

## Supplementary data: CO<sub>2</sub> sequestration in a UK North Sea analogue for geological carbon storage

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### **Background Data used in Calculating Equilibrium Dolomite Line (Figs 2, 3, and 4)**

Current reservoir temperature is estimated to be 80 – 85 °C (Wilkinson et al., 2009)

Isotopic composition of the CO<sub>2</sub> gas in Fizzy: two gas samples gave similar results: δ<sup>13</sup>C CO<sub>2</sub> of 4.3 and 4.6 ‰ V-PDB (Wilkinson, 2009).

Porewater oxygen isotope ratio of the Rotliegend Sandstone in Fizzy is unknown; following Wilkinson et al. (2009) values from the Leman Field are utilised (δ<sup>18</sup>O = 0.3 to 0.4 ‰ V-SMOW; Warren and Smalley, 1992).

### **Oxygen Isotope Fractionation Factor**

Dolomite-water <sup>18/16</sup>O fractionation factor of Deines (1974):

$$1000 \ln \alpha_{dol-water} = 2.73 \cdot (10^6 \cdot T_{(K)}^{-2}) + 0.26 \quad (1)$$

### **Carbon Isotope Fractionation Factor**

No <sup>13/12</sup>C fractionation factor for the dolomite-water system could be found in the literature. The carbon isotope equilibrium fractionation for a dolomite/CO<sub>2</sub> system is calculated via known fractionation factors. Deines (2004) presents an equation that calculates the relationship for the fractionation between Mg-calcite and calcite that can be used to predict the dolomite-calcite fractionation for a Mg-mole fraction of 0.5. He determined the following relationship:

$$1000 \ln a_{Mg\_Cal-Cal} = \left[ \begin{array}{l} 0.013702 - 0.10957 \cdot \frac{10^3}{T_{(K)}} + 1.35940 \cdot \frac{10^6}{T_{(K)}^2} \\ - 0.329124 \cdot \frac{10^9}{T_{(K)}^3} + 0.0304160 \cdot \frac{10^{12}}{T_{(K)}^4} \end{array} \right] \cdot X^{1.5} \quad (2)$$

Where X is the mole fraction of Mg; for dolomite X = 0.5. Combining with the calcite/CO<sub>2</sub> fractionation factor of Deines et al. (1974; Eqn. 3)

$$1000 \ln a_{Cal-CO_2} = 1.194 \cdot (10^6 \cdot T_{(K)}^{-2}) - 3.63 \quad (3)$$

The carbon isotope fractionation can be calculated. Combining:

$$a_{Dol-Cal} = \frac{\delta(dolomite) + 1000}{\delta(calcite) + 1000} \quad (4) \quad \text{and} \quad a_{Cal-CO_2} = \frac{\delta(calcite) + 1000}{\delta(CO_2) + 1000} \quad (5)$$

with

$$\delta(sample) = \delta^{13}C = \left( \frac{\left( \frac{^{13}C}{^{12}C} \right)_{sample}}{\left( \frac{^{13}C}{^{12}C} \right)_{standard}} - 1 \right) \cdot 1000 \text{‰} \quad (6)$$

the dolomite in equilibrium with CO<sub>2</sub> can be calculated from:

$$\delta(dolomite) = [a_{Dol-Cal} \cdot a_{Cal-CO_2} \cdot (\delta(CO_2) + 1000)] - 1000 \quad (7)$$

**Table DR1. Carbon and Oxygen Stable Isotope Data, Selective Extraction Method**

Sample	Time (min)	Yield (%)	$\delta^{13}\text{C}$ ‰ V-PDB	$\delta^{18}\text{O}$ ‰ V-PDB
<b>Fizzy water leg</b>				
1A	45	0.9	-15.5	-13.9
1B	255	2.2	24.6	-9.4
1C	465	2.3	-0.72	-8.4
1D	1410	14.7	0.33	-7.8
1E	1830	7.3	0.05	-6.8
1F	2865	12.9	-0.39	-6.2
1G	3270	5.1	-1.1	-5.1
1 (final)	(-)	54.2	-3.8	-5.5
4A	60	0.3	failed	
4B	270	0.5	-5.0	-15.5
4C	510	0.6	-11.0	-14.0
4D	1510	3.1	-0.99	-7.4
4E	1910	2	-4.0	-10.9
4 (final)	(-)	93.5	-1.9	-4.0
5uw1	30		failed	
5uw2	210		-6.2	-14.4
5uw3	370		-8.9	-17.3
5uw4			failed	
5uw5	1315		-2.0	-10.8
5uw6	1740		-1.1	-12.0
5 (final)			-3.3	-4.9
<b>Fizzy gas leg</b>				
8A	50	0.5	39.9	-12.9
8B	280	1.3	-1.8	-9.4
8C	465	2	-1.2	-9.8
8D	1410	11	-0.34	-6.6
8E	1830	6.3	-0.37	-6.2
8F	2865	11	-0.11	-6.0
8G	3270	4.9	-0.62	-5.4
8 (final)	(-)	63	-2.8	-4.5
9A	65	1.8	-15.2	-22.1
9B	275	1.4	-8.8	-21.1
9C	515	1.8	-9.7	-18.7
9D	1515	3.2	-3.5	-13.3
9E	1915	3.2	-0.25	-10.3
9 (final)	(-)	88.6	-8.2	-11.3
10_1	30		-13.2	-12.1
10_1	210		failed	
10_1	410		failed	
10_1	1420		-1.7	-9.1
10_1	1875		-3.5	-9.7
10_1	2905		-1.8	-8.9
10_1	3320		failed	
10_1 (final)	(-)		-6.1	-8.9
10_2	30		-12.3	-19.2

