

Sedimentary phosphate formation in warm shallow waters: new insights into the palaeoceanography of the Permian Phosphoria Sea from analysis of phosphate oxygen isotopes

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Abstract

Oxygen isotopic analyses of the structural phosphate ($\delta^{18}\text{O}_p$) in sedimentary phosphorites of the Upper Permian Phosphoria Formation reveal that phosphogenesis occurred across a broad range of palaeoenvironments. The $\delta^{18}\text{O}_p$ values from well-preserved hand-picked phosphate-grain separates range from 20.2 to 13.7 (± 0.5)‰ SMOW, with the lowest values in the most landward shallow-water deposits and the highest values in the most basinward deeper water deposits. The relationship between the maximum burial depth and $\delta^{18}\text{O}_p$ is opposite to that predicted if burial diagenesis was responsible for the isotopic signature of these phosphate grains. This suggests that the regional trend in oxygen isotopic data is not due to burial diagenesis. The range in oxygen isotopic values does correspond to the potential range of palaeotemperatures in the shallow and broad epicontinental Phosphoria Sea. The range is 14–42°C (± 3.5 °C) assuming a seawater $\delta^{18}\text{O}$ of -2.5 ‰ SMOW. Palaeotemperatures along an offshore to onshore transect indicate that upwelling involved temperate (14–26°C; mean of 21°C) but not cold waters, and that warming across the palaeoshelf resulted in mean shallow-water temperatures of 34–37°C. The latter values approximate those predicted by climate and ocean circulation models. These warm palaeotemperatures provide further evidence that phosphogenesis in the epicontinental Phosphoria Sea occurred under palaeoceanographic conditions that were different from modern phosphorite depositional systems. This suggests that a purely actualistic approach to the interpretation of the Phosphoria phosphorites is not valid. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Phosphoria Rock Complex (PRC; Phosphoria, Park City, and Goose Egg formations) is a succession of phosphorite–siltstone–chert–carbonate–evaporite

lithologies that were deposited on the western margin of North America during Permian time (latest Leonardian through Guadalupian series). These deposits contain five to six times the total phosphorus in today's oceans (McKelvey et al., 1959; Sheldon, 1989). Coincident with the phosphate are organic carbon contents that average >4 wt% and are locally as high as 30 wt% (Maughan, 1984). These characteristics have long been cited as evidence for a coastal upwelling system in the Phosphoria Sea. Upwelling is also predicted by both conceptual and numerical

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atmospheric circulation models (Parrish, 1982; Kutzbach and Ziegler, 1994; Golonka et al., 1994) and palaeowind directions that suggest a net offshore movement of surface waters by Ekman transport (Sheldon et al., 1967; Parrish and Peterson, 1988).

In general, the process of phosphate formation (phosphogenesis) is believed to involve the release of elemental phosphorus through the bacterial-breakdown of organic matter, and the subsequent precipitation of carbonate–fluoroapatite as the mineral francolite (cf. Jarvis, 1992; Krajewski et al., 1994; Trappe, 1998). It is likely that all stages in this process involve bacteria. Phosphate may precipitate on or near the seafloor in muddy organic matter-rich sediments, but subsequent winnowing and reworking is believed to be necessary to concentrate these precipitates (peloids, ooid-like and nodular grains) into phosphorite beds (Baturin, 1982; Föllmi, 1990; Trappe, 1998). At the scale of an individual bed, these concepts are widely regarded as applicable to the PRC (e.g. Hiatt, 1997; Trappe, 1998; Stephens and Carroll, 1999).

At the larger scale of a regional palaeoceanographic system, the origin of the extensive phosphate deposits in the PRC has been more enigmatic. The traditional view of the Phosphoria system is that upwelling occurred along a shelf margin and involved cold, nutrient-rich oceanic waters (e.g. Wardlaw, 1980, 1995; Parrish, 1982; Sheldon, 1984; Wardlaw and Collinson, 1984). McKelvey et al. (1959) and Sheldon (1963) proposed this model based on analogy to modern continental margin upwelling systems. More recent research on the Phosphoria has expanded our view of these rocks. It now appears that the Phosphoria depositional basin was a relatively shallow (<200 m; Sheldon, 1984; Peterson, 1984), semi-restricted epicontinental embayment (Scotese and Langford, 1995; Trappe, 1998). Phosphogenesis occurred not only in the deeper portions of the basin, but also in shallower, inner-shelf settings (Sheldon, 1984; Peterson, 1984; Trappe, 1998; Stephens and Carroll, 1999; Hendrix and Byers, 2000). Numerical modeling results indicate that mean summer air temperatures over the shallow Phosphoria Sea may have been as high as 35–40°C (Kutzbach and Ziegler, 1994; Golonka et al., 1994; Barron and Fawcett, 1995), and wind-driven coastal upwelling was a seasonal phenomenon (Kutzbach and Ziegler, 1994). Elevated salinities and stratification of

the water column have also been proposed based on stratigraphic associations and biomarker evidence (Hite, 1978; Dahl et al., 1993; Trappe, 1998; Stephens and Carroll, 1999).

The shallow nature of the basin and the evaporation necessary to generate elevated salinities suggests that water temperatures in the Phosphoria Sea should have been warm—much warmer than any modern phosphogenetic system. One prior effort to use oxygen isotope palaeothermometry on the Phosphoria phosphorites did indeed find evidence of warm waters (33.7–40.4°C; Piper and Kolodny, 1987), but utilized only a few samples from a single locality. Others have argued that palaeothermometry results may be biased by burial diagenesis (McArthur et al., 1986; Shemesh et al., 1988), although these arguments were based on limited sample sets that had no stratigraphic or regional context. Herein we present a new isotopic data collected along a regional basin-to-shoreline transect in the thickest phosphorite-rich unit in the PRC. Our data shows no relationship to maximum burial depth. Rather, the results suggest that phosphorites were deposited across a broad temperature spectrum from temperate (but not cold) waters in more basinward settings to very warm waters in the shallowest portions of the Phosphoria Sea.

2. The Phosphoria Rock Complex

Deposition of the PRC occurred in the Phosphoria Sea (Fig. 1), which formed in a shallow marginal foreland basin on the western margin of North America at a palaeolatitude of about 20°N (Scotese and Langford, 1995). This sea was partially separated from the Panthalassa Ocean by an island arc system, and was bounded to the north by low relief palaeohighs, to the south by the Ancestral Rockies, and to the east by evaporite basins (Sheldon et al., 1967; Trappe, 1998). PRC deposits extend over several thousand square kilometers in Wyoming, eastern Idaho, southwestern Montana, and northern Utah (McKelvey et al., 1959).

