

Isotopic constraints on the genesis and age of autochthonous glaucony in the Oligo-Miocene Torquay Group, south-eastern Australia

JONATHAN C. KELLY¹, JOHN A. WEBB and ROLAND MAAS

Department of Earth Sciences, La Trobe University, Bundoora, Victoria, Australia 3083

ABSTRACT

The Oligo-Miocene Torquay Group at Bird Rock in south-eastern Australia comprises a sequence of fine-grained skeletal carbonates and argillaceous and glauconitic sandstones, deposited in a cool-water, mid-shelf environment. The Bird Rock glaucony is autochthonous and consists predominantly of randomly interstratified glauconitic smectite, which constitutes bioclast infills and faecal pellet replacements. The results of Rb–Sr and oxygen isotopic analysis of samples taken from a single glauconitic horizon (the BW horizon) indicate that the glaucony developed through a series of simultaneous dissolution–crystallization reactions, which occurred during very early diagenesis in a closed or isochemical system, isolated from the ambient marine environment. The constituent ions of the glaucony were derived primarily from terrigenous clay minerals, but considerable potassium may have been sourced indirectly from sea water, through potassium enrichment of clay precursors. The pore fluids associated with glauconitization were marine derived, but progressively modified by the dissolution–crystallization of detrital clay minerals and autochthonous glaucony. Rb–Sr data for the BW horizon indicate that dating glauconies may be somewhat problematic, as co-genetic glauconitic minerals can show a range of initial strontium compositions, which reflect the incorporation of strontium derived from mineralogical precursors and/or contemporaneous sea water. Rb–Sr isochrons indicate that the glaucony of the BW horizon formed at 23 ± 3 Ma. This age is in good agreement with both the established biostratigraphy and a $^{87}\text{Sr}/^{86}\text{Sr}$ age for the horizon (23 ± 1 Ma), but could only be determined using the independent age constraint and the estimate of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of contemporaneous sea water provided by analysis of associated biogenic carbonate.

Keywords Diagenesis, geochemistry, geochronology, glaucony, oxygen isotopes, Rb–Sr isotopes.

INTRODUCTION

The term glaucony refers to the petrographic facies in which glauconitic minerals are abundant (Odin & Matter, 1981; Odin & Dodson, 1982).

¹Present address: Woodside Energy Ltd, 1 Adelaide Tce., Perth, Western Australia, Australia 6000 (E-mail: Jon.Kelly@woodside.com.au)

Glauconitic minerals are iron- and potassium-rich aluminophyllosilicates and typically constitute sand-sized, ellipsoidal green pellets that have an earthy or lustrous appearance (Triplehorn, 1966; McRae, 1972; Odin & Matter, 1981; Odin & Fullagar, 1988). Glaucony occurs in the surficial sediments of every ocean and in marine sedimentary rocks from all parts of the geological column (Galliher, 1935; McRae, 1972; Odin & Fullagar, 1988).

Radiometric dates of glauconies have been used widely to determine the depositional age of sedimentary rocks and have provided numerous age constraints for the calibration of the relative time scale (Odin *et al.*, 1978; Odin, 1982; Craig *et al.*, 1989). Yet the reliability of isotopic dates from glaucony has often been questioned, in part due to problems that can be attributed to an incomplete understanding of the glauconitization process (Odin *et al.*, 1978; Odin & Dodson, 1982; Craig *et al.*, 1989; Clauer *et al.*, 1992a; Stille & Clauer, 1994).

Glaucony is generally regarded as an halmyrolytic phenomenon, which develops in response to chemical interactions between sea water and sediments during periods of slow sedimentation (Odin & Matter, 1981; Fairbridge, 1983). Nevertheless, several different mechanisms of glauconitization have been postulated, including the layer lattice theory of Burst (1958a,b) and Hower (1961), the verdissement theory of Odin & Matter (1981) and the two-stage evolutionary model of Clauer *et al.* (1992a,b).

The layer lattice theory invokes solid-state transformation of degraded clay precursors to glauconitic minerals through ionic exchange with the marine environment (Burst, 1958a,b; Hower, 1961). The verdissement theory suggests that glaucony is the product of neoformation (i.e. precipitation from a fluid phase), with constituent ions being derived from both the enclosing sediment and sea water (Odin & Matter, 1981). The two-stage glauconitization model is a refinement of the verdissement theory and involves initial dissolution of clay precursors with concomitant crystallization of a glauconitic phase in the precursor-dominated environment, followed by second-stage maturation and potassium enrichment in equilibrium with sea water (Clauer *et al.*, 1992a,b).

In contrast to these theories, in a recent investigation of glaucony in the Torquay Group of south-eastern Australia, Kelly & Webb (1999) suggested that it is unnecessary to invoke ionic exchange with sea water to explain the development of glaucony; the chemical constituents of glauconitic minerals may be derived primarily from argillaceous matrix material.

Kelly & Webb (1999) concluded that the glauconitization of the Torquay Group sediments occurred in isolation from the open-marine environment under very shallow burial conditions, and involved ions derived largely from argillaceous matrix material. They also provided evidence that glauconitization must involve local

iron and potassium enrichment, but did not identify the actual mechanism of glauconitic mineral formation.

The aim of this study is to elucidate further the genesis of glaucony in the Oligo-Miocene Torquay Group of the Torquay Basin, south-eastern Australia, using a combination of oxygen and Rb–Sr isotopic techniques. This research attempts to identify the mechanism of formation of glauconitic minerals in the Torquay Group and tests the theory that glauconitization occurs in isolation from the open-marine environment.

In addition, this study employs Rb–Sr isotopic data from the glauconitic minerals and associated clay fraction, together with Sr isotope data from associated biogenic carbonate, in an attempt to determine the age of formation of the glaucony and to identify potential problems with existing dating methods.

GEOLOGICAL SETTING, PETROLOGY AND BULK CHEMISTRY

The Torquay Basin lies on Australia's south-eastern margin, in southern Victoria, and contains a Tertiary stratigraphy of terrestrial and marine siliciclastics and marine carbonates (Reeckmann, 1981; Abele, 1988; Webb *et al.*, 1995). At Bird Rock, south-west of Torquay, the Oligo-Miocene Torquay Group is exposed in coastal cliffs (Fig. 1).

The Torquay Group at Bird Rock consists of the Jan Juc and overlying Puebla Formations and comprises a sequence of fine-grained skeletal carbonates and argillaceous and glauconitic sandstones (Fig. 2), which were deposited in a cool-water, mid-shelf environment (Abele, 1979; Boreen & James, 1995; Kelly & Webb, 1999). Kelly & Webb (1999) gave full petrological descriptions of the Bird Rock lithologies; however, the pertinent features of the glauconitic sediments are summarized below.

The glauconitic Bird Rock lithologies are mid-to dark-grey/green, very poorly lithified and intensely bioturbated. They are poorly sorted and contain abundant and diverse skeletal grains, and minor quartz and feldspar, in a brown to dark-brown organic-rich matrix of smectite and lesser kaolinite.

Glauconitic minerals constitute 10–20% of the glauconitic lithologies and consist predominantly of randomly interstratified glauconitic smectite, which forms bioclast infills and faecal pellet replacements. The carbonate bioclasts that host

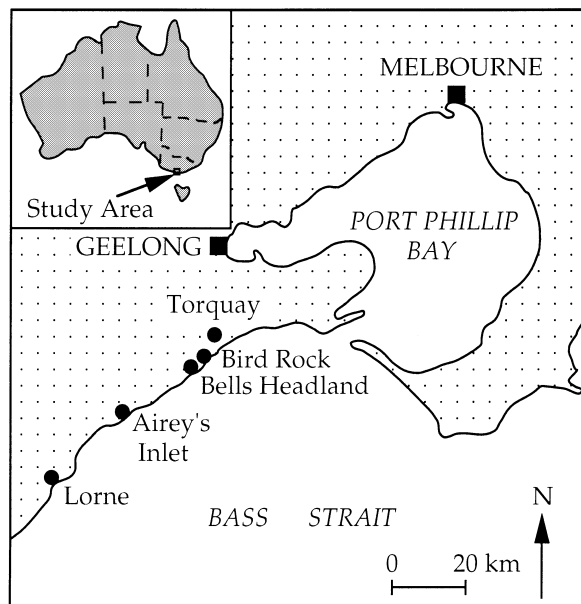


Fig. 1. Map showing the location of the Bird Rock study area.

glauconitic minerals are commonly partially or completely dissolved to form mouldic porosity.

Textural features, such as patches of diffuse glaucony in the matrix and gradational boundaries between pelletal glaucony and surrounding matrix, clearly show that the glaucony is autochthonous. The poorly sorted character of the glauconitic Bird Rock sediments verifies this; if the glauconitic grains had been transported, they would have been concentrated in texturally mature sediments by hydraulic sorting.

