

### ***Samples and Methods***

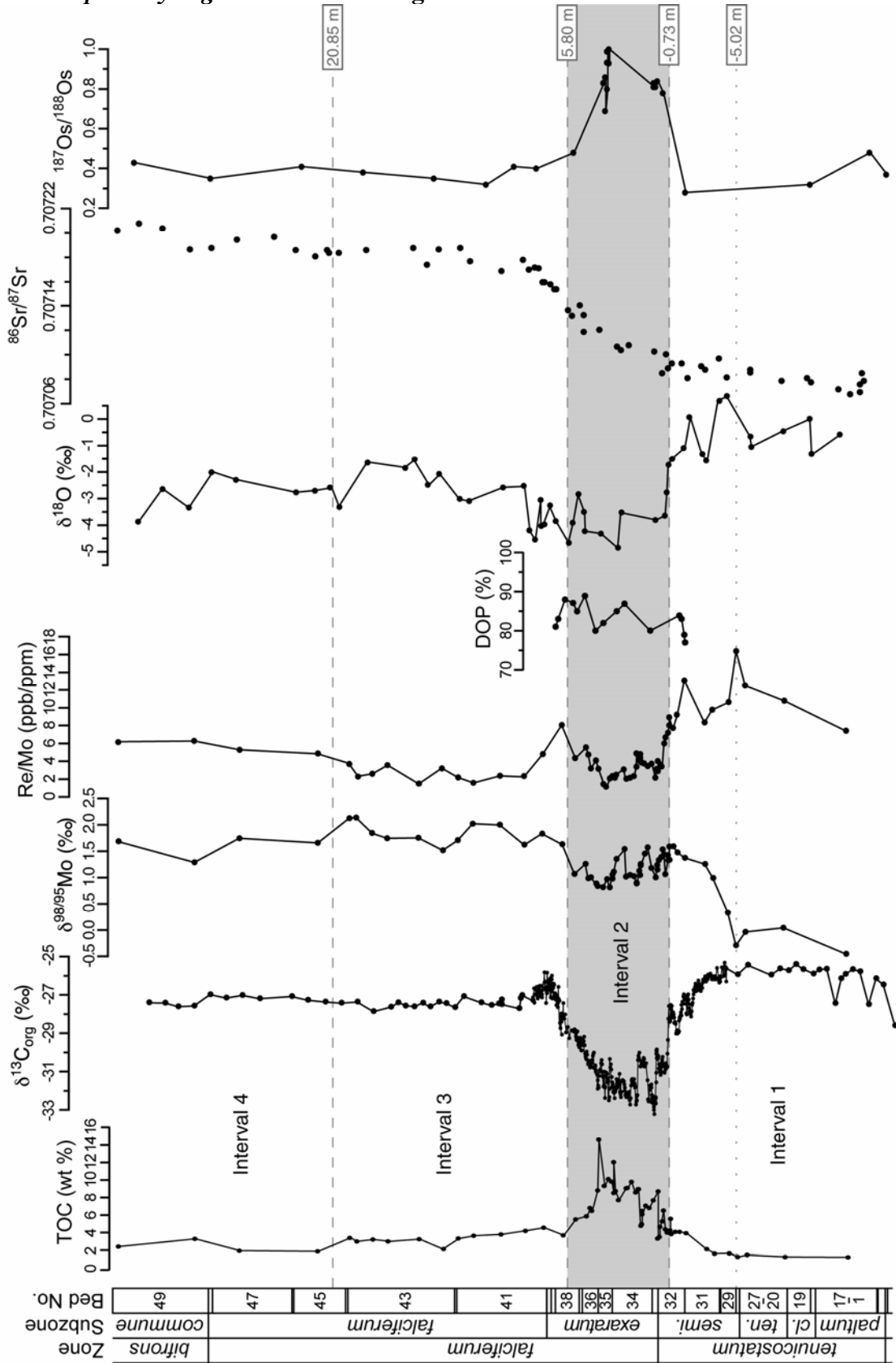
Samples were collected from the Whitby Mudstone Formation (Toarcian), now exposed along the Yorkshire coast, UK, and were obtained from three localities (Table DR1); Saltwick Bay (NZ 916111), Port Mulgrave (NZ 798176) and Hawsker Bottoms (NZ 944082). For detailed locality maps and site descriptions see Howarth (1962, 1973 & 1992) and Rawson and Wright (1995). Samples are predominantly organic-rich mudrocks that are stratigraphically equivalent to similar organic-rich deposits throughout Central and Western Europe (e.g. the ‘Schistes Carton’ from the Paris Basin, France, and the ‘Posidonia Shale’ from the Posidonienschiefer Basin, Germany) (Jenkyns, 1988; Röhl *et al.*, 2001). The samples that we have analysed constitute part of a high resolution sample set through the succession and are accurately correlated with samples used in a recent high resolution  $\delta^{13}\text{C}_{\text{org}}$  study (Kemp *et al.*, 2005; Kemp, 2006). Fourier transform analysis of these high resolution  $\delta^{13}\text{C}_{\text{org}}$ ,  $\text{CaCO}_3$ , S and TOC data (Kemp *et al.*, 2005; Kemp, 2006) has shown that sedimentation rates in the Cleveland Basin remained approximately constant throughout Intervals 1 and 2 (Figs. 1 and 2).

