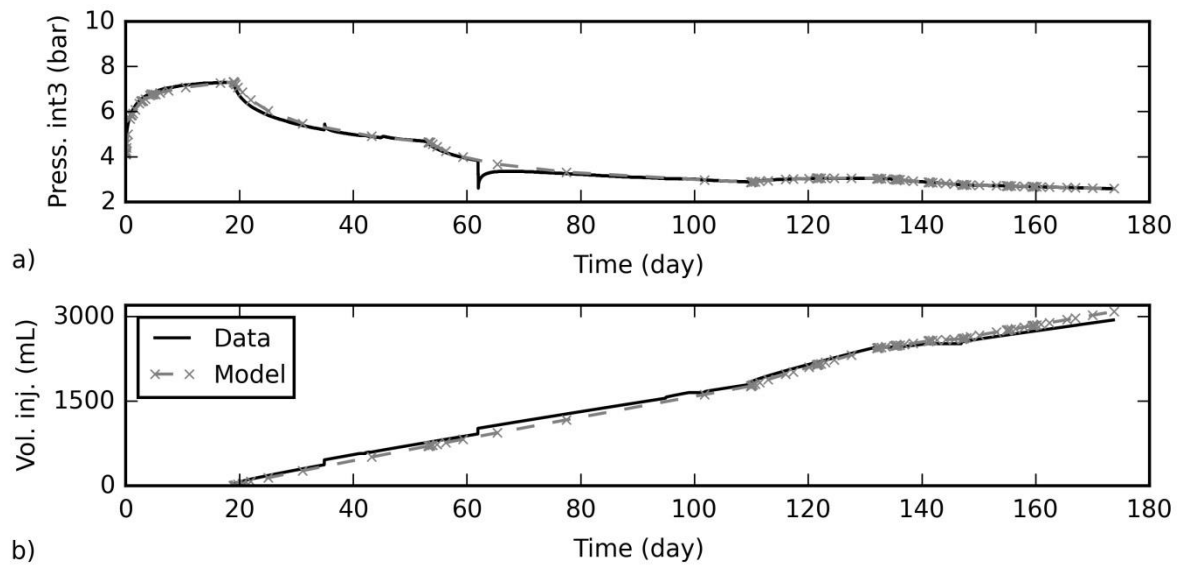


## Appendices (supplementary information)

### Appendix A: Modelling – supplementary data



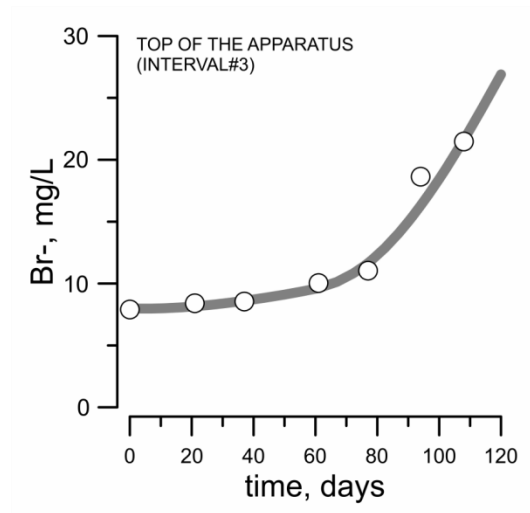
**Figure A 1: Observation and modelling of stage B (the modelling has been done between February 13<sup>th</sup> and August 6<sup>th</sup> 2015) – a) pressure in interval 3 for the whole period; b) injected volume**

**Table A 1: Initial mineralogical composition of the cement annulus, and chemical composition of the associated porewater. Kinetic parameters for the minerals considered in the simulations are also given. The parameters “Log rate” and “Ea” are the kinetic constant (mol/m<sup>2</sup>/s) at near-neutral pH, and the activation energy (kJ/mol) at 25°C, respectively**