Other authigenic components are very minor and include pyrite, siderite, phosphate and iron oxides. Pyrite commonly occurs as cubic and framboidal grains rimming and in partial replacement of glauconitic pellets; these textures suggest that pyrite post-dates the development of glaucony in the Bird Rock lithologies.

Textural features show that glaucony has replaced argillaceous matrix; together with bulk chemical data (Kelly & Webb, 1999), this indicates that the elemental constituents of the Bird Rock glaucony were derived largely, if not entirely, from primary detrital clay. However, the Bird Rock glaucony contains more iron (up to 15 wt% Fe_2O_3) and more potassium (up to 2.6 wt% K_2O) than the argillaceous matrix (Kelly & Webb, 1999), so glauconitization must have involved iron and potassium enrichment.

The glauconitic sediments are intensely bioturbated and contain a diverse benthic fauna, indicating that oxic bottom-water conditions prevailed

during their accumulation. In oxic sea water, iron has a very low solubility, whereas under reducing conditions, it is soluble as ferrous iron (Garrels & Christ, 1965; James, 1966; Harder, 1980; Drever, 1988). Thus, the inferred iron enrichment during the development of the Bird Rock glaucony indicates that glauconitization occurred in isolation from the oxic waters of the open ocean, under relatively low Eh conditions in the very shallow burial environment (Kelly & Webb, 1999).

METHODS

Prominent glauconitic strata in the Bird Rock section include an ≈ 40 -cm-thick bed, here called the burrow or BW horizon, which lies at the boundary between the Jan Juc and Puebla Formations (Fig. 2). Glaucony from this layer infills numerous olive-grey burrows in the underlying Jan Juc Formation. Kelly & Webb (1999) sampled several intervals of the Bird Rock section, but the current study focuses entirely on samples taken from the BW horizon.

Aliquots of the $<2\text{-}\mu\text{m}$ clay and glauconitic fractions from the BW horizon were analysed using the Rb–Sr and oxygen isotopic techniques. The $<2\text{-}\mu\text{m}$ clay fraction consists largely of smectite, with lesser kaolinite, and so will subsequently be identified as the smectitic component.

Before isotopic analysis, the samples were leached in a 1 N HCl ultrasonic bath for 10 min at room temperature to remove potential contaminants such as carbonate and adsorbed Rb and Sr (Kralik, 1984; Clauer *et al.*, 1992a; Stille & Clauer, 1994). Each leached sample (residue) was repeatedly rinsed with Milli-Q water to remove salts (Clauer *et al.*, 1992a; Stille & Clauer, 1994). The residues were then split into aliquots for oxygen and Rb–Sr isotopic determinations. The HCl leachates were also preserved for Rb–Sr isotopic analysis.

Oxygen isotope analytical methods

Oxygen isotope analysis was conducted according to the methods of Clayton & Mayeda (1963), using ClF_3 as the oxidizing reagent. These methods involve a 1-hour pre-analytical heating step at 400 °C under vacuum, which effectively removes interlayer and adsorbed air and water from the clay samples, such that only the oxygen of the silicate framework is analysed (Clayton & Mayeda, 1963; Savin & Epstein, 1970; O'Neil & Kharaka, 1976; Pokrovskii & Golovin, 1989).

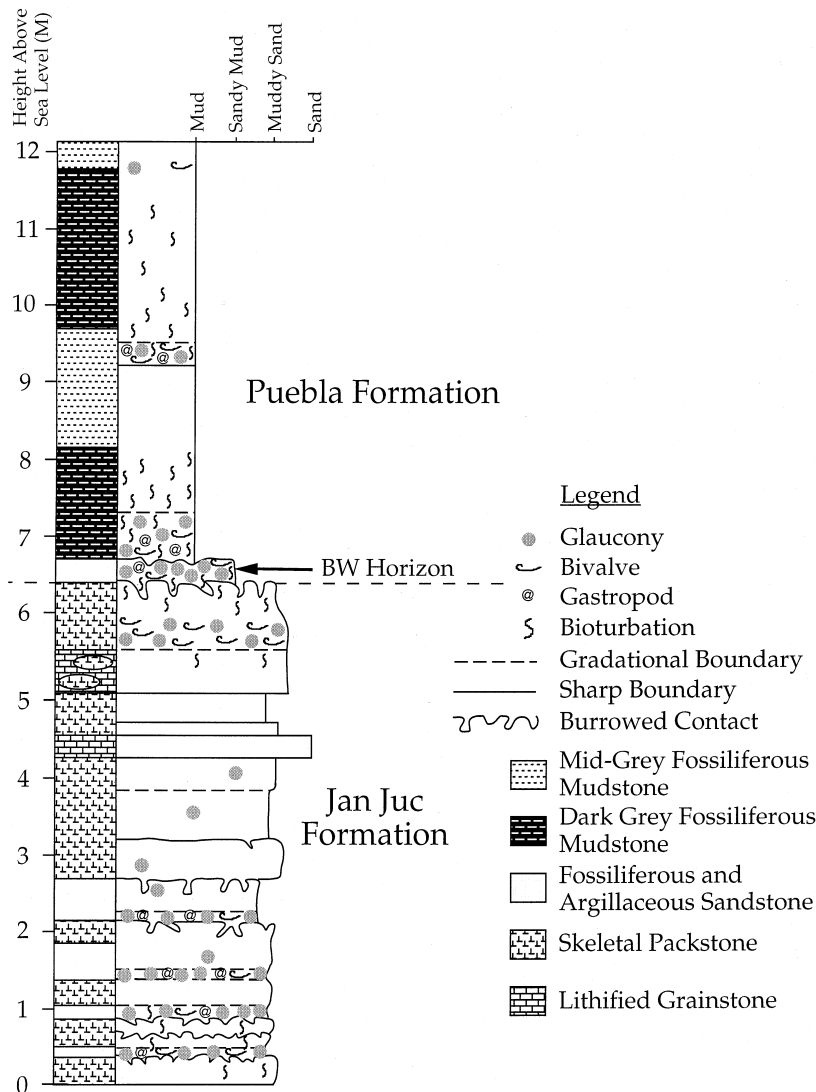


Fig. 2. The stratigraphic succession at Bird Rock (modified after Van Der Linden, 1997).

Oxygen isotopic ratios were measured on a Finnigan MAT 252 mass spectrometer. Values of $\delta^{18}\text{O}$ are reported in parts per thousand (‰) relative to V-SMOW. The precision of this analysis was better than $\pm 0.2\text{‰}$.

Rb–Sr analytical methods

The sample residues were dissolved in Teflon beakers by $\text{HF-HNO}_3\text{-HCl}$ digestion at $100\text{ }^\circ\text{C}$. The dissolved samples were then aliquoted for potassium and Rb–Sr determinations.

Potassium determinations were made by inductively coupled plasma–atomic emission spectrometry (ICP–AES) on a GBC Integra XM, using potassium chloride standard solutions. The precision of this analysis was better than 2% relative.

The Rb–Sr aliquots and HCl leachates of the various samples were spiked with a $^{87}\text{Rb}/^{84}\text{Sr}$ tracer, dried down and then redissolved in 1 N HCl. Refractory fines were removed by centrifugation before column chemistry. Rb and Sr fractions were separated by standard cation exchange chromatography using HCl eluants. Sr was loaded on single Ta filaments with dilute phosphoric acid. Rb was loaded on double Re filaments using HCl.

Isotopic analyses were made on a Finnigan MAT 262 multicollector mass spectrometer. Sr isotopic ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Results for the SRM 987 standard ($\pm 2\text{SD}$) are: $^{87}\text{Sr}/^{86}\text{Sr} = 0.71022 \pm 6$. Typical within-run precision ($\pm 2\sigma_{\text{mean}}$) for $^{87}\text{Sr}/^{86}\text{Sr}$ is $\leq \pm 0.00004$ and the reproducibility for $^{87}\text{Rb}/^{86}\text{Sr}$ is $\pm 0.5\%$.

Sr analysis

A mixture of planktonic foraminiferal taxa, hand picked from the disaggregated whole-rock sample, was analysed for Sr using the technique described above. Before analysis, the foraminifera were cleaned ultrasonically in Milli-Q water and then dissolved with 1 N HCl. Insoluble residue was removed by centrifugation.

OXYGEN ISOTOPE GEOCHEMISTRY

Glauconitic pellets separated from the BW horizon were subdivided into a number of different paramagnetic fractions using a Frantz magnetic separator (Kelly & Webb, 1999). Each fraction has a different potassium content (Table 1) and represents a particular stage in the progressive chemical evolution of the glaucony; glauconitic minerals evolve through the gradual incorporation of potassium (Cimbalnikova, 1971; Thompson & Hower, 1975; Odin & Matter, 1981). Thus, isotopic analysis of the different fractions should provide constraints on the mechanism of glauconitization in the Bird Rock sediments.