All samples were prepared and analysed at The Open University. Rock samples were crushed in an agate TEMA or in a ceramic mortar before digestion in sealed PFA vials using a 3:1 mixture of c.  $\text{HNO}_3$  and c.  $\text{HCl}$ . Samples were digested for 5–7 days at  $\sim 130^\circ\text{C}$ , which ensured the complete oxidation of the organic matter, and the oxidation and dissolution of the authigenic redox-sensitive metals. Prior to dissolution, an isotopic double spike of  $^{100}\text{Mo}$  and  $^{97}\text{Mo}$ , and a  $^{185}\text{Re}$  single spike, were added to accurately

weighed sample aliquots. Both Mo and Re were purified using a new, highly efficient single pass anion exchange procedure that gave ~100 % recovery of Mo and Re (Pearce and Cohen, In Prep.). Isotopic analyses were performed using a Nu Instruments MC-ICP-MS connected to a DSN-100 desolvation nebuliser. Mo-isotope compositions were resolved offline using the Newton-Raphson deconvolution procedure (Albarède and Beard, 2004), with data normalised to an in-house Mo standard (Fisher Chemicals Batch No. 9920914-150). The long-term reproducibility of this standard is 0.12 ‰ (2 $\sigma$ ). Repeat analyses of IAPSO seawater salinity standard yielded a mean  $\delta^{98/95}\text{Mo}$  composition of  $2.55 \pm 0.05$  ‰ (2 sd, n=6); analyses of basalt standard BHVO-2 gave a mean  $\delta^{98/95}\text{Mo}$  composition of  $0.19 + 0.1$  ‰ (2 sd, n=6); and repeat measurements of an in-house organic-rich mudrock yielded a mean  $\delta^{98/95}\text{Mo}$  value of  $0.88 + 0.1$  ‰ (2 sd, n=16). Mo and Re concentrations were calculated by isotope dilution. Total organic carbon (TOC) was determined using a LECO Instruments CNS-2000 elemental analyser.