10_2	210		-4.0	-11.6
<b>Sample</b>	<b>Time (min)</b>	<b>Yield (%)</b>	<b><math>\delta^{13}\text{C}</math> ‰ V-PDB</b>	<b><math>\delta^{18}\text{O}</math> ‰ V-PDB</b>
<b>Fizzy gas leg (continued)</b>				
10_2	410		-1.2	-13.1
10_2	1420		-0.2	-10.2
10_2	1865		-3.0	-11.1
10_2	2905		failed	
10_2	3305		-4.2	-11.3
10_2 (final)	(-)		-5.1	-7.1
<b>Rotliegend Sandstone below Orwell F ield</b>				
11A	30		-9.3	-14.5
11B	210		-4.7	-10.6
11C	370		-6.2	-12.0
11D	1315		-3.3	-8.3
11E	1735		-4.5	-8.3
11 (final)	(-)		-3.0	-4.5
14A	50	0.9	failed	
14B	270	1.4	-8.3	-17.0
14C	465	1.6		
14D	1410	3	-5.7	-12.9
14E	1830	1.6	-7.3	-14.8
14F	2860	2.8	-6.1	-13.4
14G	3270	2.3	-5.4	-12.3
14 (final)	(-)	86	-5.9	-8.7
13A	65	1.2	failed	
13B	275	1.2	failed	
13C	515	2.9	-20.1	-18.7
13D	1515	3.3	-8.3	-16.0
13E	1915	3.3	-7.4	-8.5
13 (final)	(-)	88.1	-6.0	-7.9
16A	30		-3.1	-9.1
16B	210		-4.0	-13.4
16C	410		-3.7	-13.7
16D	1420		failed	
16E	1870		-4.4	-11.6
16F	2900		failed	
16G	3310		-4.9	-11.7
16 (final)	(-)		-2.5	-7.3

**Table DR2. Carbon and Oxygen Stable Isotope Data, Whole Rock Analysis, Rotliegend Sandstone Below Orwell Field**

Well	Depth (drillers) / m	Sample number	$\delta^{13}\text{C}$ ‰ V-PDB	$\delta^{18}\text{O}$ ‰ V-PDB
50/26a-7	7656.5	MW-07-11	-2.4	-4.4
50/26a-7	7686	MW-07-12	-1.5	-4.1
50/26a-2	7959	MW-07-16	-0.1	-4.6
50/26a-2	7968	MW-07-17	-2.1	-7.6
50/26a-2	7980	MW-07-18	-0.7	-4.3
50/26a-2	8030	MW-07-19	-1.6	-6.0
50/26a-2	8007	MW-07-20	0.1	-5.3

### Comparison of Whole-Rock and Selective Extraction Experiments using Internal Laboratory Dolomite Standard

The standard used for this experiment was purchased as ‘dolomite’ from Ward’s Natural Science Establishment, Inc, Rochester, New York, here referred to as EUDOL. It is ‘pure’ dolomite by X-ray diffraction (XRD) though this does not eliminate the possibility that there are small quantities (< 1 - 2 % ?) of other minerals, especially calcite. ‘Whole-rock’ stable C and O analyses were conducted (Table 3), only 4 were deemed necessary as the results are reasonably reproducible suggesting that the dolomite sample is fairly homogeneous, at least after crushing. The reproducible whole-rock data do not prove that there is no isotopic zonation or other heterogeneity in the standard, merely that any such heterogeneity is homogenised by sample preparation.