The oxygen isotope data for the smectitic and glauconitic fractions display significant variation (Table 1). The smectitic fraction has the highest $\delta^{18}\text{O}$ value (26.41‰), the most evolved glaucony has the lowest $\delta^{18}\text{O}$ value (20.27‰), and the less evolved glauconitic fractions display a fairly narrow range of intermediate values (23.39–22.30‰).

The oxygen isotopic composition of clay minerals is controlled by two factors: the isotopic character of the water in contact with the clays at the time of formation; and the temperature of the

environment during their growth (Savin & Epstein, 1970; Faure, 1986; Hoefs, 1987). The isotopic fractionation factors for clay–water systems approach unity with increasing temperature (Savin & Epstein, 1970; Faure, 1986; Hoefs, 1987).

Clay minerals that form in terrestrial environments usually develop at higher temperatures and in waters with lower ^{18}O contents than those that form in the marine environment (Yeh & Savin, 1976; Clauer *et al.*, 1990). Consequently, terrigenous clays usually display comparatively low $\delta^{18}\text{O}$ values, typically in the 15–20‰ range, whereas authigenic marine clays are characterized by markedly higher values of around 26–31‰ (Savin & Epstein, 1970; Yeh & Savin, 1977; Clauer *et al.*, 1990).

The smectitic fraction of the BW horizon is thought to be of continental origin, as it has a non-marine initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (see below). However, its $\delta^{18}\text{O}$ value (26.41‰) is very high in relation to typical terrigenous clay minerals and is consistent with isotopic equilibration with oceanic waters.

Post-formational oxygen isotopic exchange between clay minerals and water only occurs when cation–oxygen bonds are broken and reformed and is generally very slow at sedimentary temperatures (Savin & Epstein, 1970; James & Baker, 1976; O'Neil & Kharaka, 1976; Yeh & Savin, 1976). Exchange of this type is controlled by the accessibility of water to the interlayer cation region and can therefore be significant in clays with a large proportion of expandable layers (James & Baker, 1976; O'Neil & Kharaka, 1976). However, the exchange is unlikely to achieve equilibrium at sedimentary temperatures unless considerable chemical or mineralogical alteration

Table 1. Oxygen isotope data for the smectitic and glauconitic fractions of the BW horizon.

Sample	K ₂ O (wt%)	$\delta^{18}\text{O}$ (mineral) (‰SMOW)	$\delta^{18}\text{O}$ (H ₂ O) (‰SMOW)	T _{Equil} (°C)
Smectitic fraction	2.30	26.41	-0.47	17.2
Glaucony (0.55)	3.46	23.39	-3.49	32.7
Glaucony (0.5)	3.84	22.30	-4.58	38.9
Glaucony (0.45)	4.31	23.25	-3.63	33.5
Glaucony (0.4)	4.90	20.27	-6.61	51.6

$\delta^{18}\text{O}$ (mineral) is the measured isotopic composition of the mineral fraction. $\delta^{18}\text{O}$ (H₂O) is the calculated isotopic composition of the water associated with mineral formation, assuming a formation temperature of 15 °C.

T_{Equil} is the calculated temperature of oxygen equilibration assuming marine formation waters ($\delta^{18}\text{O} = \text{‰}$).

The numbers in brackets denote the current (amps) required to attract the glaucony on a magnetic separator set with a lateral inclination of 15° and a longitudinal inclination of 20°; the more evolved/potassic glaucony shows a greater paramagnetic susceptibility, i.e. a lower current is required.

occurs (James & Baker, 1976; Yeh & Savin, 1976). Thus, the marine oxygen signature displayed by the smectitic fraction of the BW sediment probably reflects extensive alteration of terrigenous clay minerals subsequent to deposition in the marine environment.

The glauconitization of the Bird Rock sediments occurred under suboxic, partially reducing conditions in the very shallow burial environment, probably at a depth of centimetres to metres below the sediment–water interface (Kelly & Webb, 1999). Therefore, it is likely that the glaucony developed at a temperature around that of the ambient marine environment; palaeowater temperature estimates for the Torquay Group of between 12 and 17 °C have been made on the basis of oxygen isotopes and calcareous nannofossil assemblages (Dorman & Gill, 1959; Siesser, 1979).

Using the measured oxygen isotopic compositions of the glauconitic samples (Table 1), an assumed formation temperature of 15 °C and the fractionation equation for smectitic minerals (Eq. 1), the isotopic character of the waters associated with the formation of the Bird Rock glaucony ($\delta\text{H}_2\text{O}$) may be estimated (Fig. 3). The Bird Rock glaucony comprises glauconitic smectite; therefore, the fractionation equation for smectitic minerals has been used.

$$\delta_{\text{smectite}} - \delta_{\text{H}_2\text{O}} \cong (2.58 \cdot 10^6 \cdot T^2) - 4.19[T \text{ in } ^\circ\text{C}] \quad (1)$$

(O'Neil, 1979; Faure, 1986; Savin & Lee, 1988; Kharaka & Thordsen, 1992).

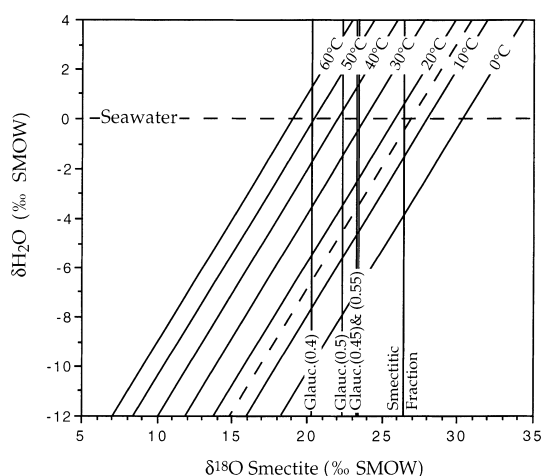


Fig. 3. Oxygen isotope fractionation between water and smectite as a function of temperature. The oxygen isotope compositions of the smectitic and glauconitic fractions of the BW horizon; the $\delta^{18}\text{O}$ of sea water and the 15 °C isotherm (dashed) are shown for reference purposes.

The estimated $\delta\text{H}_2\text{O}$ -values for the various glauconitic fractions (Table 1) suggest that the glauconitic minerals formed in equilibrium with waters that were depleted by 3.5–6.6 ml⁻¹ $\delta^{18}\text{O}$ relative to typical ocean water; open marine waters have an oxygen isotope composition of $0 \pm 1\text{‰}$ (Savin & Epstein, 1970; Faure, 1986; Hoefs, 1987; Pokrovskii & Golovin, 1989). The fact that the glaucony appears to have formed in contact with waters that were isotopically distinct from typical oceanic water indicates that the glauconitization process occurred in isolation from the open-marine environment. Petrographic and geochemical evidence also suggests this (see above).

Clay minerals forming at sedimentary temperatures are preferentially enriched in ^{18}O compared with the waters with which they equilibrate (O'Neil, 1979; Faure, 1986; Hoefs, 1987; Pokrovskii & Golovin, 1989). Thus, continuing clay formation in a closed sediment system will result in the gradual depletion of ^{18}O in the interstitial waters and will produce clay minerals with progressively more depleted oxygen isotopic signatures. The magnitude of such depletion will depend largely on the sediment–water ratio in the system and the amount of clay formed, and will be greatest in sediments with low porosity and permeability, e.g. compacted shale (Lawrence *et al.*, 1975; Faure, 1986; Kharaka & Thordsen, 1992; Mozley & Carothers, 1992). Porewater ^{18}O depletion as a consequence of clay authigenesis has been reported by several previous workers (e.g. Lawrence *et al.*, 1975; Perry *et al.*, 1976; Pokrovskii & Golovin, 1989).

The Bird Rock glaucony represents a clear example of such progressive ^{18}O depletion, as it shows a general trend of decreasing $\delta^{18}\text{O}$ with increasing potassium content (Fig. 4), i.e. the $\delta^{18}\text{O}$ decreases as the glaucony becomes more evolved. This trend is consistent with the development of glaucony through a series of dissolution–crystallization reactions in a closed or isochemical system. The potassium– $\delta^{18}\text{O}$ trend displayed by the glauconitic fractions can be extended through to the low-potassium smectitic fraction (Fig. 4), which has a marine oxygen signature, providing strong evidence that the smectitic fraction is the genetic precursor of glaucony in the Bird Rock sediments and that the porewaters involved in the glauconitization process were marine derived.

