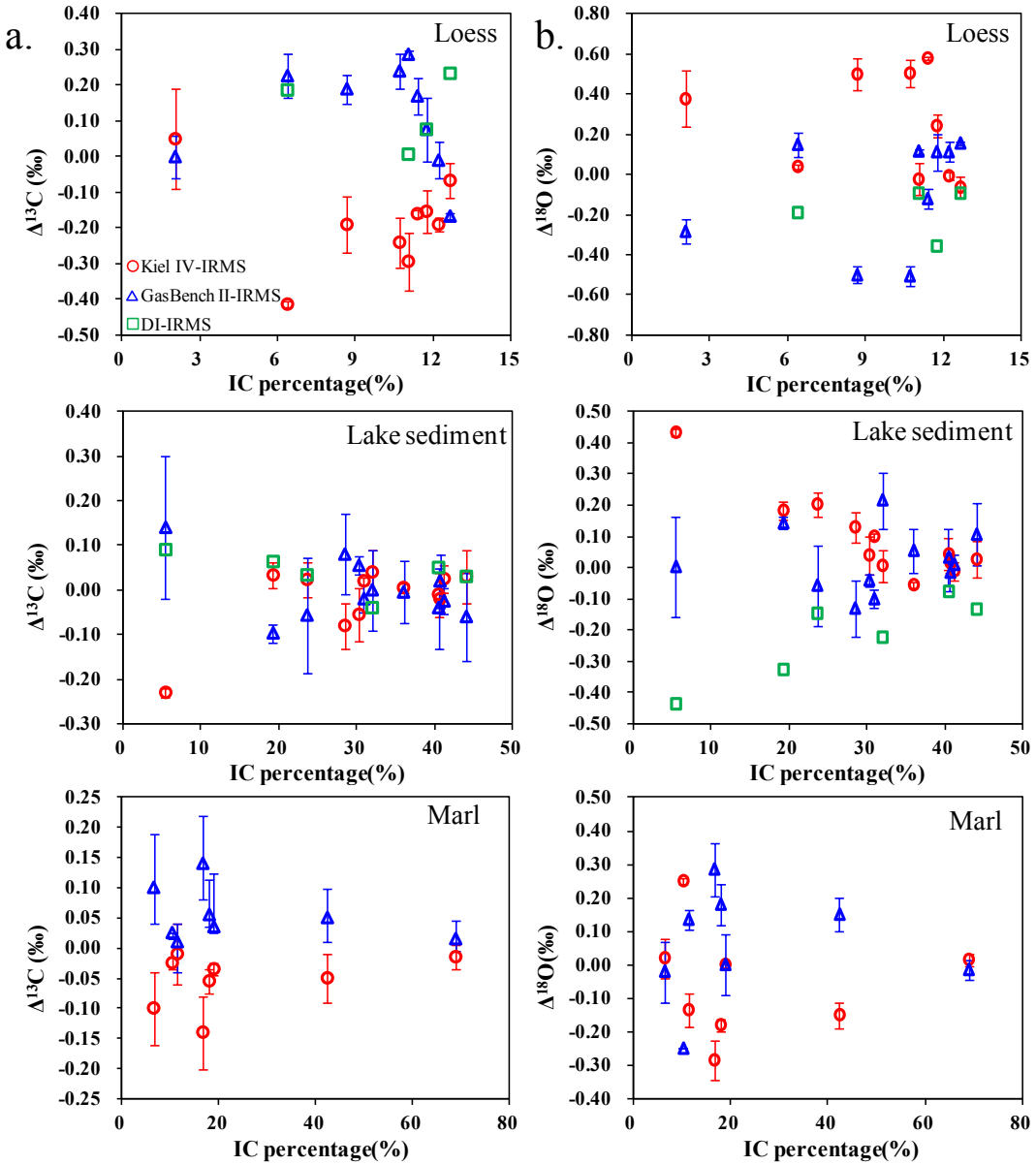


Fig. S3 Changes in $\Delta^{13}C$ and $\Delta^{18}O$ values of loess, lake sediment and marl along with carbonate (IC) percentage.

