EARLY-DIAGENETIC REE-PHOSPHATE MINERALS (FLORENCITE, GORCEIXITE, CRANDALLITE, AND XENOTIME) IN MARINE SANDSTONES: A MAJOR SINK FOR OCEANIC PHOSPHORUS

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ABSTRACT. Early-diagenetic REE-phosphate minerals are widespread, although minor (<0.005-0.14 wt percent), constituents of Archaean to Cretaceous sandstones from Australian sedimentary basins. Authigenic florencite ((REE)Al₃(PO₄)₂(OH)₆), crandallite (CaAl₃(PO₄)₂(OH)₆), and gorceixite (BaAl₃(PO₄)₂(OH)₆) occur as clusters of minute crystals (<0.1-10 μm in width) within pockets of clay matrix lining detrital quartz surfaces and less common within altered mica and feldspar grains. Rare florencite crystals form along the surface of detrital monazite grains, and in one locality, crandallite and gorceixite crystals line cavities left after grain dissolution. The aluminophosphate minerals commonly display compositional zoning, with major cation interchange between REE, Sr²⁺, Ca²⁺, and Ba²⁺, and minor anion interchange between PO₄³⁻, SO₄²⁻, and CO₃²⁻. Xenotime (YPO₄), which contains minor amounts of Th, U, and REE, forms pyramidal, dentate overgrowths (<1-20 μm) on detrital zircon grains and locally partly surrounds detrital quartz surfaces. Authigenic apatite is generally less abundant than diagenetic aluminophosphate and occurs as minute, pore-filling and grain-lining crystals.

The authigenic phosphate minerals precipitated shortly after burial within the zone of sulfate reduction and methanogenesis. The phosphates probably formed from P and REE released into marine sediment pore waters following bacterial decomposition of organic matter and reduction of hydrous iron oxides, as well as from partially dissolved and altered detrital minerals (monazite, clay matrix, feldspar, and mica). For the aluminophosphates, the critical factor controlling their precipitation site is the availability of Al (and to a lesser extent adsorbed REE and P), whereas xenotime crystals mostly precipitate on isomorphous substrates (for example, detrital zircon grains).

Given the widespread occurrence of early-diagenetic aluminophosphates and xenotime in Australian marine-deposited sandstones, it seems surprising that they have not been noticed elsewhere. However, their minute crystal size (<0.1-10 μm) and low concentration (generally <0.05 wt percent) probably hindered their previous identification by conventional microscopic techniques, while their marked insolubility at low temperatures rendered them inert to sequential solvent extraction geochemistry. Accordingly, these minerals represent a previously unrecognized marine sink for reactive P. Estimates from this study show that the global flux of oceanic P removed through the precipitation of the REE-phosphates (conservatively 7.56 × 10¹⁰ moles yr⁻¹) may be of equal importance to other major sinks (for example, carbonate fluorapatite, organic-P). If so, then the total reactive P output is prob-
ably considerably greater than previous estimates and, for the oceanic P cycle to remain in a steady state, implies a decrease in the output of other sinks or an increase in the P input. A higher output of reactive P will also reduce estimates of the oceanic residence time of P (from this study, between 11-20 ka). As P is crucial for sustaining marine life, such changes in the P budget of the oceans may affect estimates of the biomass of marine organisms, the biotic fixation of CO₂, and therefore predictions of global climatic change.

**INTRODUCTION**

Most studies on phosphate diagenesis have focused on areas of oceanic upwelling, where P concentrations are locally high (Berner, 1990). However, recent work on shallow marine and shelf deposit sediments reveals that phosphate diagenesis is also prevalent in non-upwelling areas (Krom and Berner, 1981; Berner, 1990; Ruttenburg and Berner, 1993). By far the most commonly reported authigenic phosphate mineral is francolite or carbonate fluorapatite (Ca₅(PO₄, CO₃, OH)₃F), which has been observed forming on present-day continental shelves (Froelich and others, 1982; Jahnke and others, 1983; Ruttenberg and Berner, 1993). However, other authigenic phosphate minerals have also been reported, including vivianite (Fe₃(PO₄)₂·8H₂O), goyazite (Sr₂Al₃(PO₄)₂(OH)₆), crandallite (CaAl₃(PO₄)₂(OH)₆), xenotime (YPO₄), rhabdophane ((REE, Th)PO₄·nH₂O), monazite ((REE, Th)PO₄), and florencite ((REE)(Al₃(PO₄)₂(OH)₆)₅ (Emerson and Widmer 1978; Berner, 1980; Milodowski and Hurst, 1989; Spötl, 1990; Milodowski and Zalasiewicz, 1991; Rasmussen and Glover, 1994). The abundant existence of authigenic REE-phosphates has been predicted from solubility data (Jonasson and others, 1985; Byrne and Kim, 1993), but the literature suggests that such minerals are extremely rare in the sedimentary record.

This paper shows that authigenic REE-phosphates are ubiquitous, though volumetrically minor, components of marine-deposited sandstones in sedimentary basins of all ages across a wide area of Australia. The phosphates are present as early-diagenetic mineral precipitates and are probably widespread in sandstones elsewhere. These authigenic minerals may represent an important, and previously overlooked, sink for P in seawater, and so their effects on the oceanic P budget could be significant.

**METHODS**

Most samples were derived from subsurface cores, while material from the Grampians Group and Stirling Range Formation are from outcrop. Covered and polished thin sections were examined under a polarizing microscope. Polished thin sections were examined by a JEOL JSM-6400 Scanning Microscope equipped with a Link Systems energy-dispersive X-ray microanalyser (operating conditions were 15 kV accelerating voltage and 3 nA beam current). Florencite and xenotime were analyzed on an ARL SEMQ microprobe (operating conditions were 20
in marine sandstones

kV accelerating voltage and a 5 nA beam current). Core chips (15-25 mm in width) were examined with the SEM. X-ray diffraction (XRD) analyses were carried out on a Philips PW1700 automatic diffractometer to determine major mineral compositions.

The proportion of authigenic phosphates within each sample was calculated using the JEOL JSM-6400 Scanning Microscope by first randomly selecting 5 to 10 fields of view (about 1.1 by 0.8 mm) for each polished thin section. A thermal-wax instantaneous photograph was taken of the fields, and then high magnification was used to locate and identify (with a Link Systems EDX microanalyser) any authigenic phosphate minerals within each field of view. The area occupied by each aggregate of authigenic phosphate crystals was then measured. The total area of authigenic REE-phosphate crystals (in μm²) within each field was divided by the total area of the field of view (8.8 × 10⁵ μm²) to give area percent for the diagenetic phosphate minerals. As the texture and composition of the sandstones are homogeneous, the area percent of the authigenic REE-phosphates is proportional to the volume percent of those minerals in the rock (see Krumbein and Pettijohn, 1938; Galehouse, 1971). The volume percent of each of the REE-phosphates was converted to wt percent by multiplying volume percents by the specific gravity of each of the REE-phosphates (see Galehouse, 1971).

GEOLOGICAL SETTING

Sandstone units from sedimentary basins throughout Western Australia and a unit from Victoria were examined for the presence of authigenic phosphate minerals (fig. 1). One or more of the REE-phosphate minerals (florencite, crandallite, gorceixite, and xenotime) were found in each sedimentary unit (table 1). A brief description of each of the selected units follows.