One sample does not plot directly on the potassium–oxygen isotope trend of the Bird Rock clay minerals (Fig. 4); this may reflect a transient perturbation of the clay–water system as a result

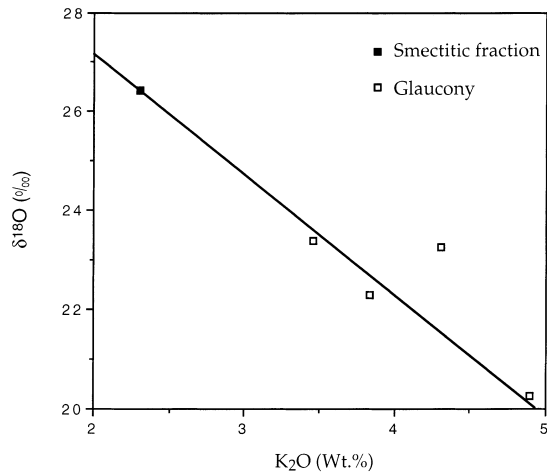


Fig. 4. Variation in the potassium content and oxygen isotope composition of the glauconitic and smectitic fractions of the BW horizon.

of the influx of marine-derived oxygen through bioturbation.

Low $\delta^{18}\text{O}$ values in the authigenic components of marine sediments have previously been attributed to three other possible mechanisms: precipitation from marine-derived waters with oxygen compositions modified by intense sulphate reduction; precipitation from fluids containing significant amounts of isotopically light fresh water; and equilibration or re-equilibration at elevated temperatures during burial (Savin & Epstein, 1970; Pokrovskii & Golovin, 1989; Sass *et al.*, 1991; Mozley & Carothers, 1992; Mozley & Burns, 1993; Ayalon & Longstaffe, 1995).

The first of these mechanisms, intense sulphate reduction, cannot be responsible for the depleted oxygen composition of the Bird Rock glaucony because pyrite, the principal product of sulphate reduction, is only a very minor component of the sediments, and petrographic evidence indicates that it post-dates the development of glaucony (see above).

The second mechanism, precipitation under the influence of fresh water, is very unlikely because the glauconitic sediments were deposited in a mid-shelf environment and contain a diverse benthic fauna characteristic of normal sea-water salinity (Abele, 1979; Webb *et al.*, 1995; Kelly & Webb, 1999). The potassium– $\delta^{18}\text{O}$ trend displayed by the smectitic and glauconitic fractions (Fig. 4) also indicates that the sediments were deposited in normal marine waters (see above). Furthermore, it is unlikely that the glauconitic strata were affected by circulating meteoric fluids during burial, as they are likely to have had low permeability in the burial environment, being

relatively fine grained, clay rich and poorly sorted (Kelly & Webb, 1999). The preservation of the metastable carbonate minerals aragonite and Mg-calcite (Reeckmann, 1981) and significant amounts of organic matter (Kelly & Webb, 1999) in the sediments attests to restricted groundwater circulation.

In addition, geochronological evidence suggests that the glauconitization of the BW horizon occurred at ≈ 23 Ma, in the Early Miocene, during early diagenesis (see below). A relative sea-level fall of sufficient magnitude to increase the hydraulic gradient and drive meteoric waters through the Bird Rock sequence did not occur until the Late Miocene–Pliocene, when the region was uplifted as a result of the Australian continent being placed into compression following arc collision to the north (Hill *et al.*, 1995). Thus, the low $\delta^{18}\text{O}$ of the glauconitic minerals cannot relate to precipitation from fluids with a significant fresh water component.

The third explanation of the depleted $\delta^{18}\text{O}$ signatures of the glaucony, equilibration or re-equilibration at elevated temperatures during burial, is also unlikely. Assuming normal marine formation waters, the most evolved glauconitic fraction of the BW horizon has an oxygen isotopic composition that equates to an equilibration temperature of 52°C (Eq 1; Fig. 3; Table 1), $\approx 35^\circ\text{C}$ higher than the temperature of the depositional environment. Using the present-day geothermal gradient for the Torquay area, $\approx 40^\circ\text{C km}^{-1}$ (Mehin & Link, 1994), this temperature corresponds to a burial depth of ≈ 900 m. The Bird Rock sediments were overlain by a maximum of only 350 m of sediment by the early Middle Miocene; subsequent sediment accumulation in the Torquay region has been restricted to thin fluvial sequences (Abele, 1979, 1988; Webb *et al.*, 1995). Consequently, the depleted oxygen composition of the Bird Rock glaucony cannot relate to equilibration at elevated temperature in the burial environment.

Furthermore, the smectitic fraction of the glauconitic BW sediment preserves a pristine low-temperature marine oxygen signature (Table 1); it is very unlikely that the glauconitic minerals were selectively affected by isotopic resetting at elevated temperature, while the co-existing smectitic fraction remained undisturbed.

Depleted oxygen isotopic compositions, similar to those of the Bird Rock glaucony, are commonly reported for glauconies from Recent sea-floor sediments (Friedrichsen, 1984; Keppens & O'Neil, 1984; Clauer *et al.*, 1992b). This also

indicates that low $\delta^{18}\text{O}$ values in glauconitic minerals are not necessarily a product of isotopic exchange with meteoric fluids or at elevated temperature and suggests that the mechanism and conditions of glauconitization are quite uniform, i.e. glauconitization always involves dissolution–crystallization reactions in a closed or isochemical system.

RUBIDIUM–STRONTIUM ISOTOPE GEOCHEMISTRY

Compared with the smectitic fraction of the BW sediment, the glauconitic fractions contain more Rb (135–202 p.p.m. vs. 89 p.p.m.) and considerably less Sr (6–10 p.p.m. vs. 98 p.p.m.; Table 2). These relative proportions appear to be closely related to potassium content; the Rb/Sr ratios display an excellent positive correlation with potassium (Fig. 5). Given the geochemical similarity of potassium and rubidium (Faure & Powell, 1972; Faure, 1986) and the knowledge that potassium occupies interlayer sites within glauconitic structures (Hower, 1961; Odin & Matter, 1981), the correlation between the Rb/Sr ratio and the K content indicates that Rb and Sr are also interlayer cations and suggests that the glauconitization process involves the progressive incorporation of K and Rb and concomitant expulsion or exclusion of Sr. These hypotheses are in agreement with the conclusions of Hower (1961), Clauer *et al.* (1992a) and Stille & Clauer (1994).

The Rb–Sr isotopic composition of the smectitic and glauconitic fractions (Table 2) can be used to constrain the process of glauconitization

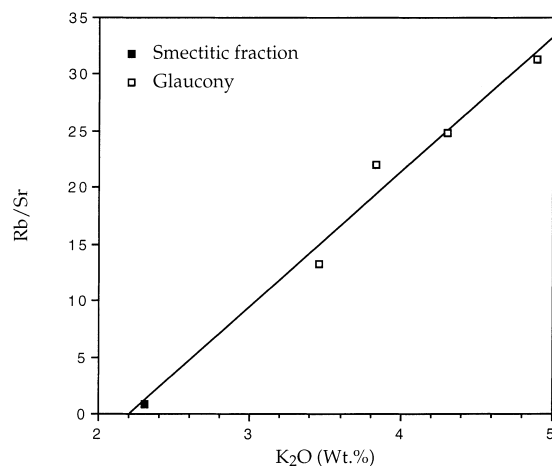


Fig. 5. Variation in the potassium content and Rb/Sr ratio of the glauconitic and smectitic fractions of the BW horizon.

further. The Rb–Sr data show considerable deviation from a single line of best fit on a standard isochron plot (Fig. 6A). The close correlation between the Rb/Sr ratio and the potassium content of the samples (Fig. 5) suggests that the scatter on the isochron plot is a primary feature of the smectite–glaucony system. If the scatter related to secondary processes, involving the differential movement of Rb and/or Sr, it is unlikely that the Rb/Sr ratio would show such a good correlation with potassium, which is a primary constituent of glauconitic minerals.

Biogenic marine carbonate incorporates strontium from sea water without isotopic fractionation and very efficiently excludes rubidium (Faure & Powell, 1972; Hurst, 1986; Hess *et al.*, 1989). Therefore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of planktonic foraminifera extracted from the glauconitic BW

Table 2. Rb–Sr isotopic data for the BW horizon.

Sample	Rb (p.p.m.)	Sr (p.p.m.)	Rb/Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Initial $^{87}\text{Sr}/^{86}\text{Sr}$
Smectitic fraction	89.13	98.18	0.91	2.622	0.71322	0.7124
Smectitic leachate					0.70887	
Glaucyony (0.55)	134.60	10.16	13.25	38.305	0.72205	0.7095
Glaucyony (0.55) leachate					0.70840	
Glaucyony (0.5)	166.40	7.54	22.07	63.844	0.72897	0.7081
Glaucyony (0.5) leachate					0.70867	
Glaucyony (0.45)	182.90	7.38	24.78	71.779	0.73674	0.7133
Glaucyony (0.45) leachate					0.70843	
Glaucyony (0.4)	201.90	6.44	31.35	90.818	0.74183	0.7122
Glaucyony (0.4) leachate					0.70857	
Planktonic forams					0.70829	

The leachate samples are the 1 N HCl leachates of the smectitic and glauconitic fractions.