Analytical method is as described in the Methods section of the main paper. A temperature of 25 °C was used for all analyses except for the final extractions of samples C20227 and C20228 which were at 100 °C. Dashes (-) in the data tables indicate a failed analysis, usually due to a small gas yield. Times are in minutes after the start of the extraction. Graphs show both whole-rock (‘bulk’) values and selective extractions with arrows showing the order of the extractions, from first to last.

**Table DR3. ‘Whole-Rock’ Analyses of EUDOL Internal Laboratory Dolomite Standard**

Sample	Yield $\mu\text{mol/mg}$	$\delta^{13}\text{C}$ ‰ V-PDB	$\delta^{18}\text{O}$ ‰ V-PDB
EUDOL	10.8	0.8	-14.0
EUDOL	10.8	0.6	-14.2
EUDOL	11.2	0.7	-14.3
EUDOL	10.9	0.5	-14.2

### Test of selective extraction method 1 - Sample C20227

Figure DR1. Comparison of whole-rock and selective extraction of standard sample C20227 (note expanded scales). First extraction has circle around data point.

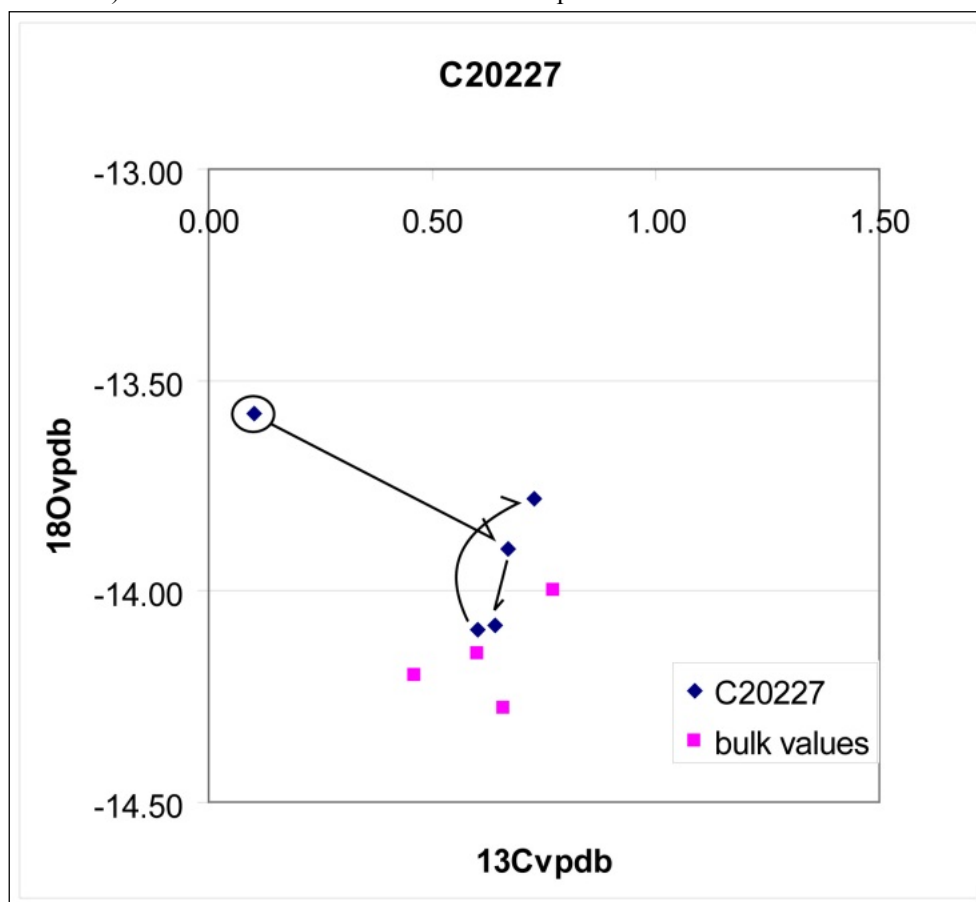


Table DR4. Selective Extraction of Standard Sample C20227

	$\delta^{13}\text{C} \text{ ‰ V-PDB}$	$\delta^{18}\text{O} \text{ ‰ V-PDB}$	time / minutes	Yield $\mu\text{mol/mg}$
C20227 I	0.10	-13.58	30	15.3
C20227 II	0.67	-13.90	125	42.2
C20227 III	0.64	-14.08	240	38.4
C20227 IV	0.60	-14.09	350	29.1
C20227 V	0.73	-13.78	1495	363.8

The first extraction shows a relatively light C and relatively heavy O composition. This could be due to small amounts of calcite or other rapidly dissolving minerals. The following extractions show a stable C ratio and slightly varying O ratios, with a small offset in  $\delta^{18}\text{O}$  (c. 0.5 ‰) between whole rock and selective extraction data that is small compared to the range found in the Fizzy and Orwell data.

