

Detailed Methodology

The Amoco Production Company Rebecca K. Bounds core (E006; 38.489628 °N, -101.974552 °W) was drilled in Greeley County, Kansas (Figure 1; Dean and Arthur, 1998). The core includes a 47 meter thick section of the Niobrara Formation, from the Carlile boundary to the middle of the Smoky Hill Member. The USGS Portland #1 core (E099; 38.37667°N, -105.02167°W) was drilled in Freemont County, Colorado (Figure 1; Dean and Arthur, 1998). The Portland core includes a 75-meter thick Niobrara Formation section including the Fort Hays Member and a partial Smoky Hill Chalk Member. The Bounds and Portland cores were sampled at 1 m and 0.5 m resolution, respectively, at the USGS Core Research Center in Denver, CO. Samples were ground to <75 µm and homogenized in an alumina shatterbox at the University of Michigan.

Analyses for Al, Fe, and Mo concentrations were completed at ALS Laboratories in Vancouver, BC. Whole rock samples were digested with perchloric, hydrofluoric, nitric, and hydrochloric acids. Concentrations were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). GBM908-10, GBM908-5, OREAS 90 and MRGeo08 standards were used to verify elemental concentrations.

Pyrite Fe extractions were made following Canfield et al. (1986). The pyrite fraction is stoichiometrically determined following precipitation of chromium reducible sulfide as ZnS. Sequential iron extractions were completed following Poulton and Canfield (2005) at the University of Michigan. Carbonate-associated Fe (Fe_{carb}), magnetite Fe (Fe_{mag}), and Fe (oxyhydr)oxides (Fe_{ox}) are considered highly reactive (HR) because these phases react with sulfide on timescales of months to years (Poulton and Canfield, 2005). These three phases were separated using the following sequential extraction: Fe_{carb} phase was extracted in 10 mL 1 M Na-acetate (pH 4.5; shake for 48 hours), the Fe_{ox} phase was extracted in 10 mL of citrate-buffered Na-dithionite (pH 4.8; shake for 2 hours), and the Fe_{mag} phase was extracted in 10 mL ammonium oxalate (pH 3.2, shake for 6 hours). Concentrations of Fe_{carb} , Fe_{ox} , and Fe_{mag} were measured on ICP-MS (Thermo iCAP Q) within the STARLAB at Central Michigan University. Analytical precision and accuracy, determined from replicate analyses ($n=21$) of a certified standard (SCP Science) were better than 5%. Calculated pyrite Fe concentrations generally replicated with <5% precision. All geochemical data discussed in this paper are archived in Pangaea (www.pangaea.de).

XAFS spectroscopy consists in two complementary techniques: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). XANES provides information on the oxidation state, ligand type, presence of double bonds, and coordination chemistry; while interatomic distances, coordination number, and type of nearest atoms can be determined following EXAFS data interpretation.

Sample holders were prepared from a 1 mm thick Teflon plate by cutting rounded holes as samples slots. Samples (as powder) were transferred and flattened to obtain an even surface in sample slot that were sealed with Kapton tape. X-ray Absorption Fine Structure (XAFS) analyses were run at beamline 13-BM-D at the Advanced Photon Source (APS) – Argonne National Laboratory. Si (111) double crystal monochromator was used in conjunction with harmonic rejection mirrors. Fluorescence X-rays were measured using a Canberra 16 element

Ge detector. The incident beam intensity was detuned by ~20 – 30% to reject higher-order harmonic frequencies.

The Mo K-edge is located at 20000 eV. All spectra were collected with energy and wave number resolution prior to the edge (19800 – 19950 eV); across the Mo K-edge (19950 – 20050 eV); and throughout the EXAFS region (20050 – 20800 eV) at 5 eV, 0.5 eV, and 0.05 Å⁻¹, respectively. At least three spectra per sample were merged to improve signal-to-noise ratio and energy resolution. Energy calibration was maintained by simultaneous measurements of a Mo(0) foil in transmission mode as an internal standard. The first and fourth peaks in the first derivative of the Mo(0) foil were assigned 20000.0 and 20039.1 eV. For data interpretation, jordisite (an amorphous Mo(IV)S₂ phase) and five other Mo standards were also characterized: Mo(IV)O_{2(s)}, Mo(IV)S_{2(s)}, Mo(VI)O_{3(s)}, Mo(VI)O₄²⁻_(l), and Mo(VI)S₄²⁻_(l) (Dahl et al., 2013; Ardakani et al., 2016). All data were processed and analyzed using the Demeter software package containing Athena and Artemis (Ravel and Newville, 2005).

