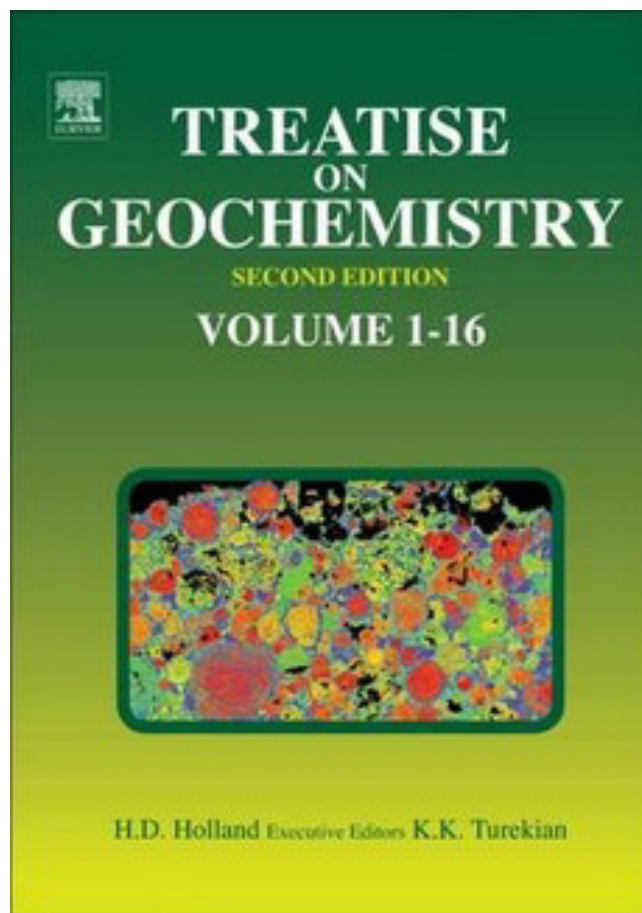


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13.12 Geochemistry of a Marine Phosphate Deposit: A Signpost to Phosphogenesis

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13.12.1 Introduction

Phosphorus is a critical element in many biologically active compounds (e.g., DNA, RNA, ATP, and bone apatite), an essential nutrient for all living things. As Isaac Asimov (1974) wrote, “we are able to substitute nuclear power for coal power, and plastics for wood, and yeast for meat, and . . . , but for phosphorus there is neither substitute nor replacement.” In the fullest sense, it is the limiting nutrient among the list of essential nutrients for plant and animal growth. Its major use today is as fertilizer to enhance crop yields. Its major source is marine sedimentary phosphate deposits, or phosphorites (Bentor, 1980; McKelvey et al., 1952), that provide approximately 80% of the world phosphate supply (US Geological Survey, 2006).

Sedimentary phosphate deposits are found in rocks of all ages, but the larger deposits are distributed unevenly both geographically and stratigraphically (Cook and McElhinny, 1979). Approximately 75% of the world demand comes from marine sedimentary rocks of (1) Precambrian to Cambrian age that occur in Australia, China, Mongolia, and Russia; (2) Cretaceous to Tertiary age that occur along the northern rim of Africa from Morocco to Tunisia, Egypt, Israel, and Jordan; and (3) Tertiary age that are present along the eastern seaboard of the United States from North Carolina to Florida.

The igneous phosphate deposit on the Kola Peninsula (Luzin et al., 1993; Notholt and Sheldon, 1986) has supplied Russia with a major part of its phosphate demand for more than half a century, but it constitutes only about 10% of the world production. Insular phosphate deposits, whose source was bird guano (Hutchinson, 1950), were important sources of phosphate during the latter part of the nineteenth century. On the Chincha Islands off the coast of Peru, the guano achieved a thickness of 45 m. The deposits on islands in the central Pacific Ocean, for example, Makatea, Baker, Nauru, and Ocean (Ellis, 1935; Elschner, 1913; Montaggioni et al., 1985), formed from guano leached of phosphate by rainwater and seawater. The water, on contact with the underlying coral, reacted to precipitate pelletal

carbonate fluorapatite (CFA) coeval with the formation of a pinnacled karst platform, or karrenfeld (Piper et al., 1991). These deposits were discovered approximately 100 years ago and provided a few percent of the world demand throughout much of the twentieth century. Mining on Nauru has only recently virtually ceased. A submerged phosphate deposit on Mataiva Atoll (Rossfelder, 1990) has not been exploited.

The geochemistries of the igneous and insular deposits are extremely interesting, but the discussion in this chapter is limited to the geochemistry of the marine sedimentary deposits. Phosphate occurs in these deposits primarily as the mineral francolite, a CFA with a stoichiometry adapted by Kolodny and Luz (1992) from McClellan and Lehr (1969). Kolodny and Luz noted several trace elements that substitute for the major elements in the lattice structure, notably the rare earth elements (REE), U, Sr, and the oxyion of SO_4^{2-} , and discussed the isotopes of C, S, O, Sr, and U (Figure 1). This rather complex isotopic composition and trace-element substitution enhances the use of the geochemistry of the CFA as a record of the marine environment within which phosphorites accumulate.

13.12.2 Statement of the Problem

The accumulation of phosphate along the continental shelves of southwest Africa (Baturin, 1971, 1982) and western South America (Burnett and Froelich, 1988) as pelletal and nodular concretions calls for a comparison of the biogeochemistry and the seawater hydrography under which these deposits are accumulating with the depositional conditions under which the ancient marine deposits formed (Bentor, 1980). The deposit on the continental shelf of Peru is accumulating within the eastern boundary Peru Current under conditions of intense coastal upwelling of nutrient-enriched waters into the photic zone from a few tens of meters depth (Richards, 1980), similar to conditions along SW Africa (Calvert and Price, 1983;

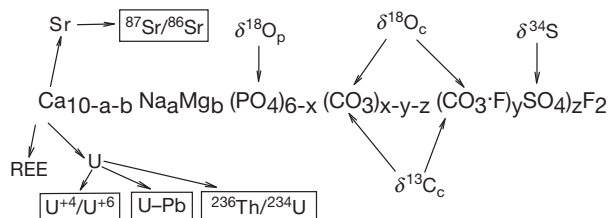


Figure 1 Stoichiometry of carbonate fluorapatite advanced by Kolodny and Luz (1992), which was adapted from McClellan and Lehr (1969).

Kuypers et al., 2005). Primary productivity along the Peru coast (Chavez and Barber, 1987) is perhaps the highest in the ocean today. Oxidation of the fraction of organic detritus that settles out of the photic zone maintains suboxic to rarely anoxic conditions between 100 and 500 m in the water column (Codispoti, 1980; Dugdale et al., 1977; Richards, 1975), corresponding to the depth interval over which CFA is accumulating (Burnett and Froelich, 1988). The organic matter that escapes oxidation in the water column and settles onto the shelf is oxidized largely in the surface and near-surface sediments, leading to the precipitation of CFA in the uppermost few millimeters to centimeters of the sediment (Burnett et al., 1988).

Kazakov (1937) was the first to propose a connection between the accumulation of marine phosphate deposits and ocean upwelling. He viewed the CFA as precipitating within the water column. It is now clear from age-dating and $\delta^{13}\text{C}$ analyses of the CFA that precipitation occurs mostly in the upper few millimeters to centimeters of the sediment (Burnett et al., 1988; Kolodny, 1981), not in the water column. Nevertheless, Kazakov's observations have been crucial to the advancement of a comprehensive understanding of these deposits. Although the exact relationship among the various diagenetic reactions occurring within the sediments that control the precipitation of CFA remains unclear (e.g., Goldhammer et al., 2010; Schuffert et al., 1994), its precipitation at and near the benthic boundary is well established, with minor precipitation extending to depths greater than several centimeters.

Deciphering the water-column chemistry and hydrography of the ancient phosphogenic environments from a comparison of their elemental geochemistry with the geochemistry and hydrography of modern phosphogenic environments is limited (Bentor, 1980), even though many of the physical and geochemical properties of the ancient deposits are shared with modern deposits. For example, the Peru deposit is composed of hardgrounds, nodules, gravels, pelloids, and micronodules to ocean depths as great as 400 m (Garrison and Kastner, 1990). Their distribution within the sediments can be interrupted by units of silty diatomaceous mud (Garrison and Kastner, 1990), possibly a result of a highly variable sedimentation rate of the lithogenous fraction that may reflect the high tectonic activity of the environment. The Pungo River Formation is one member of the series of Tertiary phosphate deposits along the eastern margin of the United States (Riggs, 1979; Riggs et al., 1982). The deposit exhibits somewhat similar textures that are related to reworking at shallow seafloor depths during ocean transgression/regression events (Riggs et al., 1997), rather than to tectonic activity. Similarly, the Permian Phosphoria Formation in

the northwestern United States was apparently deposited during a series of ocean transgression/regression events (Sheldon, 1984) that may not have, however, resulted in extensive reworking of the deposit (Sheldon, 1989).

The stratigraphy and mineral resources of many of the world's phosphate deposits (Ames, 1994; Baker and Allen, 1990; Bentor, 1980; Cabezon, 1989; Cook and Shergold, 1986; Eganov et al., 1984; Föllmi, 1996; Hein, 2004; Ilyin et al., 1989; Nathan and Shiloni, 1989; Prévôt and Lucas, 1980; Riggs, 1984; Riggs et al., 1990; Southgate, 1986; Trappe, 1998) have been presented in three volumes edited by Cook and Shergold (1986), Notholt et al. (1989), and Burnett and Riggs (1990). Most (1) suffered reworking during their deposition, such as the Tertiary deposits of the eastern United States (Riggs et al., 1990, 1997), the Cretaceous deposits of the Paris Basin (Jarvis, 1992), and the Cambrian/Precambrian deposits in the Georgina Basin of Australia (Southgate, 1986); (2) were altered during burial, as were the Cambrian deposits in Kazakhstan (Ilyin et al., 1989); and/or (3) were strongly leached during weathering, as were the deposits in Morocco (Lucas et al., 1980; McArthur, 1980). These processes led to an enrichment of CFA following deposition but likely masked much of the original geochemical signature of deposition.

The focus here is on the Meade Peak Member (MPM) of the Phosphoria Formation for the following reasons: (1) It provides about 12% of the US production (Jasinski et al., 2004) and is an important supplier to the world phosphate market (US Geological Survey, 2006); (2) its composition has been measured in great detail (Gulbrandsen, 1966; Herring and Grauch, 2004; Herring et al., 2001; Hiatt and Budd, 2001, 2003; McKelvey et al., 1959; Medrano and Piper, 1995; Piper et al., 2000); and (3) its composition has largely survived alteration since deposition, suggesting that its present elemental composition reflects the marine biology, water-column chemistry, and hydrography of the Phosphoria Sea during deposition. An examination of the geochemistry of the deposit at the single location at the Hot Springs mine (Figure 2), sampled underground along a mine adit (Gulbrandsen, 1979; Piper et al., 2000), suggests that the MPM may have experienced less alteration at this site than at natural outcrops and surface exposures in mining areas located elsewhere within the vast area of its distribution (Grauch et al., 2004; McKelvey et al., 1959).