The PRC is composed of three unconformity-bounded sequences (Fig. 2). Phosphate (as francolite) occurs throughout all three sequences, but phosphorites (beds with >10% francolite) are concentrated in the Meade Peak and Retort members of the

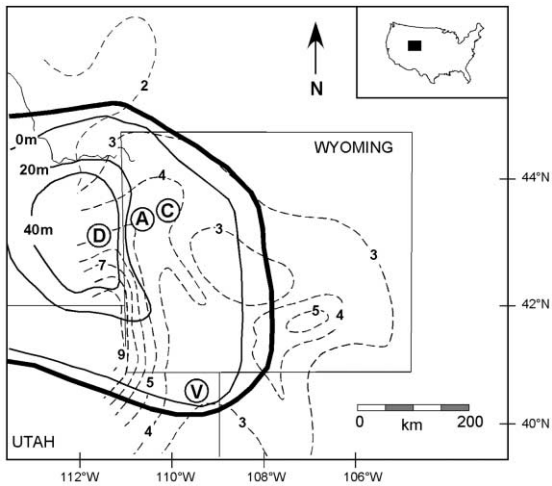


Fig. 1. Map of the study area showing limit (bold solid line) of the Phosphoria Sea during Meade Peak deposition (black box on inset map shows location of the study area). Isopach contours (in meters) of the Meade Peak Member are in solid lines (from Maughan (1984)) and estimated maximum burial depths (in kilometers) for the entire Phosphoria rock complex are in dashed lines (from Maughan (1983)). The position of the four stratigraphic sections utilized in this study are indicated by letters (D = Dry Ridge; A = Astoria Hot Springs, C = Crystal Creek; V = Vernal-Brush Creek). Exact locations of each section can be found in Hiatt (1997).

Phosphoria Formation in the upper two sequences. These phosphorite-rich units have long been interpreted to represent peak upwelling in the Phosphoria Sea. Our focus is the Meade Peak Member, which is the larger of the two phosphate-rich deposits. The Meade Peak is a seaward-thickening wedge of sediments whose depocenter was in southeastern Idaho (Fig. 1; Maughan, 1984). To the east, the Meade Peak pinches out into green shales and carbonates, which in turn grade into red beds and eventually evaporites in central Wyoming (Fig. 2; Maughan, 1983; Peterson, 1984). Palinspastic reconstructions and regional facies patterns in the entire PRC have been interpreted to suggest a shelf margin just to the east of the Meade Peak depocenter (e.g. McKelvey et al., 1959; Peterson, 1984), but no distinctive shelf-margin facies in the Meade Peak has ever been described. Phosphate in this unit occurs in grain-supported phosphorites, dolomitic siltstones, carbonates, and sandstones. Phosphate grain types include peloids, ooids, bioclasts and intraclasts.

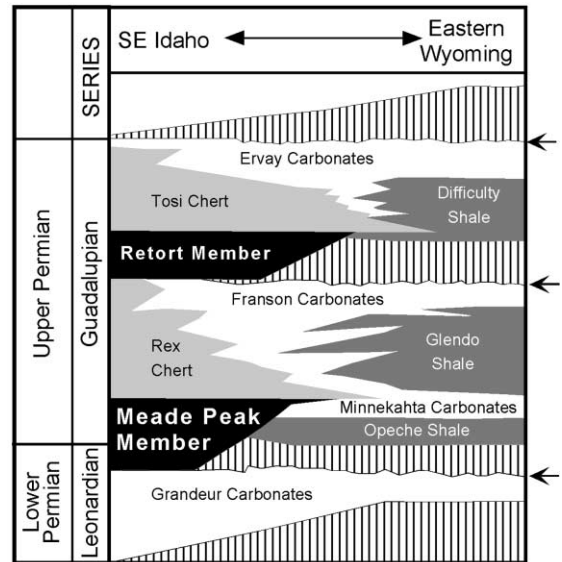


Fig. 2. Generalized stratigraphic relationships in the Phosphoria rock complex (modified from Maughan (1984)). Arrows denote tops of unconformity-bounded sequences; vertical lines denote hiatuses.

3. Methods

3.1. Field and analytical methods

Phosphate samples were collected from four stratigraphic sections that form an offshore to onshore transect through the Meade Peak Member (Fig. 1). These sections were chosen for their stratigraphic completeness (e.g. Fig. 3) and lack of visible chemical or textural alteration. The Dry Ridge section (a mine bulldozer trench) lies within the phosphate-rich depocenter of the Meade Peak in a position that most prior workers have labeled slope (e.g. Maughan, 1984) or shelf margin (e.g. Stephens and Carroll, 1999). The Astoria Hot Springs (road cut; Fig. 3A) and Crystal Creek (natural exposure) sections are on the margins of the main depocenter and they, along with the most landward section (Vernal-Brush Creek, a fresh mine exposure; Fig. 3B) are located on what was a broad ramp-like palaeoshelf. Lithologic units in each of the four sections were described in detail, and samples were collected on a decimeter scale.

Isotopic analysis of oxygen from the structural phosphate ($\delta^{18}\text{O}_p$) within the sedimentary francolite was performed using 10–30 mg samples of

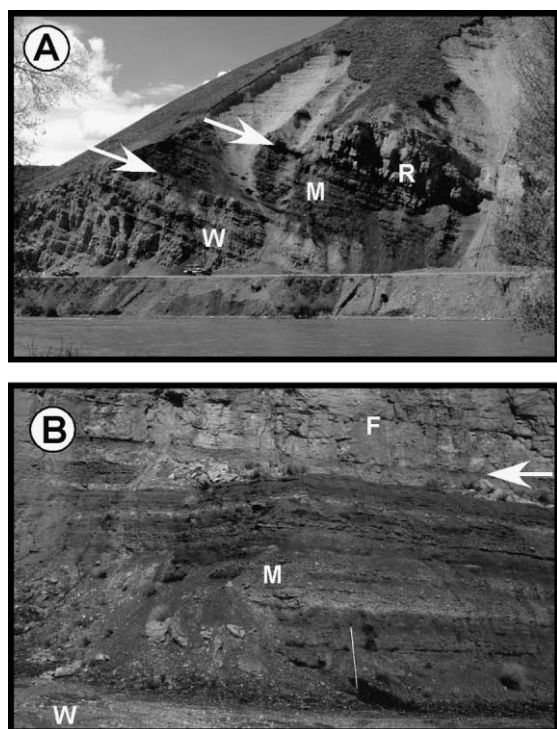


Fig. 3. Outcrop exposures of two measured sections utilized in this study. (A) The Meade Peak Member (M) at the Astoria Hot Springs road cut 40 k south of Jackson, Wyoming. The contact with the overlying Rex Chert (R) and the underlying Lower Permian Wells Formation (W) are shown by the white arrows. Note automobiles for scale. (B) Meade Peak Member at the Vernal-Brush Creek section, Vernal, Utah. The staff in the foreground is 1.5 m tall and rests atop sandstones of the Wells Formation. The contact between the Meade Peak and the overlying dolomite of the Franson Member (F) is shown by the white arrow.

individual, hand-picked phosphate peloids. These individual grains were isolated by first disaggregating the granular phosphorite rock, sieving the resultant material into size fractions, and then passing the sand fractions through a magnetic susceptibility separator to remove glauconitic and pyritic grains. A heavy liquid separation (undiluted acetylene tetrabromide, $\rho = 2.96$ at 25°C) was then used to remove carbonate and silicate grains. The remaining sample, which XRD analyses showed to be 100% francolite, was washed multiple times with acetone and deionized water, and dried in an oven at 80°C for 12 h. Individual phosphatic peloids were handpicked from these concentrated and washed splits. Only the best-preserved peloids that exhibited no phosphate

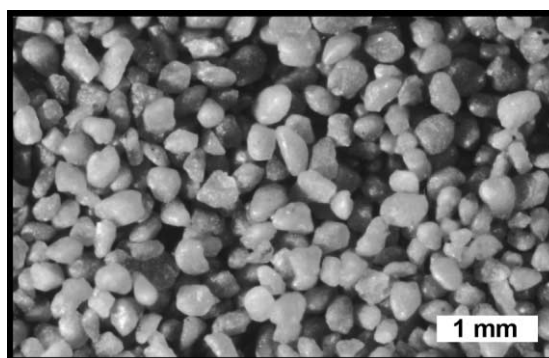


Fig. 4. Photomicrograph in reflected light of exceptionally well-preserved, fine-grained, translucent phosphate peloids typical of the samples from which cement and matrix-free grains were hand-picked for isotopic analysis (sample VBC-12.5 from the Vernal-Brush Creek section).

cement on their surfaces were chosen for analysis, with good preservation indicated by the lack of any visible discoloration or leaching of peloid surfaces when viewed at magnifications of $30\times$ with a binocular microscope (Fig. 4).