1. The mid-Archaean Lalla Rookh Formation of the Lalla Rookh Basin, Pilbara Craton (drill-hole SRD 11), consists of a 2 to 3 km thick sequence of prehnite-pumpellyite to lowermost greenschist facies metasedimentary rocks, mostly sandstone with minor conglomerate, siltstone, and claystone, deposited in alluvial, fluvial, and lacustrine environments (Krapez and Furnell, 1987);

2. The late-Archaean Hardey Formation (Taylor Creek Sequence) of the Hamersley Basin, Pilbara Craton (drill-hole 94014) consists of about 1400 m of prehnite-pumpellyite facies metasedimentary rocks, mainly feldspathic sandstone with minor conglomerate, mudstone, and tuff deposited in a fluvial to lacustrine environment (Blake, 1993);

3. The Neoproterozoic Stirling Range Formation (outcrop) consists of a 1600 m thick sequence of greenschist facies metasedimentary rocks (sandstone, with minor siltstone and claystone), deposited in shallow marine environments (Cruse and others, 1993);

4. The Late Cambrian to Early Ordovician Tumblagooda Group of the Perth and Carnarvon Basin (Wandagee no. 1), is a thick sequence (up to 3 km) deposited in fluviatile to shallow marine environments (Hock-
Fig. 1. Map of Western Australia and Victoria showing the location of samples from oil wells, mineral exploration drill-holes, and surface outcrops.
TABLE 1

Sedimentary formations studied for early-diagenetic phosphate minerals

<table>
<thead>
<tr>
<th>Formation</th>
<th>Age</th>
<th>Location</th>
<th>Authigenic phosphates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birdrong Sandstone</td>
<td>Early Cretaceous</td>
<td>Carnarvon Basin, Western Australia</td>
<td>✓* ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>Cockleshell Gully Formation</td>
<td>Early Jurassic</td>
<td>Perth Basin, Western Australia</td>
<td>✓ ✓ - - -</td>
</tr>
<tr>
<td>Permo-Triassic Sandstones</td>
<td>L. Perm-E Triassic</td>
<td>Perth Basin, Western Australia</td>
<td>✓ ✓ - ✓ ✓</td>
</tr>
<tr>
<td>Kennedy Group</td>
<td>Permian</td>
<td>Carnarvon Basin, Western Australia</td>
<td>✓ ✓ - - -</td>
</tr>
<tr>
<td>Keyling Formation</td>
<td>Early Permian</td>
<td>Bonaparte Basin, Western Australia</td>
<td>- ✓ ✓ - -</td>
</tr>
<tr>
<td>Pillara Limestone</td>
<td>M-Late Devonian</td>
<td>Canning Basin, Western Australia</td>
<td>✓ - - - -</td>
</tr>
<tr>
<td>Grampians Group</td>
<td>Late Silurian</td>
<td>Grampians Basin, Victoria</td>
<td>✓ ✓ ✓ ✓ -</td>
</tr>
<tr>
<td>Tumblagooda Group</td>
<td>L. Cam-Early Ord</td>
<td>Perth/Carnarvon Basin, Western Australia</td>
<td>✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>Stirling Range Formation</td>
<td>Neoproterozoic</td>
<td>Albany-Fraser Mobile Belt</td>
<td>✓ ✓ - - -</td>
</tr>
<tr>
<td>Hardey Formation</td>
<td>late-Archaean</td>
<td>Pilbara Craton, Western Australia</td>
<td>✓ ✓ - - -</td>
</tr>
<tr>
<td>Lalla Rookh Formation</td>
<td>mid-Archaean</td>
<td>Pilbara Craton, Western Australia</td>
<td>✓ ✓ - - -</td>
</tr>
</tbody>
</table>

*The symbol (✓) signifies the presence of this mineral phase, whereas the symbol (−) indicates its absence in the sample.

ing, 1988; Gorter and others, 1994). In Wandagee no. 1, the unit contains mainly marine facies, intercalated with continental facies, and consists of well-sorted, fine- to medium-grained quartz, with minor K-feldspar, heavy minerals, and lithic fragments. The authigenic mineral assemblage is dominated by K-feldspar and quartz overgrowths and trace pyrite, calcite, and Ti-dioxide;

5. The Late Silurian Grampians Group of the Grampians Basin, Victoria (outcrop), is a thick sequence (up to 6 km) of sandstone and minor mudstone and conglomerate, which was deposited in coastal environments. The sandstones are moderately to well sorted, consisting mainly of quartz (up to 95 percent) and minor feldspar, muscovite, tourmaline, and zircon (George, 1994);

6. The Middle to Late Devonian Pillara Limestone (drill-hole PCD 16) is a thick sequence (about 500 m) of shallow marine limestone and calcareous shale (Playford, 1980). The sample is from a thin (0.5-1.0 m) intercalated lens of arkosic siltstone and sandstone;

7. The mid-Permian Kennedy Group of the Carnarvon Basin (Dillson no. 1) consists of fine- to coarse-grained sandstone and minor siltstone, deposited on a broad shallow-marine shelf in nearshore and shoreface environments (Moore and others, 1980). The sandstones are composed of quartz (50-65 percent), with minor altered feldspar (up to 5 percent) and mica (up to 2 percent) and trace amounts of lithic fragments, carbonaceous matter, heavy minerals, and detrital clay. They have undergone complex diagenetic modification with the early precipitation of
significant quantities of siderite, kaolinite, and quartz. Following an influx of oil, diagenesis continued with the precipitation of quartz, kaolinite, and zoned calcite (Rasmussen and Glover, 1994);

8. The Permian Keyling Formation of the Bonaparte Basin (Turtle no. 1) consists mainly of sandstone and siltstone, deposited in fluvial to marine environments (Mory, 1988). In Turtle no. 1, the sandstone is mainly composed of quartz (60-70 percent), with minor feldspar, mica, lithic fragments, and heavy minerals. The diagenetic textures suggest early precipitation of kaolinite and quartz, followed by an influx of oil, and late formation of calcite and barite cements (Rasmussen and others, 1993);

9. The Permo-Triassic sandstones (Dongara nos 4, 11, 12, and 24; Mondarra nos 1 and 3; Yardarino nos 1 and 2) of the northern Perth Basin, consist mainly of sandstone, with interbedded siltstone and claystone. They were deposited over a major erosional surface in fluvio-deltaic, nearshore marine and strandline environments. The sandstones consist mainly of quartz (45-80 percent), with minor feldspar (up to 5 percent), mica (up to 1 percent), lithic fragments (trace), heavy minerals (up to 2 percent), organic matter (trace), and clay matrix (trace). The early-diagenetic mineral assemblage changes from the basin margin toward the basin centre. Near the basin margin, authigenic kaolinite, siderite, pyrite, and quartz are dominant, whereas, further basinward, the early-diagenetic assemblage consists of chlorite, pyrite, albite, and quartz. After early diagenesis, several hydrocarbon influxes moved through the sandstones thereby inhibiting mineral precipitation. When the hydrocarbon had flowed away, quartz, calcite, barite, and illite precipitated (Rasmussen and Glover, in press);

10. The Cockleshell Gully Formation of the central Perth Basin (Gingin nos 1 and 2) is a thick sequence of sandstone, siltstone, claystone, and coal deposited in a fluvio-lacustrine setting during the Early Jurassic (Cockbain, 1990). The sandstone intervals in Gingin nos 1 and 2 are composed of quartz, feldspar, mica, organic matter, lithic fragments, and heavy minerals. The diagenetic mineral assemblage consists mainly of quartz and kaolinite, with minor siderite, calcite, chlorite, barite, and pyrite (Rasmussen and others, 1993); and

11. The Early Cretaceous Birdrong Sandstone of the Carnarvon Basin (Rough Range no. 1) is a thin transgressive unit, deposited in a shoreface to nearshore environment (Hocking, 1990). In Rough Range no. 1, the sandstone contains medium- to coarse-grained quartz, with minor glauconite and rare feldspar, heavy minerals, and lithic fragments. The sandstone is mainly cemented by authigenic calcite and minor quartz, siderite, pyrite, and Ti-dioxides.