The following properties of the MPM are considered: (1) the distribution of elements hosted by a largely nonreactive lithogenous fraction of the sediment; (2) the accumulation rates of trace metals – Cd, Cu, Ni, Zn, Cr, Mo, U, and V – that are now present as metal sulfides, oxyhydroxides, organic complexes and that also substitute in CFA and the silicate minerals (Piper, 2001); (3) the accumulation of the REE that substitute for Ca within the CFA (Ilyin, 1998; Kolodny and Luz, 1992; Piper, 2001); and (4) the composition of the stable oxygen and carbon isotopes of the CFA and associated carbonate minerals (Hiatt and Budd, 2001, 2003; Kolodny and Luz, 1992; Piper and Kolodny, 1987; Shemesh et al., 1988). The interest here, however, is in the original sources of the elements – terrigenous siliciclastic debris and seawater – rather than in their current host phases. The analysis of the samples collected at an interval of approximately 25–50 cm at the Hot Springs mine (Piper et al., 2000), without regard to lithology (Figure 3), allows the elements to be partitioned between these two sources,

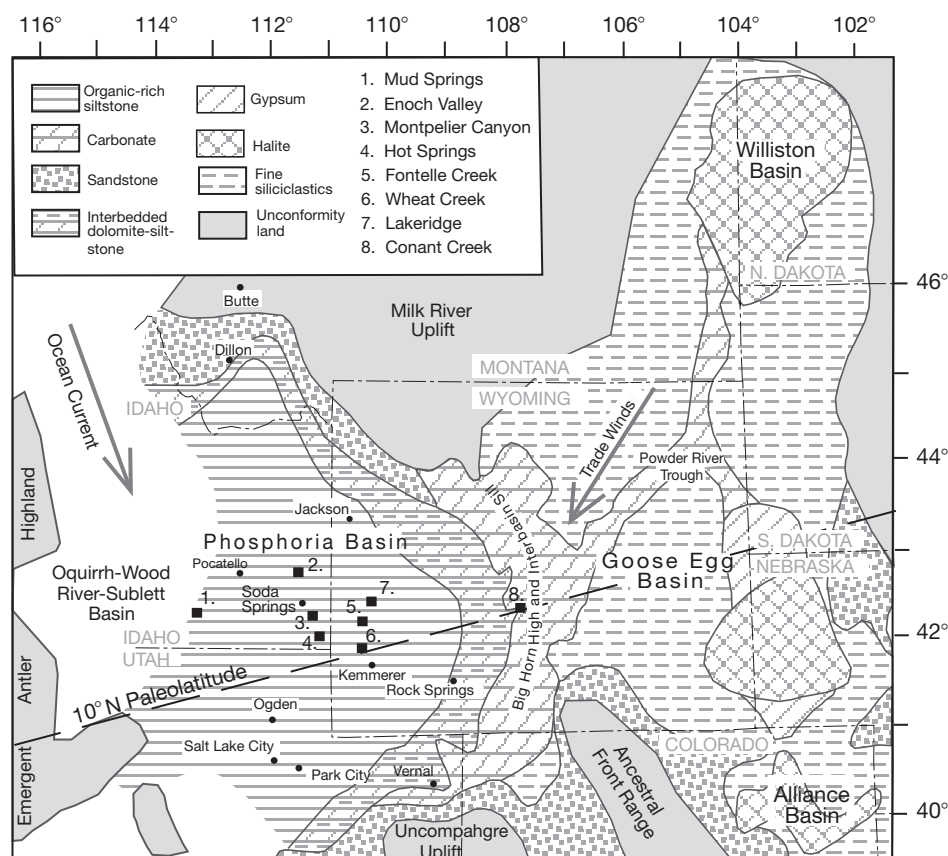


Figure 2 Map of the Phosphoria Basin. Station locations (1–8) have been sampled for chemical analysis (Gulbrandsen, 1979; Medrano and Piper, 1995; Sheldon et al., 1963). Paleolatitude was reported by Sheldon (1964). Adapted from Maughan EK (1994) Phosphoria Formation and its resource significance in the western interior, U.S.A. In: Embry AF, Beauchamp B, and Glass DJ (eds.) *Pangea: Global Environments and Resources*, CSPG Memoir 17, pp. 479–495. Calgary, AB: Canadian Society of Petroleum Geologists.

whereas their rates of accumulation may establish the biogeochemistry and hydrography of the Phosphoria Sea. A similar partitioning of elements in other deposits, even if retained only partially, may also allow these aspects of deposition to be deciphered, although perhaps less definitively.

13.12.3 The MPM: Local Setting

The Phosphoria Formation is perhaps the largest single phosphate deposit in the world (Trappe, 1998). In the central region of the formation (Figure 2), where it is composed mostly of black phosphatic mudstones and phosphorites (Sheldon 1989), it has been designated the MPM (Figure 3). It commonly exhibits a friable, laminated texture that is present on a sub-millimeter scale observed in thin sections to decimeter-thick beds that can be traced over thousands of square kilometers (Sheldon, 1989). The member exhibits a “general absence of wave marks and cross-bedding” (McKelvey et al., 1959). Although such features are present in the formation (Trappe, 1998), they are likely restricted to the margins of the basin. The MPM maintains a relatively uniform thickness of 50–55 m throughout much of the region (McKelvey et al., 1959).

Sulfide minerals, mostly pyrite and sphalerite, are common throughout the member (Piper and Perkins 2004), plus the

ammonium feldspar buddingtonite (Knudsen et al., 2000). Organic-carbon (C_{org}) commonly achieves concentrations of 10% (Herring et al., 2001; Maughan, 1994; Piper et al., 2000) and rarely more than 20%. Organic matter, approximately 1.5 times C_{org} (Powell et al., 1975), exhibits a depth profile similar to that of the heavy mineral zircon (see following sections). Taken together, these properties suggest that within the central region of the Phosphoria Sea, the MPM suffered minimal winnowing and reworking during deposition. Chemical alteration following deposition is represented by the precipitation of several trace elements and minerals in small veins and as overgrowths (Grauch et al., 2004). However, the interelement relationships that are discussed here indicate that alteration following deposition may have been on a limited scale with minimal loss of major and trace elements.

The MPM extends over an area of $\sim 21\,500\text{ km}^2$ of the full $350\,000\text{ km}^2$ extent of the Phosphoria Formation (McKelvey et al., 1959; Sheldon 1989). It accumulated within the Phosphoria Sea located along the western margin of North America (Figure 2) at 10° – 20°N latitude in the belt of trade winds (Scotese and Langford, 1995; Sheldon, 1964). Its deposition extended for a period of approximately 3.75 My, beginning in Kungurian time (Gradstein et al., 2004) and continuing into Wordian time (Figure 3), spanning the boundary between the *Mesogondolella idahoensis* and *Mesogondolella serrata* conodont

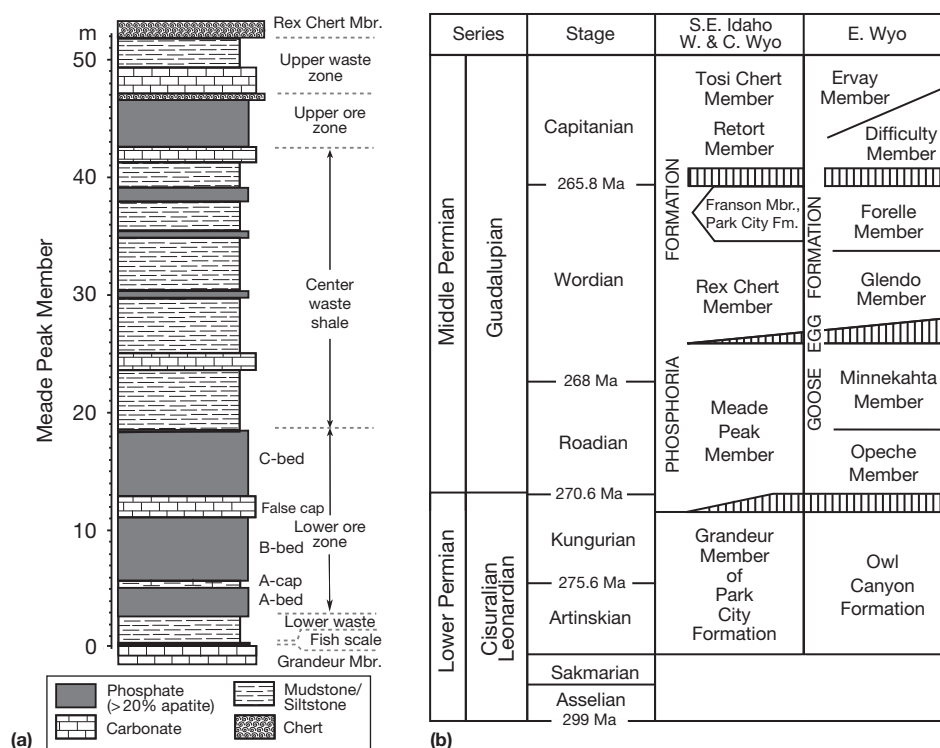


Figure 3 (a) Stratigraphic column of the Phosphoria Formation in southeast Idaho/western Wyoming and (b) its relationship to formations of correlative ages to the east. Field names and mining terms are listed in the right-hand column of frame (a). The waste zones, which are not recovered during mining, contain significant phosphorus contents but in relatively thin beds that are separated by less rich shales and mudstones. Ages are estimated from Gradstein et al. (2004).

biozones (Wardlaw and Collinson, 1980). The sea occupied a foreland basin that was only partially isolated from the open ocean (Hein, 2004; Hiatt and Budd, 2001) by an island arc to the west (Stevens et al., 2005). Phosphate deposition extended from the shallow areas of the basin in Wyoming, Montana, Utah, and Nevada into the deeper parts of the basin in western Wyoming and southeastern Idaho, where the basin depth was likely in the range of 300–350 m (Piper, 2001). The breadth of the deposit in the Phosphoria Sea may be explained by the extent of high primary productive systems in the ocean today that can extend several hundred kilometers across continental shelves (Behrenfeld and Falkowski, 1997).

Within southeastern Idaho, the Phosphoria Formation consists mainly of chert, carbonaceous mudstone, and pelletal phosphorite. In south central Montana and northwestern Wyoming, these units intertongue with a sandy sequence, although thin units of phosphatic and cherty rocks persist over much of the area (McKelvey et al., 1959; Sheldon 1989). The beds intertongue with a dominantly carbonate sequence in central Wyoming and with red beds and evaporites of the Goose Egg Formation into eastern Wyoming (Figures 2 and 3). Correlation of these units is based on their physical stratigraphy and brachiopod and conodont biostratigraphy (Wardlaw, 1979).

The MPM alone increases in thickness from east to west, much less than the Phosphoria Formation as a whole (McKelvey et al., 1959). The accumulation of CFA was $\sim 1.46 \times 10^{17}$ g P (Sheldon, 1989), as compared to $\sim 7.4 \times 10^{17}$ g P for the entire

Phosphoria Formation (McKelvey et al., 1952). The approximate rate of accumulation of P was

$$\text{P accumulation rate} = \left[1.46 \times 10^{17} \text{ g P} \div 21\,500 \text{ km}^2 \right] \div 3.75 \text{ My} = 1.8 \text{ g P m}^{-2} \text{ year}^{-1}$$

Assuming this represents 10% of the P taken up by phytoplankton in the photic zone, that is, the approximate 10% of primary productivity that escapes oxidation in the water column to ~ 250 m in the ocean today (Berger et al., 1988; Karl and Knauer, 1991; Sarnthein et al., 1988), Redfield stoichiometry of the organic matter (Redfield et al., 1963), in which the P: C_{org} ratio is ~ 0.025 (by mass), would have required primary productivity of $720 \text{ g } C_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}$. The lack of detailed age dating limits the calculation to an average, but even this value reveals a similarity between the Phosphoria Sea and the eastern boundary current along the Peru Shelf, where primary productivity achieves $770 \text{ g } C_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}$ (Chavez and Barber 1987). This accumulation rate of P in the MPM represents about 3.4% of today's P river flux into the world's ocean (Froelich et al., 1982). The enormity of the rate can be appreciated when it is realized that the Phosphoria Sea covered 0.006% of the surface area of the ocean. Such a concentration of biological activity is present along the Peru Shelf, where $\sim 20\%$ of the total fish recovered from the world's ocean each year is taken off this coast (Chavez and Messié, 2009). The role of ocean upwelling to this catch cannot be overstated, nor can its importance to the accumulation of P within the Phosphoria Sea in Permian

time (Hiatt and Budd, 2003; McKelvey et al., 1959; Parrish, 1987; Peterson, 1980; Piper, 2001; Sheldon, 1989).