Cement, Primary minerals	Vol. %	Chemical constraint / basis species		Total dissolved concentration at 26.1°C	Unit
Portlandite	16.0	pH / H <sup>+</sup>		12.41	( - )
CSH(1.6)	53.4	Ca <sub>TOT</sub> / Ca <sup>2+</sup>		$0.5131 \times 10^{-1}$	mol/kgw
Ettringite	10.9	Mg <sub>TOT</sub> / Mg <sup>2+</sup>		$0.5812 \times 10^{-8}$	mol/kgw
Hydrotalcite	6.5	Na <sub>TOT</sub> / Na <sup>+</sup>		$0.2724 \times 10^0$	mol/kgw
C3FH6	6.5	K <sub>TOT</sub> / K <sup>+</sup>		$0.2228 \times 10^{-2}$	mol/kgw
C3AH6	6.5	Fe <sub>TOT</sub> / Fe <sup>2+</sup>		$0.8582 \times 10^{-7}$	mol/kgw
		Si <sub>TOT</sub> / H <sub>4</sub> SiO <sub>4</sub>		$0.2265 \times 10^{-5}$	mol/kgw
		Al <sub>TOT</sub> / Al <sup>3+</sup>		$0.4563 \times 10^{-4}$	mol/kgw
		Cl <sub>TOT</sub> / Cl <sup>-</sup>		$0.3350 \times 10^0$	mol/kgw
		C <sub>TOT</sub> / HCO <sub>3</sub> <sup>-</sup>		$0.5131 \times 10^{-1}$	mol/kgw
		S <sub>TOT</sub> / SO <sub>4</sub> <sup>2-</sup>		$0.2216 \times 10^{-6}$	mol/kgw
		Sr <sub>TOT</sub> / Sr <sup>2+</sup>		$0.1566 \times 10^{-4}$	mol/kgw

Mineral	Rate constant	Ea	Mineral	Rate constant	Ea
Calcite	$1.9 \times 10^{-6}$	24	Sepiolite	$5.8 \times 10^{-9}$	42
Dolomite	$3 \times 10^{-12}$	52	Quartz	$4.1 \times 10^{-14}$	88
Siderite	$1.3 \times 10^{-9}$	63	Chalcedony	$4.9 \times 10^{-13}$	76
Nesquehonite	$4.5 \times 10^{-10}$	63	Ferrihydrite 6L	$1.0 \times 10^{-9}$	15
Dawsonite	$1.3 \times 10^{-9}$	63	Pyrite	$4.0 \times 10^{-11}$	63
Ankerite	$1.3 \times 10^{-9}$	63	Portlandite	$2.2 \times 10^{-8}$	15
Mg-Illite	$8.8 \times 10^{-16}$	14	Katoite-Si	$2.8 \times 10^{-12}$	15
Mg-Fe-Chlorite	$3.0 \times 10^{-16}$	88	Ettringite	$1.1 \times 10^{-12}$	15
Phillipsite (Ca- and K-)	$4.0 \times 10^{-12}$	87	Monosulfoaluminate	$6.3 \times 10^{-12}$	15
Smectite (Ca- and K-)	$3.9 \times 10^{-15}$	48	Fe-monosulfate	$6.3 \times 10^{-12}$	15
Montmorillonite (all)	$3.9 \times 10^{-15}$	48	Hydrotalcite	$1.1 \times 10^{-12}$	15
Kaolinite	$6.9 \times 10^{-14}$	22	C3FH6 and C3AH6	$2.2 \times 10^{-8}$	15
Brucite	$5.8 \times 10^{-9}$	42	CSH (all)	$2.8 \times 10^{-12}$	15



**Figure A 2: Comparison between experimental and numerical data (chemical composition of interval 3 water). Dots are experimental data, grey lines numerical outputs.**

## *Appendix B: Analytical protocols*

### Fluid analysis

Two aliquots of each solution sample preserved in 2 mL vials with a septum and entirely filled were used to measure the dissolved organic carbon (DOC), the total inorganic carbon (DIC) and the  $\delta^{13}\text{C}$  of DOC and DIC when possible. A commercial interface coupling a liquid chromatography Isolink (LC) to a continuous-flow isotope ratio mass spectrometry (CF-IRMS) instrument was used to determine the  $\delta^{13}\text{C}$  of the DIC, according to the method described in Brandes [2009], and of the DOC according to the method described in Alberic [2011].