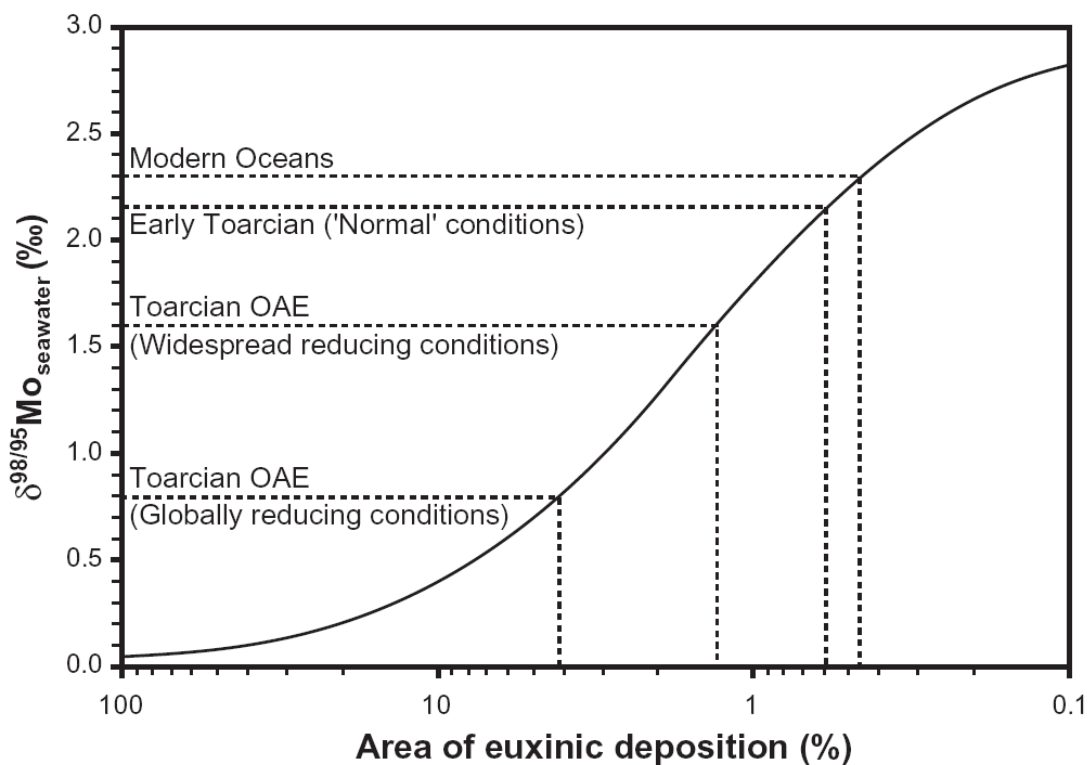
Data Repository Figures

Figure DR1



**Figure DR1.**

Variations in geochemical parameters against stratigraphical height for samples from the Early Toarcian, Yorkshire. The first 4 parameters (TOC,  $\delta^{13}\text{C}_{\text{org}}$ ,  $\delta^{98/95}\text{Mo}$  and Re/Mo ratio) and references are presented in Fig. 1 of the main paper. Additional parameters include the degree of pyritisation (DOP) (Raiswell *et al.*, 1993), which is a proxy for anoxia/euxinia; a proxy indicating seawater temperature ( $\delta^{18}\text{O}$ ) (McArthur *et al.*, 2000; Bailey *et al.*, 2003); and two proxies reflecting continental weathering flux,  $^{87}\text{Sr}/^{86}\text{Sr}$  (McArthur *et al.*, 2000) and  $^{187}\text{Os}/^{188}\text{Os}$  (Cohen *et al.*, 1999, 2004). The progressive change from oxic to euxinic conditions in the upper part of Interval 1 in the Cleveland Basin in Yorkshire is defined by the changing  $\delta^{98/95}\text{Mo}$  values and Re/Mo ratios, which increased and decreased, respectively. Low Re/Mo ratios and high DOP values indicate that conditions were persistently euxinic throughout Interval 2. The  $\delta^{18}\text{O}$  data suggest that there was a gradual increase in temperature in the upper part of Interval 1, followed by a very sudden increase in temperature at exactly the same time as the first abrupt decrease in  $\delta^{13}\text{C}_{\text{org}}$  at the boundary between Intervals 1 and 2. The proxies for continental weathering flux (the seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{187}\text{Os}/^{188}\text{Os}$  ratios) indicate that weathering rates accelerated greatly during the main part of the carbon isotope excursion.