The mean composition of the MPM at the Hot Springs mine (Table 1) is apatite (41%), lithogenous sediment (30%),

C_{org} (6.2%), calcite and dolomite (13%), and chert (~10%) (Piper et al., 2000), yielding an accumulation rate for the lithogenous fraction alone of 0.58×10^{-3} cm year⁻¹. The Phosphoria Basin was a sediment-starved basin, in which minimal dilution

Table 1 Elemental composition of four rock standards – world shale average (WSA), North American shale composite (NASC), upper continental crust (UCC), and lower continental crust (LCC) – and the lithogenous fraction and mean bulk composition of the MPM at the Hot Springs mine

Element	World shale ^a average	North American ^b shale composite	Upper continental crust ^c	Lower continental crust ^d	Hot Springs mine lithos. fraction ^e	Hot Springs mine bulk composition ^e
	(%)	(%) ^f	(%)	(%)	(%)	(%)
P	0.07	0.05	0.07–0.07	0.04	0.05	7.06
Ti	0.47	0.40	0.41–0.38	0.49	0.31	0.09
K	2.99	3.05	2.8–2.32	0.51	2.39	0.98
Ca	1.57	2.40	3.0–2.57	6.85	1.60	19.4
Mg	1.57	1.72	1.33–1.50	4.37	1.21	1.52
Fe	3.97	4.07	3.5–3.92	8.57	2.90	1.06
Mn	0.07	0.06	0.06–0.08	0.08	0.01	0.01
Al	8.83	8.27	8.04–8.15	8.94	7.85	2.55
Si	27.5	28.0	30.8–31.13	24.96	27.10 ^g	–
F	–	–	–	–	–	1.37
C _{org}	–	–	–	–	–	6.2
CaCO ₃	–	–	–	–	–	13
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
La	41	31.1	30–31	8	38	127
Ce	83	66.7	64–63	20	72	42
Pr	10.1	7.70	7.1–7.1	–	8.7	17.6
Nd	38.0	27.4	26–27	11	31	71
Sm	7.50	5.59	4.5–4.7	2.8	6.2	11.7
Eu	1.60	1.18	0.88–1.0	1.1	1.2	2.55
Gd	6.4	4.90	3.8–4.0	3.1	6.7	15
Tb	1.2	0.85	0.64–0.7	0.48	0.89	1.9
Dy	5.5	4.17	3.5–3.9	3.1	5.9	13
Ho	1.30	1.02	0.8–0.83	0.68	1.0	2.9
Er	3.8	2.84	2.3–2.3	1.9	3.7	9.2
Tm	0.6	0.48	0.33–0.3	0.24	0.48	1.25
Yb	3.50	3.06	2.2–1.96	1.5	3.6	7.4
Lu	0.60	0.46	0.32–0.31	0.25	0.46	1.15
Y	27	20.5	22–21	16	34	187
Cu	35	–	25–28	26	39	67
Cd	0.8	–	0.098–0.09	0.1	0.2	70
Cr	83	125	83–92	215	100	728
Mo	2	–	1.5–1.1	0.6	2.9	57
Ni	42	58	44–47	88	80	188
Pb	22	20	–	4	–	16
U	2.5	2.66	2.8–2.7	0.2	3.7	60
V	130	–	107–97	196	110	600
Zn	100	–	71–67	78	125	1395
Ba	580	636	550–628	259	400	153
Co	19	25.7	17–17.3	38	–	2
Ga	21	–	17–17.5	13	18–25	13
Sr	300	–	350–320	348	130	637
Th	12	12.3	10.7–10.5	1.2	12	5.2
Zr	160	200	190–193	68	240	250

^aWedepohl (1971) and Piper et al. (2000).

^bGromet et al. (1984).

^cMcLennan (2001), Rudnick and Gao (Chapter 4.1), and Wedepohl (1995).

^dRudnick and Gao (Chapter 4.1).

^eConcentrations are means for the MPM at the Hot Springs mine.

^fMajor elements adjusted by 7.5% for loss of weight on drying at 1000 °C.

^gThe Si concentration is obtained from other sites than the Hot Springs mine (Medrano and Piper, 1995).

of the marine fraction by the lithogenous fraction was a major contributor to the elevated concentration of CFA, adding to the high level of primary productivity.

13.12.4 Lithogenous Sediment Fraction

The composition of crustal reference standards (Table 1) is commonly assumed to represent the composition of the lithogenous fraction of sedimentary deposits. Sediment compositions that are similar to the upper continental crust (UCC) or other standard suggest their sources were homogenized samples of surficial crustal debris (Goldschmidt, 1954) that have been minimally altered by mechanical (grain-size sorting) and chemical (weathering) processes. Calvert and Pedersen (2007) summarized the use of Al as a proxy for this fraction of the sediment. Its concentration in felsic and mafic extrusive and intrusive igneous rocks and most metamorphic rocks and sedimentary shales varies only slightly (Wedepohl et al., 1969–1978). Aluminum is strongly conservative in weathering profiles and soil formation owing to the in situ formation of clay minerals and retention of oxyhydroxides (Bohn et al., 1979; Hem, 1969–1978; Loughnan, 1969). Thus, its concentration within a sedimentary deposit provides a reliable measure of the concentration of the lithogenous sediment fraction. Its concentration in this fraction in the MPM of 7.85% (Table 1) can be determined from extrapolation of the second-order polynomial of Al versus Ca to 1.6% Ca (Figure 4), the approximate Ca concentration in the rock standards – WSA, UCC, and NASC.

The lithogenous fraction, composed mostly of clay- and silt-size debris, is a minor component of many samples (Figure 4). Still, factor analysis (Table 2) yields a strong factor loading of Al on factor 1 and less so on factor 4. Similar positive loadings for Ga, Th, Ti, and the alkali metals suggest they too have strong lithogenous affinities and similar terrigenous sources. Subtle variations of the Al-normalized contents of these elements can reveal variations in terrigenous sediment sources, changes in sea level, and degree of sediment reworking contemporaneous with deposition. For example, the Al-normalized K contents in the MPM exhibit a decrease of

~40% above the lower ore/middle-waste boundary (Figure 5) that extends over several 1000 km² (Perkins and Piper, 2004), reflecting a decrease in K-hosting minerals. The decrease may represent a shift in the dominant sediment source from the Milk River uplift (Maughan, 1994), which was upwind from the Phosphoria Sea (Peterson, 1988) and may have had extensive exposures of Mississippian sedimentary rock (McMannis, 1965; Peterson, 1980), to the Uncompahgre uplift and Ancestral Rockies (Figure 2), which included Paleoproterozoic and Mesoproterozoic volcanogenic magmatic and juvenile mafic rocks.

Titanium exhibits a strong linear correlation with Al at each of the sites examined, reflecting a common terrigenous source, but the Ti:Al ratio varies between sites across the basin (Figures 2 and 6). Titanium is partitioned largely into the heavy minerals ilmenite (FeTiO₃) and rutile (TiO₂). Their high density and typically fine-grained texture may account for the separation of Ti and Al. Aluminum is hosted by the lower density siliciclastic minerals, for example, clay minerals and feldspars, that constitute the bulk of the fine-grained lithogenous sediment fraction (Knudsen et al., 2000). As the finer-grained heavy minerals are hydraulically equivalent to coarser-grained siliciclastic minerals, the Al-normalized Ti contents serve as proxies of the coarse component of the lithogenous fraction (Calvert and Pedersen, 2007; Shimmield and Mowbray, 1991; Spears and Kanaris-Sotiriou, 1976). Thus, the decrease in the Al-normalized Ti contents across the basin from Conant Creek (Figure 6) to Mud Springs, with the intervening sites having intermediate Ti:Al ratios, represents a decrease in grain size from east to west.

The distribution of the heavy minerals at the Hot Springs site is possibly better represented by the Ga-normalized Zr contents than by the Al-normalized Ti contents. Zirconium is hosted virtually exclusively by the heavy mineral zircon, whereas Ti can be hosted by several Al silicate minerals, as well as ilmenite and rutile (Calvert and Pedersen, 2007). Gallium, with a factor loading similar to that of Al, is also hosted largely by the lithogenous fraction (Table 2). The two were analyzed in 310 samples (Gulbrandsen, 1979) versus the 74 samples analyzed for Ti and Al (Piper et al., 2000). Even with fewer Ti and Al analyses, the Al-normalized Ti depth profile at the Hot Springs mine is similar to the Ga-normalized Zr trend (Figure 7(a)). The major exception occurs between 20 and 30 m depth that may reflect the more complex partitioning of the Ti in several minerals than the partitioning of Zr solely in zircon. Otherwise, the two ratios suggest a series of alternating coarse-grained/fine-grained intervals from the base of the MPM upward (Figure 7(a)).

The enrichments of these heavy mineral-hosted trace elements are commonly interpreted as reflecting sediment winnowing and reworking. Their distribution in the MPM, in which evidence of sediment reworking is scant, suggests an alternative interpretation. The $\delta^{18}\text{O}$ record of CFA at the Montpelier Canyon site (Piper and Kolodny, 1987), transferred to the Hot Springs section based on the P concentration profiles at the two sites (Figure 7(b); Piper, 2001), reveals relatively low water-column temperatures that are coincident with glacial events proposed by Sheldon (1984). The glacial events correspond with the normalized Zr maxima, thus indicating sea level low stands, or regressions. As the three

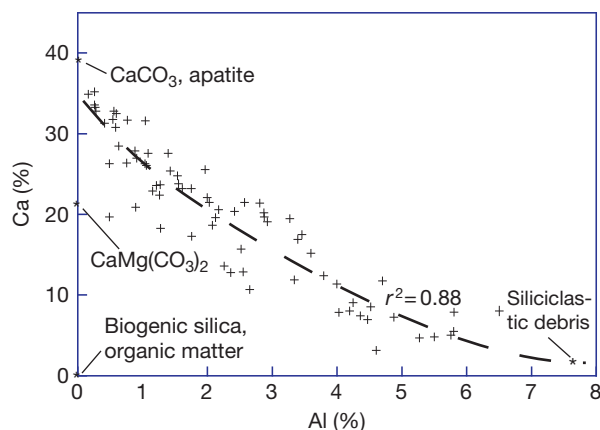


Figure 4 Relationship between Al and Ca (in wt%) in samples from the Hot Springs mine (Piper et al., 2000). The curve is a second-order polynomial, which extrapolates to 7.85% Al at 1.6% Ca.

Table 2 Orthogonal solution factor analysis, using StatView software, of samples collected at the Hot Springs mine by Gulbrandsen (1979)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Al	0.80	0.00	−0.08	0.54	−0.13	0.93
Fe	0.81	0.09	0.05	0.53	− 0.70	0.95
Ca	− 0.92	−0.03	0.13	−0.28	0.09	0.95
K	0.88	0.08	−0.10	0.40	−0.07	0.95
Li	0.76	0.39	0.16	0.04	0.11	0.76
Ti	0.95	−0.04	0.03	0.04	0.07	0.90
P	− 0.87	−0.03	0.26	−0.12	0.24	0.90
F	− 0.76	−0.02	0.37	−0.08	0.30	0.81
C _{org}	−0.09	0.87	0.05	−0.06	0.27	0.85
S	0.60	0.52	0.14	0.49	0.18	0.92
Cd	−0.27	0.16	−0.19	−0.03	0.84	0.85
Cu	0.00	0.94	0.12	0.10	0.10	0.91
Ni	0.18	0.71	0.18	0.00	0.52	0.83
Zn	−0.18	0.26	−0.14	0.01	0.90	0.93
Cr	0.17	0.84	0.30	0.00	0.06	0.82
Mo	0.19	0.30	−0.08	0.00	0.82	0.80
U	− 0.72	−0.15	0.19	0.01	0.44	0.77
V	−0.30	0.14	−0.26	−0.02	0.82	0.85
La	−0.32	0.25	0.81	0.05	−0.20	0.86
Ce	0.27	0.07	0.87	0.09	−0.22	0.90
Sm	−0.24	0.17	0.87	0.06	−0.23	0.90
Th	0.54	−0.06	0.20	0.74	−0.14	0.91
Ba	0.76	−0.06	0.39	0.06	0.06	0.07
Ga	0.80	0.24	0.10	−0.23	−0.05	0.75
Sr	− 0.70	0.25	0.43	−0.15	0.01	0.75
Variance	0.38	0.24	0.15	0.07	0.05	—

Absolute values greater than 0.5 are in bold.