### Test of selective extraction method 2 - Sample C20228

Figure DR2. Comparison of whole-rock and selective extraction of standard sample C20228 (note expanded scales). First extraction has circle around data point.

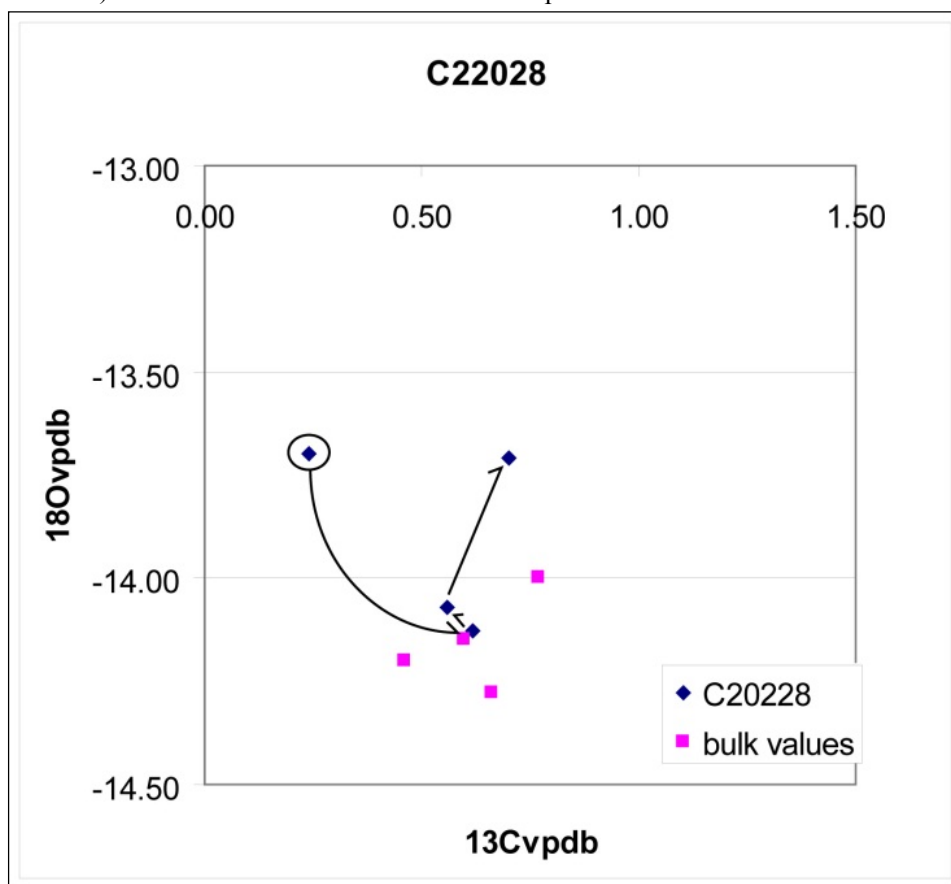


Table DR5. Selective Extraction of Standard Sample C20228

	$\delta^{13}\text{C} \text{ ‰ V-PDB}$	$\delta^{18}\text{O} \text{ ‰ V-PDB}$	time / minutes	Yield $\mu\text{mol/mg}$
C20228 I	0.24	-13.70	50	20.7
C20228 II	-	-	150	40.1
C20228 III	0.62	-14.13	270	33.3
C20228 IV	0.56	-14.07	375	27.9
C20228 V	0.70	-13.71	1615	369

Again, the first extraction shows a relatively light C and relatively heavy O composition. The second extraction failed. The following two extractions show a stable C and O within the range of the 'bulk values'. The sample was placed overnight at 100C and finally shows, like the experiment before, a trend towards a heavier O-ratio.

### Test of selective extraction method 3 - Sample C20229

Figure DR3. Comparison of whole-rock and selective extraction of standard sample C20229 (note expanded scales). First successful extraction has circle around data point.