### Carbon and oxygen isotopes on calcite

The conventional method of Rosenbaum & Sheppard [1986] was used to extract calcite from about 45 to 100 mg of bulk powder of material by acid attack with 100 % phosphoric acid at 25 °C for 24 h [McCrea, 1950]. The  $\text{CO}_2$  pressure was measured in a calibrated volume and converted into a calcite content; the uncertainty is about 5 %. The extracted  $\text{CO}_2$  was analysed for its isotopic composition using a Delta S Finnigan-Mat gas-source mass spectrometer. Reproducibility was  $\pm 0.2$  ‰ for oxygen and carbon.

### Cation exchange capacity (CEC) and aqueous leaching on claystone

Measurements of cation exchange capacity (CEC) and aqueous leaching were performed on pieces of core preserved in liquid nitrogen to preserve as best as possible the in-situ conditions. At laboratory, samples were transferred in a glove-box just before the analyses to limit oxygen contamination. Samples were not fully crushed, but precise samplings of few grams of rock were performed using a micro-drill. Measurements of CEC and adsorbed-cation concentrations (Ca, K, Mg, Na and Sr) were carried out by exchange of about 1 gram of rock powder with 20 ml of cobalt hexamine trichloride during 1 hour. The cobalt hexamine concentration of the leachate was determined colorimetrically (absorption band at 473 nm) on a UNICAM UV visible spectrometer that gives the CEC (cation exchange capacity). Strontium and major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) were determined in the exchange solution by ion chromatography with a conductivity detector (DIONEX). An amount of 200/100/100 mg of recovered powder were leached with 2/2/5 ml of deionised water that was boiled and degassed beforehand, during 24 hours. Each analysis was duplicated. After the leaching procedure, the liquid was filtrated on a 0.1  $\mu\text{m}$  filter prior to analysis. Chloride, bromide and sulphate concentrations were measured using ionic chromatography.

### $\text{CO}_2$ partial pressure measurements in claystone

The samples were conditioned in a glass container with dry He according to modified method of Girard et al. [2005]. Gas pressure, temperature, and chemical analyses of the gas were performed on a Varian star 3400 CX gas chromatograph. An aliquot of the gas was collected to be analyzed for carbon isotopes by Gas bench coupled with a Delta+XP mass spectrometer. In this paper, the isotopic signatures are reported in  $\delta$  units relative to international standards, defined by:  $\delta = (R_{\text{Sample}}/R_{\text{Standard}} - 1) \times 1000$  ‰, where R is the measured isotopic ratio in the sample and in the standard: SMOW<sup>1</sup> for oxygen, PDB for carbon.

### Microscopic observations of cement

Observations and analyses were performed on surfaces of cement that were sawed and polished with silicon carbide paper without water. Scanning electron microscope (SEM)

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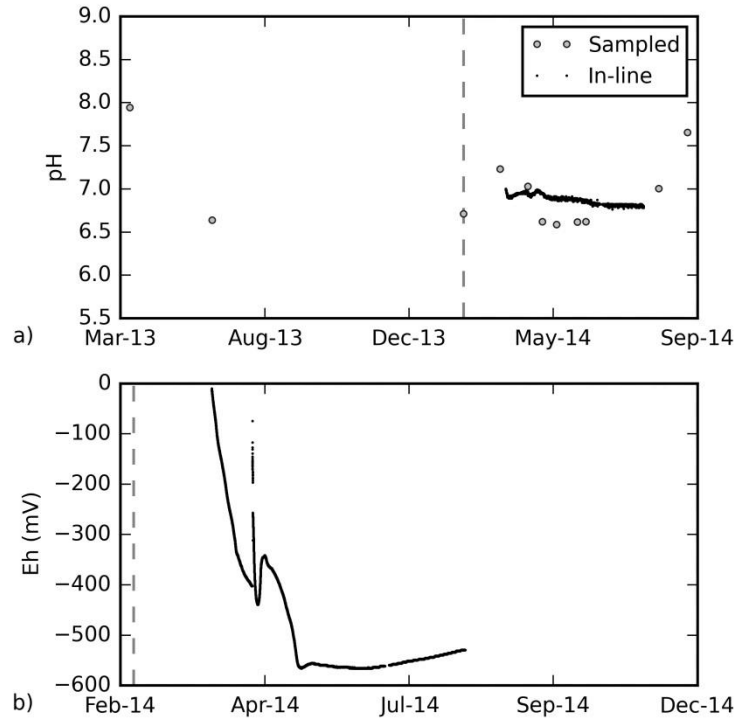
<sup>1</sup> Standard Mean Ocean Water