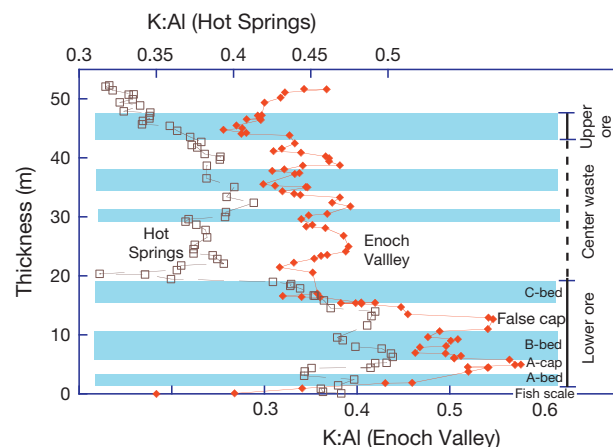


Figure 5 Relationship between K:Al ratios (three-point running average) and depth of the sediment section at the Hot Springs and Enoch Valley mines. Shaded horizontal bars are identified in the text and in the caption to Figure 7. Field names are listed for units in the lower ore zone. Thickness gives height of the MPM above the Grandeur Member.

low-temperature events (G-1, G-2, and G-3) correspond with three of the six Ga-normalized Zr maxima, the normalized Zr contents may indicate three additional low sea level stands. These possible eustatic sea level changes in the middle part of the Permian, in response to glacial events in the southern hemisphere (Fielding et al., 2008; Rygel et al., 2008), may have been as much as 70 m in the Kungurian and less in the Roadian and Wordian times (Figure 3).

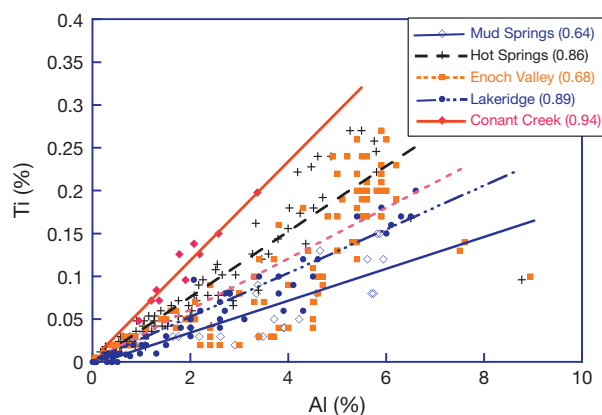


Figure 6 Relationship between Al and Ti (in wt%) in samples from sites in the Phosphoria Basin. The two extreme trends are from the eastern (Conant Creek) and westernmost sites (Mud Springs) (Figure 1). The legend gives r^2 of the linear regressions, when extrapolated to the origin. The scatter reflects in part the complex geochemistry of Ti, of it not being hosted in the sediments solely in the heavy minerals. Reproduced from Calvert SE and Pedersen TF (2007) Elemental proxies for palaeoclimatic and palaeoceanographic variability in marine sediments: Interpretation and application. In Hillaire-Marcel C and de Vernal A (eds.) *Paleoceanography of the Late Cenozoic, Part 1. Methods*, pp. 567–644. New York: Elsevier.

Correlation of this record in the MPM with the southern hemisphere glacial record, however, requires a much more detailed examination than is currently available. Still, the lower heavy mineral contents that occurred during periods of

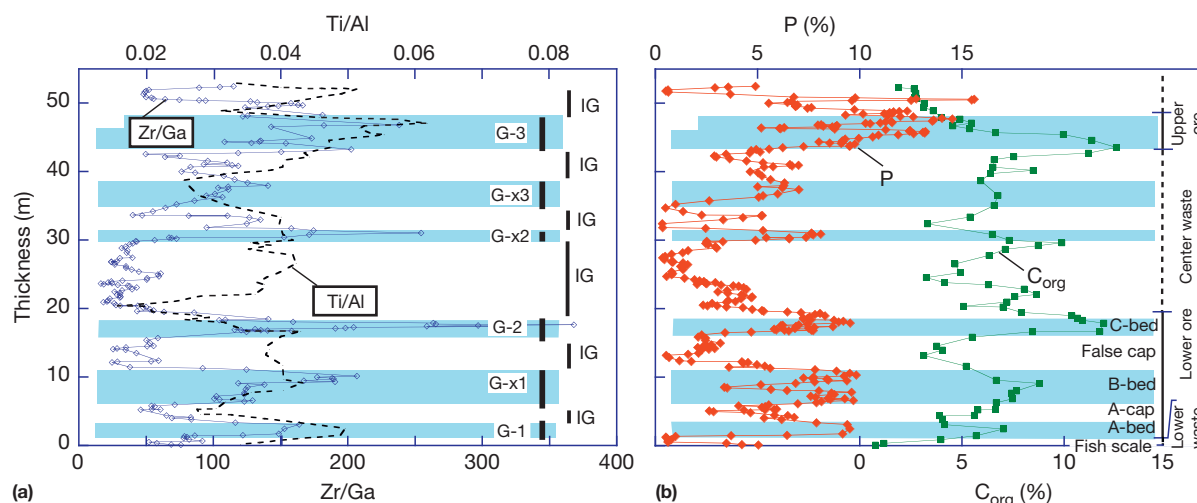


Figure 7 Relationship at the Hot Springs mine (Gulbrandsen, 1979) of (a) the Ga-normalized Zr contents (five-point running average of semiquantitative analyses) and the Al-normalized Ti contents (three-point running average) versus sediment thickness and (b) P (five-point running average of semiquantitative analyses) and C_{org} (three-point running average), both in wt%, versus sediment thickness. The shaded horizontal bars represent maxima of the Ga-normalized Zr contents. The glacial events labeled G-1 through G-4 were proposed by Sheldon (1984) and supported by $\delta^{18}\text{O}$ measurements of samples from the Montpelier Canyon site (Figure 1; Piper and Kolodny, 1987). Three possible glacial events have been added (G-x) based on maxima of the normalized Zr contents. Samples with Ga concentrations less than the detection limit (1.5 ppm) were not included in frame (a). The Ga concentration in these samples could be as low as 0.5 ppm. Field names are listed for units in the lower ore zone in frame (b).

elevated sea level, or transgression events, may reflect their greater retention in stream estuaries and the shallow margins of the basin than during low sea level regression events. The low sea level stands would have allowed the heavy minerals to be transported farther into the basin. Their high density would also account for their decrease in concentration across the basin from east to west (Figure 6). The similarity of their profiles with the C_{org} profile (Figure 7(b)) further supports the heavy mineral distributions as being a depositional feature other than one of reworking. Organic matter is the least dense component of the sediment and should be the most easily eroded and redeposited, whereas the heavy minerals should behave oppositely. The two should have mirror-image distributions if the sediments were reworked during deposition, rather than parallel distributions. The preservation of the textural evidence of the sediments, discussed earlier, and the association of high Ga-normalized Zr and Al-normalized Ti contents with high C_{org} contents suggest that the depth of the Phosphoria Sea in the central region was below the depth of sediment winnowing and reworking by waves and isolated from intense bottom currents.

Plots of trace elements versus Al (Figure 8) also provide estimates of the contribution of elements by the lithogenous fraction of those elements otherwise strongly enriched above a terrigenous source (Piper and Calvert, 2011). They include the REE, Cd, Cr, Cu, Mo, Ni, Re, Sb, Se, U, and V (e.g., Ames, 1994; Herring and Grauch, 2004; Medrano and Piper, 1995; Piper et al., 2000; Prévôt and Lucas, 1980). A curve drawn from the origin through the samples having the lowest element/Al ratios and extrapolated to 7.85% Al gives the concentration of individual trace elements in the lithogenous fraction. Their concentrations in this fraction of the sediments estimated from these plots closely approach their concentrations in the rock

standards (Table 1). The offset of elements above these curves then gives the trace-element concentrations within the seawater-derived fractions.

13.12.5 Seawater-Derived Trace Elements

The trace metals that are enriched above a lithogenous contribution in the MPM include the elements that have strong loadings on factors 2 or 5 (Table 2). Phosphorus, hosted largely by CFA, might be expected to show a strong loading on these same factors, but it has a strong negative loading on factor 1, along with Ca and F. CFA is the dominant component in many samples, the other major components being the lithogenous fraction, organic matter, and less so the carbonate minerals calcite and dolomite (Figure 4). This hierarchy predetermines the negative loading of P on factor 1 and contributes to the complex loadings of C_{org} and the trace metals.

The trace elements strongly enriched above a lithogenous contribution can be partitioned into two seawater-derived fractions – a biogenous fraction and a hydrogenous fraction (Goldberg, 1963). The biogenous fraction includes the trace nutrients Cd, Cu, Ni, and Zn (Piper 2001; Piper and Calvert, 2011). In the open ocean, the profiles of these metals exhibit low concentrations in the photic zone and elevated concentrations at depth (e.g., Boyle et al., 1976, 1977; Collier, 1984; Sclater et al., 1976), similar to the depth profiles of the major nutrients HPO_4^{2-} and NO_3^- (Sverdrup et al., 1942). The seawater profiles reflect the uptake of these nutrients in the photic zone largely by phytoplankton and their return to solution at depth through the oxidation of organic matter under oxic conditions of bacterial respiration. Their concentrations in organic matter, calculated from these profiles, normalized to

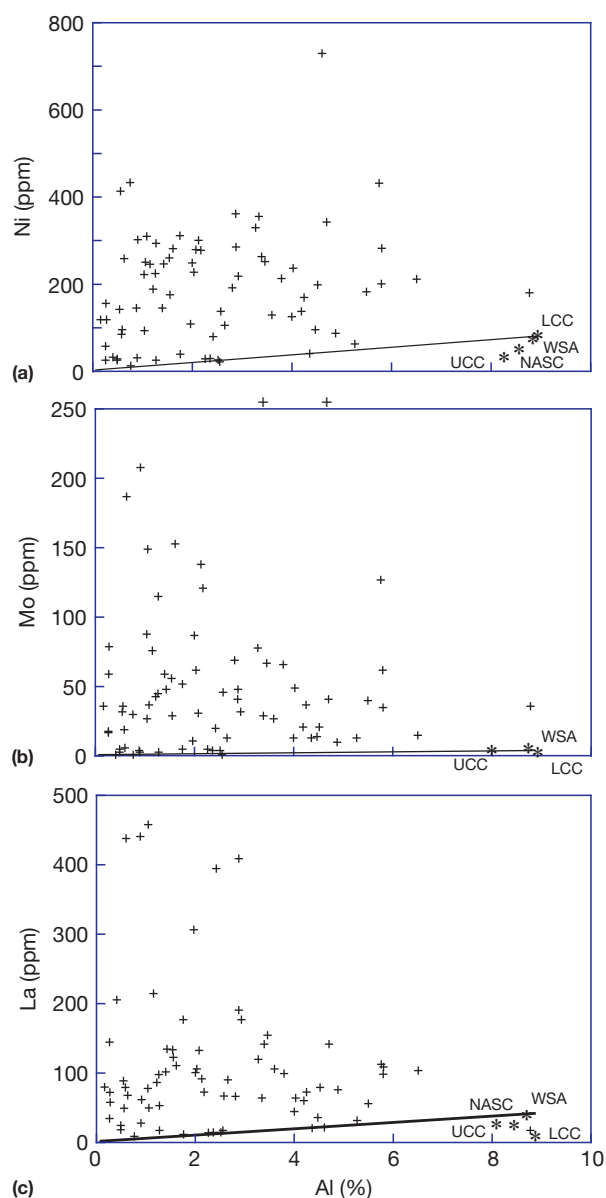


Figure 8 Relationship between Al and (a) Ni, (b) Mo, and (c) La in samples from the Hot Springs mine. The lines are drawn through the samples with the lowest Ni:Al, Mo:Al, and La:Al ratios and are interpreted to represent the element:Al ratios for the trace elements in the lithogenous sediment fraction. The other trace nutrients and redox-sensitive trace metals exhibit similar relationships with Al. The offset of samples above these lines is interpreted to represent the trace-element contribution of seawater. Rock standards – North American shale composite (NASC), world shale average (WSA), upper continental crust (UCC), and lower continental crust (LCC) – are shown with asterisks (Table 1).

the P profile (Brumsack, 1986; Piper, 2001; Piper and Dean, 2002) yield concentrations that agree closely with the mean of their P-normalized contents in organic matter-suspended phases, although their measured concentrations between individual samples vary over a wide range (Brumsack, 1986; Collier and Edmond, 1983, 1984; Martin and Knauer, 1973). Their uptake by phytoplankton in laboratory experiments (Ho

et al., 2003) further confirms their active role in the biological cycle. Their accumulation on the seafloor is thus governed largely by primary productivity in the photic zone. Additional trace nutrients include As, Sb, Se, Co, and Fe.