Oxygen was extracted from the PO_4 radical using the technique developed by O'Neil et al. (1994). All isotopic measurements were made with a Finnigan MAT 252 mass spectrometer at the USGS isotope laboratory in Denver, CO. Analytical precision ($\pm 1\sigma$) over a 12 month period was 0.4‰ SMOW ($n = 21$) for an internal apatite crystal standard and 0.8‰ SMOW ($n = 28$) for NBS-120c, a phosphate-rock standard. The latter value and the phosphate palaeotemperature equation of Longinelli and Nuti (1973a) yield an error estimate of $\pm 3.5^{\circ}\text{C}$ for calculated palaeotemperatures.

3.2. Palaeotemperature calculations

There is no universal agreement upon palaeotemperature expression for the oxygen isotopic fractionation between water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) and the phosphate radical ($\delta^{18}\text{O}_{\text{P}}$). Published equations are of four general derivations. One set is based on the observed oxygen isotopic fractionation between water and $\delta^{18}\text{O}_{\text{P}}$ in living organisms from a variety of modern environments (mostly marine) and over a temperature range of $3\text{--}28^{\circ}\text{C}$. Longinelli and Nuti (1973a) were the first to take this approach and their results were

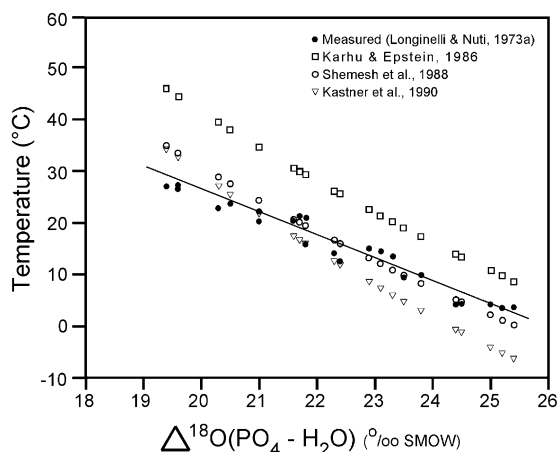


Fig. 5. Actual temperatures of formation versus calculated temperatures of formation for modern phosphate-bearing shells. Actual temperatures and measured $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_\text{P} - \delta^{18}\text{O}_\text{H}_2\text{O}$) values (solid dots) are from Longinelli and Nuti (1973a) and the solid line is their palaeotemperature expression through that data. Calculated temperatures are based on the same measured $\Delta^{18}\text{O}$ values and the equations of Karhu and Epstein (1986), Shemesh et al. (1988), and Kastner et al. (1990). Note the poor match of most calculated temperatures to observed temperatures.

confirmed by Longinelli and Nuti (1973b), Kolodny et al. (1983), and Lécuyer et al. (1996). The diversity of environments and organisms that have been sampled in these studies and the fact that each set of workers derived essentially the same results indicates that the Longinelli and Nuti (1973a) equation is not subject to significant error due to vital effects or difficulties in measuring the temperature and isotopic composition of habitat waters.

A second set of palaeotemperature expressions for $\delta^{18}\text{O}_\text{P}$ was derived by Karhu and Epstein (1986) and Shemesh et al. (1988). Both attempted to account for the decreased isotopic fractionation at higher temperatures by anchoring their expressions on one and two high-temperature points, respectively. However, these high-temperature points were not well constrained. Karhu and Epstein estimated the temperature of their single high-temperature point, and assumed $\delta^{18}\text{O}_\text{H}_2\text{O}$ values for three of their four low-temperature points. Shemesh et al.'s (1988) two high-temperature end members were an unpublished experimental value and the one estimated value of Karhu and Epstein (1986). Recognizing the limitation of their approach, Karhu and Epstein (1986), p. 1753

stated that "...the temperature vs. $\delta^{18}\text{O}$ relations we specify... must be considered a necessary convenience rather than as serious temperature scales."

A third approach was that of Kastner et al. (1990) who derived their expression by assuming: (1) that measured $\delta^{18}\text{O}_\text{P}$ and $\delta^{18}\text{O}_\text{C}$ (oxygen isotopic value of the carbonate radical) in Miocene Monterey Formation phosphorites had been diagenetically reset at various stages of burial; (2) that the diagenetic resetting of oxygen in each radical occurred simultaneously (i.e. that one radical was not more reactive than the other); (3) that oxygen fractionates into the CO_3 radical of apatite as it does into calcite (thus temperatures can be calculated rather than measured); and (4) that all such reactions in four different basins and at varying burial depths happened in an unevolved seawater ($\delta^{18}\text{O}_\text{w} = 1 - \text{‰ SMOW}$). Kastner et al. believed that the Monterey $\delta^{18}\text{O}_\text{P}$ values were explained by bacterially mediated enzymatic breakdown of the phosphate radical during progressive burial diagenesis, which allowed isotopic re-equilibrium of $\delta^{18}\text{O}_\text{P}$ and $\delta^{18}\text{O}_\text{C}$ to occur. Strictly speaking, the equation of Kastner et al. (1990) is not a calibration equation because $\delta^{18}\text{O}_\text{P}$ is the only measured parameter on which the equation is based.

The fourth approach to establishing a $\delta^{18}\text{O}_\text{P}$ palaeotemperature equation is that of Blake et al. (1997). They synthesized low-temperature (15–35°C) flourapatites by enzyme- and microbially-mediated reactions of phosphate and organic matter. Their data overlap with that of Longinelli and Nuti (1973a), which further confirms the validity of the Longinelli and Nuti equation and suggests that it is valid to a temperature of at least 35°C. Due to the size and temperature range of their database, Blake et al. (1997) cautioned that their resultant palaeotemperature expression is a provisional one, thus we did not consider it further.