Data for EXAFS were processed with the Demeter package (Athena software; Ravel and Newville, 2005). Briefly, the background absorption was subtracted and average spectrum slightly smoothed for each sample. In the fitting process, coordination numbers for each atom *i* were fixed; while total amplitude of the photon energy (A_0), interatomic distance between Mo and the *i* atom (R_i), the zero point of the energy scale (E_0), and the Debye-Waller factor (σ_i) were allowed to vary. The rest of the parameters were estimated theoretically in Artemis using FEFF8 code for calculations of atomic scattering amplitudes, including the effective scattering amplitude of backscattering X-ray photons, which depends on type and number of neighboring atoms, the effective scattering phase functions, and the mean free path.

Acceptable fits satisfied three criteria: (1) the total amplitude (A_0) was allowed to float between 0.7 and 1.1, but was fixed at the same value for all shells; (2) the energy shift (E_0) was restrained within ± 10 eV from E_0 ; (3) the Debye-Waller factors (σ_i) were allowed to float within a range of 0.003 – 0.020 Å² or fixed at 0.003 Å². To test different possibilities, scattering paths from the following atoms were fitted: Mo—O, Mo—S, Mo—Mo, and Mo—Fe. The best model fit was selected among acceptable fits based on the model run with lowest R-factor. Multiple scattering paths were evaluated, but did not contribute significantly to all spectra and thus were omitted in final fits. The EXAFS function was Fourier transformed using k^2 weighting to run model fits on Fourier transform data (R-space). The fitting domain ranged from 1.4 to 4 Å.

Figure DR1: XANES spectra of E099 samples (solid black lines), E006 samples (solid gray lines) and Mo reference compounds (dashed lines). The black dots identify the maximum absorption energy (E_m).