The hydrogenous metal fraction in marine sediments, the fraction of metals derived from seawater by precipitation/adsorption reactions, and examined here includes Cr, Mo, U, and V (Crusius et al., 1996; Piper and Calvert, 2011; Piper and Dean, 2002). Their deposition, or lack of deposition, from the water column is governed largely by redox conditions in the bottom water. A three-level hierarchy of bacterial respiration determines the redox properties of the bottom water. Within the open ocean, bacterial respiration is characterized by the reduction of O_2 , or *oxic* respiration, from the surface to the seafloor at abyssal depths. *Suboxic* respiration is present at intermediate ocean depths in limited areas of the oxygen minimum zone (OMZ), for example, in areas marginal to Peru, Namibia, and the Arabian Peninsula, where the concentration of O_2 is less than $5 \mu M$. Within these areas, bacteria reduce NO_3^- to N_2 (denitrification) and the remaining $5 \mu M$ of O_2 . Other combined nitrogen species (e.g., NH_4^+ and NO_2^-) are also lowered within the OMZ by anammox reactions (Kuypers et al., 2005) or anaerobic ammonium oxidation reactions. Suboxic conditions also occur within the water columns of all anoxic basins (e.g., in the Black Sea, Baltic Sea, Cariaco Basin, and several high-latitude fjords) at intermediate depth immediately below the oxic surface waters. Within these basins at even greater depths, that is, within the very bottom waters, bacterial respiration depletes both O_2 and NO_3^- . Bacteria then resort to *anoxic* respiration, the reduction of SO_4^{2-} to H_2S (H_2S is used to represent all forms of dissolved sulfide). Anoxic conditions are infrequently encountered in the OMZ of the open ocean, likely persisting only briefly (Codispoti, 1980; Dugdale et al., 1977), presumably when O_2 and NO_3^- have been reduced.

The seawater depth profiles of several trace metals identify the trace metals whose accumulation on the seafloor is governed by these three levels of bacterial respiration in the water column. Trace metals that accumulate from seawater (i.e., not including the commonly dominant fraction incorporated in aluminosilicate lattices of the lithogenous fraction) under oxic conditions include Fe, Mn, and several trace elements adsorbed by the oxyhydroxides of these two metals (Nameroff et al., 2002), Fe and Mn being the diagnostic elements. Vanadium, Cr, and possibly U are reduced to relatively insoluble phases and accumulate from bottom waters under suboxic to anoxic conditions (Crusius et al., 1996; Emerson and Husted, 1991; Emerson et al., 1979; Murray et al., 1983; Stumm and Morgan, 1996; Wehrli and Stumm, 1989), whereas Fe and Mo accumulate from the water column under anoxic sulfidic conditions (Calvert et al., 1996; Crusius et al., 1996; Emerson and Husted, 1991; François, 1988; Haraldsson and Westerlund, 1991; Helz et al., 1996; Jacobs et al., 1985, 1987; Kremling, 1988; Landing and Lewis, 1991; Lyons, 1997; Piper and Dean, 2002).

Of course, the accumulation of these redox-sensitive trace metals is more complicated than this simple scheme. For example, Mo may accumulate from suboxic bottom waters (Calvert and Price, 1983; McManus et al., 2006; Morford et al., 2005) following sediment diagenetic pathways rather than water-column pathways (Erickson and Helz, 2000),

owing to rate-controlled reactions of thiomolybdate species. The 'action point' at which the H_2S concentration is high enough to produce easily adsorbed thiomolybdate species over nonadsorbed MoO_4^{2-} can be within the sediment pore waters. In Peru Shelf sediments, H_2S -enriched pore waters can occur at the sediment–water interface (Froelich et al., 1988). The shallowness of this boundary within sediments apparently enhances the diffusion of Mo into the sediments from waters near the bottom, where the bottom waters themselves are suboxic. This can lead to overestimating anoxic bottom-water conditions based solely on the enrichment of Mo in the sediments above a lithogenous contribution.

These metals also act as trace nutrients, for example, V (Collier, 1984), but their accumulation within basins that exhibit O_2 -depleted bottom-water conditions is commonly dominated by their hydrogenous fraction. Similarly, the trace nutrients Cd, Cu, and Zn are removed from anoxic bottom waters (Haraldsson and Westerlund, 1991; Jacobs et al., 1985, 1987; Landing and Lewis, 1991), but their accumulation commonly is dominated by the biogenous contribution (Piper and Dean, 2002). The partitioning of the trace elements within the sediments into two marine fractions is further complicated by their lithogenous-fraction contribution. This is a severe problem for Fe in nearly all deposits, as the lithogenous fraction usually dominates the seawater-derived fraction. The adjustment necessary to estimate separately the seawater contributions of Cr, Cu, Ni, V, and Zn from the bulk trace-element concentrations in many deposits can also be significant, although the adjustment to many samples of the MPM (Table 1) is less than 15% and less than 30% in virtually all samples. This adjustment for Cd, Mo, and U in many sedimentary phosphate deposits introduces little error to the estimate of their marine fractions, owing to their low concentrations in the lithogenous fraction (Table 1). Thus, the authors limit the discussion of the biogenous fraction to Cd, Cu, Ni, and Zn and of the hydrogenous fraction to Cr, Mo, U, and V. The partitioning of As, Sb, and Se between the two marine fractions and lithogenous fraction is not as well defined as that of the earlier eight elements, but all three are strongly enriched in the MPM above a lithogenous contribution (Piper et al., 2000).

13.12.5.1 Biogenous Trace Elements

Nickel is the master trace-element proxy for the flux of planktonic organic matter that settles out of the photic zone (Piper, 2001; Piper and Calvert, 2011). In addition to its depth profile in the open ocean that is similar to those of the nutrients HPO_4^{2-} and NO_3^- (Sclater et al., 1976), its nutrient properties are further illustrated by recent studies (e.g., Muyssen et al., 2004; Price and Morel, 1991; Saito et al., 2004; Twining et al., 2004; Wang et al., 2007; Whitfield, 2001). Equally important, it exhibits a uniform depth profile within the water column of the anoxic basins the Cariaco Basin (Jacobs et al., 1987), the Framvaren Fjord (Jacobs et al., 1985), and the Black Sea (Haraldsson and Westerlund, 1991) – suggesting that among the trace nutrients, it alone is not removed from the bottom water under O_2 -depleted conditions. The lack of any increase in its concentration in the bottom waters of these anoxic basins further indicates that its biogenous fraction, once exported from the photic zone, accumulates on the seafloor (Piper and Calvert, 2011; Piper and Dean, 2002). The

strong factor loading of Ni and the other trace nutrients on factors 2 and 5 (Table 2), along with C_{org} lends additional support to a biogenous origin in the MPM.

The bulk sediment accumulation rate at the Hot Springs site was $35 \text{ g m}^{-2} \text{ year}^{-1}$, assuming a sediment density of 2.5 g cm^{-3} (Gulbrandsen and Krier, 1980). The accumulation rate of seawater-derived Ni was $5630 \mu\text{g Ni m}^{-2} \text{ year}^{-1}$, based on its average bulk concentration of 188 ppm (Piper et al., 2000) that was adjusted for its lithogenous Ni contribution. The adjustment (-27 ppm) is based on the mean Al concentration of 2.6% and the mass Ni:Al ratio for the lithogenous fraction of 1×10^{-3} (Table 1). The level of primary productivity necessary to supply this accumulation rate of Ni was $1130 \text{ g C}_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}$, where the Ni: C_{org} stoichiometric ratio of the organic matter is assumed to be 18 ppm:36% (Collier and Edmond, 1983; Piper and Dean, 2002). This compares with the earlier calculation of primary productivity of $720 \text{ g C}_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}$, based on the accumulation rate of P, and with primary productivity on the Peru Shelf of $770 \text{ g C}_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}$. Primary productivity estimated from the accumulation rates of Cd, Cu, and Zn and their concentrations in organic matter of 12, 11, and 100 ppm (Brumsack, 1986; Collier and Edmond, 1983; Martin and Knauer, 1973; Piper and Dean, 2002) was 820, 630, and $1400 \text{ g C}_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}$, respectively. The mean of $980 \text{ g C}_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}$ is quite close to the value for the Peru Shelf, considering the uncertainty of the estimates of the trace-nutrient concentrations in Permian phytoplankton and likely minor contributions of all three from the bottom water as sulfides during likely brief periods of bottom-water anoxia, Zn much more so than Cd and Cu (Piper and Dean, 2002).

Sediment-depth profiles of the Al-normalized contents of the trace nutrients at the Hot Springs mine, for which the profile of the Al-normalized Ni contents is representative of all four (Figure 9(a)), parallel the profile of P and only slightly less so the profile of the C_{org} concentrations (Figure 7(b)). These relationships and the strong factor loading of Ni on the same factor as C_{org} (Table 2) support the role of primary productivity as responsible for the elevated concentrations of the trace nutrients. The maxima further correspond to maxima of the normalized heavy mineral contents and glacial cycles (Figure 7), which possibly identify the periods of maximum CFA deposition as occurring during regression events (Peterson, 1980). Variations in the dilution of the marine fractions by the lithogenous plus carbonate fractions contribute only secondarily to these maxima. In the Miocene Pungo River deposit of North Carolina, high CFA concentrations correspond to transgression events (Riggs, 1984; Riggs et al., 1990, 2000). In that deposit, sediment reworking, elevated primary productivity, and possible low dilution by the lithogenous fraction during the transgression events may all have contributed to the enrichment of P.

13.12.5.2 Hydrogenous Trace Elements

The Al-normalized trace metal contents of Cr, Mo, V, and only slightly less so U (not shown), at the Hot Springs site exhibit depth distributions (Figure 9(b), 9(c), 9(d)) that are similar to those of the trace nutrients (Figure 9(a)). Rather than indicating that these metals also act as trace nutrients, their geochemistry confirms the importance of primary productivity in