observations were performed on a TESCAN MIRA 3 XMU equipped with a YAG-scintillator back scattered electron (BSE) detector. Elemental analyses were collected on non-coated samples at high voltage of 25 kV under low vacuum conditions ( $P \sim 30\text{-}35\text{ Pa}$ ) using an EDAX PEGASUS system (camera DIGIVIEW IV, OIM DC 6.4).

*Appendix C: Water composition evolution and analyses on the overcore samples – raw data*

**Table C 1: Analytical results from the water samples in Int.3 during the CO<sub>2</sub> injection period. Ionic strength, charge balance and TIC content have been calculated using PHREEQC v3 calculation code [Parkhurst and Appelo, 2013] and Thermoddem v2011 thermodynamic database [Blanc et al., 2012]. \*: pe value computed from Fe<sup>2+</sup> and total Fe measured contents.**

Lab-no.	Unit	ULT-9	ULT-11	ULT-13	ULT-14	ULT-16	ULT-17	ULT-19	ULT-21
Interval sampled	--	Int. 3	Int. 3	Int. 3	Int. 3	Int. 3	Int. 3	Int. 3	Int. 3
Sampling date	--	20/03/2014	16/04/2014	30/04/2014	14/05/2014	03/06/2014	11/06/2014	21/08/2014	18/09/2014
pH value (lab)		7.23	7.03	6.618	6.586	6.615	6.618	7	7.65
pe		--	--	6.176	5.172	5.15	5.146	4.511	--
Alkalinity	(eq/L)	3.45×10 <sup>-3</sup>	4.97×10 <sup>-3</sup>	6.77×10 <sup>-3</sup>	6.24×10 <sup>-3</sup>	6.38×10 <sup>-3</sup>	6.00×10 <sup>-3</sup>	5.28×10 <sup>-3</sup>	--
Ionic strength	(M)	2.87×10 <sup>-1</sup>	3.11×10 <sup>-1</sup>	2.87×10 <sup>-1</sup>	2.81×10 <sup>-1</sup>	2.82×10 <sup>-1</sup>	2.80×10 <sup>-1</sup>	2.77×10 <sup>-1</sup>	2.72×10 <sup>-1</sup>
Charge balance	(%)	-4.64	-7.36	-6.50	-6.76	-6.29	-8.08	-0.04	0.04
Na	(mol/L)	2.02×10 <sup>-1</sup>	1.96×10 <sup>-1</sup>	1.85×10 <sup>-1</sup>	1.84×10 <sup>-1</sup>	1.88×10 <sup>-1</sup>	1.84×10 <sup>-1</sup>	2.07×10 <sup>-1</sup>	2.05×10 <sup>-1</sup>
K	(mol/L)	1.44×10 <sup>-3</sup>	2.55×10 <sup>-2</sup>	2.28×10 <sup>-2</sup>	2.06×10 <sup>-2</sup>	1.57×10 <sup>-2</sup>	1.46×10 <sup>-2</sup>	1.48×10 <sup>-3</sup>	1.46×10 <sup>-3</sup>
Ca	(mol/L)	1.37×10 <sup>-2</sup>	1.34×10 <sup>-2</sup>	1.17×10 <sup>-2</sup>	1.13×10 <sup>-2</sup>	1.18×10 <sup>-2</sup>	1.12×10 <sup>-2</sup>	1.26×10 <sup>-2</sup>	1.17×10 <sup>-2</sup>
Mg	(mol/L)	1.23×10 <sup>-2</sup>	1.19×10 <sup>-2</sup>	1.10×10 <sup>-2</sup>	1.07×10 <sup>-2</sup>	1.11×10 <sup>-2</sup>	1.09×10 <sup>-2</sup>	1.20×10 <sup>-2</sup>	1.19×10 <sup>-2</sup>