AUTHIGENIC PHOSPHATES

Florencite.—Authigenic florencite \(((\text{REE})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6)\) is widespread throughout the formations examined but only in trace amounts. Quantitative analysis of the authigenic REE-phosphate content shows
that the proportion of florencite ranges up to 0.14 wt percent (avg concentration is about 0.0379 wt percent, table 2). The florencite concentration from the Permo-Triassic sandstones varies between 0.001 and 0.032 wt percent with an average around 0.016 wt percent. Most formations have average total aluminophosphate contents between 0.0085 and 0.033 wt percent.

The main habit of florencite is as clusters of minute (<1-10 μm), euhedral crystals (fig. 2A, B). In most samples, authigenic florencite is found lining detrital quartz surfaces along with a fine illitic clay matrix (fig. 2C, D, E, F). Florencite may also be found within remnants of altered alkali-feldspar, illitic-sericitic grains, muscovite, and authigenic kaolinite. In samples from the Kennedy Group, florencite is present on the partly etched surfaces of detrital monazite as minute anhedral crystals (1-3 μm) and rare euhedral crystals. In some of the deeper samples from the Permo-Triassic sandstones, florencite crystals are concentrated along with illitized clay matrix in sutured and microstylolitic contacts between quartz grains and along larger amplitude stylolites (1-5 mm).

Most florencite crystals are visible with the optical microscope under high magnification (see fig. 2A). The crystals are clear to pale yellow to pale green with moderate relief and low birefringence. Florencite crystals are rhombohedral and have a “pseudocubic” habit in thin section. Most display compositional zonation (fig. 3A) with up to four distinct layers. In the Kennedy Group their core is relatively Ca-poor and REE-rich, commonly anhedral and less than 2 μm in diameter. The core is surrounded by a zone (partly to entirely dissolved) containing less REE and more Ca. The third (and outer) zone is REE-rich and Ca-poor relative to zone 2. The Permo-Triassic sandstones contain florencite with at least

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**TABLE 2**

*Concentration of early-diagenetic phosphate minerals in marine sandstones*

<table>
<thead>
<tr>
<th>Formation</th>
<th>Well Name</th>
<th>Xenotime</th>
<th>Florencite</th>
<th>Crandallite and Gorceixite</th>
<th>Apatite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birdrong Sandstone</td>
<td>Rough Range-1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Permo-Triassic Sandstones</td>
<td>Average (over 8 wells)</td>
<td>—</td>
<td>0.0164 (0.0105)</td>
<td>—</td>
<td>0.0085 (0.006)</td>
</tr>
<tr>
<td>Dongara-4</td>
<td>—</td>
<td>—</td>
<td>0.032 (0.020)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Dongara-24</td>
<td>—</td>
<td>—</td>
<td>0.025 (0.015)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mondarra-1</td>
<td>—</td>
<td>—</td>
<td>0.001 (0.0007)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mondarra-3</td>
<td>0.00027 (0.00014)</td>
<td>—</td>
<td>0.032 (0.023)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>West White</td>
<td>—</td>
<td>—</td>
<td>0.001 (0.0007)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Point-1</td>
<td>—</td>
<td>—</td>
<td>0.0055 (0.004)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Strawberry</td>
<td>—</td>
<td>—</td>
<td>0.018 (0.012)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Hill-1</td>
<td>—</td>
<td>—</td>
<td>0.017 (0.01)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Yarndaro-1</td>
<td>0.0006 (0.0003)</td>
<td>—</td>
<td>0.14 (0.10)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mt Adam-1</td>
<td>—</td>
<td>—</td>
<td>0.0015 (0.0001)</td>
<td>0.02 (0.018)</td>
<td>—</td>
</tr>
<tr>
<td>Kennedy Group</td>
<td>Dilson-1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Grampians Group</td>
<td>Outcrop</td>
<td>0.0002 (0.0001)</td>
<td>0.0015 (0.0001)</td>
<td>0.02 (0.018)</td>
<td>—</td>
</tr>
<tr>
<td>Tumblagooda Group</td>
<td>Wandagee-1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Average concentration (over 5 formations)</td>
<td>0.00006 (0.00003)</td>
<td>0.0379 (0.0261)</td>
<td>0.0079 (0.0064)</td>
<td>0.00178 (0.00126)</td>
<td>—</td>
</tr>
</tbody>
</table>

*Concentration in Weight % (Volume %)*
Fig. 2(A) Cluster of euhedral “pseudocubic” florencite crystals within an altered potassic-aluminosilicate grain. Clear adjacent grains are quartz. Transmitted light photograph, Dillson no. 1, 2392.6 m. Field of view is about 0.1 mm.

(B) Small cluster of florencite crystals displaying compositional zonation. Some crystals show signs of partial dissolution of one or more zones. Florencite crystals are within a kaolinite-illite aggregate. Backscattered-electron (BSE) image, Mondarra no. 3, 2840.15 m.

(C) Rounded quartz grain partly surrounded by a lining of detrital illite clay, containing several clusters of florencite (see arrows). The detrital illite and florencite are engulfed in syntaxial quartz. Transmitted light photograph, Mondarra no. 1, 2708.5 m. Field of view about 0.5 mm.
Fig. 2(D) Dense clusters of minute florencite (white) crystals lining the detrital surface of a quartz grain. Some florencite is engulfed in syntaxial quartz. BSE image, Mondarra no. 3, 2840.15 m.

(E) Close-up of several large zoned florencite crystals within a pocket of clay matrix along a detrital quartz surface. Clay mineral at the top of the photograph is authigenic kaolinite. Transmitted light photograph, Mondarra no. 1, 2708.5 m. Field of view about 0.1 mm.

(F) Cluster of florencite crystals within partly illitized detrital clay on a quartz grain. BSE image, Mount Adam No. 1, 3543.0 m.
Fig. 3(A) Minute florencite crystal displaying compositional zonation. “Darker” core contains higher proportions of Ca and less REE than the two “lighter” outer zones. BSE image, Dongara no. 4, 1693.2 m.

(B) Thin lining of crandallite-gorceixite (light gray) around a dissolved grain. Surrounding minerals are quartz and a fine pore-filling illitic clay. BSE image, outcrop sample (MG-4) from the Grampians Group.

(C) Well-rounded detrital zircon grain partly surrounded by illitized kaolinite and quartz. Note serrated zircon surface (top left of zircon). BSE image, Mondarra no. 3, 2840.15 m.
Fig. 3(D) Close-up BSE image of zircon from (C). The zircon surface is partly overgrown by minute dentate crystals of xenotime and thorite. BSE image, Mondarra no. 3, 2840.15 m.

(E) Close-up of zircon grain surface (dark gray), with overgrowths of xenotime (light gray) and thorite (white). BSE image, Mondarra no. 3, 2840.15 m.