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were calculated using the 23 Ma Sr age of the BW horizon.

For explanation of the numbers in brackets, refer to Table 1.

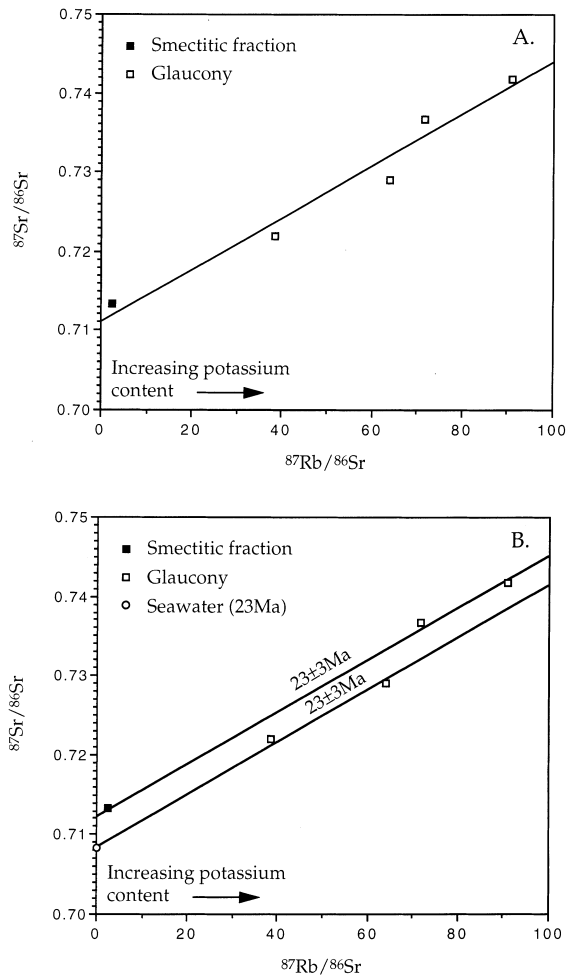


Fig. 6. Rb–Sr isochron diagrams for the smectitic and glauconitic fractions of the BW horizon. (A) A single line of best fit. (B) Two 23 Ma isochrons. The value for 23 Ma sea water was plotted using $\text{Rb}/\text{Sr} = 0.12/8$ p.p.m. (Drever, 1988) and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70829$ (from analysis of planktonic foraminifera).

horizon (Table 2) provides a measure of the marine Sr composition at the time of deposition. Correlation of this value (0.70829) with the established marine Sr isotope curves (Hess *et al.*, 1989; Hodell *et al.*, 1991; Miller *et al.*, 1991) gives a sedimentary age of 23 ± 1 Ma (Fig. 7). This date is in agreement with biostratigraphic evidence that indicates that the Oligo-Miocene boundary (23.8 Ma; Young & Laurie, 1996) lies just above or below the BW horizon and the stratigraphic boundary between the Jan Juc and Puebla Formations (Siesser, 1979; Carter, 1990; Chaproniere, 1992; Fig. 2).

The HCl leachates of the smectitic and glauconitic fractions have Sr isotope compositions (Table 2) that are very close to the sea-water value. This indicates that the leaching process

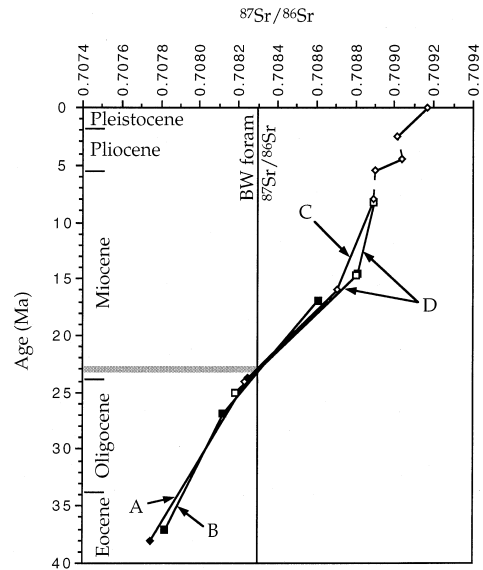


Fig. 7. Correlation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of planktonic foraminifera from the BW horizon with a composite marine Sr evolution curve for the 0–40 Ma period (timescale after Young & Laurie, 1996). The curve comprises linear regression segments from: (A) Miller *et al.* (1988); (B) Hess *et al.* (1989); (C) Hodell *et al.* (1991); (D) Miller *et al.* (1991). The line segments have been normalized on the basis of an SRM 987 value of 0.71022.

removed extraneous marine-derived Sr, which may occur adsorbed to the clay minerals or in mineral impurities (e.g. salts, phosphate and carbonate; Clauer, 1982; Clauer *et al.*, 1990, 1992a), but removed little or no Sr from the clay mineral lattices. If the leaching process removed structural Sr from the clay minerals, the leachates would have more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, given the initial Sr ratios of the clay minerals (see below) and their significant Rb content (Table 2). In addition, the correlation between the Rb/Sr ratio and the potassium content (Fig. 5) would probably be destroyed by the removal of clay-lattice Sr.

The $^{87}\text{Sr}/^{86}\text{Sr}$ age of the BW sediment can be used to calculate the initial Sr ratios of the smectitic and glauconitic fractions (using standard methods, e.g. Faure, 1986). The smectitic fraction has an initial Sr ratio (0.7124) that is significantly higher than that of contemporaneous sea water (Table 2; Fig. 8). The relatively radiogenic Sr signature of the smectitic fraction indicates that it retained considerable detrital Sr despite the intense halmyrolitic alteration evident from its oxygen isotope composition (see above). Clay minerals that form in continental soil profiles display analogous decoupled Rb–Sr and

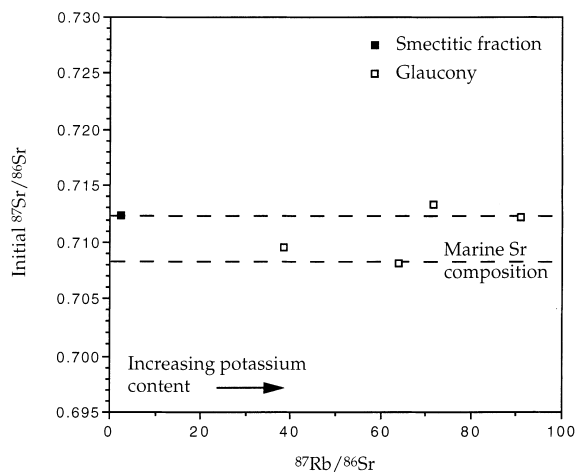


Fig. 8. Variation of the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ($t = 23$ Ma) for the smectitic and glauconitic fractions of the BW horizon. The initial Sr ratio of the smectitic fraction and the Sr composition of contemporaneous sea water (from analysis of planktonic foraminifera) are shown as dashed lines for reference.

oxygen isotopic behaviour; the Sr composition of pedogenic clay usually resembles that of the parent rock or mineral (Dasch, 1969; Clauer, 1979b), whereas the oxygen composition of such clay generally reflects the composition of the environmental water (Savin & Epstein, 1970; Lawrence & Taylor, 1971; O'Neil, 1987).

The two least evolved glauconitic fractions have initial Sr ratios that are close to the marine value (Fig. 8; Table 2); this is also true of their oxygen isotope values, as discussed previously (Table 1). Thus, the least evolved glauconitic fractions appear to record the Sr and oxygen isotope composition of the porewaters of formation. This demonstrates the importance of the fluid phase to the glauconitization process and suggests that the formation of glauconitic minerals in the Bird Rock sediments involved dissolution–recrystallization, rather than solid-state transformation. If glauconitization involved the solid-state transformation of precursor clays, the initial Sr isotope composition of the first formed glaucony would be close to that of the smectitic fraction as a result of isotopic inheritance (Clauer, 1979a).

The initial Sr compositions of the two most evolved glauconitic fractions are comparatively radiogenic and are very similar to that of the smectitic fraction (Fig. 8; Table 2). These Sr ratios confirm the genetic link between the smectitic fraction and the authigenic glaucony and provide evidence for the progressive evolution of the pore fluids associated with glauconitization. The

attendant pore fluids were initially dominated by sea water, but gradually evolved towards the composition of the smectitic fraction. The smectitic fraction has a high Sr content (98 p.p.m) relative to sea water (8 p.p.m.; Drever, 1988). Therefore, the dissolution of the smectitic fraction in a closed system containing marine-derived pore fluids would progressively change the composition of the fluid phase until the original marine Sr signature was completely overwhelmed by the terrigenous Sr signature of the smectitic fraction.