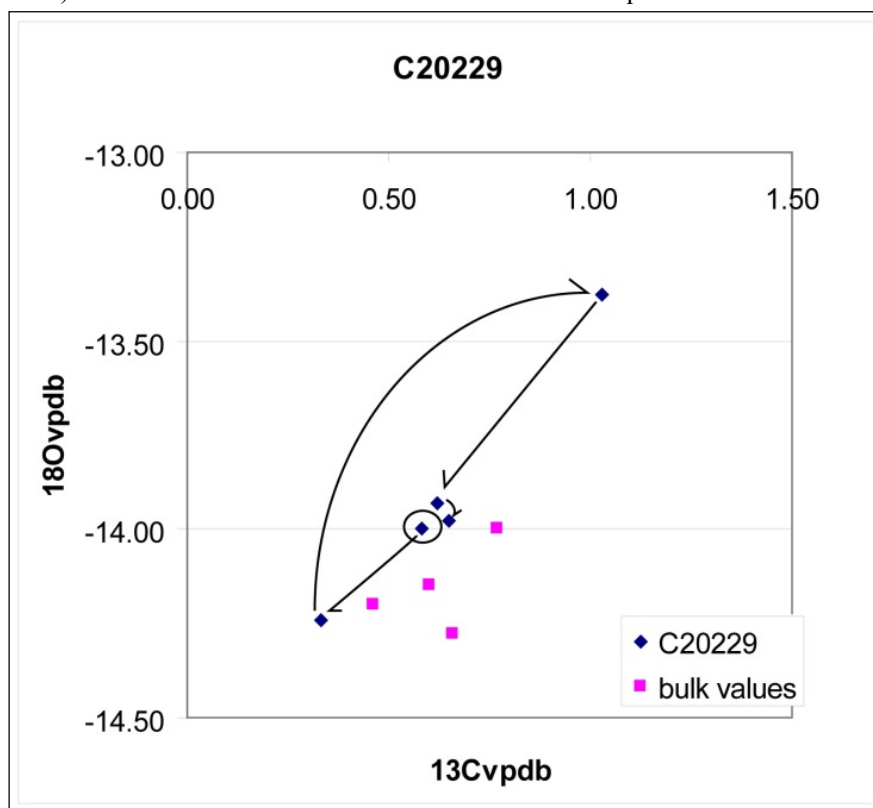


Table DR6. Selective Extraction of Standard Sample C20229

	$\delta^{13}\text{C} \text{ ‰ V-PDB}$	$\delta^{18}\text{O} \text{ ‰ V-PDB}$	time / minutes	Yield $\mu\text{mol/mg}$
C20229 I	-	-	30	15.1
C20229 II	0.58	-14.00	180	43.2
C20229 III	0.33	-14.24	270	38
C20229 IV	1.03	-13.38	425	39.1
C20229 V	-	-	1450	130
C20229 VI	0.65	-13.98	1815	40
C20229 VII	0.62	-13.93	2895	not determined

The first extraction failed so that any anomalous mineral or artefact will not be recognized in this experiment. Extraction 4 is clearly anomalous, while the others are close to the whole-rock values. Even extraction 4 is shows significantly less deviation from the whole-rock values than is found in the data from Fizzy and Orwell.



#### Test of selective extraction method 4 - Sample C20230

Figure DR4. Comparison of whole-rock and selective extraction of standard sample C20230 (note expanded scales). First successful extraction has circle around data point.

