

GSA DATA REPOSITORY ITEM DR2009125

APPENDIX 1: SAMPLE PREPARATION:

Samples were ground in a Si-nitride ball mill, sieved, ashed to burn off organic matter and digested using nitric and hydrofluoric acids. An aliquot of each sample was taken to determine elemental concentrations by ICP-MS (Thermo X-Series). Most elements were analyzed using a multi-element external standard solution and an internal standard of 3 ppb Be, In and Bi to monitor for drift in instrument sensitivity due to matrix or other effects. Mo concentrations were additionally determined by isotope dilution using a calibrated ^{97}Mo spike solution. These accurate Mo concentration data provided a baseline against which to determine the yield of Mo chemical separation and purification procedures (>95% yield is important to assure no significant isotope fractionation during these procedures). The Mo from the remainder of the samples was separated and purified by two-stages of ion exchange chemistry, with particular attention to removing Zr (using an anion exchange column; AG1X-8 100-200 mesh resin) and Fe (using a cation exchange column; AG50WX-8, 200-400 mesh). The only difference between this chromatography and procedures cited in the main text is that Mo was eluted from the cation column in 0.5 M HCl instead of 1.5 M HCl, taking advantage of the higher partition coefficient of Mo in the weaker acid to achieve a cleaner separation of Mo from Fe. An aliquot of each processed solution was then analyzed by ICP-MS to determine Mo concentrations for yield assessment and to monitor for impurities that could complicate isotopic analysis. Prior experience (e.g., Arnold et al., 2004b) as well as experience gained during this study demonstrated the importance of sample purity to prevent instability in instrumental mass fractionation, and particularly instability in the relative fractionation behaviors of Mo and Zr.

Data are reported using the δ notation, relative to our in-house standard (Johnson Matthey Chemical, Specpure lot #702499I), where

$$\delta^{98/95}\text{Mo} = \left(\frac{{}^{98}\text{Mo}/{}^{95}\text{Mo}_{\text{sample}}}{{}^{98}\text{Mo}/{}^{95}\text{Mo}_{\text{standard}}} - 1 \right) \times 1000$$

Modern seawater has a value of $2.34 \pm 0.20\%$ (2σ) on this scale (Arnold et al., 2004).

Where necessary, published DOP values were supplemented with measurements made as part of this study. Reactive iron was extracted with the boiling HCl method (Berner, 1970; Canfield, 1989; Lyons, 1997; Raiswell et al., 1994) and measured by the Ferrozine method (To et al., 1999; Viollier et al., 2000), while the chromium volatile sulfur method measured weight percent pyrite sulfur (Canfield et al., 1986). Ideal pyrite stoichiometry was assumed in calculating DOP; pyrite iron is divided by the sum of reactive iron and pyrite iron (Raiswell et al., 1988; Werne et al., 2002).

APPENDIX 2: DATA ARCHIVE

Table 1. $\delta^{98/95}\text{Mo}$ values of samples measured at University of California, Santa Barbara. n is the number of replicate Neptune measurements. Each entry indicates a separate chemical extraction and purification, beginning from a separate powder split. 2σ for an individual chemistry represents the internal error on replicate measurements of the same purified solution while the 2σ for replicate chemistries represents the external error for samples from that depth.

Table 2: Elemental concentration data corresponding to the isotope data are from (Sageman et al., 2003), as determined by ICP-MS after multi-acid total digestion. DOP and Fe-HCl measurements in bold were determined in the course of this study. SDO-1, a Devonian Ohio shale reference material available from the USGS, is shown for comparison.

References Cited

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	$\delta^{98/95}\text{Mo}$	2σ	n	<i>average of replicate chemistries</i>		
				$\delta^{98/95}\text{Mo}$	2σ	n
Geneseo Formation						
162.72	0.85	0.10	3	0.85	0.10	3
163.12	1.16	0.13	3			
replicate	1.22	0.05	3	1.19	0.11	6
164.7	1.28	0.02	3			
replicate	1.25	0.07	3	1.26	0.05	6
166.9	1.21	0.03	3			
replicate	1.20	0.05	3	1.21	0.04	6
167.1	1.01	0.09	3			
replicate	1.09	0.11	3	1.05	0.12	6
169.62	1.32	0.15	3	1.32	0.15	3
170.97	1.00	0.10	3			
replicate	1.05	0.07	3	1.03	0.10	6
Oatka Formation						
329.48	1.36	0.11	3	1.36	0.11	3
333.12	1.69	0.12	3			
replicate	1.74	0.11	3	1.72	0.12	6
334.63	1.89	0.08	3	1.89	0.08	3
335.87	1.74	0.04	3			
replicate	1.79	0.07	4	1.77	0.07	7
336.69	1.86	0.10	3			
replicate	1.92	0.04	4	1.89	0.09	7
338.53	1.66	0.11	4			
replicate	1.64	0.03	3	1.65	0.08	7
341.09	1.96	0.04	3	1.96	0.04	3
341.61	1.48	0.07	3			
replicate	1.46	0.04	3	1.47	0.06	6

Sample	Org C (wt %)	Al (wt%)	Ti (wt%)	V (ppm)	Cr (ppm)	Mn (ppm)	Fe-HCl (wt %)	Fe-pyr (wt %)	Mo (ppm)	DOP	Mo/Al	Mo/Ti
Geneseo Formation									paper			
162.72 (core depth in m)	1.84	9.12	0.4	183	99	341	1.76	1.15	15	0.39	0.00016	0.0038
163.12	1.05	8.13	0.37	258	98	273	1.66	0.43	33	0.21	0.00041	0.0089
164.7	5.79	6.76	0.3	133	55	372	1.35	0.98	6	0.42	0.00009	0.0020
166.9	2.83	6.29	0.27	269	47	303	1.21	0.49	28	0.29	0.00045	0.0104
167.1	6.40						0.42		23	0.58		
169.62	4.84	8.54	0.32	166	96	254	0.87	0.60	4	0.41	0.00005	0.0013
170.97	2.84						0.88		1	0.33		
Oatka Formation												
329.48 (core depth in m)	0.8	3.43	0.14	55	13	417	0.91	1.00	2	0.52	0.00006	0.0014
333.12	8.68	7.61	0.32	277	85	146	0.67	4.55	173	0.87	0.00227	0.0541
334.63	11.19	6.29	0.27	328	54	120	0.36	7.56	251	0.95	0.00399	0.0930
335.87	9.51	6.32	0.29	310	53	154	0.50	5.41	192	0.92	0.00304	0.0662
336.69	17.3	6.48	0.26	421	58	129	0.58	6.35	394	0.92	0.00608	0.1515
338.53	4.81	8.54	0.38	150	85	186	0.68	1.80	15	0.73	0.00018	0.0039
341.09	0.39	0.23	0.02	4	0	173	0.11	1.72	1	0.94	0.00043	0.0050
341.61	18.08						0.12		250	0.81		
SDO-1	8.98	6.50	0.42	160	66	325			134		0.00206	0.0318