The smectitic fraction and the two most evolved glauconitic fractions had approximately the same Sr ratios during the time of glauconitic mineral formation (Fig. 8) and appear to have remained closed with respect to Rb and Sr since that time (see above). Therefore, Rb–Sr isotopic data for these fractions can be used to determine the age of glaucony formation in the BW sediment (Faure & Powell, 1972; Faure, 1986). The smectitic and most evolved glauconitic samples define a linear array on a Rb–Sr isochron diagram (Fig. 6B). The gradient of this line indicates that the most evolved glauconitic fractions formed at 23 ± 3 Ma, which is in close agreement with the $^{87}\text{Sr}/^{86}\text{Sr}$ age for the BW horizon (23 ± 1 Ma). In addition, the two least evolved glauconitic fractions define a 23 ± 3 Ma isochron that has a marine initial Sr ratio (Fig. 6B). The age uncertainties for the isochron dates were calculated using methods similar to those of Kalsbeek & Hansen (1989).

The age of glaucony formation for both early formed and relatively evolved fractions is indistinguishable from the depositional age of the BW horizon (≈ 23 Ma; see previous discussion), so it can be concluded that glauconitization occurred early in the diagenetic history of the Bird Rock sediments.

Implications for Rb–Sr dating of glaucony

The conventional Rb–Sr method of dating glauconies can be used to date a single glauconitic fraction, but it relies on the assumption that the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the glaucony is identical to that of contemporaneous sea water (Harris, 1982; Keppens & Pasteels, 1982; Clauer *et al.*, 1992a). The results of the current study, along with those of Clauer (1979a), Clauer *et al.* (1992a) and Stille & Clauer (1994), demonstrate that this assumption may often be invalid, as glauconies do not necessarily form in isotopic equilibrium with sea water.

The Rb–Sr isochron technique of dating glauconies does not rely upon presumed equilibration with sea water, but is based on an assumption of homogeneous initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in genetically related glauconitic fractions (Clauer, 1982; Harris, 1982). The results of the current investigation show that this assumption may also be invalid, as the different glauconitic fractions of a single horizon do not always have the same initial Sr ratios. The Rb–Sr isochron dates for the glaucony of the BW horizon agree with both $^{87}\text{Sr}/^{86}\text{Sr}$ chronostratigraphy and the established biostratigraphy (see above), but could only be determined using the independent age constraint and the estimate of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of contemporaneous sea water provided by analysis of associated biogenic carbonate.

GLAUCONITIZATION UNDER CLOSED-SYSTEM CONDITIONS

Rb–Sr and oxygen isotopic data indicate that the Bird Rock glaucony formed in a closed chemical system isolated from the marine depositional environment. The inference of closed-system conditions contrasts sharply with the open-system layer lattice and verdissement models of glauconitization, which involve ionic exchange between precursor sediments and the marine macroenvironment (Burst, 1958a,b; Hower, 1961; Odin & Matter, 1981). Nevertheless, Pokrovskii & Golovin (1989) and Stille & Clauer (1994) provided independent isotopic evidence confirming that glauconitization occurs in a confined microenvironment, isotopically closed to external supply. The two-stage glauconitization model of Clauer *et al.* (1992a,b) also invokes closed-system conditions for the neoformation of glaucony before subsequent maturation and potassium enrichment in equilibrium with sea water. The results of the present study, along with those of Stille & Clauer (1994) and Kelly & Webb (1999), suggest that the second stage of the model of Clauer *et al.* (1992a,b) is unnecessary to explain the genesis of glaucony.

Chemical isolation may be a common prerequisite for the formation or alteration of authigenic silicates and has been inferred for the neoformation of pedogenic kaolinite, the dissolution–recrystallization of sedimentary smectites in black shales and the diagenetic conversion of smectite to illite (Perry & Hower, 1970; Yeh & Savin, 1977; Clauer *et al.*, 1990).

Kelly & Webb (1999) showed that the glauconitization of the Bird Rock sediments involved iron

and potassium enrichment. Consequently, the confined chemical environment in which glauconitization occurs must be sufficiently permeable to allow short-distance mobility of these cations on the scale of millimetres to centimetres.

The closed-system conditions necessary for glauconitization probably occur only in impermeable sediments; the high permeability of coarse-grained, texturally mature sediments would inhibit the development of chemically isolated microenvironments.

SOURCE OF THE CHEMICAL CONSTITUENTS OF GLAUCONY

The evidence presented here indicates that the Bird Rock glaucony precipitated from marine-derived pore fluids. However, aluminium, silica and iron, three of the principal chemical components of glaucony, have very low concentrations in normal sea water (Drever, 1988). Chemical, petrographic and isotopic data indicate that these ions were derived primarily from dissolution of detrital argillaceous matrix (as discussed previously). Dissolution of primary clay minerals occurs during early diagenesis in all types of marine sediments (Mackin & Aller, 1984a,b; Aplin, 1993) and produces concentrated pore fluids that can precipitate authigenic aluminosilicates (Hurd, 1973; Froelich *et al.*, 1979; Mackin & Aller, 1984a,b; Aplin, 1993).

Profiles of dissolved silica in the pore fluids of marine sediments usually show low silica concentrations in surface sediments increasing downwards to constant values within a metre of the sediment–water interface (Hurd, 1973; Mackin & Aller, 1984a,b). The activity of silica is not buffered by quartz or amorphous silica, but more likely by clay mineral dissolution and precipitation reactions (Hurd, 1973; Mackin & Aller, 1984a,b).

The behaviour of aluminium during early diagenesis is very poorly understood, and pore-water aluminium data are scant (Mackin & Aller, 1984a; Aplin, 1993). However, in the East China Sea, Mackin & Aller (1984b) found relatively high aluminium concentrations in the water immediately overlying the sediment–water interface, declining downwards into the porewaters. Similar bottom-water aluminium enrichment was recorded in the Pacific Ocean by Oriens & Bruland (1986). Mackin & Aller (1984b) attributed the elevated aluminium concentrations in the vicinity of the sediment–water interface to the

dissolution of detrital clays and suggested that aluminium is buffered to low levels in the porewaters by the formation of authigenic clays.

The activity of iron in the pore fluids of marine sediments is largely controlled by redox. In oxic conditions, iron has a very low solubility and forms minerals such as haematite, goethite and smectite; under reducing conditions, iron is soluble, and the dissolution of iron-bearing minerals is possible (Carroll, 1958; Garrels & Christ, 1965; James, 1966; Harder, 1980; Drever, 1988). Thus, relatively high concentrations of iron commonly occur at a depth of millimetres to metres below the sediment–water interface as a result of reductive dissolution following oxygen depletion (Froelich *et al.*, 1979; Mackin & Aller, 1984a,b; Van Der Loeff, 1990; Canfield *et al.*, 1993).

Potassium, another essential constituent of glaucony, is relatively abundant in ocean water (399 p.p.m.; Drever, 1988), but experimental evidence suggests that glauconitic minerals only form in solutions with much higher potassium contents (Harder, 1980; Murav'yev *et al.*, 1985). Potassium enrichment of porewaters will occur during dissolution of detrital clays that contain potassium as the dominant interlayer cation. Terrestrial clay minerals have their exchange sites occupied chiefly by calcium, but this is commonly replaced by potassium when such clays encounter sea water (Carroll, 1958; Drever, 1988). Ionic exchange of this type may have produced significant potassium enrichment in the terrigenous clays of the Bird Rock sediments. Thus, the potassium in the Bird Rock glaucony was probably sourced both directly and indirectly from sea water.

CONCLUSIONS

1 The Bird Rock glaucony is autochthonous and developed through a series of simultaneous dissolution–crystallization reactions, which occurred during very early diagenesis, probably at a depth of centimetres to metres below the sediment–water interface.

2 The glauconitization process occurred in chemical isolation from the ambient marine environment in a closed or isochemical system.

3 The constituent ions of the glaucony were derived primarily from terrigenous clay. However, the potassium may have been directly and indirectly sourced from sea water, the latter through potassium enrichment of clay precursors.

4 The pore fluids associated with glauconitization were marine derived, but progressively modified by the dissolution–crystallization of detrital clay minerals and autochthonous glaucony.

5 Rb–Sr dating of glauconies may be problematic as co-genetic glauconitic minerals can incorporate strontium derived from mineralogical precursors and/or contemporaneous sea water, and thus show a range of initial strontium compositions.

6 Rb–Sr isochrons indicate that the glaucony of the BW horizon formed at 23 ± 3 Ma. This age is in good agreement with both the established biostratigraphy and a $^{87}\text{Sr}/^{86}\text{Sr}$ age for the horizon (23 ± 1 Ma), but could only be determined using the independent age constraint and the estimate of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of contemporaneous sea water provided by analysis of associated biogenic carbonate.

ACKNOWLEDGEMENTS

This research was conducted using the technical resources of the Victorian Institute of Earth and Planetary Sciences and was supported by a La Trobe University Postgraduate Research Scholarship. The authors wish to thank J. Metz, I. Cartwright and D. Murray for their technical assistance. This manuscript benefited from reviews by R. S. Haszeldine, J. M. Huggett and P. S. Mozley.