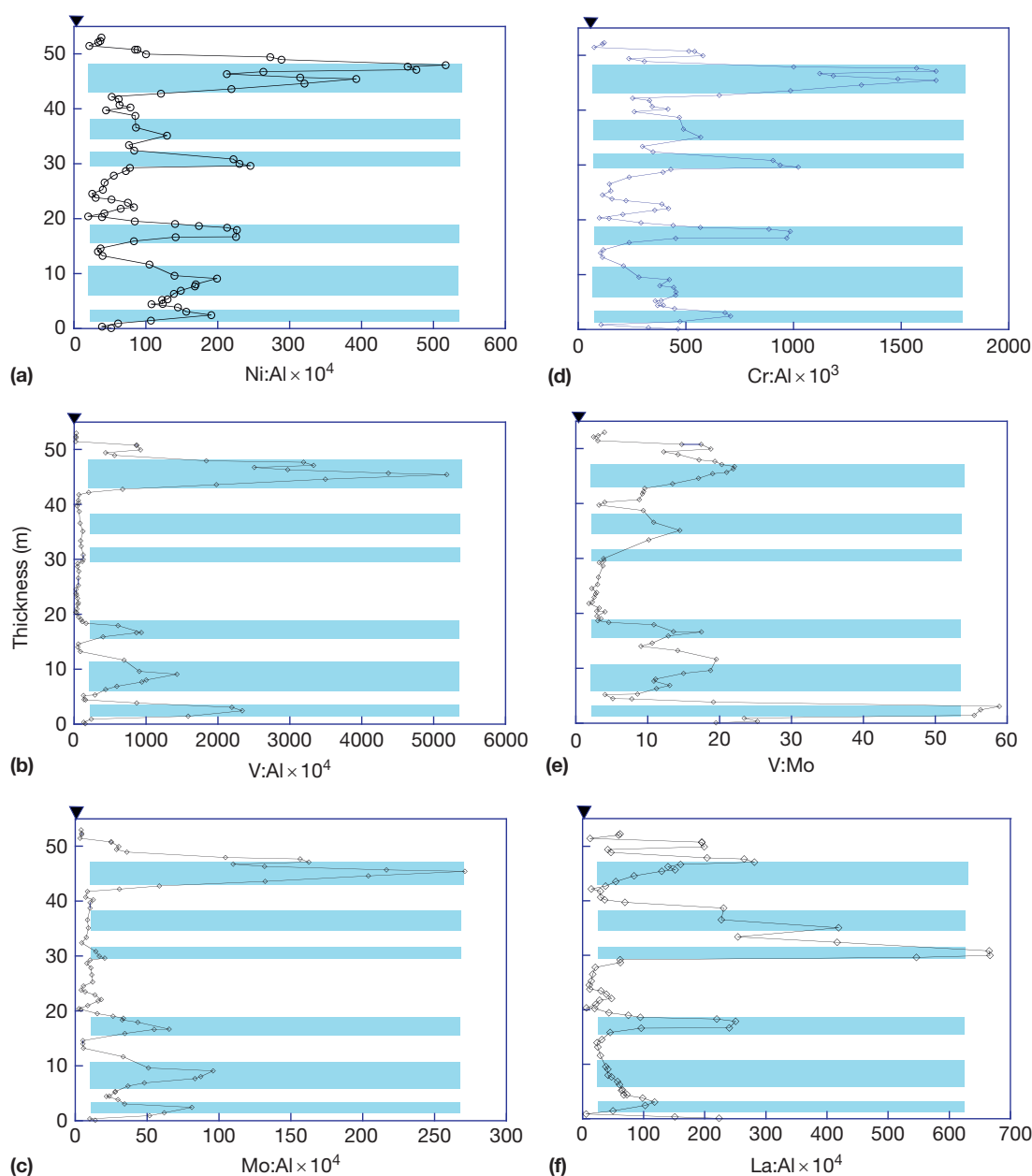


Figure 9 Relationship of sediment thickness in the Meade Peak Member at the Hot Springs mine with (a) Al-normalized Ni contents, (b) Al-normalized V contents, (c) Al-normalized Mo contents, (d) Al-normalized Cr contents, (e) marine V:Mo ratios after adjusting for a lithogenous contribution, and (f) Al-normalized La contents. Values represent three-point running averages. See Figure 7 for an explanation of the shaded bars. The filled triangle at the top of each frame is the ratio in the lithogenous model and in frame (e) the V:Mo ratio in seawater. The normalized contents of Cd, Cu, Zn, and U exhibit essentially identical trends to that of the normalized Ni contents.

determining the redox conditions of the bottom water that contributed to their deposition from seawater. The elevated Al-normalized contents of these trace metals within modern environments, as discussed earlier, are supportive of O_2 depletion in the bottom waters of the Phosphoria Sea. The elevated ratios of Cr:Mo and V:Mo in the MPM (Figures 9(e) and 10) further identify the bottom water as having been dominantly suboxic. Under fully anoxic conditions that might have persisted for the entire period of deposition of an individual sample (c.3000 years), the sample would have been expected to have a V:Mo ratio that was less than 1, similar to the ratio of surface sediments from the Black Sea (Piper and Calvert, 2011)

and Cariaco Basin (Piper and Dean, 2002), which have remained anoxic for the past several 1000 years. One sample in the MPM (at 21 m) has a ratio that is less than 1 and only four of 75 samples have ratios between 1 and 2 (Piper et al., 2000).

Anoxic conditions were likely achieved in the bottom water of the Phosphoria Sea but only for brief periods of time. For example, the sample with the highest Mo concentration of 695 ppm in the lower waste (Figure 3) has a V:Mo ratio of 3.7 (Figure 9(d)). The interval between 20 and 28 m has an average V:Mo ratio less than 2.7 and a Mo concentration that averages 50 ppm. The coupled high Mo concentrations and low V:Mo ratios suggest that the bottom water may have

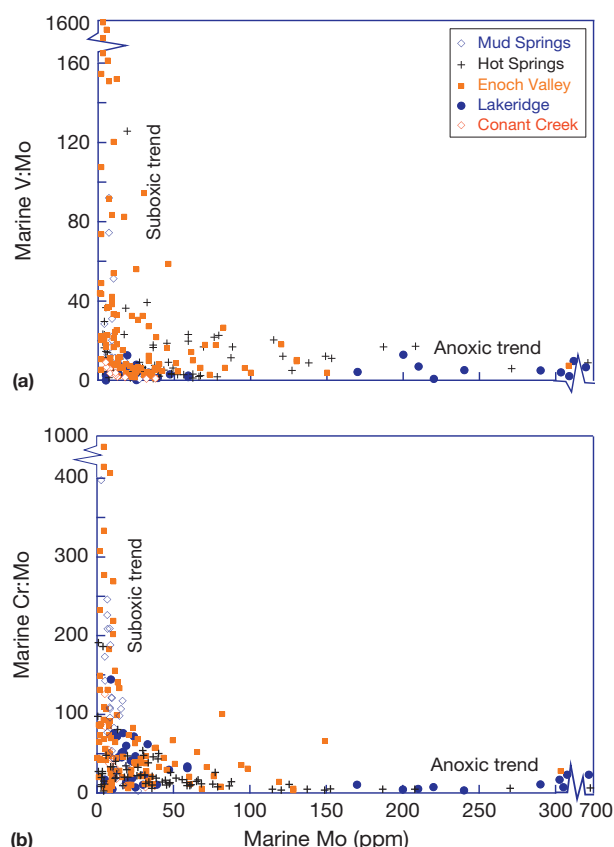


Figure 10 Relationship between (a) marine Mo and V:Mo ratios and (b) marine Mo and Cr:Mo ratios in the MPM at five sites in southeastern Idaho (Figure 1). Bulk elemental concentrations (Medrano and Piper, 1995; Piper, et al., 2000) have been adjusted for a lithogenous contribution (Piper, et al., 2000) to yield elemental concentrations in the marine fraction alone. The suboxic trend, based on samples with elevated marine V:Mo and Cr:Mo ratios and relatively low marine Mo concentrations, identifies samples at sites where bottom-water conditions were suboxic at the time of deposition, mostly samples from Mud Springs and Conant Creek. The anoxic trend, based on samples with elevated marine Mo concentrations, identifies sites where bottom-water conditions fluctuated largely between suboxic and anoxic conditions mostly samples from Hot Springs and Lakeridge, plus Wheat Creek and Fontenelle Creek (not shown). Samples from Enoch Valley (plus Montpelier Canyon – not shown) occur within both trends. Uncertainties in the marine model-calculated concentrations approach 30% at concentrations less than approximately 15 ppm V and 5 ppm Mo. Thus, bottom-water conditions of bacterial respiration are uncertain for those samples that plot near the origin, for which conditions may even have been oxic.

achieved fully anoxic conditions, more so than throughout the rest of the section. The authors are, however, unable to determine the persistence of fully anoxic bottom waters beyond this qualitative estimate, even for these two intervals.

The bottom waters during the accumulation of most of the remaining sediment section were dominantly suboxic, although the sediment pore waters at the benthic boundary may have been permanently anoxic. Under the Erickson and Helz (2000) scheme noted earlier, the diffusion of MoO_4^{2-} into the sediments followed by its reaction to readily adsorbed thiomolybdate species may partially account for the elevated

Mo concentrations. In the sediments on the Peru Shelf, Mo has a concentration of as much as 60 ppm (W. E. Dean, unpublished data) and on the Namibia shelf 100 ppm (Calvert and Price, 1983). Suboxic bottom waters (Codispoti, 1980; Dugdale et al., 1977; Kuypers et al., 2005) and anoxic near-surface sediment pore waters are reported for both shelves (Calvert and Price, 1983; Froelich et al., 1988; Goldhammer et al., 2010).

Samples from the Mud Springs site (Figure 10) plot largely along the suboxic trend (elevated V:Mo ratios and low Mo contents). Samples from the Conant Creek site, for which only ten samples were analyzed, plot near the origin but have large uncertainties in the estimates particularly of the marine V concentrations. The most severe redox conditions in the bottom water at these two sites were suboxic, with oxic conditions likely prevailing during times represented by the samples that plot nearest the origin. Surface-sediment pore waters that may have been anoxic at both sites could account for the accumulation of Mo. Conversely, the samples from the Hot Springs and Lakeridge sites (Figure 10) and Fontenelle/Wheat Creek samples (not shown) plot mostly along the anoxic trend. The bottom waters at these sites may have been anoxic for a significant period of time, with surface-sediment pore waters likely permanently anoxic. Samples from the Montpelier Canyon (not shown) and Enoch Valley sites plot along both trends, suggesting that the bottom waters were dominantly suboxic, but with anoxic sediment pore waters contributing to the accumulation of Mo. The Cr:Mo ratios, which exhibit similar distributions to the V:Mo ratios, support the interpretation of bottom-water conditions at these eight sites and the similar marine chemistries for V and Cr.

The separation of the sites based on the levels of bottom-water anoxia identifies the Hot Springs, Lakeridge, and Fontenelle Creek sites, with Mo concentrations as high as 695, 670, and 575 ppm, respectively, as located in the deepest part of the basin. Samples from the Enoch Valley and Montpelier Canyon sites plot along both axes. Thus, the seafloor at these sites may have had an intermediate depth. The samples from the Mud Springs site in the far west plot along the V:Mo axis and samples from the Conant Creek site in the extreme east (Figure 2) plot near the origin. They likely represent the shallowest sites. The seafloor depths at these sites thus define the Phosphoria Basin as a bathymetric feature. This bathymetry allowed for a relatively uniform thickness of the MPM over much of southeastern Idaho, western Wyoming, and north-eastern Utah (McKelvey et al., 1959).

Goldhammer et al. (2010) have emphasized that the accumulation of CFA on the Namibian shelf occurs under anoxic bottom-water conditions and that this may be a prerequisite for CFA accumulation. Unfortunately, they do not consider the suboxic conditions within the OMZ of this shelf (Kuypers et al., 2005). Indeed, they fail even to mention suboxia. It may be that CFA accumulates within the more extreme redox environment, possibly weakly, but the distributions of the V:Mo and Cr:Al ratios (Figure 9(d) and 9(e)) and their relationship with P concentrations (Figure 7(b)) in the Phosphoria Formation are indicative of the much greater importance of suboxic than anoxic bottom-water conditions during phosphogenesis. H_2S was likely present in the very surface sediments of the Phosphoria Sea, as it is on the Peru Shelf (Froelich et al., 1988), but there also the OMZ is dominantly suboxic (Dugdale et al., 1977).

The absence of CFA deposition in the permanently anoxic Black Sea or Cariaco Basin further places a limit on phosphogenesis under anoxic bottom-water conditions. The water-column geochemistry of the Black Sea adds additional support to this interpretation. Shaffer (1986) reported a HPO_4^{2-} shuttle across the suboxic–anoxic interface of the water column that is confirmed by Yakushev et al. (2008). The shuttle of HPO_4^{2-} is expressed by its depletion in the suboxic zone and enrichment in the immediately underlying anoxic waters, relative to a smoothly increasing concentration with depth that would have been achieved by the oxidation of settling organic matter in the absence of the HPO_4^{2-} shuttle. The carrier phase of P across the suboxic/anoxic boundary and its dissolution in the anoxic layer has not been identified. Yakushev et al. (2008) dismissed an Fe phase because of the significantly greater concentrations of HPO_4^{2-} than Fe and lack of a clear relationship between the dissolved concentration profiles of the two. Thus, it is conceivable that it could be a Ca phosphate phase. Regardless of the solid phase, anoxic conditions contribute to its dissolution on its settling into the anoxic bottom waters.