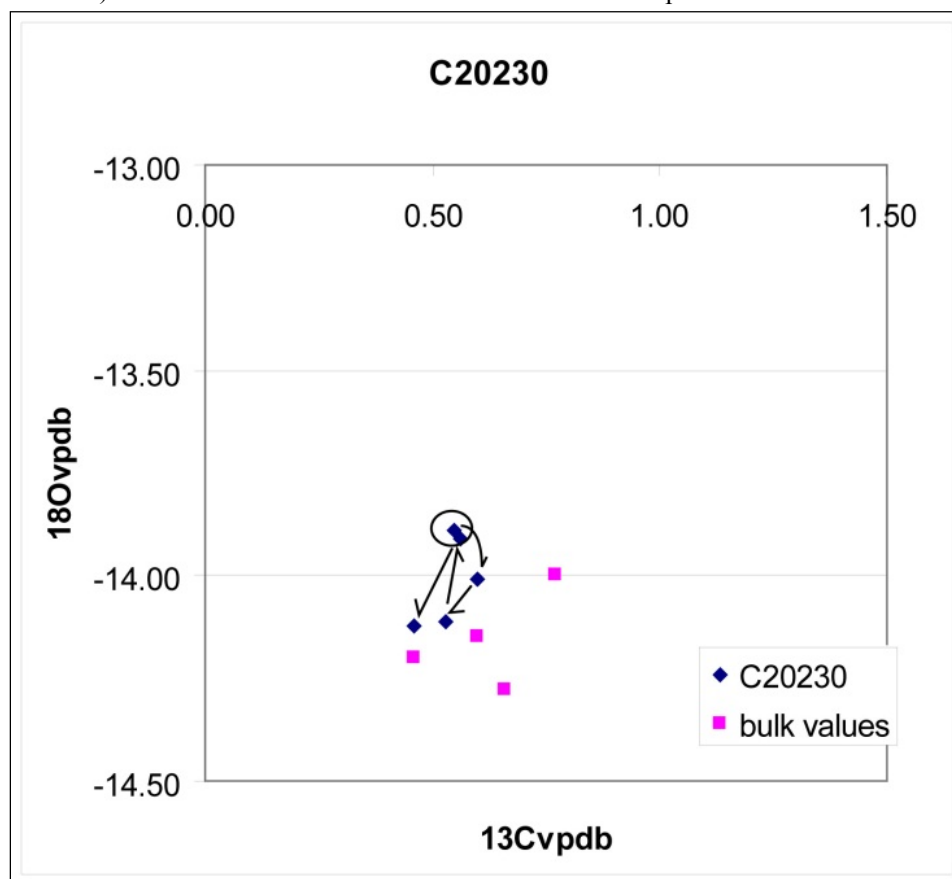


Table DR7. Selective Extraction of Standard Sample C20230

	$\delta^{13}\text{C} \text{ ‰ V-PDB}$	$\delta^{18}\text{O} \text{ ‰ V-PDB}$	time / minutes	Yield $\mu\text{mol/mg}$
C20230 I	-	-	30	4
C20230 II	0.55	-13.89	145	49.1
C20230 III	0.60	-14.01	265	43.7
C20230 IV	0.53	-14.11	420	40.7
C20230 V	-	-	1430	134
C20230 VI	0.56	-13.91	1790	34.1
C20230 VII	0.46	-14.12	2880	not determined

The first extraction failed. The remaining selective extraction analyses are very close to the whole-rock values.

### Test of selective extraction method 5 - Sample C20231

Figure DR5. Comparison of whole-rock and selective extraction of standard sample C20231 (note expanded scales). First successful extraction has circle around data point.

