

Table S1a Information on IsoJarTM samples of Funaki et al. (2012)

| Sample ID | Sampling date* (dd/mm/yyyy) | Analysis date* (dd/mm/yyyy) | Sampling depth of cores (ground level -m) | $\delta^{13}\text{C}_{\text{CH}_4}$ (‰ VPDB) | $\delta^{13}\text{C}_{\text{CO}_2}$ (‰ VPDB) |
|-----------|--------------------------------|--------------------------------|--|---|---|
| PB1-1 | 17/12/2007 | 12/02/2008 | 262.9 | -52.8 | +4.7 |
| PB1-2 | 18/12/2007 | 12/02/2008 | 274.4 | -48.8 | -2.6 |
| PB1-3 | 18/12/2007 | 12/02/2008 | 280.4 | -41.1 | -4.6 |
| PB1-4 | 18/12/2007 | 12/02/2008 | 288.0 | -53.3 | +4.2 |
| PB1-5 | 18/12/2007 | 12/02/2008 | 289.5 | -51.1 | +2.1 |
| PB1-6 | 19/12/2007 | 12/02/2008 | 299.2 | -53.6 | +3.7 |
| PB1-7 | 20/12/2007 | 12/02/2008 | 307.7 | -53.9 | +5.6 |
| PB1-8 | 21/12/2007 | 13/02/2008 | 316.9 | -50.6 | +4.1 |
| PB1-9 | 21/12/2007 | 13/02/2008 | 325.5 | -54.2 | +5.0 |
| PB1-10 | 22/12/2007 | 13/02/2008 | 336.1 | -52.4 | +9.3 |
| PB1-11 | 22/12/2007 | 13/02/2008 | 343.0 | -53.4 | +9.1 |
| PB1-12 | 23/12/2007 | 13/02/2008 | 355.0 | -49.1 | +12.2 |
| | | 14/02/2008 | | | |
| PB1-13 | 18/01/2008 | 14/02/2008 | 367.0 | -55.5 | +6.8 |
| PB1-14 | 19/01/2008 | 14/02/2008 | 375.7 | -55.8 | +6.2 |
| PB1-15 | 20/01/2008 | 14/02/2008 | 385.0 | -54.7 | +8.7 |
| PB1-16 | 20/01/2008 | 14/02/2008 | 397.3 | -54.8 | +9.8 |
| PB1-17 | 21/01/2008 | 15/02/2008 | 405.7 | -51.8 | +3.9 |
| PB1-18 | 22/01/2008 | 15/02/2008 | 416.0 | -47.7 | -0.2 |
| PB1-19 | 23/01/2008 | 15/02/2008 | 425.4 | -56.1 | +3.6 |
| PB1-20 | 24/01/2008 | 15/02/2008 | 435.0 | -56.2 | +4.1 |
| PB1-21 | 24/01/2008 | 15/02/2008 | 445.0 | -53.8 | +3.0 |
| PB1-22 | 25/01/2008 | 18/02/2008 | 455.0 | -52.9 | +2.3 |
| PB1-23 | 26/01/2008 | 18/02/2008 | 465.0 | -53.6 | +3.5 |
| | | 21/02/2008 | | | |
| PB1-24 | 28/01/2008 | 18/02/2008 | 485.0 | -55.8 | +4.8 |
| | | 21/02/2008 | | | |
| PB1-25 | 30/01/2008 | 20/02/2008 | 504.0 | -51.9 | +0.7 |
| PB1-26 | 31/01/2008 | 20/02/2008 | 515.0 | -45.7 | +2.2 |
| PB1-27 | 31/01/2008 | 20/02/2008 | 520.0 | -49.5 | +0.9 |

*These information are unpublished data in Funaki et al. (2012).