Sr	(mol/L)	3.16×10 <sup>-4</sup>	3.11×10 <sup>-4</sup>	2.74×10 <sup>-4</sup>	2.53×10 <sup>-4</sup>	2.67×10 <sup>-4</sup>	2.66×10 <sup>-4</sup>	3.04×10 <sup>-4</sup>	3.00×10 <sup>-4</sup>
Fe	(mol/L)	1.70×10 <sup>-4</sup>	1.42×10 <sup>-4</sup>	3.41×10 <sup>-4</sup>	3.43×10 <sup>-5</sup>	4.51×10 <sup>-5</sup>	8.54×10 <sup>-5</sup>	2.09×10 <sup>-4</sup>	--
Fe <sup>2+</sup>	(mol/L)	--	--	6.35×10 <sup>-5</sup>	2.48×10 <sup>-5</sup>	3.18×10 <sup>-5</sup>	6.07×10 <sup>-5</sup>	1.43×10 <sup>-4</sup>	9.73×10 <sup>-5</sup>
Al	(mol/L)	2.22×10 <sup>-7</sup>	7.66×10 <sup>-6</sup>	4.33×10 <sup>-7</sup>	2.06×10 <sup>-7</sup>	1.60×10 <sup>-7</sup>	1.22×10 <sup>-7</sup>	2.36×10 <sup>-7</sup>	--
NH <sub>4</sub>	(mol/L)	4.02×10 <sup>-4</sup>	5.02×10 <sup>-4</sup>	8.35×10 <sup>-4</sup>	5.43×10 <sup>-4</sup>	5.08×10 <sup>-4</sup>	5.14×10 <sup>-4</sup>	6.44×10 <sup>-4</sup>	6.97×10 <sup>-4</sup>
Si	(mol/L)	1.88×10 <sup>-4</sup>	2.20×10 <sup>-4</sup>	2.54×10 <sup>-4</sup>	2.27×10 <sup>-4</sup>	2.32×10 <sup>-4</sup>	2.28×10 <sup>-4</sup>	1.84×10 <sup>-4</sup>	1.66×10 <sup>-4</sup>
Cl	(mol/L)	2.58×10 <sup>-1</sup>	2.88×10 <sup>-1</sup>	2.65×10 <sup>-1</sup>	2.61×10 <sup>-1</sup>	2.59×10 <sup>-1</sup>	2.61×10 <sup>-1</sup>	2.35×10 <sup>-1</sup>	2.36×10 <sup>-1</sup>
SO <sub>4</sub>	(mol/L)	9.50×10 <sup>-3</sup>	1.06×10 <sup>-2</sup>	8.49×10 <sup>-3</sup>	8.17×10 <sup>-3</sup>	8.29×10 <sup>-3</sup>	8.55×10 <sup>-3</sup>	8.99×10 <sup>-3</sup>	9.06×10 <sup>-3</sup>
TIC (calculated)	(mol/L)	3.67×10 <sup>-3</sup>	5.52×10 <sup>-3</sup>	8.97×10 <sup>-3</sup>	8.50×10 <sup>-3</sup>	8.54×10 <sup>-3</sup>	8.02×10 <sup>-3</sup>	5.94×10 <sup>-3</sup>	--
Br	(mol/L)	1.07×10 <sup>-4</sup>	1.09×10 <sup>-4</sup>	1.28×10 <sup>-4</sup>	1.40×10 <sup>-4</sup>	2.37×10 <sup>-4</sup>	2.73×10 <sup>-4</sup>	1.94×10 <sup>-4</sup>	1.97×10 <sup>-4</sup>
I	(mol/L)	5.63×10 <sup>-6</sup>	1.33×10 <sup>-5</sup>	1.07×10 <sup>-5</sup>	7.37×10 <sup>-6</sup>	6.88×10 <sup>-6</sup>	5.88×10 <sup>-6</sup>	9.58×10 <sup>-6</sup>	--



**Figure C 1: Interval 3 sampled and in-line water evolution over the experiment duration. a) pH and b) Eh**

**Table C 2: Average anion concentrations measured by leaching with milliQ water and given in mmole per 100 g of rock, and exchanged cations concentrations and cation exchange capacity measured by cobalt hexamine technique.**