(F) Numerous xenotime euhedra (white) and minor florencite (gray) lining a quartz grain. BSE image, Mondarra no. 3, 2840.15 m.
four distinct zones, with the core and zone 3 Ca-rich and REE-poor relative to zones 2 and 4. In places, one or more zones have been partly dissolved. In the Kennedy Group there appears to be minor anion substitution by \( \text{SO}_4^{2-} \) (about 0.8 wt percent) for \( \text{PO}_4^{3-} \) in the florencite crystal structure; however, accurate analysis of florencite was not possible due to their minute crystal size.

Clusters of florencite crystals may surround early-diagenetic pyrite and siderite, although in places, florencite is partly embedded in siderite. In the Permian Kennedy Group, some florencite crystals within remnants of altered feldspar grains occur within the center of siderite rhombs. These crystals are smaller than adjacent florencite appear to have formed during the precipitation of zone 1 (the core) and zone 2, and then been surrounded by siderite cement. Florencite is engulfed by later quartz and calcite cement. Early florencite seems to have been higher in REE, and lower in Ca, than later florencite.

**Crandallite and gorceixite.**—Authigenic crandallite \( \text{(CaAl}_3\text{(PO}_4\text{)}_2\text{(OH)}_6) \) and gorceixite \( \text{(BaAl}_3\text{(PO}_4\text{)}_2\text{(OH)}_6) \) were found in the Birdrong Sandstone, Tumblagooda Group and the Grampians Group. In the Birdrong Sandstone, the dominant aluminophosphate is gorceixite, which is present in trace amounts \( (0.0085 \text{ wt percent}) \) along detrital quartz surfaces, within pockets of recrystallized detrital clay and within highly altered and leached aluminosilicate grains. Gorceixite crystals are commonly engulfed by syntaxial quartz overgrowths or pore-filling calcite cement.

In sandstones of the Tumblagooda Group, trace quantities of crandallite and gorceixite \( (0.011 \text{ wt percent}) \), as well as florencite \( (0.033 \text{ wt percent}) \) occur within pockets and linings of detrital clay on quartz surfaces. In both the Birdrong Sandstone and Tumblagooda Group, the main habit of crandallite and gorceixite is as isolated to dense clusters of minute \( (<1.5 \mu m) \), pseudocubic crystals. Both crandallite and gorceixite contain minor concentrations of REE and Sr and in the Tumblagooda Group contain high concentrations of \( \text{SO}_4 \). Larger crystals \( (2-5 \mu m) \) commonly display compositional zonation due to substitution between Ba, Ca, REE, and Sr and between \( \text{PO}_4 \) and \( \text{SO}_4 \).

In the Grampians Group, gorceixite and crandallite are the main aluminophosphate minerals \( (0.014 \text{ and } 0.0064 \text{ wt percent respectively}) \), while florencite is rare \( (0.00015 \text{ wt percent}) \). The aluminophosphates occur in three habits: as thin rims lining cavities left by grain dissolution (fig. 3B), as irregular masses of intergrown “bladed” crandallite and gorceixite, and as crystals infilling partly dissolved K-feldspar. The cavity-lining aluminophosphates are relatively common, with up to 50 occurrences in one polished thin section \( (about 2 \text{ by } 4 \text{ cm}) \). The enclosing rims appear to be composed of minute crystals which have grown outward simultaneously, although in places, larger elongate rods and rhombohedral crystals have formed. The aluminophosphates are zoned, with a “darker” center (using BSE imaging) composed of crandallite and a “lighter” rim of gorceixite. In places, three zones are observable, with the center and outer rim composed of gorceixite and the middle zone of
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crandallite. Rare, zoned pseudocubic crystals have been incorporated into the cavity-lining crusts. The aluminophosphate linings are commonly surrounded by quartz cement. Most cavities enclosed by crandallite-gorceixite are rounded and relatively equant in shape and have a uniform grain size (about 20-50 \( \mu m \) in diam), although rarely, the precursor grains were blocky or elongate. The abundance, shape, and size of the dissolved grains is similar to that of heavy minerals within the sandstone, particularly zircon.

In other samples from the Grampians Group, crandallite and gorceixite are intergrown, with crandallite occurring as randomly-oriented clusters of “bladed” crystals and gorceixite filling interstitial positions. The crandallite-gorceixite aggregates range in size between 10 to 40 \( \mu m \) and are commonly associated with fine pore-filling clay. Gorceixite also occurs within cleavage planes and fractures dissecting partly dissolved alkali-feldspar grains, and within the framework of highly altered feldspar grains. Most of these gorceixite crystals are anhedral and minute (< 1 \( \mu m \) in width), but some larger euhedra (up to 4 \( \mu m \) in width) display compositional zonation, with a “darker” core and zone 3 composed of Ca-rich gorceixite and a “lighter” zone 2 and outer rim composed of Ca-poor gorceixite.

Xenotime.—Authigenic xenotime (YP\( _{04} \)) occurs in most formations (table 1); however, its average concentration (0.00006 wt percent) is lower than for the aluminophosphates or apatite. The main habit of authigenic xenotime is as irregular to pyramidal overgrowths around detrital zircon grains (fig. 3C, D, E). The overgrowths range in size from minute (<0.5 \( \mu m \)) dentate serrations which line the rounded zircon surface to large pyramidal prisms up to 12 \( \mu m \) long and 20 \( \mu m \) wide. The xenotime overgrowths are present on up to 75 percent of zircon grains, particularly on smaller grains. Rarely, xenotime has precipitated so closely as to surround up to 50 percent of zircon grain surfaces. The larger xenotime crystals (observable with the polarizing microscope) are in optical continuity with their detrital zircon cores and are clear and colorless. Xenotime euhedra are also present on the detrital quartz grain surfaces (fig. 3F), overgrown by quartz cement.

Xenotime overgrowths are composed of Y and PO\( _4 \), with minor amounts of Th, U, and REE. Rare xenotime overgrowths are zoned, with variations in the BSE image gray level due to changes in the proportion of U and Th relative to REE. Some of the xenotime overgrowths are surrounded by siderite, Ti-dioxide, cryptocrystalline silica, and quartz cement, suggesting that they preceded the formation of these authigenic minerals. In the Permo-Triassic sandstones, chlorite platelets have partly impeded the growth of xenotime overgrowths on zircon, suggesting precipitation postdated chlorite formation.

Rare detrital xenotime grains in the Kennedy Group and Permo-Triassic sandstones are partly etched and pitted. However, these samples do not display any enrichment in early-diagenetic xenotime, suggesting that detrital xenotime dissolution may have been a deep burial phenom-
ena. In the Permo-Triassic sandstones of the northern Perth Basin, the xenotime overgrowths are more common in regions unaffected by meteoric water influx.

**Apatite.**—Authigenic apatite is a trace constituent (up to 0.067 wt percent, avg 0.00178 wt percent) and is generally less abundant than the REE-aluminophosphates, although within parts of the Permo-Triassic sandstones (for example, Dongara no. 24) concentrations of apatite are greater than florencite. Authigenic apatite occurs as isolated crystals and clusters of minute (<1-10 μm) crystals (fig. 4A) within partly dissolved and altered grains of potassic feldspar, mica, and albite. In samples from the Permo-Triassic sandstones, apatite lines detrital quartz surfaces (fig. 4B) and is itself surrounded by quartz and siderite cement. Locally, there are two linings of apatite crystals, separated by quartz and siderite cement (fig. 4C, D).