**Figure DR2.****Figure DR2.**

Fluctuations in the areal extent of marine euxinia in the Early Toarcian expressed as a percentage of total seafloor area, calculated using the steady-state model of Ling *et al.*, (2005). Because no data are available on the extent of sites of suboxic and anoxic sediment accumulation in the Toarcian, the model assumes that the variations in  $\delta^{98/85}\text{Mo}$  resulted solely from the expansion and contraction of sites of oxic and euxinic sediment accumulation. The overall decrease in  $\delta^{98/95}\text{Mo}$  indicates that the area of seafloor that was

highly reducing increased periodically by at least an order of magnitude during the Toarcian OAE, and was likely to have encompassed much, if not all, of the continental shelf at that time. Strongly reducing conditions may also have extended into the deep ocean basins, as suggested by the presence of a discrete organic-rich horizon of Toarcian age in allochthonous cherts in Japan (Hori, 1997); at present our data cannot confirm this possibility.

Table DR1

Interval	Sample	Exposure	Ammonite Subzone	Height (m)	TOC (wt %)	$\delta^{98/95}\text{Mo}$ (‰)	[Mo] (ppm)	[Re] (ppb)	Re/Mo (ppb/ppm)
4	Tco 01-62*	S.B.	<i>commune</i>	34.67	2.55	1.68 ± 0.03	7.47	45.97	6.16
	Tco 01-50*	S.B.	<i>commune</i>	29.79	3.41	1.28 ± 0.04	15.86	99.74	6.29
	Tfa 01-44	S.B.	<i>falciferum</i>	26.89	2.08	1.74 ± 0.03	3.34	17.55	5.26
	Tfa 01-34	S.B.	<i>falciferum</i>	21.87	2.03	1.65 ± 0.03	3.92	19.00	4.85
3	Tfa 01-30*	S.B.	<i>falciferum</i>	19.87	3.53	2.12 ± 0.02	15.83	58.54	3.70
	Tfa 01-29	S.B.	<i>falciferum</i>	19.37	3.12	2.14 ± 0.03	42.97	111.32	2.59
	Tfa 01-27	S.B.	<i>falciferum</i>	18.37	3.34	1.84 ± 0.04	33.55	86.04	2.56
	Tfa 01-25	S.B.	<i>falciferum</i>	17.38	3.14	1.74 ± 0.03	23.10	90.15	3.90
	Tfa 01-21*	S.B.	<i>falciferum</i>	15.38	3.41	1.75 ± 0.05	30.49	63.05	2.07
	Tfa 01-18	S.B.	<i>falciferum</i>	13.88	2.26	1.51 ± 0.03	15.84	50.28	3.17
	Tfa 01-16	S.B.	<i>falciferum</i>	12.88	3.45	1.71 ± 0.04	22.52	48.76	2.17
	Tfa 01-15*	S.B.	<i>falciferum</i>	11.88	3.80	2.02 ± 0.03	39.30	83.50	2.12
	Tfa 01-04	P.M.	<i>falciferum</i>	10.20	3.92	2.00 ± 0.04	26.09	61.63	2.36
	Tfa 00-85	H.B.	<i>falciferum</i>	8.65	4.33	1.62 ± 0.03	34.69	97.11	2.80
	Tfa 00-32	P.M.	<i>falciferum</i>	7.44	4.69	1.83 ± 0.03	15.90	75.89	4.77
Tex 00-81	H.B.	<i>exaratum</i>	6.15	3.84	1.62 ± 0.08	9.50	76.21	8.02	
2	Tex 97-46*	P.M.	<i>exaratum</i>	5.42	5.63	1.07 ± 0.03	4.09	17.71	4.33
	Tex 00-22	P.M.	<i>exaratum</i>	4.68	5.97	1.25 ± 0.03	7.58	41.91	5.53
	Tex 00-24	P.M.	<i>exaratum</i>	4.50	6.93	0.98 ± 0.03	4.91	23.08	4.71
	Tex 00-25	P.M.	<i>exaratum</i>	4.30	6.61	1.00 ± 0.07	6.26	19.97	3.19
	Tex 06-38	P.M.	<i>exaratum</i>	4.01	8.90	0.88 ± 0.03	6.43	26.21	4.08
	Tex 06-28	P.M.	<i>exaratum</i>	3.86	14.67	0.83 ± 0.04	7.53	23.75	3.15
	Tex 97-39*	P.M.	<i>exaratum</i>	3.53	9.40	0.81 ± 0.04	14.44	20.76	1.44
	Tex 97-27*	P.M.	<i>exaratum</i>	3.31	10.19	0.97 ± 0.05	15.57	20.99	1.35
	Tex 06-16	P.M.	<i>exaratum</i>	3.08	9.91	0.81 ± 0.03	11.22	23.02	2.05
	Tex 06-08	P.M.	<i>exaratum</i>	2.95	8.64	1.05 ± 0.03	7.57	17.50	2.31
	Tex 06-06	P.M.	<i>exaratum</i>	2.92	12.12	0.97 ± 0.04	6.23	13.63	2.19
	Tex 06-01	P.M.	<i>exaratum</i>	2.81	8.84	1.11 ± 0.06	7.78	16.56	2.13
	Tex 00-74	H.B.	<i>exaratum</i>	2.68	7.84	1.35 ± 0.04	7.46	18.51	2.48
	Tex 00-73	H.B.	<i>exaratum</i>	2.18	9.14	1.53 ± 0.04	5.50	16.82	3.06
	Tex 00-16	P.M.	<i>exaratum</i>	2.08	9.21	1.01 ± 0.03	7.19	14.56	2.03
	Tex 01-02	P.M.	<i>exaratum</i>	1.80	9.89	1.04 ± 0.03	7.12	15.27	2.14