Algeo and Lyons (2006) have shown that Mo:C_{org} ratios in sediments currently accumulating in modern silled anoxic basins are indicative of the degree of isolation of the basin. There is no such relationship for the MPM; the ratios are randomly distributed (Piper et al., 2000) for both the glacial (low sea level) and interglacial (high sea level) periods (Figure 7(a)), suggesting that the exchange of water between the ocean and the Phosphoria Sea was unrestricted during the entire period of deposition. The Mo:C_{org} ratios also exhibit a distribution similar to that of sediments from the Namibian Shelf (Figure 11), further supporting the interpretation of the free exchange of water between the Phosphoria Sea and the open ocean.

Whereas the threshold for the accumulation of these trace elements is governed by redox properties of the water column, their actual rate of accumulation is governed by the hydrography of the basin. The level of bacterial respiration in the bottom

waters merely represents the balance between the level of primary productivity in the photic zone that determines the settling flux of C_{org} into the bottom water and the advection of open ocean water into the bottom water. The advection of bottom water into the Phosphoria Sea, expressed as a residence time (RT), can be estimated from the accumulation rates of the redox-sensitive trace metals. If one assumes that the concentration of V in the imported water was 1.8 ppb (Pacific Ocean; Collier, 1984), of which roughly 50% accumulated by adsorption/precipitation reactions, the case for the Cariaco Basin and Black Sea (Emerson and Huested, 1991; Jacobs et al., 1987; Piper and Calvert, 2011; Piper and Dean, 2002), then the RT of the 250 m of bottom water, or 25 l cm^{-2} , is given by the V available in the bottom water divided by the V accumulation rate on the seafloor. Its accumulation rate is calculated from the bulk sediment accumulation rate of $1.4 \times 10^{-3} \text{ cm year}^{-1}$, the bulk sediment density of 2.5 g cm^{-3} , the mean marine V concentration in the sediments of 565 ppm, and the level of V removal from the bottom water of ~50%:

$$\begin{aligned} \text{RT}_{(V)} &= [25 \text{ l cm}^{-2} \times 1.8 \mu\text{g} - \text{V l}^{-1} \times 50\%] \\ &\div [1.4 \times 10^{-3} \text{ cm year}^{-1} \times 2.5 \text{ g cm}^{-3} \times 565 \text{ ppm}] \\ &= 11 \text{ years} \end{aligned}$$

The development of severe O₂ depletion in bottom waters of marine basins is commonly interpreted as reflecting stagnant conditions. A mean bottom-water RT in the Phosphoria Sea of 11 years was certainly not a stagnant condition.

13.12.5.3 A Circulation Model

The rate of upwelling of nutrient-enriched bottom water into the photic zone of the Phosphoria Sea necessary to maintain the high level of primary productivity and the accumulation of CFA on the seafloor for c.3.75 My can be estimated from the recharge of P equal to the loss of $1.8 \text{ g P m}^{-2} \text{ year}^{-1}$, calculated earlier from the settling of organic matter (Figure 12). The open-ocean eastern boundary current that supplied nutrients to the basin may have been ancestral to the Californian Current. If one assumes that the concentration of P in the upwelling water was $1.9 \mu\text{M}$, its approximate concentration in the California Current at 150 m depth, then the rate of upwelling was 30 m year^{-1} . For a photic zone that was 50–75 m, the RT of water in the photic zone would have been approximately 2 years.

The advection of bottom water into the basin from the open ocean, calculated above from the accumulation rate of V, can also be calculated from the balance between the rate of oxidation of organic matter settling out of the photic zone and the import of O₂-charged open-ocean seawater to depth in the basin, that is, from the balanced loss of oxidants and reductants in the bottom water at steady state. The calculation was presented by Perkins and Piper (2004) in a slightly different format. The major differences here are the O₂ concentration assumed for the imported water, the period of deposition of the MPM of 3.75 My (Figure 3) as estimated from Gradstein et al. (2004), and the percentage of primary productivity oxidized in the bottom water of 8%, whereby 2% of the 10% that settles out of the photic zone survives oxidation and accumulates on the seafloor. The latter is based on the mean

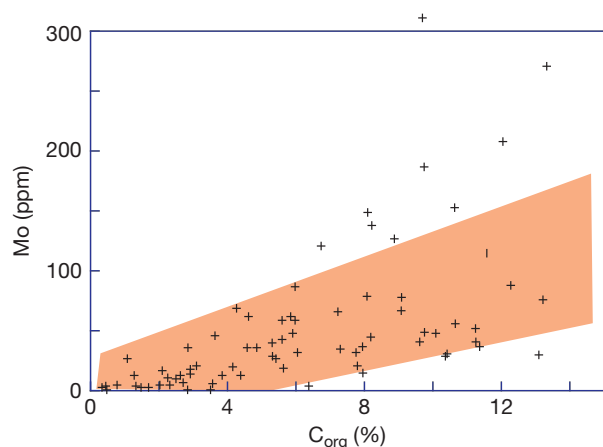


Figure 11 The relationship between Mo and C_{org} in samples from the MPM at the Hot Springs site. The shaded area encloses samples from the Namibian shelf, southwest Africa (Algeo and Lyons, 2006).

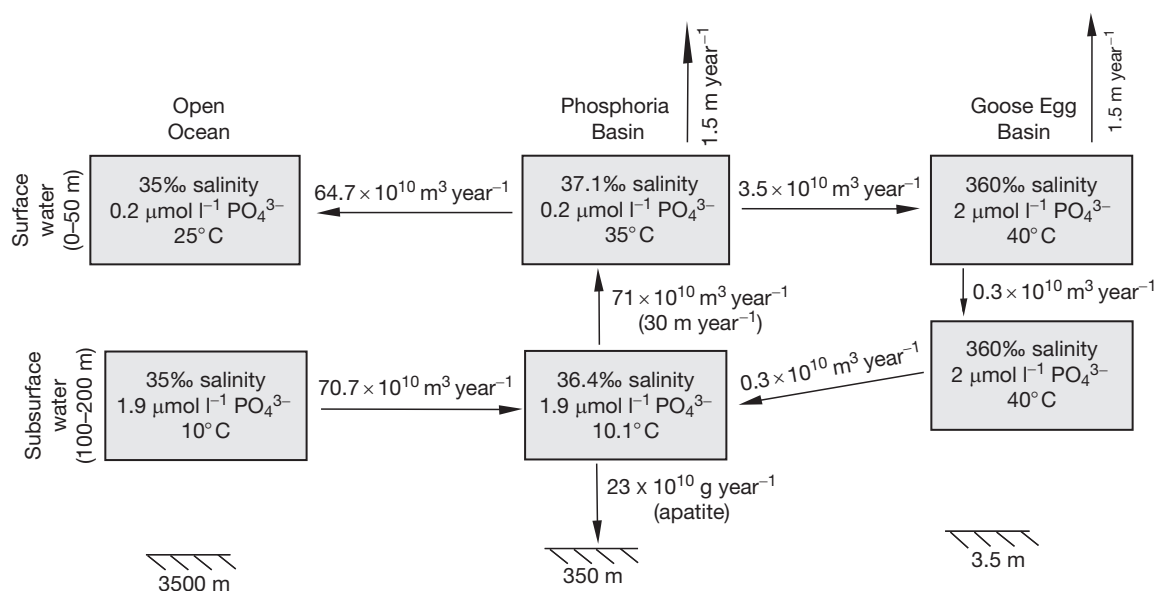


Figure 12 A circulation model for the Phosphoria Basin. The upwelling rate is based on the mean accumulation rates of the trace nutrients Cd, Cu, Ni, and Zn. Advection of bottom water is based on the mean accumulation rate of the redox-sensitive trace metal V. The rate of exchange of water between the Phosphoria Basin and the Goose Egg Basin assumes an evaporation rate of 1.5 m year^{-1} (Penman, 1948) and an area of evaporation in the Goose Egg Basin that equaled the area of phosphogenesis in the Phosphoria Basin.

concentration of C_{org} in the MPM of 6.2% (Table 1). Because the trace metals define the bottom waters as having been dominantly suboxic and only intermittently anoxic, SO_4^{2-} reduction is not considered in the calculation. Similar to the replenishment of P to the photic zone, the major oxidizing agents of O_2 and NO_3^- must be replenished in the bottom water at a rate that balances their loss in the oxidation of C_{org} . An O_2 concentration of $160 \mu\text{M}$ in the water imported into the basin is assumed, its approximate concentration in seawater within the California Current at 150 m depth (Thomas and Seibert, 1974), and a NO_3^- concentration of $15 \mu\text{M}$, which represents an arbitrary adjustment owing to its partial loss by anammox reactions (Kuypers et al., 2005) within the bottom water. Regardless of the NO_3^- concentration one might have assumed, however, its contribution to the calculation is small, relative to that of O_2 . Thus, the rate of oxidation of 8% of primary productivity in the bottom water is

$$\begin{aligned} \text{Rate of oxidants reduced} &= \text{Rate of } C_{\text{org}} \text{ oxidized} \\ &= [(720 \times 0.08 \text{ g C m}^{-2} \text{ year}^{-1} \times 4 \text{ equiv mol}^{-1} \\ &\quad \div 12 \text{ g C per mol C}] \div 250 \text{ m} \\ &= (19 \text{ equiv } C_{\text{org}} \text{ m}^{-2} \text{ year}^{-1}) \\ &\quad \div (250 \times 10^3 \text{ l m}^{-2}) \\ &= 77 \mu \text{equiv l}^{-1} \text{ year}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Concentration of oxidants} &= 160 \mu \text{mol O}_2 \text{ l}^{-1} \\ &\quad + 15 \mu \text{mol NO}_3^- \text{ l}^{-1} \\ &= 640 \mu \text{equiv O}_2 \text{ l}^{-1} \\ &\quad + 75 \mu \text{equiv NO}_3^- \text{ l}^{-1} \\ &= 715 \mu \text{equiv l}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Bottom-water RT} &= (715 \mu \text{equiv oxidants l}^{-1}) \\ &\quad \div (77 \mu \text{equiv } C_{\text{org}} \text{ l}^{-1} \text{ year}^{-1}) \\ &= 9.3 \text{ years} \end{aligned}$$

The RT agrees closely with the RT of 11 years that was calculated from the accumulation rate of V.

The exchange rate of water between the evaporite Goose Egg Basin to the east (Figure 2) and the Phosphoria Sea (Figure 12) can be calculated from the evaporation of seawater in the Goose Egg Basin of approximately 1.5 m year^{-1} (Penman, 1948) and the precipitation of NaCl. Approximately 90% of the water imported into the Goose Egg Basin must evaporate to bring about NaCl precipitation (Harvie et al., 1980). The remaining 10% fluxed back into the Phosphoria Sea. If evaporation occurred within the Goose Egg Basin over an area roughly equal to the area of the Phosphoria Sea itself (Figure 2), then the salt in the water fluxing back into the Phosphoria Sea would have equaled 4% of the salt introduced from the open ocean. Although this is not an insignificant amount of salt, it would have had a negligible impact on the accumulation of P, limited to a slight increase in the stability of the water column of the Phosphoria Sea and indirectly to the maintenance of O_2 depletion in the bottom waters.

13.12.6 Rare Earth Elements

Unlike the marine fraction of metals that defines the local geochemistry and hydrography of seawater, the REE may have recorded the geochemistry of the open ocean (Wright et al., 1987). They are an extremely coherent group of elements, having similar chemical properties in seawater, sediments, and sedimentary rocks. They exhibit a 3+ valence state and a slightly decreasing ionic radius with increasing atomic number (Elderfield, 1988; Goldberg et al., 1963). Exceptions are Ce, which can be oxidized to the 4+ valence and Eu which can be reduced to the 2+ valence. These differences lead to differences in their relative concentrations in mafic versus felsic

source rocks and in seawater versus rivers. The differences are easily compared when concentrations are normalized on an element-by-element basis to their concentrations in one of the rock standards (Piper, 1974) and the concentrations plotted against atomic number (Figure 13).