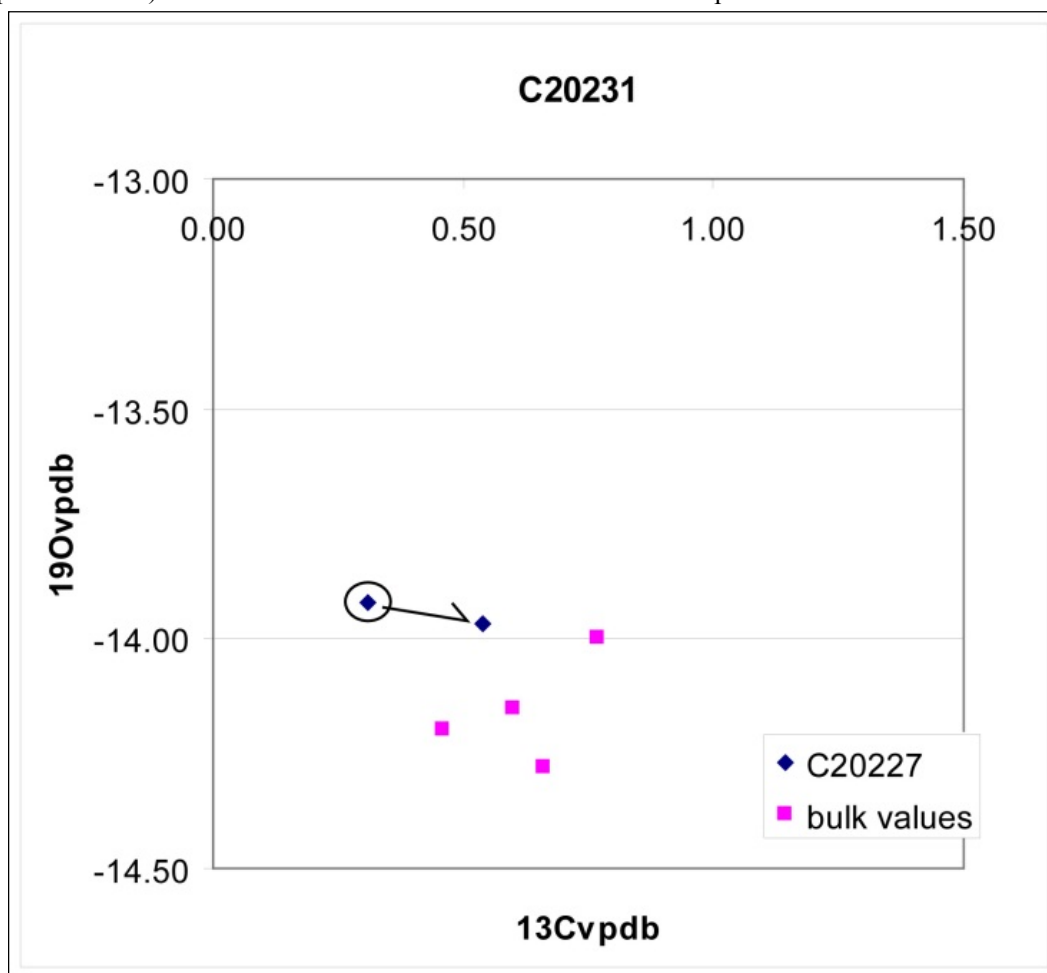


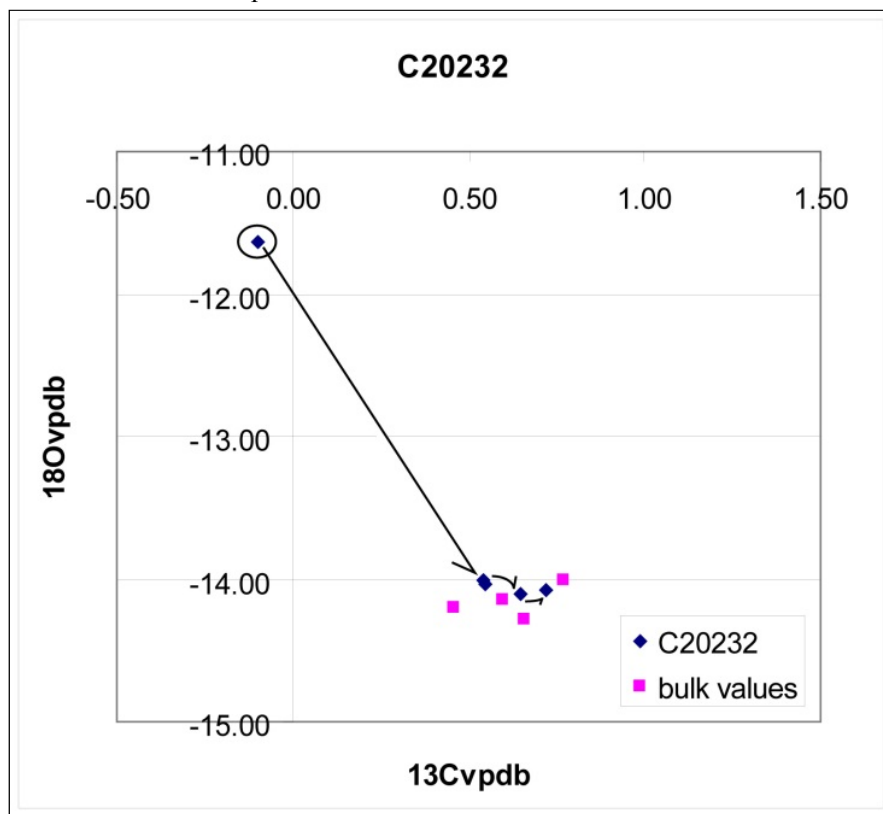
Table DR8. Selective Extraction of Standard Sample C20231

	$\delta^{13}\text{C} \text{ ‰ V-PDB}$	$\delta^{18}\text{O} \text{ ‰ V-PDB}$	time / minutes	Yield $\mu\text{mol/mg}$
C20231 I	-	-	30	3.4
C20231 II	0.31	-13.92	155	27.5
C20231 III	0.54	-13.97	260	43.1
C20231 IV	-	-	400	44.5
C20231 V	-	-	1455	145

Most of the extractions failed. The second extraction shows a slightly lighter O ratio than measurements of the third extraction, but given the low yields experienced in this experiment the results should perhaps be discounted.

### Test of selective extraction method 6 - Sample C20232

Figure DR6. Comparison of whole-rock and selective extraction of standard sample C20232. First extraction has circle around data point.



**Table DR9. Selective Extraction of Standard Sample C20232**

	$\delta^{13}\text{C} \text{ ‰ V-PDB}$	$\delta^{18}\text{O} \text{ ‰ V-PDB}$	time / minutes	Yield $\mu\text{mol/mg}$
C20232 I	-0.10	-11.64	40	25.3
C20232 II	0.54	-14.01	170	54.1
C20232 III	0.55	-14.03	285	35.8
C20232 IV	0.65	-14.11	405	30.3
C20232 V	0.72	-14.08	1485	not determined

The first extraction shows a light C and heavy O composition. It could be due to rock heterogeneity, i.e. calcite dissolution which would perhaps be unusually abundant in this sample. Note that the heavy initial oxygen value is not seen in the analysis of the Fizzy and Orwell data. The remaining extractions show stable C and O ratios within the range of the 'bulk values'.