Table S1b Information on IsoJarTM samples of Funaki et al. (2012)

| Sample ID | Sampling date* (dd/mm/yyyy) | Analysis date* (dd/mm/yyyy) | Sampling depth of cores (ground level -m) | $\delta^{13}\text{C}_{\text{CH}_4}$ (‰ VPDB) | $\delta^{13}\text{C}_{\text{CO}_2}$ (‰ VPDB) |
|-----------|--------------------------------|--------------------------------|--|---|---|
| SAB1-1 | 31/10/2008 | 04/02/2009 | 150.2 | -31.5 | -1.7 |
| SAB1-2 | 05/11/2008 | 04/02/2009 | 160.0 | | -5.4 |
| SAB1-3 | 05/11/2008 | 04/02/2009 | 170.0 | | -5.2 |
| SAB1-4 | 06/11/2008 | 04/02/2009 | 180.0 | -26.3 | -10.0 |
| SAB1-5 | 06/11/2008 | 06/02/2009 | 190.0 | -31.4 | -5.4 |
| SAB1-6 | 07/11/2008 | 06/02/2009 | 200.0 | -54.5 | +3.7 |
| SAB1-7 | 07/11/2008 | 06/02/2009 | 210.0 | -13.4 | -7.0 |
| SAB1-8 | 07/11/2008 | 06/02/2009 | 220.0 | -49.9 | -2.4 |
| SAB1-9 | 08/11/2008 | 06/02/2009 | 230.0 | -55.9 | -6.8 |
| SAB1-10 | 08/11/2008 | 10/02/2009 | 240.0 | -37.6 | -2.0 |
| SAB1-11 | 08/11/2008 | 10/02/2009 | 250.0 | -40.3 | -9.5 |
| SAB1-12 | 09/11/2008 | 10/02/2009 | 260.0 | -15.0 | -12.4 |
| SAB1-13 | 09/11/2008 | 10/02/2009 | 270.0 | -53.8 | +3.1 |
| SAB1-14 | 10/11/2008 | 10/02/2009 | 280.0 | -48.1 | -2.7 |
| SAB1-15 | 20/11/2008 | 10/02/2009 | 290.0 | -43.6 | -8.4 |
| SAB1-16 | 11/11/2008 | 12/02/2009 | 300.2 | -52.1 | -0.9 |
| SAB1-17 | 03/12/2008 | 12/02/2009 | 310.1 | -48.8 | -2.4 |
| SAB1-18 | 04/12/2008 | 12/02/2009 | 320.0 | -38.4 | -9.0 |
| SAB1-19 | 13/12/2008 | 12/02/2009 | 330.1 | -50.2 | -0.6 |
| | | 25/02/2009 | | | |
| SAB1-20 | 14/12/2008 | 12/02/2009 | 340.0 | -50.2 | +2.9 |
| SAB1-21 | 15/12/2008 | 19/02/2009 | 350.0 | -52.1 | +6.5 |
| SAB1-22 | 15/12/2008 | 19/02/2009 | 360.0 | -37.0 | -2.3 |
| SAB1-23 | 16/12/2008 | 19/02/2009 | 370.0 | -50.2 | +0.5 |
| SAB1-24 | 16/12/2008 | 19/02/2009 | 379.4 | -33.6 | -3.7 |
| SAB1-25 | 18/12/2008 | 19/02/2009 | 399.0 | -46.3 | +0.4 |
| SAB1-26 | 06/01/2009 | 20/02/2009 | 410.0 | -50.3 | +3.6 |
| SAB1-27 | 07/01/2009 | 20/02/2009 | 420.7 | -41.4 | -3.5 |
| SAB1-28 | 08/01/2009 | 20/02/2009 | 430.0 | -45.9 | -2.6 |
| SAB1-29 | 08/01/2009 | 20/02/2009 | 440.0 | -40.1 | +0.8 |
| SAB1-30 | 09/01/2009 | 24/02/2009 | 450.0 | -31.6 | -0.1 |
| SAB1-31 | 11/01/2009 | 24/02/2009 | 470.0 | -46.8 | +0.8 |
| SAB1-32 | 11/01/2009 | 24/02/2009 | 480.0 | | -4.0 |
| SAB1-33 | 12/01/2009 | 24/02/2009 | 490.0 | -20.5 | -2.0 |
| SAB1-34 | 13/01/2009 | 24/02/2009 | 500.0 | -23.0 | -4.7 |
| SAB1-35 | 13/01/2009 | 25/02/2009 | 510.0 | -48.0 | -6.4 |

*These information are unpublished data in Funaki et al. (2012).