REFERENCES

- Abele, C.** (1979) *Geology of the Anglesea Area, Central Coastal Victoria*. Memoir 31. Geological Survey of Victoria, 71 pp, Melbourne.
- Abele, C.** (1988) Torquay–Anglesea–Aireys Inlet. In: *Victorian Geology Excursion Guide* (Eds I. Clarke and B. Cook), pp. 119–132. Australian Academy of Science, Canberra.
- Aplin, A.C.** (1993) The composition of authigenic clay minerals in recent sediments: links to the supply of unstable reactants. In: *Geochemistry of Clay–Pore Fluid Interactions* (Eds D.A.C. Manning, P.L. Hall and C.R. Hughes), pp. 81–106. The Mineralogical Society Series 4. Chapman & Hall, London.
- Ayalon, A. and Longstaffe, F.J.** (1995) Stable isotope evidence for the origin of diagenetic carbonate minerals from the Lower Jurassic Inmar Formation, southern Israel. *Sedimentology*, **42**, 147–160.
- Boreen, T.D. and James, N.P.** (1995) Stratigraphic sedimentology of Tertiary cool-water limestones, SE Australia. *J. Sed. Res.*, **B65**, 142–159.
- Burst, J.F.** (1958a) 'Glauconite' pellets: their mineral nature and applications to stratigraphic interpretations. *Bull. Am. Assoc. Petrol. Geol.*, **42**, 310–327.

- Burst, J.F.** (1958b) Mineral heterogeneity in 'glauconite' pellets. *Am. Mineral.*, **43**, 481–497.
- Canfield, D.E., Jorgensen, B.B., Fossing, H., Glud, R., Gundersen, J., Ramsing, N.B., Thamdrup, B., Hansen, J.W., Nielsen, L.P. and Hall, P.O.J.** (1993) Pathways of organic carbon oxidation in three continental margin sediments. *Mar. Geol.*, **113**, 27–40.
- Carroll, D.** (1958) Role of clay minerals in the transportation of iron. *Geochim. Cosmochim. Acta*, **14**, 1–27.
- Carter, A.N.** (1990) Time and space events in the Neogene of south-eastern Australia. In: *Pacific Neogene Events; Their Timing Nature and Interrelationship* (Ed. R. Tsuchi), pp. 183–193. University of Tokyo Press, Japan.
- Chaproniere, G.C.H.** (1992) The distribution and development of Late Oligocene and Early Miocene reticulate globigerines in Australia. *Mar. Micropaleontol.*, **18**, 279–305.
- Cimbalnikova, A.** (1971) Chemical variability and structural heterogeneity of glauconites. *Am. Mineral.*, **56**, 1385–1391.
- Clauer, N.** (1979a) A new approach to Rb-Sr dating of sedimentary rocks. In: *Lectures in Isotope Geology* (Eds E. Jager and J.C. Hunziker), pp. 30–51. Springer-Verlag, Berlin.
- Clauer, N.** (1979b) Relationship between the isotopic composition of strontium in newly formed continental clay minerals and their source material. *Chem. Geol.*, **27**, 155–124.
- Clauer, N.** (1982) The rubidium-strontium method applied to sediments: certitudes and uncertainties. In: *Numerical Dating in Stratigraphy* (Ed. G.S. Odin), pp. 245–276. John Wiley and Sons, UK.
- Clauer, N., O'Neil, J.R., Bonnot-Courtois, C. and Holtzapffel, T.** (1990) Morphological, chemical, and isotopic evidence for an early diagenetic evolution of detrital smectite in marine sediments. *Clay Mineral.*, **38**, 33–46.
- Clauer, N., Keppens, E. and Stille, P.** (1992a) Sr isotopic constraints on the process of glauconitization. *Geology*, **20**, 133–136.
- Clauer, N., Stille, P., Keppens, E. and O'Neil, J.R.** (1992b) The glauconitization process: constraints from the strontium, neodymium and oxygen isotope geochemistry of Recent glauconies. *CR Acad. Sci. Paris (Series II)*, **315**, 321–327.
- Clayton, R.N. and Mayeda, T.K.** (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta*, **27**, 43–52.
- Craig, L.E., Smith, A.G. and Armstrong, R.L.** (1989) Calibration of the geologic time scale: Cenozoic and Late Cretaceous glauconite and non-glauconite dates compared. *Geology*, **17**, 830–832.
- Dasch, E.J.** (1969) Strontium isotopes in weathering profiles, deep-sea sediments, and sedimentary rocks. *Geochim. Cosmochim. Acta*, **33**, 1521–1552.
- Dorman, F.H. and Gill, E.D.** (1959) Oxygen isotope palaeotemperature measurements on Australian fossils. *Proc. Roy. Soc. Victoria*, **71**, 73–98.
- Drever, J.I.** (1988) *The Geochemistry of Natural Waters*, 2nd edn. Prentice Hall, New Jersey, 437 pp.
- Fairbridge, R.W.** (1983) Syndiagenesis-anadiagenesis-epidiagenesis: phases in lithogenesis. In: *Diagenesis in Sediments and Sedimentary Rocks 2*. Developments in Sedimentology 25B (Eds G. Larsen and G.V. Chillingar), pp. 17–113. Elsevier, Amsterdam.
- Faure, G., (ed.)** (1986) *Principles of Isotope Geology*, 2nd edn. John Wiley and Sons, USA, 589 pp.
- Faure, G. and Powell, J.L.** (1972) *Strontium Isotope Geology*. Springer-Verlag, Berlin, 188 pp.
- Friedrichsen, H.** (1984) Oxygen and hydrogen isotope studies on glauconites. *Terra Cognita*, **4**, 218.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. and Maynard, V.** (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta*, **43**, 1075–1090.
- Galliher, E.W.** (1935) Geology of glauconite. *Bull. Am. Assoc. Petrol. Geol.*, **19**, 1569–1601.
- Garrels, R.M. and Christ, C.L.** (1965) *Solutions, Minerals, and Equilibria*. Harper & Row and John Weatherhill, Japan, 450 pp.
- Harder, H.** (1980) Synthesis of glauconite at surface temperatures. *Clay Mineral.*, **28**, 217–222.
- Harris, W.B.** (1982) Rubidium-strontium glaucony ages, southeastern Atlantic coastal plain, USA. In: *Numerical Dating in Stratigraphy* (Ed. G.S. Odin), pp. 593–606. John Wiley and Sons, UK.
- Hess, J., Stott, L.D., Bender, M.L., Kennet, J.P. and Schilling, J.-G.** (1989) The Oligocene marine microfossil record: age assessments using strontium isotopes *Paleoceanography*, **4**, 655–679.
- Hill, K.C., Hill, K.A., Cooper, G.T., O'Sullivan, A.J., O'Sullivan, P.B. and Richardson, M.J.** (1995) Inversion around the Bass Basin, SE Australia. In: *Basin Inversion* (Eds J.G. Buchanan and P.G. Buchanan), *Geol. Soc. Spec. Publ.*, **88**, 525–547.
- Hodell, D.A., Mueller, P.A. and Garrido, J.R.** (1991) Variations in the strontium isotopic composition of seawater during the Neogene. *Geology*, **19**, 24–27.
- Hoefs, J.** (1987) *Stable Isotope Geochemistry*, 3rd edn. Springer-Verlag, Berlin, 241 pp.
- Hower, J.** (1961) Some factors concerning the nature and origin of glauconite. *Am. Mineral.*, **46**, 313–334.
- Hurd, D.C.** (1973) Interactions of biogenic opal, sediment and seawater in the central equatorial Pacific. *Geochim. Cosmochim. Acta*, **37**, 2257–2282.
- Hurst, R.W.** (1986) Strontium isotopic chronostratigraphy and correlation of the Miocene Monterey Formation in the Ventura and Santa Maria Basins of California. *Geology*, **14**, 459–462.
- James, A.T. and Baker, D.R.** (1976) Oxygen isotope exchange between illite and water at 22 °C. *Geochim. Cosmochim. Acta*, **40**, 235–239.
- James, H.L.** (1966) Chemistry of the iron-rich sedimentary rocks. In: *Data of Geochemistry*, 6th edn, Chapter W. *US Geol. Surv. Prof. Pap.*, **440-W**, W1–W59.
- Kalsbeek, F. and Hansen, M.** (1989) Statistical analysis of Rb-Sr isotope data by the bootstrap method. *Chem. Geol.*, **73**, 289–297.
- Kelly, J.C. and Webb, J.A.** (1999) The genesis of glaucony in the Oligo-Miocene Torquay Group, Southeastern Australia: petrographic and geochemical evidence. *Sed. Geol.*, **125**, 99–114.
- Keppens, E. and O'Neil, J.R.** (1984) Oxygen isotope variations in glauconies. *Terra Cognita*, **4**, 224.
- Keppens, E. and Pasteels, P.** (1982) A comparison of rubidium-strontium and potassium-argon apparent ages on glauconies. In: *Numerical Dating in Stratigraphy* (Ed. G.S. Odin), pp. 225–243. John Wiley and Sons, UK.
- Kharaka, Y.K. and Thordsen, J.J.** (1992) Stable isotope geochemistry and origin of waters in sedimentary basins. In: *Lecture Notes in Earth Science 43: Isotopic Signatures and*