Interval	Sample	Exposure	Ammonite Subzone	Height (m)	TOC (wt %)	$\delta^{98/95}\text{Mo}$ (‰)	[Mo] (ppm)	[Re] (ppb)	Re/Mo (ppb/ppm)
2	Tex 00-72	H.B.	<i>exaratum</i>	1.59	8.70	$1.02 \pm 0.05$	5.96	13.77	2.31
	Tex 97-09	P.M.	<i>exaratum</i>	1.38	9.04	$0.89 \pm 0.04$	6.04	20.23	3.35
	Tex 97-08	P.M.	<i>exaratum</i>	1.38	9.04	$0.88 \pm 0.01$	5.78	28.09	4.86
	TC05-A01	P.M.	<i>exaratum</i>	1.21	4.91	$1.12 \pm 0.04$	6.44	26.33	4.09
	Tex 00-14	P.M.	<i>exaratum</i>	1.16	5.08	$1.04 \pm 0.02$	6.75	32.20	4.77
	Tex 00-71	H.B.	<i>exaratum</i>	1.14	6.61	$1.25 \pm 0.04$	3.83	16.80	4.39
	TC05-A02	P.M.	<i>exaratum</i>	1.09	6.21	$1.22 \pm 0.04$	3.64	14.06	3.87
	TC05-A03	P.M.	<i>exaratum</i>	0.89	7.19	$1.45 \pm 0.03$	3.73	13.88	3.72
	Tex 00-13	P.M.	<i>exaratum</i>	0.67	6.93	$1.57 \pm 0.04$	3.82	13.21	3.46
	Tex 97-28	P.M.	<i>exaratum</i>	0.42	7.80	$1.18 \pm 0.06$	6.12	22.66	3.70
	Tex 97-32	P.M.	<i>exaratum</i>	0.15	8.80	$1.00 \pm 0.05$	7.31	15.47	2.11
	TC05-B01	P.M.	<i>exaratum</i>	0.06	3.47	$1.23 \pm 0.06$	7.96	24.68	3.10
	TC05-B02	P.M.	<i>exaratum</i>	0.04	3.63	$1.14 \pm 0.05$	6.80	19.68	2.89
	TC05-B03	P.M.	<i>semicelatum</i>	-0.01	4.80	$1.33 \pm 0.04$	3.99	15.91	3.99
	TC05-B04	P.M.	<i>semicelatum</i>	-0.16	5.39	$1.38 \pm 0.04$	4.35	15.64	3.59
	Tse 97-36*	P.M.	<i>semicelatum</i>	-0.25	6.65	$1.53 \pm 0.04$	4.06	13.87	3.42
	TC05-C01	H.B.	<i>semicelatum</i>	-0.36	4.52	$1.43 \pm 0.04$	4.28	25.55	5.97
	Tse 00-68	H.B.	<i>semicelatum</i>	-0.46	4.16	$1.06 \pm 0.03$	6.70	44.59	6.66
	TC05-C02	H.B.	<i>semicelatum</i>	-0.63	4.39	$1.32 \pm 0.08$	5.93	42.55	7.18
	Tse 00-15	P.M.	<i>semicelatum</i>	-0.65	5.70	$1.42 \pm 0.04$	3.32	39.97	12.03
TC05-C03	H.B.	<i>semicelatum</i>	-0.68	4.09	$1.33 \pm 0.04$	4.87	38.88	7.98	