Apatite is composed of Ca and PO₄ and commonly displays compositional zonation, with a darker core (with BSE imaging). Unlike the aluminophosphates, apatite crystals are rarely associated with pockets of clay matrix along detrital quartz surfaces. Some altered potassic-aluminosilicate grains contain dense clusters of anhedral to euhedral apatite crystals (up to 10 μm in width). In places, adjacent pore-filling siderite has engulfed and locally replaced clusters of apatite. In parts of the Permo-Triassic sandstones, apatite crystals partly engulf early-diagenetic chlorite platelets and are themselves embedded in authigenic albite, calcite, and quartz. Petrographic textures indicate that apatite precipitated during early diagenesis, postdating chlorite and pyrite, and preceding authigenic siderite, quartz, kaolinite, illite, albite, and calcite.

**DISCUSSION**

*Phosphorus and REE cycling in the marine environment.*—The concentration of phosphorus in seawater is very low (about 0.6 ppm; Krauskopf, 1977), with most inflowing phosphorus removed from the oceans in the form of organic-P, incorporated into phytoplankton in the euphotic zone of the water column (Berner and Berner, 1987). Seawater P concentrations may also be reduced by adsorption onto hydrous Fe-oxide particles and clay minerals, by incorporation into skeletal debris and biogenic calcium carbonate, and by mineral precipitation (Berner, 1973; Froelich and others, 1982; Berner and others, 1993). However, the concentration of dissolved phosphate in marine pore water below the sediment-water interface may be locally highly enriched compared to seawater (Sholkovitz, 1973; Martens and others, 1978), as P is released back into the sediment pore water during bacterial decomposition of organic compounds (Berner, 1980; Burnett, 1977; Baturin and Bezrukov, 1979; De Lange, 1986). Phosphorus adsorbed onto the surfaces of clay and iron oxyhydroxide particles may also be re-released shortly after burial during anoxic reduction (Froelich and others, 1977; Krom and Berner, 1981; Borgaard, 1983; Watanabe and Tsunogai, 1984). Pore-water phos-
Phosphate concentrations may also be increased by the dissolution of phosphatic skeletal debris (Suess, 1981).

The concentrations of REE in the ocean range from 1 to 2 part per trillion (ppt) near the surface to 4 to 6.5 ppt for the deep sea (Elderfield and Greaves, 1982), while river water has REE concentrations between 47.5 to 192 ppt (Martin and others, 1976; Hoyle and others, 1984; Elderfield and others, 1990). Ocean water is thus depleted in the REE relative to river water (Piper, 1974a; Martin and others, 1976) with several processes apparently responsible (fig. 5): adsorption of REE onto ferromanganese nodules (Elderfield and others, 1981a) and surfaces of detrital clay (Spurn, 1965; Piper, 1974a; Dypvik and Brunfelt, 1979; Fleet, 1984); adsorption onto hydrous Fe-oxide particles including hydrothermal plume precipitates (Piper, 1974b; Elderfield and others, 1981b; German and others, 1990), inorganic complexation with various anions (for example, CO$_3^{2-}$, PO$_4^{3-}$, SO$_4^{2-}$) (Cantrell and Byrne, 1987; Wood, 1990; Byrne and Kim, 1990; Byrne and others, 1991), organic adsorption, halmyrolytic reactions between volcanic material and seawater (Fleet, 1984), incorporation of REE into biogenic material (Bernat, 1975; Wright and others, 1987), and incorporation into minerals (for example, calcite/aragonite, glauconite, barite, phosphorites) by precipitation or fixation (Goldschmidt, 1954; Guichard and others, 1979; Altschuler 1980). Moreover, it has been suggested that marine REE concentrations may also be reduced by REE-phosphate mineral precipitation (Jonasson and others, 1985; Byrne and Kim, 1993). The latter process has been inferred from solubility product determinations for hydrous REE phosphates which indicate that these phases are very insoluble.

Although the seawater REE concentration is very low, immediately below the sediment-water interface, REE concentrations may be between 10 to 50 times that of seawater (Elderfield and Sholkovitz, 1987; Sholkovitz and others, 1989). The high concentrations appear to be due to anoxic reduction of Fe- and Mn-(hydr-)oxides, resulting in the release of adsorbed REE. The REE concentration may also be increased by the release of REE adsorbed onto clay mineral surfaces (Balashov and Girin, 1969; Roaldset and Rosenqvist, 1971) and from the partial dissolution and surface reactions of REE-bearing minerals (for example, monazite, apatite, xenotime) and early-diagenetic dissolution of fish debris.

**REE-phosphate formation.**—The sediment pore-water from which florencite, crandallite, gorceixite, xenotime, and apatite precipitated must have been locally enriched in REE, Y, Ca, Ba, and P. The availability of Ca and Ba ions in ocean water is not restrictive, but marine concentrations of REE, Y, and dissolved phosphate are very low (Turekian, 1969). However, as has been shown above, the concentration of REE and P in pore waters of organic-rich coastal sediments may be greatly increased during early diagenesis, by the bacterial decomposition of organic matter, suboxic or anoxic reduction of hydrous Fe-oxides, leaching of adsorbed REE on clay mineral surfaces, and dissolution of REE- and P-bearing minerals and skeletal debris.
Fig. 4(A) Euhedral crystal of early-diagenetic apatite within a pore filled by authigenic chlorite. BSE image, Mount Adam no. 1, 3543.0 m.

(B) Rounded quartz grain lined by a thin rim of authigenic apatite crystals (white). BSE image, Dongara no. 24, 1632.0 m.
Fig. 4(C) Rounded quartz grain surrounded by a thin lining of authigenic apatite (bottom right) and siderite crystals (light gray). Pore-filling clay (top right) is authigenic kaolinite. BSE image, Dongara no. 24, 1632.0 m.

(D) Close-up of part of quartz grain from (C). Two thin linings of authigenic apatite are present (see arrows), the first around the original detrital surface and the second within quartz and siderite cement. The second phase of apatite precipitation was apparently preceded by some quartz and siderite formation. BSE image, Dongara no. 24, 1632.0 m.
Fig. 5. Schematic section showing controls and site of authigenic REE-phosphate precipitation. The reactive phosphorus influx values are from Berner and Rao (1994) and Graham and Duce (1979).
The close association between aluminophosphates and detrital clay in most samples examined here is significant. It may be explained by the clay minerals acting as a source of Al, which they release shortly after burial as they undergo transformation within the marine pore water. As the solubility of Al is extremely low in low-temperature aqueous fluids (Garrels and Christ, 1965), the site of Al release (the clay mineral substrate) was probably also the nucleation site, where the various ions (REE, Ca^{2+}, Ba^{2+}, Sr^{2+}, PO_{4}^{3−}, and SO_{4}^{2−}) in the pore water combined to precipitate as aluminophosphate crystals. During clay mineral alteration and transformation, adsorbed P and REE may also have been released. Similarly, aluminophosphates within altered alkali-feldspar and mica probably also derived Al from the substrates of these grains. The main sources of REE in the aluminophosphates were probably detrital clay, which commonly lines detrital quartz surfaces and locally fills grooves and indentations of quartz grains, and Fe-(hydr-)oxides, onto whose surfaces REE are commonly adsorbed and consequently released during suboxic or anoxic reduction.