Fig. 5 illustrates how the various palaeotemperature equations relate to each other. The $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_\text{P} - \delta^{18}\text{O}_\text{H}_2\text{O}$) values and corresponding temperatures actually measured by Longinelli and Nuti (1973a) are shown as solid dots, and the solid line is a linear regression through those known (i.e. the Longinelli and Nuti expression). The other trends are the temperatures calculated when the same known $\delta^{18}\text{O}$ values input into the equations of Karhu and Epstein (1986), Shemesh et al. (1988),

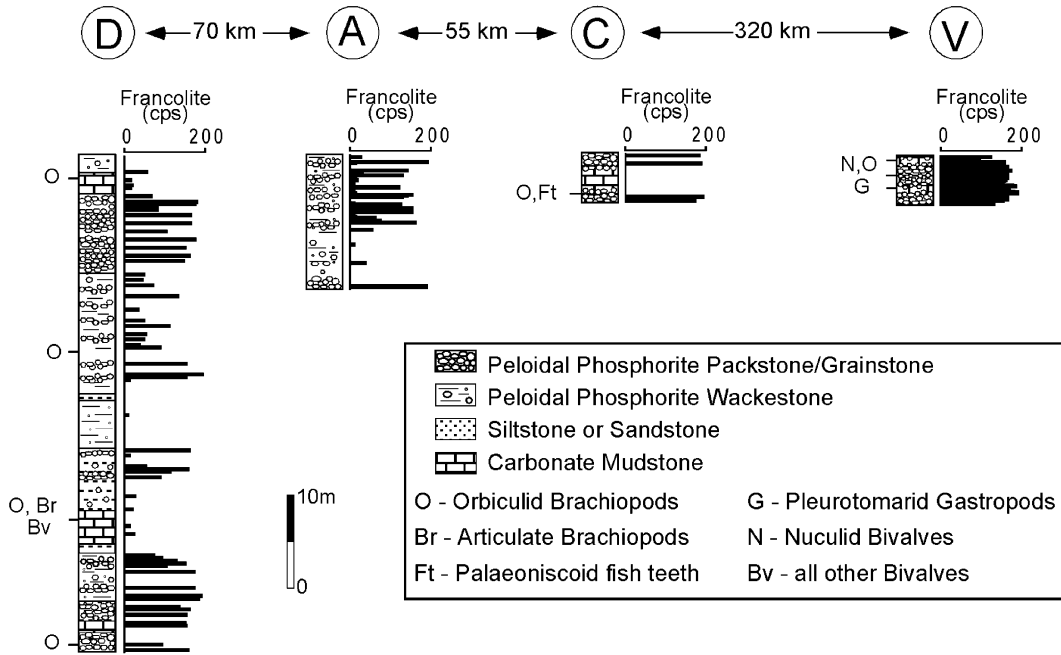


Fig. 6. Basinward (left) to shoreward (right) stratigraphic trends in fauna, lithofacies and sedimentary phosphate of the Meade Peak Member at the Dry Ridge (D), Astoria Hot Springs (A), Crystal Creek (C), and Vernal-Brush Creek (V) sections. Francolite values are in x-ray diffraction counts per second and equate to the positions of phosphorite beds (>190 cps equates to 100% francolite).

and Kastner et al. (1990). Note that the calculated temperatures do not match those actually measured by Longinelli and Nuti (1973a). The deviations between calculated and observed temperatures represent the errors in those equations. The expression of Karhu and Epstein is particularly poor over all $\delta^{18}\text{O}$ and temperatures that correspond to earth surface conditions. The expression of Kastner et al. is poor at $\delta^{18}\text{O}$ greater than 23‰ (i.e. temperatures less than 10°C); the expressions of Kastner et al. and Shemesh et al. also predict higher than observed temperatures at $\delta^{18}\text{O}$ values less than 21‰ (i.e. temperatures greater than ~22°C).

Given the results shown in Fig. 5, we thus estimated palaeotemperatures using the most widely accepted and confirmed equation, that of Longinelli and Nuti (1973a). Unlike the expressions of Karhu and Epstein (1986) and Shemesh et al. (1988), this calibration does not attempt to force the regression through one or two poorly constrained high temperature values, nor does it require multiple assumptions, as is the case with the equation of Kastner et al. (1990).

4. Results

4.1. Sedimentology

The Meade Peak Member at the Dry Ridge (52 m thick), Astoria Hot Springs (11.6 m thick) and Crystal Creek (8.1 m thick) locations has many similarities (Fig. 6). Sediments in all three are gray to black due to organic carbon contents that are up to 16 wt% (Hiatt, 1997). Phosphorites comprise about 25% of all three sections with individual beds ranging in thickness from centimeters to one meter at Dry Ridge, and centimeters to decimeters in the other two sections (Fig. 6). All of the phosphorites in these sections are planar bedded; none showed any visible evidence of cross bedding. Each phosphorite is grain-supported and dominated by fine-grained peloids, has a sharp base, and about 15% have erosional bases that scour the underlying bed. About half exhibit a coarse sand or pebble lag and a fining-upward texture. Intercalated with the phosphorites at Crystal Creek and Astoria Hot Springs are thin-bedded non-fossiliferous, non-laminated silty

dolomite mudstones. Intercalated facies at the Dry Ridge locality consist of bioturbated siltstone, silty carbonate mudstones, and fine- to medium-grained sandstones with hummocky cross-stratification. Previous workers referred to these lithofacies as shales, but petrographic examination reveals that the 'shales' are in fact siltstones and fine-grained sandstones, as also noted by Carroll et al. (1998). At all three localities, the intercalated dolomite mudstones and siltstones also contain phosphate primarily as widely dispersed peloids.

Macrofossils are relatively uncommon in the Meade Peak Member, but each location in the transect presented here has a unique assemblage. Macrofossils are rare in the Dry Ridge section (Fig. 6), but when present, they only occur in dolomitic mudstones and consist of small bivalves, the articulate brachiopods *Leiorhynchoidea* and *Lissochonetes*, and poorly-preserved inarticulate orbiculid brachiopods; brachiopods that are indicative of dysaerobic environments in the late Palaeozoic (Kammer et al., 1986; Alexander, 1994). No macrofossils were observed at Astoria Hot Springs. The only macrofossils observed at Crystal Creek were small mechanically reworked fish teeth (order Palaeoniscoidea) and fragments of inarticulate orbiculid brachiopods, both of which occur in a coarse-grained basal phosphorite (Fig. 6).

The macrofaunal assemblage and thickness of the Dry Ridge section suggests it formed in the deepest water setting, whereas the coarse-grained and well sorted nature of the phosphorites and the dominance of carbonate facies places the Crystal Creek section in a mid-shelf position. The Astoria Hot Springs section is between the two and along the palaeoshelf-margin defined by Peterson (1984). The dark colors, abundance of organic matter, absence of infauna, and scarcity of nektonic and epifauna suggest a dominance of anoxic conditions in all three settings.

The most landward section is Vernal-Brush Creek where the Meade Peak Member is only 7 m thick (Figs. 3 and 6). All sedimentary rocks in this section are light to dark gray; the organic carbon content is very low and textural preservation of phosphate bioclasts and peloids is superb. Decimeter-thick phosphorite beds comprise 60% of the section. None of the phosphorites showed any visible evidence of cross bedding and all are planar bedded. They do not exhibit fining-upward textures; rather, all are well sorted and

consist of either fine-grained peloids or medium-grained mixtures of peloids and small intraclasts. Intercalated lithologies are thin to very thin beds of non-laminated dolomitic wackestones and silty dolomites (Fig. 6), both of which typically contain small phosphate peloids. Macrofossils, when present in the Vernal-Brush Creek section, occur in bioturbated wackestones, or as abraded lags in the phosphorites. These fossils consist of inarticulate orbiculid brachiopods, and phosphatized nuculid bivalves and pleurotomarid gastropods (Fig. 6), with the latter two being typical of nearshore, shallow-water settings in the Late Palaeozoic (Stevens, 1966). The faunal content, low-energy nature of the intercalated carbonates, proximity of this section to shoreline deposits (Stephens and Carroll, 1999), and its distance from the palaeoshelf margin all indicate deposition in a nearshore, shallow-water setting. Relative to the other three sections, the gray colors, paucity of organic carbon, and faunal assemblage at the Vernal-Brush Creek section suggest dysaerobic rather than anoxic conditions (Kammer et al., 1986).