**3. Table**

Table S1 Contents of carbonate and organic carbon contained in carbonate nodules, loess, lake sediments and marl.

| Type | Sample No. | Carbonate percentage (%) | Organic carbon content (%) |
|---|---|---|---|
| Carbonate nodules | HD02-1 | 73.59 | - |
| | HD02-2 | 74.57 | - |
| | HD02-3 | 86.43 | - |
| | HDPE-205 | 28.46 | - |
| Loess | LT-L1 | 10.70 | 0.25 |
| | LT-L3 | 8.67 | 0.09 |
| | LP-3 | 11.73 | 1.95 |

| | | | |
|---|---|---|---|
| | LP-5 | 12.64 | 0.49 |
| | LP-7 | 11.03 | 0.43 |
| | LP-13 | 12.20 | 0.38 |
| | LP-17 | 2.06 | 0.22 |
| | LYX-S201 | 11.38 | 0.65 |
| | TGL | 6.38 | 0.24 |
| Lake sediment | DH-281 | 28.44 | 2.35 |
| | DH-491 | 40.65 | 2.61 |
| | DH-495 | 41.18 | 2.73 |
| | DH-537 | 35.97 | 2.27 |
| | DH-539 | 30.25 | 1.77 |
| | DH-541 | 30.90 | 1.83 |
| | XY3-1-06 | 19.25 | 5.42 |
| | XY3-1-130 | 5.46 | 2.02 |
| | XY3-2-40 | 23.59 | 2.70 |
| | XY3-2-150 | 40.46 | 3.61 |
| | XY3-3-15 | 44.03 | 6.21 |
| | XY3-3-91 | 31.96 | 7.40 |
| Marl | B32-3 | 6.43 | 0.42 |
| | B34-17 | 17.93 | 0.17 |
| | B34-18 | 11.33 | 1.10 |
| | B34-21 | 10.27 | 1.19 |
| | B34-27 | 68.84 | 0.10 |
| | B34-36 | 18.88 | 1.15 |
| | B34-37 | 42.33 | 0.12 |
| | B34-38 | 16.61 | 0.48 |

Table S2 $\delta^{13}C$ and $\delta^{18}O$ values of geological samples measured using Kiel IV-IRMS, GasBench II-IRMS and DI-IRMS.