As mentioned above, the most likely source of phosphorus is organic matter which releases phosphorus during bacterial decomposition. Up to 50 percent of organic matter (and incorporated P) sinks through the water column on continental shelves and reaches the sea floor (Müller and Suess, 1979). Once organic matter reaches the sediment-seawater interface, it is decomposed by aerobic organisms using dissolved oxygen and releasing various nutrients, including phosphate. Richards (1965) expressed this reaction as:

$$(\text{CH}_2\text{O})_{106}\text{(NH}_3)_{16}\text{(H}_3\text{PO}_4) + 138\text{O}_2 \rightarrow 106\text{CO}_2 + 122\text{H}_2\text{O} + 16\text{NHO}_3 + \text{H}_3\text{PO}_4$$

Below the oxic zone, organic matter is decomposed by organisms using progressively less efficient oxidants ($\text{O}_2$, $\text{NO}_3$, $\text{MnO}_2$, $\text{Fe}_2\text{O}_3$, $\text{SO}_4^{2−}$, $\text{CO}_2$) (Froelich and others, 1979), with the continual release of phosphate with burial. In shallow marine environments, where sedimentation rates and primary productivity are high, organic matter decomposition by organisms using $\text{SO}_4^{2−}$ is prominent (Jørgensen, 1982; Van der Weijden, 1992; Canfield and others, 1993). Also important in releasing P is the anoxic reduction of iron (hydr-)oxides (Krom and Berner, 1981), which may be present in shelf sediments in similar quantities to organic-P (Ruttenberg, 1993). The common occurrence of early-diagenetic pyrite and siderite in most samples attests to the relatively high concentration of iron (probably in the form of oxides/hydroxides) prior to its incorporation into pyrite and siderite.

The presence of authigenic florencite crystals on the surfaces of detrital monazite (REE-phosphate) from the Permian Kennedy Group suggests that the REE required for florencite (and possibly xenotime) precipitation may also be derived from detrital-heavy minerals. In sandstones from the Kennedy Group there is evidence of minor dissolu-
tion of detrital monazite and xenotime, with many mineral surfaces displaying minute pits and grooves, and in some samples, partly dissolved fission damage tracks are visible. Although detrital monazite grains were probably a source of REE and P in the Kennedy Group, the contribution was probably minor as the proportion of florencite (0.14 wt percent) within the sandstones is several orders of magnitude greater than the volume of REE and P which could have been released from partly dissolved heavy minerals. Furthermore, samples from the Permo-Triassic sandstones with 1 to 2 wt percent heavy mineral contents do not display any enrichment in authigenic xenotime or florencite, relative to heavy mineral-deficient sandstones. Thus, it seems that a detrital REE source, though locally important, is not necessary for the formation of authigenic florencite.

Crandallite-gorceixite crystals from the Grampians Group have a different habit to the other aluminophosphates. In one locality they line cavities left by grain dissolution, which have the abundance, shape, and size of heavy minerals. The dissolved grains were chemically less stable than zircon, rutile, monazite, xenotime, rutile, ilmenite, and tourmaline, which are still present in the sandstones. Given the presence of granitoid intrusions and amphibolite schists proximal to the Grampians Group, possible heavy mineral precursors of the dissolved grain include the epidote group of minerals, particularly epidote \((\text{Ca}_2\text{Fe}^{3+}\text{Al}_2\text{O} \cdot \text{OH} \cdot \text{Si}_2\text{O}_7 \cdot \text{SiO}_4)\) and allanite \((\text{Ca}, \text{Mn}^{2+}, \text{Ce})_2 (\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_3 \cdot \text{OH} \cdot \text{Si}_2\text{O}_7 \cdot \text{SiO}_4)\). These minerals are relatively unstable in the sedimentary environment and rarely survive deep burial (Morton, 1984). Both minerals would have acted as sources of Al, Ca, and some REE, and, from previous observations, aluminophosphates commonly precipitate in close proximity to a mineral source of Al (for example, detrital clay, mica and feldspar) or REE (for example, monazite).

Unlike the REE, little is known of the geochemistry of Y in the marine environment (Bau and Dulski, 1994). Although the aqueous geochemistry of the REE and Y is similar (Wood, 1990), the REE form stronger surface-complexes with Fe-(hydr-)oxides than does Y (Bau and others, in press). Nevertheless, the source of Y (as well as P and other REE) required for xenotime formation was probably the same as for the REE in the aluminophosphates. For authigenic xenotime, the site of precipitation is generally along the surfaces of detrital zircon grains which acted as isomorphous templates, although rare xenotime crystals precipitated within detrital clay along detrital quartz surfaces.

The size of authigenic aluminophosphate and apatite crystals \((<0.1 \text{ to } 10 \mu\text{m})\) from the sediments studied is similar to the size of apatite particles (one to several microns in width) found in modern phosphorites (Glenn and Arthur, 1988) and aluminophosphates from Permian marine sediments (Spötl, 1990). The relatively uniform crystal size is also consistent with results from crystal growth experiments carried out in modified seawater solutions by Van Cappellen and Berner (1991), who predicted that fluorapatite crystals that nucleate and precipitate near the sediment-
water interface should be restricted in size to 0.1 and 10 μm during burial.

Francolite precipitation is considered an early diagenetic event, and in areas of coastal upwelling, its formation is restricted to the top few tens of centimeters of the sediment column (Glenn, 1990). These regions experience relatively rapid deposition and burial, so that apatite crystals only grow over short time spans. For example, apatite growth times from the western Mexican continental margin were restricted to about 1000 yrs (Van Cappellen and Berner, 1988), and generally range between 500 and 2000 yrs for modern phosphorites (Van Cappellen and Berner, 1991).

Phosphate precipitation in marine sediments has been reported from three geochemical zones: the sub-oxic zone; the zone of sulfate reduction, associated with the formation of diagenetic pyrite; and the zone of microbial methanogenesis, commonly associated with siderite precipitation (see Benmore and others, 1983; Coleman, 1985; Morad and Al-Aasm, 1994). Regarding the authigenic phosphates described here, florencite commonly surrounds and is partly embedded in siderite cement, though locally, florencite and apatite crystals are engulfed in early-diagenetic siderite. This indicates that most authigenic phosphates formed contemporaneously with siderite, but some apparently began precipitating earlier. The latter contention is supported by the presence of significant amounts of SO$_4^{2-}$ (about 0.8 wt percent) in the structure of the aluminophosphate minerals from the Kennedy Group and Tumblagooda Group, showing that sulfate was still available in the sediment pore-water during phosphate precipitation. Thus, the phosphates probably started forming within the zone of sulfate reduction and carried on precipitating through the zone of microbial methanogenesis (fig. 6). It is uncertain whether authigenic phosphate crystals precipitated in the sub-oxic zone. Phosphorus and REE are commonly adsorbed onto the surfaces of metal (hydr-)oxides in the oxic zone, reducing the concentration of these elements in pore fluids (Krom and Berner, 1980; Sundby and others, 1992; Slomp and van Raaphorst, 1993).

The complex compositional zonation displayed by most aluminophosphate crystals probably reflects the changing concentration of cations (for example, Ca$^{2+}$, REE, Ba$^{2+}$, and Sr$^{2+}$) and anions (PO$_4^{3-}$, SO$_4^{2-}$, and CO$_3^{2-}$) in the sediment pore-water during precipitation. Once precipitation is initiated, the concentration of phosphate is reduced, but the pore-water alkalinity increases due to continued organic matter degradation, resulting in incorporation of structural carbonate into the phosphate and an increase in its solubility (Jahnke, 1984; Glenn and others, 1988). The period of carbonate incorporation probably coincides with the time of formation of Ca-rich and REE-deficient zones within florencite crystals (as shown by samples from the Permo-Triassic sandstones and Kennedy Group), because these zones are commonly partly dissolved and in extreme cases completely absent.
The majority of P in the ocean is removed by marine organisms (for example, phytoplankton) living in surface waters. However, some of the P is released back into the ocean as the organic matter decomposes while descending through the water column. On continental shelves, about 50 percent of organic-P reaches the ocean floor, as compared to 1 percent in the deep ocean (Müller and Suess, 1979; Jørgensen, 1983). Clay particles settling out of suspension, adsorb REE and P onto their mineral surfaces. At the sediment-sea water interface, REE and P may also be adsorbed onto Fe-(hydr-)oxide surfaces.