### Test of selective extraction method 7 - Sample C20233

Figure DR7. Comparison of whole-rock and selective extraction of standard sample C20233. First extraction has circle around data point.

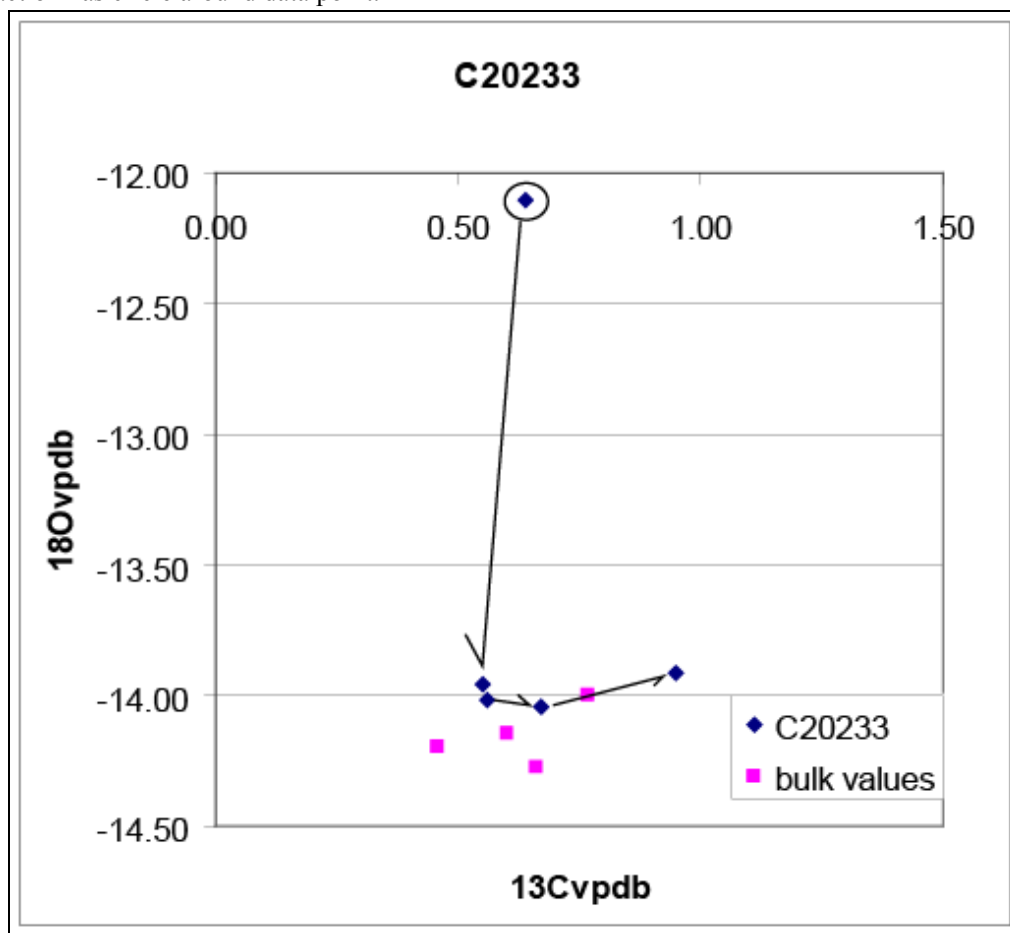


Table DR10. Selective Extraction of Standard Sample C20233

	$\delta^{13}\text{C}$ ‰ V-PDB	$\delta^{18}\text{O}$ ‰ V-PDB	time / minutes	Yield $\mu\text{mol/mg}$
C20233 I	0.64	-12.10	30	12.6
C20233 II	0.55	-13.96	160	45.1
C20233 III	0.56	-14.02	275	40.3
C20233 IV	0.67	-14.04	385	32.3
C20233 V	0.95	-13.91	1455	not determined

The first extraction shows a very heavy O composition. The following extractions show stable O ratio and a slightly varying C ratio which becomes slightly heavier with increasing time.

## **Test of Selective Extraction Method: Discussion and Conclusions**

The selective extraction analyses generally lie within the range of whole-rock analyses. Only a minority lie more than 0.5 ‰ away from the whole-rock data, and these are the initial selective extraction analyses which might be due to a reactive contaminant mineral (calcite?) within the dolomite standard present in concentrations too low for detection by XRD.

In contrast to the selective extraction analyses of the Orwell and Fizzy samples, the selective extraction test analyses lack anomalously light  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. It could hence be concluded that the anomalously light  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values from Orwell and Fizzy are not artefacts of the selective extraction technique, but reflect genuine compositional variation within the sample material.