Table S2 Information on IsoJar™ samples and analytical results of head-space gases

| Sample no. | Sampling date (dd/mm/yyyy) | Analysis date (dd/mm/yyyy) | Sampling depth of cores (ground level -m) | C ₂ H ₆ (ppm) | C ₃ H ₈ (ppm) | $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$ (‰ VPDB) |
|------------|-------------------------------|-------------------------------|--|--|--|---|
| IJ1 | 10/11/2016 | 16/1/2017 | 384.9–385.9 | 1 | nd* | 59.0 |
| IJ2 | 06/12/2016 | 16/1/2017 | 395.0–396.0 | 15 | nd* | 48.7 |
| IJ3 | 19/12/2016 | 08/03/2017 | 413.4–415.4 | 15 | nd* | 44.0 |
| IJ4 | 02/12/2016 | 19/12/2016 | 394.5–395.0 | 5 | nd* | 54.3 |
| IJ5 | 10/11/2016 | 17/01/2017 | 384.9–385.9 | 1 | nd* | 53.5 |
| IJ6 | 06/12/2016 | 17/01/2017 | 395.0–396.0 | 26 | nd* | 46.0 |
| IJ7 | 19/12/2016 | 08/03/2017 | 415.4–416.3 | 21 | nd* | 35.8 |
| IJ8 | 19/12/2016 | 08/03/2017 | 413.4–415.4 | 2 | nd* | 20.9 |
| IJ9 | 10/11/2016 | 29/11/2016 | 382.8–383.8 | 18 | 2 | 72.9 |
| IJ10 | 10/11/2016 | 16/01/2017 | 384.9–385.9 | 15 | nd* | 55.2 |
| IJ11 | 06/12/2016 | 16/01/2017 | 395.0–396.0 | 35 | nd* | 64.5 |
| IJ12 | 06/12/2016 | 08/03/2017 | 394.5–396.0 | 4 | nd* | 39.7 |
| IJ13 | 10/11/2016 | 29/11/2016 | 383.8–384.9 | 37 | 2 | 61.3 |
| IJ14 | 10/11/2016 | 17/01/2017 | 384.9–385.9 | 1 | nd* | -2.0 |
| IJ15 | 06/12/2016 | 17/01/2017 | 395.0–396.0 | 24 | nd* | 49.7 |
| IJ16 | 19/12/2016 | 08/03/2017 | 413.4–415.4 | 9 | nd* | 40.7 |
| IJ17 | 10/11/2016 | 29/11/2016 | 382.8–383.8 | 5 | 1 | 64.7 |
| IJ18 | 10/11/2016 | 16/01/2017 | 383.8–384.9 | 11 | nd* | 58.1 |
| IJ19 | 06/12/2016 | 16/01/2017 | 395.0–396.0 | 37 | 2 | 62.9 |
| IJ20 | 19/12/2016 | 08/03/2017 | 413.4–415.4 | 21 | nd* | 60.6 |
| IJ21 | 10/11/2016 | 29/11/2016 | 383.8–384.9 | 5 | nd* | 50.0 |
| IJ22 | 10/11/2016 | 17/01/2017 | 383.8–384.9 | 10 | nd* | 29.5 |
| IJ23 | 06/12/2016 | 17/01/2017 | 395.0–396.0 | 24 | nd* | 47.0 |
| IJ24 | 19/12/2016 | 08/03/2017 | 413.4–415.4 | 28 | nd* | 44.0 |
| IJ25 | 19/12/2016 | 08/03/2017 | 415.4–416.3 | 33 | nd* | 46.7 |
| IJ26 | 22/02/2017 | 27/02/2017 | 470.0–470.4 | 17 | nd* | 69.9 |
| IJ27 | 22/02/2017 | 27/02/2017 | 470.0–470.4 | 16 | nd* | 68.6 |
| IJ28 | 22/02/2017 | 27/02/2017 | 470.0–470.4 | 11 | nd* | 70.6 |

*nd = not detected.