Organic matter is decomposed by organisms using oxygen, releasing carbon dioxide, water, nitrate, and phosphate. In the oxic zone, pore-water phosphate released from degraded organic matter in deeper layers and phosphate from sea water may in part be adsorbed onto the surfaces of Fe-(hydr-)oxides. The REE released in underlying geochemical zones and from sea water may also be captured and adsorbed onto the surfaces of Fe-(hydr-)oxides.

In the zone of sulfate reduction, organic matter is decomposed by bacteria using sulfate as an electron acceptor, producing hydrogen disulfide and phosphate, as well as ammonia, carbon dioxide, and water. Iron and manganese oxides are reduced (releasing REE and P) and combine with hydrogen disulfide to form pyrite. REE and P adsorbed onto detrital clay surfaces are released during clay transformation and locally nucleate and precipitate on substrates releasing Al (for example, detrital clay, feldspar, and mica). Yttrium and P combine and precipitate on isomorphous templates (for example, zircon).

Decomposition of organic matter continues within the zone of methanogenesis, with the release of phosphate, as well as methane and carbon dioxide. In the presence of Fe, siderite or Fe-rich carbonates may form. Aluminophosphate precipitation and crystal growth continues with the ongoing transformation of detrital clay (releasing adsorbed P, REE, and Al) and dissolution and alteration of detrital aluminosilicate grains (releasing Al). Yttrium and P continue to precipitate, enlarging xenotime overgrowths on detrital zircon grains.

Fig. 6. Schematic diagram showing the main processes operating near the sediment-water interface, resulting in the release of P, REE (+Y), and Al, and the precipitation of REE-phosphates.
Comparison with other studies.—It has been recognized that authigenic carbonate fluorapatite is a major sink for reactive P in the marine environment (Froelich and others, 1982; Ruttenberg and Berner, 1993). Ruttenberg (1993) estimated that about 50 percent of phosphorus in the ocean is lost through authigenic mineral precipitation. Recent work (Jonasson and others, 1985) has demonstrated from laboratory experiments that hydrous REE-phosphates (rhabdophane and xenotime) should also form in seawater shortly after burial. These experimental observations are, in fact, supported by the common occurrence of early-diagenetic florencite, crandallite, gorceixite, and xenotime in sandstones, highlighting that REE-phosphates do form in marine pore waters and are stable through deep burial.

In the comprehensive study by Ruttenberg and Berner (1993) of phosphorus in modern marine shelf sediments, REE-phosphates were not identified. They estimated the quantity of phosphorus tied up in various components by sequential extraction techniques using various solvents at low temperatures (Ruttenberg, 1992). However, aluminophosphates and xenotime are extremely insoluble in acids at temperatures below about 450°C (Norrish, 1968) and so may not have been released and identified as “authigenic-P.” It is more likely that the REE-phosphates were included with the more insoluble “detrital-P” or “organic-P” fractions, or, most likely, that they passed through the extraction cycle undetected. If so, the proportion of reactive P lost through authigenic mineral precipitation as estimated by Ruttenberg and Berner (1993) may well be too low, perhaps by a significant amount.

In the marine sandstones studied here, diagenetic florencite, crandallite, gorceixite, and xenotime are generally more abundant than authigenic apatite. However, the concentration of apatite may have been greater in the fraction <0.1 μm, which is difficult to detect with the SEM. It is also difficult to determine what proportion of P was incorporated into the sands as organic-P, calcareous-P, Fe bound-P, and loosely sorbed-P, as these components may have been remobilized during burial as they were subjected to increasing pressure and temperature conditions and changing pore-water chemistry. Hence it is impossible to compare directly the sequential extraction results of Ruttenberg and Berner (1993) with those in this study. However, in subsequent calculations, it will be assumed that their study correctly identified the fluxes of organic-P, calcareous-P, Fe bound-P, loosely sorbed-P, and authigenic apatite-P and failed to detect REE-phosphate-P. Although this approach may somewhat exaggerate the total-P flux (if some REE-phosphate-P has been counted twice), the flux of REE phosphate is, if anything, underestimated by this method.

Global applicability of these results.—It could be argued that the location of the sediments studied here along a western continental margin (western Australia) may have seen the sediments exposed to unusually high levels of dissolved phosphorus upwelling in nutrient-rich currents. There is, however, no evidence from the sedimentary record of up-
welling conditions (for example, phosphorite deposits). Furthermore, plate reconstructions show that several of the sandstones were deposited in restricted basins due to the juxtaposition of greater India along the southwest margin of Australia during much of the Palaeozoic. Also, due to the effects of plate rotation, much of the Western Australian continental shelf faced northward at the time of sediment deposition. So it seems unlikely that the samples studied here were disproportionately influenced by phosphate-rich upwelling. The results can probably be generalized to other marginal marine and shelf situations.

Another consideration is the rarity of reported occurrences of these minerals in marine sandstones from other localities. Previous studies of authigenic aluminophosphate minerals are mostly restricted to samples where the crystals are either unusually large (up to 2 mm long elongate rhombohedra; Pouliot and Hofmann, 1981) or present in particularly high concentrations (up to 15 wt percent) and typically between 5 and 10 wt percent: Spötl, 1990). However, results from this study suggest that authigenic aluminophosphates are more common as minute crystals (0.1-10 μm width) present in trace quantities (commonly <0.1 wt percent) and have probably been overlooked or dismissed as insignificant trace minerals in previous studies. It is therefore suggested that the REE-phosphates are probably globally widespread in marine-deposited sandstones elsewhere.

Phosphorus burial flux.—To calculate the oceanic geochemical flux of an element, it is commonly assumed that the ocean is in a steady state, that is, the rate of addition of the element into seawater (input) is balanced by its rate of removal (output). The major P input is river water (Froelich and others, 1982), with atmospheric input accounting for less than 10 percent (Graham and Duce, 1979). For phosphorus, the natural fluvial input is difficult to quantify due to the effect of human activity on river nutrient levels (Meybeck, 1982). Furthermore, it is unknown what proportion of phosphorus eroded from continents is “solubilizable” or reactive in river water and how phosphorus behaves during mixing with ocean water (Froelich and others, 1982). It is therefore simpler to calculate the output of P lost through the burial of phosphate-bearing components within marine sediments.

The burial flux of P has been estimated in previous studies (Froelich and others, 1982; Ruttenberg 1993) (table 4). In the study by Froelich and others (1982), the P burial flux was calculated for sediments from upwelling margins and the deep sea. The reactive P burial flux was estimated to be about 3.8 × 10^10 moles yr⁻¹. The main P sinks were identified as organic-bound P and P associated with biogenic carbonate.