4.2. Oxygen isotope data

Oxygen isotopic data from the phosphate radical ($\delta^{18}\text{O}_\text{P}$) of the Meade Peak phosphorites range from 13.7 to 20.2‰ SMOW ($n = 38$; Table 1). Fig. 7 shows the $\delta^{18}\text{O}_\text{P}$ data in stratigraphic and a general palaeogeographic context and shows that the $\delta^{18}\text{O}_\text{P}$ signature of the phosphorites varies regionally as a function of depositional setting. Lower values occur in the eastern, more shoreward sections. From west (Dry Ridge) to east (Vernal-Brush Creek), mean and standard deviations for the four sections studied are 18.6 ± 0.8 , 16.9 ± 0.5 , 15.5 ± 1.6 , and 14.9 ± 0.7 ‰ SMOW.

5. Discussion

The process of francolite precipitation begins at or slightly below the sediment–water interface, and thus the oxygen isotopic composition of the phosphate peloids should reflect bottom water conditions (e.g. Kolodny and Luz, 1992). Phosphogenesis can continue into the early burial setting where it typically involves francolite replacement of carbonate skeletal grains and precipitation of francolite cement (e.g.

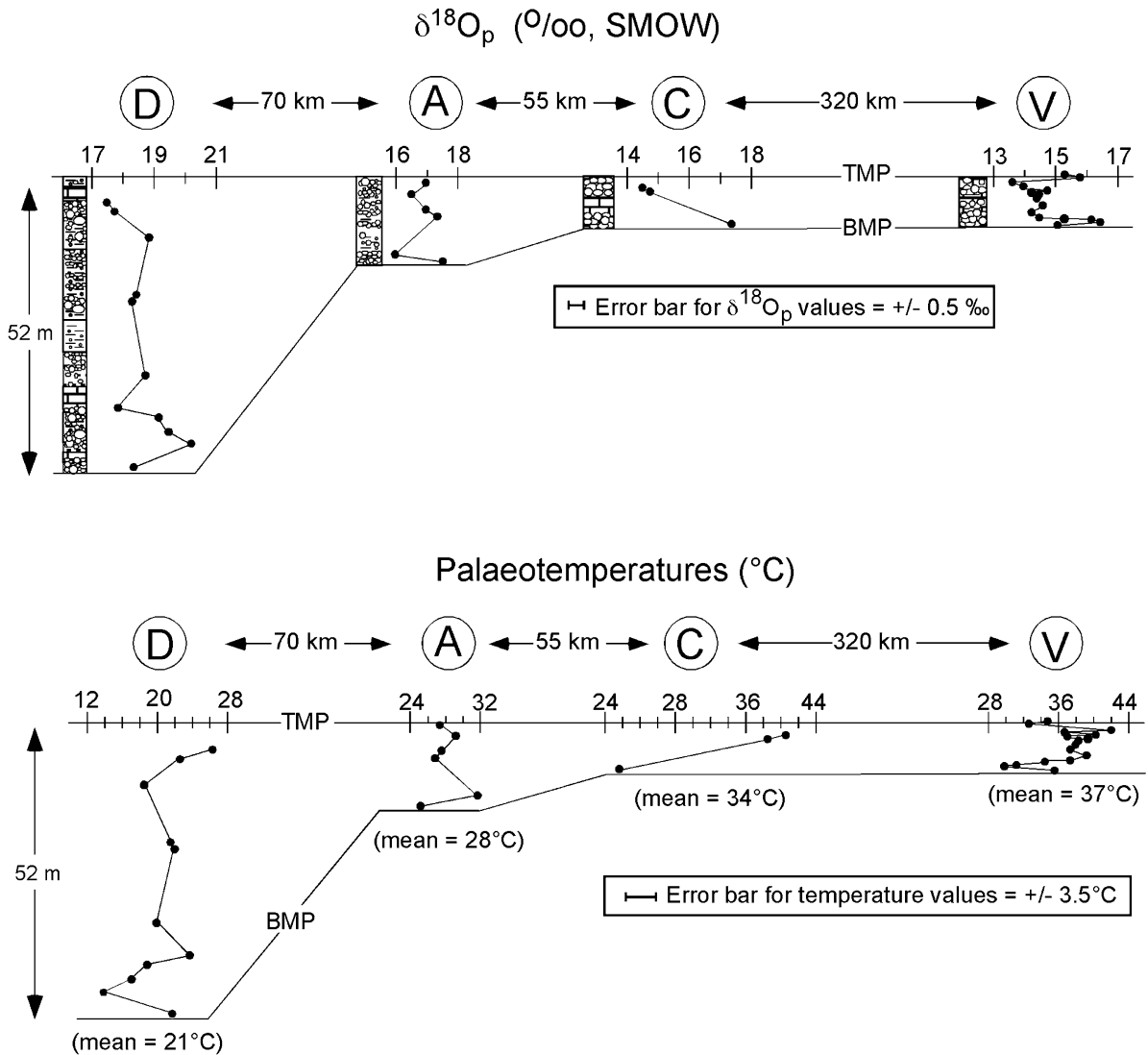


Fig. 7. (A) Stratigraphic plots of observed $\delta^{18}\text{O}_p$ values and (B) calculated palaeotemperatures of phosphogenesis in the Meade Peak Member. The sections are arranged with the most basinward to the left and the most landward to the right. (D = Dry Ridge; A = Astoria Hot Springs, C = Crystal Creek; V = Vernal-Brush Creek). BMP is the unconformity at the base of the Meade Peak Member, and TMP is the top of the Meade Peak.

Trappe, 1998). Because of these potential early diagenetic effects, extraction of palaeoenvironmental signals from phosphorites requires the careful selection of materials and the ability to analyze very small samples. This requirement was met in this study due to our ability to focus on single grains of well-preserved, cement-free, fine-grained sand-sized phosphate peloids.