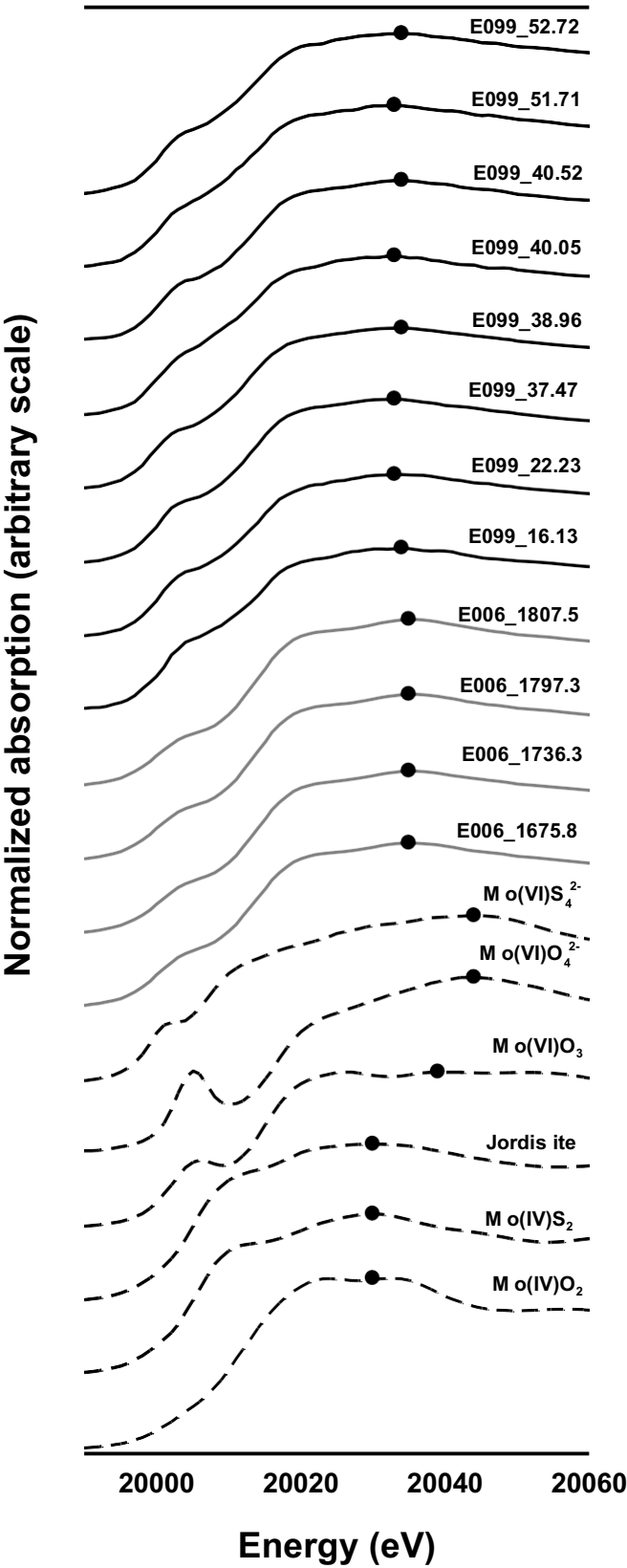


Figure DR2. Mo concentrations and average oxidation states for U.S. Geological Survey Portland (black) and Amoco Rebecca Bounds (gray) samples.

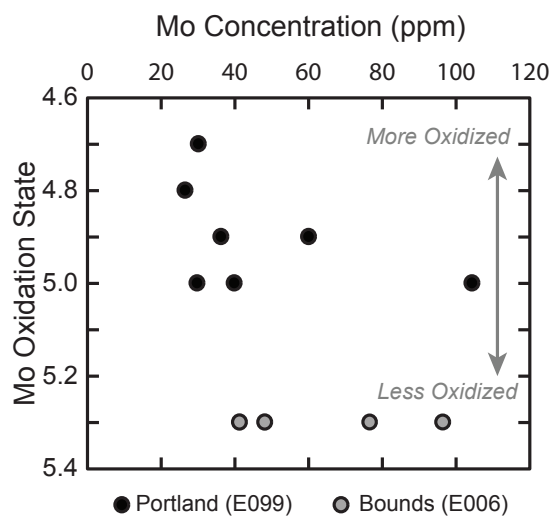


Table DR1: E_m (eV) and derived Mo oxidation state

Samples	E_m (eV)	Average Mo oxidation state
Reference materials		
Mo(IV)O ₂	20030.0	4.0
Mo(VI)O ₃	20038.0	6.0
E006_1675.8	20035.1	5.3
E006_1736.3	20035.0	5.3
E006_1797.3	20035.0	5.3
E006_1807.5	20035.1	5.3
E099_16.13	20033.2	4.8
E099_22.23	20033.5	4.9
E099_37.47	20033.8	4.9
E099_38.96	20033.9	5.0
E099_40.05	20032.7	4.7
E099_40.52	20033.9	5.0
E099_51.71	20032.9	4.7
E099_52.72	20033.9	5.0

Table DR2: EXAFS Fit in R space from R = 1–4 Å

Samples	Mo--O			Mo--S			R factor
	n	r (Å)	σ^2	n	r (Å)	σ^2	
E006_1675.8	3	1.70±0.07	0.003*	1	2.35±0.04	0.005±0.003	0.07
E006_1736.3	3	1.70±0.03	0.003*	1	2.34±0.06	0.006±0.008	0.06
E006_1797.3	3	1.69±0.03	0.005±0.006	1	2.36±0.07	0.011±0.009	0.03
E006_1807.5	3	1.70±0.03	0.004±0.006	1	2.36±0.08	0.012±0.011	0.03
E099_16.13	2	1.68±0.07	0.003*	2	2.33±0.09	0.004±0.006	0.15
E099_22.23	2.3	1.72±0.02	0.003*	1.7	2.39±0.03	0.003*	0.05
E099_37.47	2.7	1.70±0.02	0.006*	1.3	2.37±0.03	0.003*	0.04
E099_38.96	2.4	1.70±0.01	0.003*	1.6	2.37±0.02	0.003*	0.02
E099_40.05	1.3	1.70±0.04	0.003*	2.7	2.38±0.05	0.003±0.003	0.09
E099_40.52	2.4	1.71±0.03	0.005±0.003	1.6	2.39±0.04	0.003*	0.06
E099_51.71	1.6	1.70±0.03	0.003*	2.4	2.37±0.04	0.008±0.004	0.08
E099_52.72	2.4	1.70±0.05	0.005±0.009	1.6	2.36±0.07	0.003±0.005	0.008