| Type | Sample No. | $\delta^{13}C$ | | | $\delta^{18}O$ | | |
|---|---|---|---|---|---|---|---|
| | | Kiel IV | GasBench II | Duel Inlet | Kiel IV | GasBench II | Duel Inlet |
| Carbonate nodules | YAL-S0-C | -5.72 | -5.72 | -5.70 | -9.48 | -9.16 | -9.48 |
| | YAL-S1-B | -4.20 | -4.27 | -4.01 | -8.61 | -8.58 | -8.96 |
| | YAL-S2-2B | -4.97 | -4.98 | -5.06 | -8.82 | -8.69 | -9.15 |
| | TJK-S15 | -8.14 | -8.17 | -8.16 | -10.35 | -10.08 | -10.33 |
| | HD02-1 | -8.63±0.09 | -8.59±0.07 | - | -7.10±0.02 | -6.63±0.10 | - |
| | HD02-2 | -6.62±0.03 | -6.70±0.07 | - | -7.15±0.05 | -6.94±0.14 | - |
| | HD02-3 | -8.62±0.15 | -8.81±0.08 | - | -7.00±0.01 | -6.84±0.08 | - |
| | HDPE-205 | -8.03±0.06 | -7.93±0.09 | - | -7.02±0.08 | -7.00±0.04 | - |
| Loess | LT-L1 | -5.98±0.07 | -5.50±0.05 | - | -7.97±0.11 | -8.98±0.09 | - |
| | LT-L3 | -4.98±0.08 | -4.60±0.04 | - | -8.36±0.04 | -9.36±0.09 | - |
| | LP-3 | -5.41±0.06 | -5.18±0.09 | -5.18 | -8.54±0.12 | -8.67±0.03 | -9.14 |
| | LP-5 | -2.79±0.05 | -2.89±0.01 | -2.49 | -8.51±0.02 | -8.29±0.13 | -8.54 |
| | LP-7 | -4.96±0.08 | -4.38±0.01 | -4.66 | -8.80±0.15 | -8.66±0.06 | -8.87 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | LP-13 | -3.61±0.02 | -3.43±0.05 | -3.22 | -7.96±0.13 | -7.84±0.04 | -8.06 |
| | LP-17 | -2.74±0.14 | -2.79±0.06 | -2.84 | -8.42±0.10 | -9.08±0.17 | -8.89 |
| | LYX-S201 | -3.80±0.01 | -3.47±0.05 | -3.65 | -6.90±0.10 | -7.60±0.05 | -7.94 |
| | TGL | -2.27±0.01 | -1.63±0.06 | -1.67 | -9.48±0.11 | -9.37±0.31 | -9.71 |
| Lake sediment | DH-281 | -2.47±0.05 | -2.31±0.09 | - | -1.90±0.09 | -2.16±0.14 | - |
| | DH-491 | 1.16±0.03 | 1.20±0.06 | - | -5.88±0.03 | -5.91±0.08 | - |
| | DH-495 | 0.53±0.03 | 0.48±0.03 | - | -7.06±0.11 | -7.04±0.05 | - |
| | DH-537 | 0.07±0.01 | 0.06±0.07 | - | -4.82±0.04 | -4.71±0.04 | - |
| | DH-539 | -0.99±0.06 | -0.88±0.02 | - | -4.61±0.02 | -4.69±0.09 | - |
| | DH-541 | -1.42±0.01 | -1.46±0.03 | - | -4.27±0.01 | -4.47±0.02 | - |
| | XY3-1-06 | 0.94±0.03 | 0.81±0.02 | 0.97 | -5.72±0.07 | -5.76±0.38 | -6.23 |
| | XY3-1-130 | -0.31±0.01 | 0.06±0.16 | 0.01 | -6.33±0.12 | -6.76±0.23 | -7.20 |
| | XY3-2-40 | -0.33±0.04 | -0.41±0.13 | -0.32 | -6.62±0.06 | -6.88±0.23 | -6.97 |
| | XY3-2-150 | -1.31±0.05 | -1.34±0.09 | -1.25 | -7.66±0.14 | -7.67±0.20 | -7.78 |
| | XY3-3-15 | 0.52±0.06 | 0.43±0.10 | 0.52 | -8.14±0.11 | -8.06±0.14 | -8.30 |
| | XY3-3-91 | 0.78±0.05 | 0.74±0.09 | 0.70 | -10.65±0.14 | -10.44±0.15 | -10.88 |
| Marl | B32-3 | -0.38±0.06 | -0.18±0.09 | - | -8.53±0.02 | -8.57±0.02 | - |
| | B34-17 | -0.64±0.02 | -0.53±0.06 | - | -6.67±0.09 | -6.31±0.11 | - |
| | B34-18 | -0.63±0.05 | -0.61±0.03 | - | -7.87±0.09 | -7.60±0.07 | - |
| | B34-21 | -0.46±0.01 | -0.41±0.00 | - | -7.21±0.06 | -7.71±0.09 | - |
| | B34-27 | 0.73±0.02 | 0.76±0.03 | - | -6.23±0.10 | -6.26±0.05 | - |
| | B34-36 | 0.06±0.01 | 0.13±0.09 | - | -6.72±0.03 | -6.72±0.11 | - |
| | B34-37 | 0.51±0.04 | 0.61±0.05 | - | -6.23±0.01 | -5.93±0.05 | - |
| | B34-38 | 0.74±0.06 | 1.02±0.08 | - | -6.65±0.07 | -6.08±0.13 | - |