It has been shown that some ancient phosphorites are the product of long distance transport (e.g. Glenn et al., 1994; Trappe, 1998), and that the $\delta^{18}\text{O}_p$ of phosphate can be reset by metamorphism (McArthur, 1985), extreme tropical weathering, or recrystallization in 'normal' burial environments due to bacterial-enzymatic breakdown of the phosphate radical (e.g. Kastner et al., 1990). Therefore, to use $\delta^{18}\text{O}_p$ data as a

Table 1
Isotopic results and calculated palaeotemperatures

Sample ^a	$\delta^{18}\text{O}_p$ (‰ SMOW)	Palaeotemperature ^b (°C)
<i>Dry Ridge (D)</i>		
DR-159.5	17.3	26.2
DR-156.0	17.7	24.5
DR-140.0	18.9	19.3
DR-105.0	18.4	21.7
DR-101.0	18.3	21.8
DR-69.0	18.8	19.9
DR-40.0	17.8	23.9
DR-35.5	19.1	18.7
DR-26.0	19.4	17.1
DR-19.5	20.2	13.7
DR-7.5	18.3	21.9
<i>Astoria Hot Springs (A)</i>		
AHS-71.3	17.0	27.6
AHS-62.1	16.6	29.3
AHS-54.3	17.0	27.7
AHS-49.8	17.2	26.9
AHS-27.0	16.0	31.9
AHS-26.6	17.5	25.2
<i>Crystal Creek (C)</i>		
CRC-12.5	14.5	38.3
CRC-10.5	14.7	37.4
CRC-2.0	17.4	25.8
<i>Vernal-Brush Creek (V)</i>		
VBC-23.0	15.3	34.7
VBC-22.5	15.9	32.5
VBC-20.0	13.7	42.0
VBC-19.5	14.9	36.6
VBC-17.0	14.5	38.3
VBC-16.0	14.0	40.4
VBC-15.5	14.8	37.0
VBC-14.0	14.2	39.5
VBC-12.5	14.5	38.5
VBC-12.0	14.6	37.9
VBC-11.0	14.4	38.7
VBC-9.0	14.7	37.4
VBC-5.0	14.2	39.6
VBC-2.5	14.8	37.2
VBC-1.1	15.2	35.1
VBC-1.0	16.2	31.0
VBC-0.5	16.5	29.7
VBC-0.0	15.1	35.8

^a Sample number refers to footage in the measured sections through the Meade Peak Member. The lowest number for each location corresponds to the base of the Meade Peak Member.

^b Palaeotemperatures were calculated using the equation of Longinelli and Nuti (1973a) and assuming $\delta^{18}\text{O}_{\text{SW}} = -2.5\text{‰ SMOW}$.

means of determining palaeo-bottom water temperatures of the Phosphoria Sea it is necessary to first demonstrate that the $\delta^{18}\text{O}_p$ signal is not a product of burial recrystallization and that there has not been significant cross-shelf transport of phosphate grains. The former is difficult because, as Kastner et al. (1990) pointed out, there are no petrographic or geochemical criteria that discriminate primary palaeoenvironmental $\delta^{18}\text{O}_p$ signals from those that represent burial diagenesis.

5.1. Primary isotopic signal or burial recrystallization?

McClellan (1980) and McArthur (1985) noted that several geochemical parameters in Meade Peak francolites varied with burial depth and were also different from most Miocene and younger francolites from around the world. In particular, they noted that the carbonate in the phosphate crystal structure and $\text{Na}/\text{P}_2\text{O}_5$ ratios systematically decreased from east–west. Since maximum burial depths increase to the west, these workers suggested that the geochemical signatures of the PRC phosphorites had been altered by burial, which would also explain the deviation in geochemical signatures relative to unaltered Neogene phosphorites. Subsequently, $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}_p$ in a small number of Meade Peak phosphorites were found to covary and be 5 to 10‰ lower than most Miocene and younger phosphorites (McArthur et al., 1986; Shemesh et al., 1988). These data were also interpreted to reflect burial alteration by McArthur et al. (1986) and Jarvis et al. (1994), although systematic variations in Meade Peak isotopic values with respect to burial depth were never demonstrated. In fact, many workers currently believe that $\delta^{18}\text{O}_p$ values of pre-Cretaceous phosphorites, to varying degrees, represent diagenetic processes (e.g. Jarvis et al., 1994).

We do not dispute the possibility that $\delta^{18}\text{O}_p$ values of some phosphorites have indeed experienced burial alteration. However, we see two potential flaws in the above arguments when applied to the Meade Peak phosphorites. First is that burial alteration may explain the trends seen in geochemical parameters like Na and CO_3 , but applying this hypothesis to $\delta^{18}\text{O}_p$ data ignores the fact that some geochemical proxies are much less likely to alter than others. The

chemical bonds in the phosphate radical are very strong, certainly much stronger than those in the CO_3 radical, and not readily susceptible to breakdown by inorganic reactions (e.g. Kastner et al., 1990; Kolodny and Luz, 1992; O'Neil et al., 1994; Blake et al., 1997). Cations that substitute in the phosphate structure, CO_3 contents, and $\delta^{18}\text{O}_\text{C}$ values should thus alter far more readily than $\delta^{18}\text{O}_\text{P}$. Shemesh et al. (1988) recognized this relationship and pointed out that the phosphate radical is the geochemical parameter most likely to retain a primary depositional signal.

Changes in the $\delta^{18}\text{O}_\text{P}$ value with burial are only possible if bacterially-mediated reactions led to the breakage of the P–O bonds (e.g. Kolodny et al., 1983). Kastner et al. (1990) argued for such a process in the Miocene Monterey Formation of California. Their data, which has a similar range of values as those reported here, show that samples with low $\delta^{18}\text{O}_\text{P}$ values, which they interpreted as recrystallized, experienced the greatest burial depths. However, unlike samples from the Meade Peak, Monterey phosphorites are associated with dolomites that exhibit very high $\delta^{13}\text{C}$ values (up to +10‰ PDB) which are suggestive of methanogenesis. As Kolodny and Luz (1992) pointed out, the bacterial processes that led to the breakage of the P–O bonds are likely the same ones that produced methanogenesis. This in turn suggests that bacterially mediated burial alteration of the Meade Peak phosphatic peloids would be indirectly implicated by evidence for methanogenesis. However, such evidence is lacking as no Meade Peak phosphorites or interbedded dolomite has $\delta^{13}\text{C}$ values that would suggest a relationship between $\delta^{18}\text{O}_\text{P}$ values and burial-related methanogenesis (Hiatt, 1997).

The second potential flaw in the burial alteration hypothesis is the assumption that Miocene and younger phosphorites define the primary isotopic composition of francolites regardless of geologic age. This assumption suggests that any phosphorite whose $\delta^{18}\text{O}_\text{P}$ values differ from those of young phosphorites must have experienced diagenetic recrystallization. Implicit in this assumption is that all sedimentary francolites have formed under similar environmental conditions, which ignores secular changes in ocean water chemistry and the diverse palaeoenvironmental settings in which ancient

phosphorites are known to have formed (e.g. Cook et al., 1990; Glenn et al., 1994). In fact, it is becoming clear that the Meade Peak phosphorites did not form under conditions like any Neogene or Quaternary phosphogenetic environment (Dahl et al., 1993; Hiatt, 1997; Trappe, 1998; Stephens and Carroll, 1999); thus those younger deposits are not reasonable analogs for the Meade Peak phosphorites. Shemesh et al. (1988; p. 2571) pointed out that “it is quite possible that the Recent is an anomalous time in this respect, i.e. Recent phosphorites are found in relatively deep water and in a sea with a sharp thermal structure.”