The later work, by Ruttenberg and Berner (1993) showed that continental margins are probably more important as areas for reactive P burial, with an output flux about 5 times greater (about 18.5 × 10^10 moles yr⁻¹) than for upwelling areas. The higher output flux is mostly due to additional removal of non-volcanogenic iron-bound P in deltaic
environments and burial of carbonate fluorapatite, biogenic apatite and biogenic carbonate in shelf environments (Ruttenberg, 1993).

In this study, the quantity of reactive P buried through authigenic phosphate precipitation was calculated for each mineral (ALP) by the following equation:

\[
\text{Burial Flux (moles-P yr}^{-1}\text{)} = SR \times (\text{wt\% ALP/100} \times \text{SD})/\text{MW}_{\text{ALP}} \times M_{\text{ALP}} \times MS_{\text{ALP}} \times A_{\text{Ocean}}
\]

Sedimentation rates (SR) in coastal environments, the dominant sites of sand deposition, are generally quite high (> 0.3 cm yr\(^{-1}\); Gibbs, 1981; Ingall and Van Cappellen, 1990; Alexander and others, 1991); however, a relatively conservative value (0.1 cm yr\(^{-1}\)) was used in these calculations. The average concentration of each mineral is shown in table 2 (for
example, the average concentration for florencite is 0.0379 wt percent). A sediment density of 2.65 g cm$^{-3}$ and an initial sand porosity of 40 percent (Atkins and McBride, 1992) were also assumed, giving a sand density (SD) of about 1.59 g cm$^{-3}$. The molecular weight of one mole of authigenic phosphate is represented by $MW_{(ALP)}$ (for florencite the molecular weight is about 490 g). The number of moles of PO$_4$ in 1 mole of authigenic phosphate is represented by $(M_{(ALP)}$; 1 mole of florencite contains two moles of PO$_4$). The proportion of marine sandstones with diagenetic REE-phosphates ($MS_{(ALP)}$) was estimated to be about 7 percent. This was calculated from (1) the abundance of sandstones in the Phanerozoic sedimentary rock record (ranges from 14 to 40 percent (Kuenen, 1941; Krynine, 1948; Ronov and Migdisov, 1971; Holland, 1984), with an average between 20.1 and 34 percent (Poldervaart, 1955; Horn and Adams, 1966; Ronov, 1982); an average of 20.1 percent was used here); (2) the proportion of marine sedimentary rocks deposited on continents during the Phanerozoic (approx 70 percent; Ronov, 1982); and (3) the proportion of marine-deposited sandstones which contain measurable concentrations of authigenic REE-phosphate minerals (about 62.5 percent from this study; 50 percent was used here). To give global flux values (in moles-P yr$^{-1}$), the estimated burial rate (in moles-P cm$^{-2}$ yr$^{-1}$) was multiplied by the area of the oceans ($A_{(Ocean)}$; 3.61 $\times$ 10$^{18}$ cm$^2$; Chester, 1990).

From this equation, the total burial flux of P through REE-phosphate precipitation is estimated to be about 7.56 $\times$ 10$^{10}$ moles yr$^{-1}$ (table 3, subtracting the output from apatite), which is of similar magnitude to authigenic-P (authigenic carbonate fluorapatite, biogenic apatite, and phosphorus-bearing carbonates; between 2.2 and 9.1 $\times$ 10$^{10}$ moles yr$^{-1}$; Ruttenberg, 1993). This suggests that the quantity of phosphorus sequestered through REE-phosphate precipitation is of major importance to the global P budget (table 4), constituting perhaps a third to a half of all phosphorus burial in marine sediments. If so, then the oceanic residence time of phosphorus will be significantly smaller (11 ka for maximum P-output estimate; 20 ka for minimum P-output estimate) than previous estimates (between 16 and 38 ka; Ruttenberg, 1993).

If the oceanic P cycle is to maintain mass balance, then the increase in burial flux caused by the discovery of a new sink (that is, authigenic REE-phosphates) must be compensated for by the decreased output in another sink or by enhanced input. Recent work on the behavior of phosphorus in river and estuarine waters (Fox and others, 1986; Froelich, 1988) shows that the quantity of reactive P carried by suspended material (adsorbed onto hydrous iron and aluminium oxides and associated with organic material) is significantly higher than previously thought (up to three times greater than that carried in solution by rivers; Rao and Berner, 1993; Berner and Rao, 1994). Extrapolating results from the Amazon River, Berner and Rao (1994) estimate a global solubilized sediment P flux of 3.5–6 $\times$ 10$^{10}$ moles yr$^{-1}$, which translates to a total pre-human P flux to the oceans of 5 to 8.5 $\times$ 10$^{10}$ moles yr$^{-1}$ after
including the natural dissolved P flux of about 1.5 to 2.5 \times 10^{10} \text{ moles yr}^{-1}; Froelich and others, 1982). While there is uncertainty in the estimates of the input of P from rivers and output through sediment burial, these values are about 2 to 5 times smaller than the modified P output (15.5 \times 10^{10} - 26 \times 10^{10} \text{ moles yr}^{-1}) and may suggest that the proportion of reactive P in river-borne suspended material may be significantly higher still or that the size of some marine sinks has been exaggerated.

Implications.—The concentration of phosphorus in the oceans is an important factor in controlling atmospheric CO$_2$ levels (Broecker, 1982). Phosphorus is an essential nutrient in sustaining life (Holland, 1978), and its concentration in the ocean is thought to limit the growth of phytoplankton which remove CO$_2$ from surface waters and the atmosphere through photosynthesis. Atmospheric CO$_2$ plays an important role in maintaining the Earth's surface temperature and has a major impact on climate variation (Berner and Berner, 1987). Thus, changes in the volume of P removed from the oceans and buried as relatively inert authigenic minerals should have a significant influence on the carbon cycle. In the light of the results of this paper (that is, the ubiquitous nature of early-diagenetic REE-phosphate minerals in marine sandstones), the P budget should be revised, implying a shorter P residence time in the ocean. This may therefore impact on the abundance and distribution of marine life and the capacity of the ocean to absorb CO$_2$, thereby influencing global climates.

Conclusions

Authigenic aluminophosphates (florencite, crandallite, and gorceixite) and xenotime are volumetrically minor but widespread components of Archaean to Cretaceous sandstones from Australian sedimentary basins. The minute crystal size (<0.1-10 \mu m in width) and low concentration of the aluminophosphates and xenotime have probably hindered their previous identification by optical methods, while their insolubility at low temperatures may have prevented their separation and recognition by sequential solvent extraction techniques.

The REE-phosphates precipitated shortly after burial, probably within the zone of sulfate reduction and microbial methanogenesis. Rapid increase in pore-water phosphate following organic matter degradation and Fe-(hydr-)oxide reduction, combined with clay mineral transformation and REE-bearing mineral dissolution, resulted in the precipitation of the aluminophosphates and xenotime.

The presence of early-diagenetic REE-phosphate minerals in larger quantities than carbonate fluorapatite in marine sandstones suggests these previously-unrecognized authigenic minerals may be an equally important sink for P in seawater. Estimates of the burial flux of reactive P by REE-phosphate precipitation (7.56 \times 10^{10} \text{ moles yr}^{-1}) is comparable with the combined burial flux for authigenic carbonate fluorapatite, calcareous-P, and biogenic apatite; between 2.2 \times 10^{10} and 9.1 \times 10^{10}
mole yr⁻¹). The identification of this new sink has implications for the residence time of P in the oceans and through nutrient modulation of the photosynthetic biomass may impact on oceanic and atmospheric CO₂ levels and hence the global climate.

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