	Cl	SO4		Na	K	Ca	Sr	Mg	$\Sigma$ cations	CEC
	mmol/100 g			meq/100g						
BCS 5A - 8.45-8.55m	0.87	0.35		7.22	1.57	4.89	0.09	2.13	15.91	14.26
BCS 5A - 9.48-9.58m	0.89	0.34		7.16	1.49	4.70	0.08	2.26	15.68	14.55
BCS 5A - 10.08-10.10m near	1.09	0.37		7.38	1.99	5.29	0.08	2.00	16.74	15.79
BCS 5A - 10.08-10.10m far	1.04	0.37		7.46	2.02	5.42	0.09	1.97	16.96	15.54
BCS 5A - 10.65-10.71m near	1.33	0.49		6.98	1.53	5.83	0.10	2.74	17.17	15.65
BCS 5A - 10.65-10.71m far	1.26	0.37		6.29	1.87	6.09	0.08	2.38	16.70	15.72
BCS 5A - 12.08-12.12m near	1.53	2.29		5.87	1.08	4.92	0.72	2.26	14.84	11.99
BCS 5A - 12.08-12.12m far	1.50	2.49		8.16	1.53	6.09	0.83	3.22	19.84	16.53
REFERENCE	0.75	<0.45		6.54	0.97	4.53	0.00	3.01	15.04	

**Table C 3: Clay core outgassing - Measurements of CO<sub>2</sub> partial pressure and alkanes, and  $\delta^{13}\text{C}$  of CO<sub>2</sub>; Carbon and oxygen isotopes on calcite in the core samples**

	2 days	2 7 days				71 days	161 days				Alkanes (%)					
	$\delta^{13}\text{C}_{\text{CO}_2}$	P total	% O <sub>2</sub>	% N <sub>2</sub>	P CO <sub>2</sub>	$\delta^{13}\text{C}$	P total	% O <sub>2</sub>	% N <sub>2</sub>	P CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>14</sub>
BCS 5A - 8.45-8.55m	24.6	882	10.05	85.05	14.2	-6.2	831	11.2	83.0	41.1	0.02	0.04	0.18	0.22	0.09	0.08
BCS 5A - 9.48-9.58m		857	0.10	18.57	2.3	-8.7	854	0.0	31.7	14.9	0.21	0.21	0.54	0.47	0.16	0.08
BCS 5A - 10.02-10.08m near		907	0.40	15.53	0.7	-12.2	979	0.2	39.7	14.9	0.05	0.06	0.22	0.25	0.08	0.05
BCS 5A - 10.02-10.08m far	-10.0	582	0.07	73.22	2.7	-8.7	408	0.1	8.2	14.7	0.14	0.15	0.42	0.39	0.12	0.06
BCS 5A - 10.15-10.18m near	-5.1	738	0.20	20.65	7.6	-5.0	733	0.1	27.4	22.6	0.05	0.06	0.20	0.21	0.06	0.04
BCS 5A - 10.15-10.18m far	-8.2	623	0.14	44.03	4.8	-7.0	908	0.0	30.4	14.7	0.07	0.09	0.29	0.29	0.09	0.05
BCS 5A - 10.65-10.71m near	2.6	825	0.93	91.33	37.0	-10.2	871	<	91.9	45.2	0.10	0.13	0.44	0.40	0.13	0.07
BCS 5A - 10.65-10.71m far	-0.4	885	0.07	15.65	8.7	0.0	843	0.1	25.7	16.4	0.05	0.08	0.25	0.26	0.08	0.05
BCS 5A - 12.08-12.12m		988	1.56	46.84	8.5	-7.0	997	2.7	89.4	39.8	0.21	0.18	0.42	0.36	0.12	0.07

**Table C 4: Carbon and oxygen isotopic composition of calcite extracted from cement at the both interfaces (clay and steel)**

Core samples	External contact with clay			Internal contact with steel		
	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ SMOW)	Calcite content (%)	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ SMOW)	Calcite content (%)
BCS5-OC – depth (m)						
8.32 m	-19.4	19.8	22	-32.6	13.1	19
8.84 m	-26.0	16.5	20	-35.2	11.3	11
9.54 m	-24.0	18.2	18			
9.79 m	-19.4	17.6	19			
10.12 m	-20.0	17.1	14	-40.3	17.2	9



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