Table S3 Information on IsoJarTM samples and analytical results of head-space gases for Section 3.1.2

| Sample no. | Sampling date (dd/mm/yyyy) | Analysis date (dd/mm/yyyy) | C ₂ H ₆ (ppm) | C ₃ H ₈ (ppm) | $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$ (‰ VPDB) |
|------------|-------------------------------|-------------------------------|--|--|---|
| IJ29 | 28/06/2017 | 25/07/2017 | 2 | 4 | 62.5 |
| IJ30 | 28/06/2017 | 25/07/2017 | 1 | 3 | 89.8 |
| IJ31 | 28/06/2017 | 25/07/2017 | 2 | 5 | 88.2 |
| IJ32 | 28/06/2017 | 25/07/2017 | 2 | 5 | 97.8 |
| IJ33 | 28/06/2017 | 25/07/2017 | 3 | 5 | 102.4 |
| IJ34 | 28/06/2017 | 26/07/2017 | 3 | 4 | 88.7 |
| IJ35 | 28/06/2017 | 26/07/2017 | 8 | 9 | 71.0 |
| IJ36 | 28/06/2017 | 26/07/2017 | 11 | 9 | 102.8 |
| IJ37 | 28/06/2017 | 26/07/2017 | 5 | 2 | 71.0 |
| IJ38 | 28/06/2017 | 26/07/2017 | 4 | 2 | 72.4 |
| IJ39 | 28/06/2017 | 27/07/2017 | 7 | 4 | 68.2 |
| IJ40 | 28/06/2017 | 27/07/2017 | 9 | 8 | 71.2 |
| IJ41 | 28/06/2017 | 27/07/2017 | 3 | 2 | 74.0 |
| IJ42 | 28/06/2017 | 27/07/2017 | 1 | 2 | 78.0 |
| IJ43 | 28/06/2017 | 27/07/2017 | 2 | 2 | 80.4 |
| IJ44 | 28/06/2017 | 27/07/2017 | 2 | 3 | 74.9 |
| IJ45 | 28/06/2017 | 28/07/2017 | 2 | 3 | 77.8 |
| IJ46 | 28/06/2017 | 28/07/2017 | 2 | 3 | 77.1 |
| IJ47 | 28/06/2017 | 28/07/2017 | 2 | 2 | 78.9 |
| IJ48 | 28/06/2017 | 28/07/2017 | 2 | 4 | 78.2 |

Table S4 Carbon isotope ratios in methane, and total inorganic carbon (TIC), methane, and TIC contents in EV samples

| Sample no. | Sampling date (dd/mm/yyyy) | Analysis date (dd/mm/yyyy) | Storage period (days) | Sampling depth of groundwater (ground level -m) | $\delta^{13}\text{C}_{\text{CH}_4}$ (‰ VPDB) | $\delta^{13}\text{C}_{\text{CO}_2}$ (‰ VPDB) | $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$ (‰ VPDB) | Concentration of dissolved CH_4 (mmol kg ⁻¹) | Concentration of total inorganic carbon (TIC) (mmol kg ⁻¹) |
|------------|-------------------------------|-------------------------------|--------------------------|---|---|---|---|---|--|
| EV1 | 26/10/2016 | 01/11/2016 | 6 | 248.5 | -56.7 | +17.1 | 73.8 | - | - |
| EV2 | 26/10/2016 | 20/12/2016 | 55 | 248.5 | -54.0 | +17.8 | 71.8 | 7.8 | - |
| EV3 | 26/10/2016 | 01/02/2017 | 98 | 248.5 | -53.7 | +17.3 | 71.0 | 8.5 | - |
| EV4 | 26/10/2016 | 01/11/2016 | 6 | 248.5 | -56.8 | +16.9 | 73.7 | 8.7 | 42 |
| EV5 | 26/10/2016 | 20/12/2016 | 55 | 248.5 | -54.5 | +16.2 | 70.6 | 6.7 | 37 |
| EV6 | 26/10/2016 | 01/02/2017 | 98 | 248.5 | -52.7 | +16.7 | 69.4 | 6.7 | 35 |