Streams that transport REE to the oceans have patterns indicative of their partitioning into two fractions – a dissolved fraction and a colloidal fraction (Elderfield, 1988; Elderfield et al., 1990). The pattern of the colloidal fraction is similar to the shale pattern (i.e., similar to the pattern of the predominant source rocks in the drainage basin), whereas the pattern of the dissolved load may exhibit faint signs of the interelement fractionation that is characteristic of seawater, a negative Ce anomaly and an increase in normalized concentrations with increasing atomic number. Upon entering the ocean, a fraction of the dissolved Ce^{3+} is oxidized to the less soluble $4+$ valence state and partitioned more strongly into suspended phases that then settle out of the water column than the $3+$ valence REE. The $3+$ REE, including Eu^{3+} and presumably the remaining Ce as Ce^{3+} , form stable complexes mostly with CO_3^{2-} (Goldberg et al., 1963) or are adsorbed onto surface films of particulate matter (Byrne and Kim, 1990). Both processes contribute to the increase in their concentrations in seawater with increasing atomic number, the pattern unique to seawater (DeBaar et al., 1985; Goldberg et al., 1963; Piepgras and Jacobsen, 1992). The two properties increase with depth in the ocean such that the bottom water in the Pacific has the strongest negative Ce anomaly and enrichment of heavy REE relative to the light REE. The increasingly negative trend of the Ce anomaly is moderately reversed within the OMZ (DeBaar et al., 1985), possibly reflecting the reduction of solid phases, which may have scavenged Ce^{4+} in the photic zone. Several seawater-derived solid phases (Figure 13), for example, CFA (Piper et al., 1988), barite (Guichard et al., 1979), phillipsite (Piper, 1974), biogenic calcite (Palmer, 1985), and biogenic silica (Elderfield et al., 1981), exhibit similar patterns, whereas ferromanganese nodules that

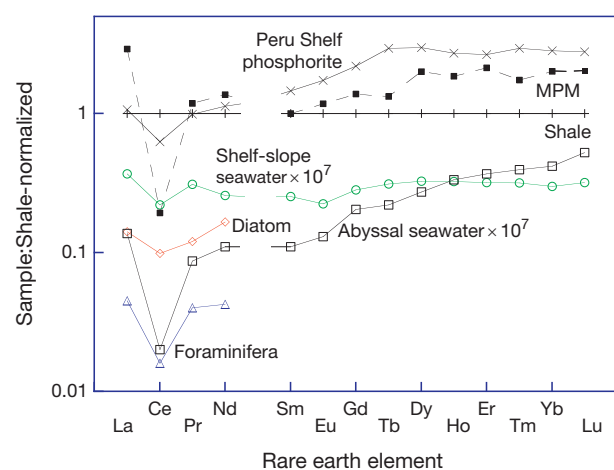


Figure 13 The REE concentrations in seawater (DeBaar et al., 1985; Elderfield, 1988; Elderfield and Greaves, 1982; Høgdahl, 1965–1968; Piepgras and Jacobsen, 1992), marine solid phases (Elderfield et al., 1981; Palmer, 1985; Piper et al., 1991), and a typical sample from the MPM at the Hot Springs mine that contains 7% P (Piper et al., 2000), all normalized on an element-by-element basis to the WSA.

accumulate in the pelagic realm exhibit a positive Ce anomaly (Elderfield et al., 1981; Piper, 1974).

Wright et al. (1987) advanced the intriguing proposal that the REE pattern of CFA in ancient phosphate deposits, specifically the Ce anomaly of biogenous apatite, might have recorded the geochemistry of ancient oceans. They reasoned that during periods of possible global anoxia (e.g., Demaison and Moore, 1980; Hallam, 2004; Meyer and Kump, 2008), the negativity of the Ce anomaly in seawater would be less than during times when the ocean was oxic, as it is currently. Following their early success, more recent work failed to support the earlier findings (Holser, 1997). Several reasons may account for this, which may not necessarily reflect a failure of Wright's original hypothesis. The Ce anomaly in surface seawater today increases in its negativity from coast and shelf environments to the open ocean (DeBaar et al., 1985; Høgdahl, 1965–1967), although Elderfield et al. (1990) documented a more complex trend in the North Atlantic Ocean. As noted earlier, the Ce anomaly becomes increasingly more negative from the surface to abyssal depths (Elderfield and Greaves, 1982; Goldberg et al., 1963; Piepgras and Jacobsen, 1992), with the exception of its value in the OMZ. A diagenetic overprint may largely have altered the REE pattern following deposition (Holser, 1997). And lastly, the Ce anomaly within individual phosphorites commonly exhibits a range of values (Jarvis, 1984; Piper, 2001) that requires the analysis of several samples, particularly samples strongly enriched in CFA that may limit the range of the anomaly of a single deposit (Figure 14). On the positive side, the pelletal CFA fraction of the sediments may retain its REE signature of deposition, similar to the retention of its isotopic signature (Shemesh et al., 1988), whereas biogenic apatites, such as conodonts and fish

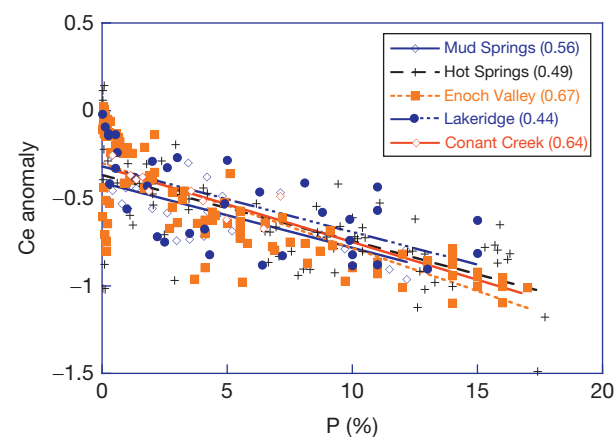


Figure 14 Relationship in the MPM between Ce anomalies and the concentrations of P, where the Ce anomaly is defined as $\log_{10} ((3 \times Ce/83)/((2 \times La/41) + (Nd/38)))$. The mean of the anomalies in samples that have P concentrations greater than 10% (greater than ~60% CFA) is -0.91 ± 0.1 . The coefficients of determination of the regressions (r^2) are listed in the legend. The scatter reflects the variation in the anomalies of the different hosts of the REE (largely Al silicates, carbonates, and CFA) and the two REE sources (terrigenous debris and seawater). The variation is seen clearly in the samples that have less than 1% CFA, which are composed mostly of calcite and dolomite, with a strongly negative Ce anomaly, and lithogenous material, with a zero anomaly. Adapted from Piper DZ (2001) Marine chemistry of the Permian Phosphoria Formation and basin, southeast Idaho. *Economic Geology* 96: 599–620.

debris (Grandjean-Lécuyer et al., 1993), may lose that record during burial.

Tens of samples of the CFA-enriched units from the MPM (Piper, 2001) and the Lisburne Group of Carboniferous age in northern Alaska (Dumoulin et al., 2011) have patterns that exhibit a Ce anomaly significantly more negative than the Ce anomaly of the Peru Shelf deposit (Figure 13). It averages -0.9 in those samples with greater than 10% P. Analyses by the authors (DZP) show that pelletal CFA-enriched samples from the Miocene Pungo River deposit in the eastern United States (Riggs et al., 2000) have Ce anomalies that are similar to the Peru Shelf deposit. Cerium anomalies of the Paris Basin phosphorites are intermediate between these two extremes (Jarvis, 1984).

According to the hypothesis of Wright et al. (1987), the REE pattern of the MPM and of the Lisburne Group may have recorded a global oxic event in the late Paleozoic. Indeed, Berner (2006) presented an O_2 model of the atmosphere for the Phanerozoic that identified a significantly elevated O_2 concentration in the late Paleozoic, owing to the rise of large vascular land plants. In his model, O_2 decreased sharply at the end of the Paleozoic and then gradually increased to reach its present value approximately 100 Ma. Since then, it has remained relatively constant and markedly lower than the late Paleozoic maximum. This explanation might account for the weak anomaly of the Miocene and modern Peru Shelf deposits and the strongly negative anomaly of the Carboniferous–Permian deposits. However, establishing a relationship between the Ce anomaly of CFA and the ambient O_2 atmospheric concentration requires confirmation from analyses of many additional samples in additional deposits.

13.12.7 Summary and Conclusions

Marine basins in which phosphorites have accumulated in the past include inland seas, ocean corridors that traversed continents, and expansive continental shelves. The hydrographic and chemical properties of these marine environments likely differed from one to the other and even during the deposition of any single deposit. Even so, interelement relationships within the seawater-derived sediment fractions may have recorded the biogeochemistry of the various basins, while element accumulation rates recorded basin hydrography. How closely the present composition of a phosphorite might reflect these seawater properties depends on the preservation of the chemical record during deposition and subsequent burial and weathering. The composition of the Permian MPM of the Phosphoria Formation has been largely retained since its deposition. Thus, its elemental composition may provide a means for deciphering the hydrography and marine chemistry of the water column under which it and other deposits accumulated.

1. The accumulation rate of the bulk sediment and of separate sediment fractions in the MPM can be estimated owing to now available reliable geologic ages established by others. The average accumulation rate of the terrigenous-derived lithogenous fraction of the MPM in the central region of the basin, where the maximum depth was approximately 350m, reflects deposition in a sediment-starved basin. Minimal dilution of the marine fraction by the lithogenous

fraction contributed prominently to the strongly elevated concentrations of the marine sediment fractions and specifically to the concentration of the carbonate–fluorapatite mineral francolite (CFA).

2. The distributions of the trace elements that are hosted by heavy minerals (e.g., Ti and Zr) reflect a series of regression–transgression events. At the Hot Springs mine site, the maxima of the Al- and Ga-normalized contents of Ti and Zr, respectively, may correspond to Permian age glacial events in the southern hemisphere. During low sea level stand regression events, the heavy minerals were transported farther into the basin than during high sea level stand transgression events, when the heavy minerals were largely retained on the shelf and in river estuaries. Thus, their distributions in the MPM are a depositional feature rather than an artifact of seafloor erosion and winnowing.
3. Accumulation rates of P, C_{org} , and the trace nutrients Ni, Cd, Cu, and Zn, as opposed to their concentrations, yield a mean level of primary productivity of $720 \text{ g C m}^{-2} \text{ year}^{-1}$, an upwelling rate of 30 m year^{-1} , and mean RT of water in the photic zone of 2 years. Aluminum-normalized trace-nutrient contents and P concentrations suggest that periods of greatest upwelling occurred during low stands of sea level, during the regression events, although mere variable accumulation rates of lithogenous sediment may also have contributed.
4. Accumulation rates of the redox-sensitive trace metals (Cr, Mo, U, and V) and the balanced loss in the bottom water between the major reductant – organic matter – that settled out of the photic zone and dominant oxidants – O_2 and NO_3^- – that were imported from the open ocean yield an RT for the bottom water of $c. 10$ years. This robust exchange with the open ocean supplied a high flux of trace metals and nutrients into the basin that supported their high accumulation rates on the seafloor and high level of primary productivity in the photic zone.
5. Interelement ratios of Cr:Mo and V:Mo recorded redox conditions of the bottom waters as being dominantly sub-oxic. The covariance between the concentration of these trace metals versus P and C_{org} concentrations identify the dependence of bottom-water O_2 depletion on the rate of primary productivity in the photic zone.
6. The exchange of water between the Phosphoria Sea and evaporite basins to the east, that is, the export of surface water from the Phosphoria Sea into these basins and reflux of brines back into the Phosphoria Sea, influenced insignificantly the accumulation of CFA and associated trace metals in the MPM. It may possibly have contributed indirectly to the maintenance of O_2 depletion in the bottom waters of the Phosphoria Sea.
7. Whereas the trace metals in phosphate deposits identify the local hydrography and biogeochemistry of the water column, the REE may have recorded global seawater redox conditions. The strongly negative Ce anomaly of the phosphate-enriched samples within the MPM suggests that seawater in the coeval open ocean was more oxic than today, in apparent agreement with a model of the O_2 concentrations of the Phanerozoic atmosphere that exhibit a uniquely elevated concentration during Permian/Carboniferous time.

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