- Sedimentary Records* (Eds N. Clauer and S. Chaudhuri), pp. 412–466. Springer-Verlag, Berlin.
- Kralik, M.** (1984) Effects of cation-exchange treatment and acid-leaching on the Rb-Sr system of illite from Fithian, Illinois. *Geochim. Cosmochim. Acta*, **48**, 527–533.
- Lawrence, J.R., Giekes, J.M. and Broecker, W.S.** (1975) Oxygen isotope and cation composition of DSDP pore waters and the alteration of Layer II basalts. *Earth Planet. Sci. Lett.*, **27**, 1–10.
- Lawrence, J.R. and Taylor, H.P., Jr** (1971) Deuterium and oxygen-18 correlation: clay minerals and hydroxides in Quaternary soils compared to meteoric waters. *Geochim. Cosmochim. Acta*, **35**, 993–1003.
- Mackin, J.E. and Aller, R.C.** (1984a) Diagenesis of dissolved aluminium in organic-rich estuarine sediments. *Geochim. Cosmochim. Acta*, **48**, 299–313.
- Mackin, J.E. and Aller, R.C.** (1984b) Dissolved Al in sediments and waters of the East China Sea: implications for authigenic mineral formation. *Geochim. Cosmochim. Acta*, **48**, 281–297.
- McRae, S.G.** (1972) Glauconite. *Earth Sci. Rev.*, **8**, 397–440.
- Mehin, K. and Link, A.G.** (1994) Source, migration and entrapment of hydrocarbons and carbon dioxide in the Otway Basin, Victoria. *Aust. Petrol. Explor. Assoc. J.*, **34**, 439–459.
- Miller, K.G., Feigenson, M.D., Kent, D.V. and Olsson, R.K.** (1988) Upper Eocene to Oligocene isotope ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$) standard section, Deep Sea Drilling Project site 522. *Paleoceanography*, **3**, 223–233.
- Miller, K.G., Feigenson, M.D., Wright, J.D. and Clement, B.M.** (1991) Miocene isotope reference section, Deep Sea Drilling Project site 608: an evaluation of isotope and biostratigraphic resolution. *Paleoceanography*, **6**, 33–52.
- Mozley, P.S. and Burns, S.J.** (1993) Oxygen and carbon isotopic composition of marine carbonate concretions: an overview. *J. Sed. Petrol.*, **63**, 73–83.
- Mozley, P.S. and Carothers, W.W.** (1992) Elemental and isotopic composition of siderite in the Kuparuk Formation, Alaska: effect of microbial activity and water/sediment interaction on early pore-water chemistry. *J. Sed. Petrol.*, **62**, 681–692.
- Murav'yev, V.I., Daynyak, L.G. and Golovin, D.I.** (1985) Changes in the composition of glauconite in contact with seawater. *Int. Geol. Rev.*, **27**, 850–858.
- O'Neil, J.R.** (1979) Stable isotope geochemistry of rocks and minerals. In: *Lectures in Isotope Geology* (Eds E. Jager and J.C. Hunziker), pp. 235–263. Springer-Verlag, Berlin.
- O'Neil, J.R.** (1987) Preservation of H, C, and O isotopic ratios in the low temperature environment. In: *Short Course in Stable Isotope Geochemistry of Low Temperature Fluids* (Ed. T.K. Kyser), *Mineral. Assoc. Can.*, **13**, 110–128.
- O'Neil, J.R. and Kharaka, Y.K.** (1976) Hydrogen and oxygen isotope exchange reactions between clay minerals and water. *Geochim. Cosmochim. Acta*, **40**, 241–246.
- Odin, G.S.** (ed.) (1982) *Numerical Dating in Stratigraphy*. John Wiley and Sons, UK, 1040 pp.
- Odin, G.S. and Dodson, M.H.** (1982) Zero isotopic age of glauconites. In: *Numerical Dating in Stratigraphy* (Ed. G.S. Odin), pp. 277–305. John Wiley and Sons, UK.
- Odin, G.S. and Fullagar, P.D.** (1988) The geological significance of the glaucony facies. In: *Green Marine Clays* (Ed. G.S. Odin), pp. 295–332. Elsevier, Chichester.
- Odin, G.S. and Matter, A.** (1981) De glauconiarum origine. *Sedimentology*, **28**, 611–641.
- Odin, G.S., Curry, D. and Hunziker, J.C.** (1978) Radiometric dates from NW European glauconites and the Palaeogene time-scale. *J. Geol. Soc. London*, **135**, 481–497.
- Orians, K.J. and Bruland, K.W.** (1986) The biogeochemistry of aluminium in the Pacific Ocean. *Earth Planet. Sci. Lett.*, **78**, 397–410.
- Perry, E.A. and Hower, J.** (1970) Burial diagenesis in Gulf Coast pelitic sediments. *Clay Mineral.*, **18**, 165–177.
- Perry, E.A., Jr, Gieskes, J.M. and Lawrence, J.R.** (1976) Mg, Ca and $\text{O}^{18}/\text{O}^{16}$ exchange in the sediment-pore water system, hole 149, DSDP. *Geochim. Cosmochim. Acta*, **40**, 413–423.
- Pokrovskii, B.G. and Golovin, D.I.** (1989) Glauconite formation conditions during the Paleogene in the Eastern Mediterranean based on isotopic data. *Lithol. Mineral. Resour. (USSR)*, **24**, 375–386.
- Reeckmann, S.A.** (1981) Relationships between lithology and diagenesis in a limestone-marl facies transition: an electron microprobe study. *Sedimentology*, **28**, 643–652.
- Sass, E., Bein, A. and Almogi-Labin, A.** (1991) Oxygen-isotope composition of diagenetic calcite in organic-rich rocks: evidence for ^{18}O depletion in marine anaerobic pore water. *Geology*, **19**, 839–842.
- Savin, S.M. and Epstein, S.** (1970) The oxygen and hydrogen isotope geochemistry of clay minerals. *Geochim. Cosmochim. Acta*, **34**, 25–42.
- Savin, S.M. and Lee, M.** (1988) Isotopic studies of phyllosilicates. In: *Hydrous Phyllosilicates (Exclusive of Micas)*. Reviews in Mineralogy, Vol. 19 (Ed. S.W. Bailey), pp. 189–233. Mineralogical Society of America, Michigan.
- Siesser, W.G.** (1979) Oligocene-Miocene calcareous nannofossils from the Torquay Basin, Victoria, Australia. *Alcheringa*, **3**, 159–170.
- Stille, P.S. and Clauer, N.** (1994) The process of glauconitization: chemical and isotopic evidence. *Contrib. Mineral. Petrol.*, **117**, 253–262.
- Thompson, G.R. and Hower, J.** (1975) The mineralogy of glauconite. *Clay Mineral.*, **23**, 289–300.
- Triplehorn, D.M.** (1966) Morphology, internal structure and origin of glauconite pellets. *Sedimentology*, **6**, 247–266.
- Van Der Linden, T.E.** (1997) *Depositional facies, cyclicity, and sequence stratigraphy of the Oligo-Miocene Torquay Group, Torquay Embayment, Southeastern Australia*. Unpublished MSc Thesis, Sydney University, New South Wales, Australia, 385 pp.
- Van Der Loeff, M.M.R.** (1990) Oxygen in pore waters of deep-sea sediments. *Phil. Trans. Roy. Soc. London*, **A331**, 69–84.
- Webb, J.A., Nicolaides, S. and Kelly, J.** (1995) *Cool Water Carbonates of the Northeastern Otway Basin, Southeastern Australia*. Australasian Sedimentologists Group Field Guide Series no. 6. Geological Society of Australia, 60 pp, Melbourne.
- Yeh, H.W. and Savin, S.M.** (1976) The extent of oxygen isotope exchange between clay minerals and sea water. *Geochim. Cosmochim. Acta*, **40**, 743–748.
- Yeh, H.W. and Savin, S.M.** (1977) Mechanism of burial metamorphism of argillaceous sediments: 3. O-isotope evidence. *Geol. Soc. Am. Bull.*, **88**, 1321–1330.
- Young, G.C. and Laurie, J.R.** (eds) (1996) *An Australian Phanerozoic Timescale*. Australian Geological Survey Organisation. Oxford University Press, Melbourne, 279 pp.

*Manuscript received 19 August 1997;
revision accepted 24 July 2000.*