The question is thus whether Meade Peak $\delta^{18}\text{O}_\text{P}$ data reflect palaeoenvironmental conditions or are a reflection of burial diagenesis. The fundamental test of these competing hypotheses requires that isotopic data be collected across the palaeoshelf and from locations that provide a range of maximum burial depths. All prior $\delta^{18}\text{O}_\text{C}$ and $\delta^{18}\text{O}_\text{P}$ datasets from the Phosphoria (e.g. McArthur et al., 1986; Piper and Kolodny, 1987; Shemesh et al., 1988), however, are too limited with respect to depositional environment, stratigraphic context, and burial depth to perform this test. Our data were collected along a west-to-east transect and thus do provide a true test of whether burial alteration affected Meade Peak $\delta^{18}\text{O}_\text{P}$ values. If burial alteration is the case, then a trend of decreasing $\delta^{18}\text{O}_\text{P}$ with increasing burial depth is predicted (e.g. Kastner et al., 1990; Jarvis et al., 1994). However, Fig. 8 shows that such a trend is not observed in our data. The lowest $\delta^{18}\text{O}_\text{P}$ values occur in the Vernal-Brush Creek section, which experienced the least amount of burial, whereas the greatest $\delta^{18}\text{O}_\text{P}$ values occur in the Dry Ridge and Astoria sections, which were the most deeply buried sections. These trends are exactly opposite of those that would result from burial alteration. We therefore conclude that none of the $\delta^{18}\text{O}_\text{P}$ values reported herein or the stratigraphic trends are the result of burial alteration. Although some minor degree of isotopic exchange cannot be completely ruled out, we accept the hypothesis that the data record a primary palaeoenvironmental signature.

5.2. Autochthonous phosphate or cross-shelf transport?

If the phosphorites were generated in outer shelf or

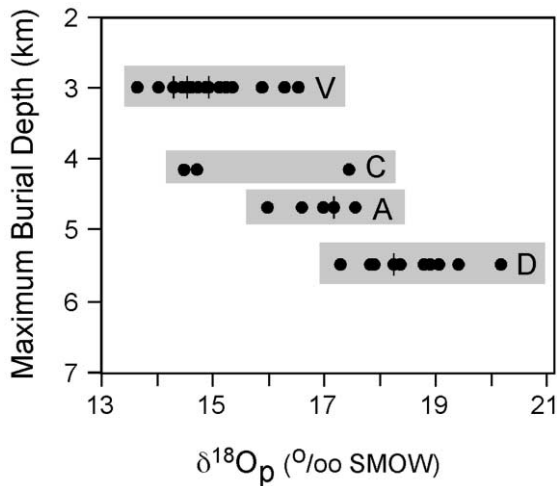


Fig. 8. Cross plot of $\delta^{18}O_p$ versus maximum burial depth for each sample locality. Maximum burial depths are from Maughan (1983), who derived these estimates by plotting the thicknesses of overlying Mesozoic rocks. Vertical lines through a data point denote two analyses of the same value. Sections are labeled as in Figs. 1, 6, and 7. (D = Dry Ridge; A = Astoria Hot Springs, C = Crystal Creek; V = Vernal-Brush Creek).

'shelf margin' settings, such as the organic-rich depocenter of the Meade Peak (Dry Ridge and Astoria Hot Springs), and subsequently dispersed up gradient and 50–100s of kilometers across the shelf to the Crystal Creek and Vernal-Brush Creek locations, then the $\delta^{18}O_p$ of the phosphorites at the latter two locations would not reflect the oceanographic conditions of their final depositional environment. Instead, any preserved geochemical signal in the phosphate grains would reflect only the narrow range of palaeoenvironmental conditions at the more seaward loci of phosphogenesis. A similar conclusion would apply if the sites of phosphogenesis were in shallow water (e.g. Vernal-Brush Creek and Crystal Creek) and phosphate peloids were subsequently transported seaward by storm and/or gravity flows. If, on the other hand, the phosphate precipitated in diverse depositional environments, then $\delta^{18}O_p$ values should reflect conditions in these environments. Even in this later case, some local (≤ 10 km) transport and reworking, possibly parallel to the coast, may have occurred. The key issue is whether there was landward or seaward transport at the scale of our section spacing, meaning many 10s to 100s of kilometers across the relatively flat and broad Phosphoria shelf.

An autochthonous origin for the phosphorites in the Dry Ridge, Astoria Hot Springs, and Crystal Creek sections has never been disputed. Since the pioneering work of McKelvey et al. (1959) to the most recent work of Stephens and Carroll (1999), and Hendrix and Byers (2000), all prior workers have considered phosphorites in these portions of the Meade Peak to be relatively autochthonous. Many of these phosphorites do have sharp bases and may exhibit graded bedding, but all lack visible evidence of current activity. These attributes plus the grain-supported textures indicate scouring and winnowing of the finer-grained material in which the peloids initially formed (McKelvey et al., 1959; Trappe, 1998). These features are typical of peloidal phosphorites in general and indicate reworking and condensation at the site of phosphogenesis (cf. Baturin, 1982; Föllmi, 1990; Jarvis, 1992); they do not *a priori* imply cross-shelf transport. In support of autochthony, the distinct, yet limited biota present in these reworked phosphorites represents only deeper water organisms; shallow-water gastropods and bivalves that would indicate cross-shelf or down-slope transport are conspicuously absent. Further, the presence of phosphate in the intervening carbonates and siltstones is typical of in situ 'pristine' phosphate deposits that were not condensed (Föllmi, 1990; Föllmi et al., 1991; Jarvis, 1992; Trappe, 1998). The lack of peloid abrasion in all phosphorites and the partial phosphatization of the mud-rich matrix in many peloidal phosphate packstones also support autochthonous phosphogenesis at the Dry Ridge, Astoria Hot Springs, and Crystal Creek sections.

Transport of phosphate grains is more likely in nearshore settings like the Vernal-Brush Creek section. At least local transport in that section is suggested by a high degree of sorting within the peloidal phosphorite beds and reports of cross-bedded phosphorites in other locations interpreted as near-shore settings (McKelvey et al., 1959; Stephens and Carroll, 1999). These attributes, however, do not require long-distance transport. In contrast, the presence of small phosphatic peloids in the intercalated carbonate muds is suggestive of in situ phosphogenesis. The palaeontology of the Vernal-Brush Creek section also provides strong evidence for an autochthonous origin. This section contains a unique fauna that includes articulated nuculid bivalves and well preserved delicate orbiculid brachiopods. The

phosphatized bivalves are shallow-water, infaunal organisms (Kammer et al., 1986), many of which are found as phosphate casts in their original burrows within the muddy units. Their lack of disarticulation indicates that they were not reworked before being phosphatized. Their *in situ* phosphatization confirms that the Vernal-Brush Creek section was indeed a site of phosphogenesis. Accordingly, we interpret the peloidal phosphorites in that section to reflect local reworking because they contain the same phosphatized fauna as the interlayered carbonate beds, but with a relatively localized source. Thus, there is no sedimentological or palaeontological evidence to support cross-shelf transport of the phosphorites in any of the four localities studied. All data support a relatively autochthonous origin for the phosphate grains with, at most, local winnowing and reworking.