TC05-C04	H.B.	<i>semicelatum</i>	-0.73	3.97	$1.58 \pm 0.04$	4.03	35.79	8.89	
1	Tse 00-67	H.B.	<i>semicelatum</i>	-0.96	4.20	$1.59 \pm 0.04$	4.59	35.25	7.68
	Tse 00-66	H.B.	<i>semicelatum</i>	-1.21	4.20	$1.48 \pm 0.05$	4.89	44.95	9.20
	Tse 00-65*	H.B.	<i>semicelatum</i>	-1.71	4.06	$1.37 \pm 0.05$	3.03	39.54	13.05
	Tse 00-63	H.B.	<i>semicelatum</i>	-3.00	2.29	$1.25 \pm 0.04$	1.15	9.61	8.33
	Tse 00-62	H.B.	<i>semicelatum</i>	-3.50	1.77	$0.99 \pm 0.02$	1.10	10.78	9.76
	Tse 00-60	H.B.	<i>semicelatum</i>	-4.50	1.79	$0.33 \pm 0.04$	0.51	5.44	10.62
	Tte 00-59	H.B.	<i>semicelatum</i>	-5.02	1.42	$-0.30 \pm 0.04$	0.39	6.39	16.37
	Tte 00-58	H.B.	<i>tenuicostatum</i>	-5.62	1.62	$-0.04 \pm 0.04$	0.49	6.07	12.48
	Tte 00-53	H.B.	<i>tenuicostatum</i>	-8.07	1.41	$0.04 \pm 0.04$	0.43	4.68	10.77
	Tpa 00-44	H.B.	<i>paltum</i>	-12.07	1.39	$-0.46 \pm 0.04$	0.41	3.01	7.38



**Table DR1.**

Sample locations and stratigraphic positions with TOC,  $\delta^{98/95}\text{Mo}$ , [Mo], [Re] and Re/Mo data for mudrocks from the Whitby Mudstone Formation, Yorkshire, UK. The  $\delta^{98/95}\text{Mo}$  measurements are presented with respect to the in-house Mo standard and uncertainties are the internal 2 s.e. of the measurement. Sample localities are Saltwick Bay (S.B.), Port Mulgrave (P.M.) and Hawsker Bottoms (H.B.). Ammonite subzones are taken from (Howarth, 1962, 1992) and heights are given with respect to the base of the *exaratum* Subzone, defined as the base of bed 33 (Howarth, 1962, 1992). Os-isotope analyses have been performed (Cohen *et al.*, 1999, 2004) on samples marked \*. Intervals 1 to 4 refer to the divisions of the succession that have made on geochemical criteria (see main text for details).

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