6. Palaeotemperatures

Palaeotemperatures for the Phosphoria Sea were calculated using the equation of Longinelli and Nuti (1973a):

$$t^{\circ}\text{C} = 111.4 - 4.3(\delta^{18}\text{O}_\text{P} - \delta^{18}\text{O}_\text{SW})$$

where $\delta^{18}\text{O}_\text{P}$ is the isotopic composition of the phosphate sample and $\delta^{18}\text{O}_\text{SW}$ is the isotopic composition of seawater. Critical to the calculation is the $\delta^{18}\text{O}_\text{SW}$ value. There is increasing evidence that Palaeozoic epicontinental seas exhibited large secular variations in their oxygen isotopic compositions, and may have had $\delta^{18}\text{O}_\text{SW}$ values as low as $-5 \pm 2\%$ SMOW relative to the modern well-mixed ocean (Veizer et al., 1997). Reported values for Late Permian $\delta^{18}\text{O}_\text{SW}$ range from -2.7 to -1.4% . For example, Mii et al. (1997) derived a $\delta^{18}\text{O}_\text{SW}$ value of -2.7% from a small number of well preserved Late Permian brachiopods, although the range of isotopic values (-4.0 to -2.2%) caused them to suspect the effects of diagenetic alteration in some of the samples. Veizer et al.'s (1997, their Fig. 9) compilation of thousands of Phanerozoic brachiopod analyses suggest a Late Permian value of -1.7 to -2.5% , and Given and Lohmann (1985) proposed a value of -1.4 based on marine cements. We consider the brachiopod-derived estimates to more likely represent Late Permian seawater because the

cement-derived estimate involves extrapolation from altered $\delta^{18}\text{O}$ values, an exercise that could easily introduce error. Based on the brachiopod data, we thus assume a $\delta^{18}\text{O}_\text{SW}$ of -2.5% SMOW for seawater in the Phosphoria Sea.

The next issue that must be assessed is whether all the waters in the Phosphoria Sea were of normal marine salinity. Small ephemeral streams may have drained into the evaporative playas to the east of the Phosphoria Sea (Sheldon et al., 1967), but there is no direct evidence for large fluvial systems feeding directly into the Phosphoria Sea. The possibility of brackish waters is thus unlikely. In fact, extreme aridity prevailed throughout the region as evidenced by the evaporitic desert deposits to the east of the Phosphoria embayment that are correlative to the Meade Peak Member (Sheldon et al., 1967). Atmospheric circulation models further support the geological evidence and predict extremely hot desert conditions regionally (e.g. Kutzbach and Ziegler, 1994; Golonka et al., 1994). Finally, Hiatt (1997) showed that the rare-earth element signatures of the PRC phosphorites record a consistent seawater signature across the palaeoshelf with no evidence for mixing with river water even in a nearshore setting. The possibility of brackish waters with an isotopic value less than -2.5% SMOW is thus unlikely.

There may have been ^{18}O -enriched evaporative brines in the innermost shelf settings due to the desert environments surrounding the Phosphoria Sea. Dahl et al. (1993) and Stephens and Carroll (1999) presented organic matter biomarker data that indicated the presence of water-column stratification at inner-shelf localities like our Vernal-Brush Creek section. Both sets of workers suggested that stratification was due to seaward-migrating evaporative brines. The brines would have been sourced from the coeval evaporite deposits to the east and their presence in inner-shelf settings is geologically reasonable. In more seaward settings, marine currents, tides, and waves would probably have led to the assimilation of those brines with the normal marine waters flowing into the embayment from the west. We believe such an argument would be especially applicable to the Dry Ridge, Astoria Hot Spring, and Crystal Creek sections that are hundreds of kilometers from the coeval evaporite playas. The assumption of normal marine salinities and a value of -2.5% SMOW for $\delta^{18}\text{O}_\text{SW}$

for those three sections is thus reasonable. Higher salinities and a $\delta^{18}\text{O}_{\text{SW}}$ value greater than -2.5‰ SMOW may be more appropriate for the Vernal-Brush Creek section, although there is no direct sedimentological, palaeontological, or geochemical, evidence that the waters were hypersaline. In particular, the presence of a marine, albeit restricted, fauna suggests that the potential for elevated salinity was probably minimal. We thus utilized a value of -2.5‰ for the Vernal-Brush Creek section also, with the realization that the resultant palaeotemperatures could represent a minimum estimate for this inner-shelf setting at the time of phosphogenesis.

Fig. 7 and Table 1 show the results of the palaeotemperature calculations for the four Meade Peak sections. These calculated palaeotemperatures suggest that temperate, but not cold waters, were associated with phosphogenesis in the most basinward (Dry Ridge) section, and increasingly warmer waters were associated with phosphogenesis in the more landward Astoria, Crystal Creek, and Vernal-Brush Creek sections. Mean palaeotemperatures increase from 21°C in the Dry Ridge section, to 28°C in the Astoria Hot Springs section, to 34 and 37°C in the Crystal Creek and Vernal-Brush Creek sections, respectively. Palaeotemperatures in the latter two sections approximate climate model predictions of the overlying air masses summer-time temperatures ($35\text{--}40^{\circ}\text{C}$; Kutzbach and Ziegler, 1994; Barron and Fawcett, 1995; Golonka et al., 1994). The warming presumably occurred as the upwelled waters slowly circulated across the broad and shallow palaeoshelf. This warming of bottom waters on the inner shelf may also have promoted phosphate formation as Van Cappellen and Berner (1991) found phosphate precipitation rates increase dramatically with increasing temperature. Warming was also not just a phenomenon of the inner shelf as indicated by the rise in palaeotemperatures between the Dry Ridge and Astoria sections. The presence of temperate waters in the vicinity of the Dry Ridge location, and the abundance of warm temperatures across the palaeoshelf, is in sharp contrast to traditional interpretations of the Phosphoria that have assumed phosphate deposition occurred in cold deep water like those that impinge on modern continental shelves (e.g. $3\text{--}16^{\circ}\text{C}$; Levitus, 1982). This was not the case in the Phosphoria Sea suggesting phosphogenesis may occur

over a much broader range of oceanographic conditions than those associated with modern phosphorites.

7. Conclusions

- The $\delta^{18}\text{O}_{\text{P}}$ signature of phosphorites in the Meade Peak Member of the Phosphoria Formation does not show systematic variations that can be related directly to burial depth.
- There is a strong correlation in the $\delta^{18}\text{O}_{\text{P}}$ data with position on the palaeoshelf, with a trend towards more ^{18}O -depleted values in a landward direction. The regional trend in the $\delta^{18}\text{O}_{\text{P}}$ data is best explained in terms of palaeoceanographic setting and appears to reflect a range of palaeoenvironmental conditions across the broad and shallow Wyoming palaeoshelf.
- Calculated palaeotemperatures ($\pm 3.5^{\circ}\text{C}$) indicate that phosphate deposition occurred in temperate waters ($14\text{--}26^{\circ}\text{C}$) in the offshore depocenter, whereas mean bottom water temperature in shallow inner-shelf settings was $30\text{--}37^{\circ}\text{C}$, which approximated the predicted overlying air temperature.
- These findings indicate that phosphogenesis in the Permian Phosphoria Sea occurred under a much wider range of oceanographic conditions than do analogous processes in the modern oceans. Recognizing the broad range of environments in which phosphogenesis and associated high organic productivity occurred in the geologic past has important implications for understanding palaeoproductivity in ancient oceans.

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