

Exhumed hydrocarbon-seep authigenic carbonates from Zakynthos Island (Greece): concretions not archaeological remains

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Running Header: **Hydrocarbon-seep authigenic carbonates, Zakynthos**

Highlights

- Exposure of columnar and slab-like structures in the modern shallow subtidal of Greece promoted research into possible classical archaeological remains.
- This research shows the structures are actually exhumed fossil hydrocarbon seep concretions.
- Ferroan dolomite mineralogy and stable carbon isotopes are diagnostic of methane oxidation and authigenesis in the sulphate-methane transition zone.
- A rare example of hydrocarbon-seep authigenic carbonates in a shallow shelf setting.

Abstract

In Zakynthos Island (Greece), authigenic cementation of marine sediment has formed pipe-like, disc and doughnut-shaped concretions. The concretions are mostly composed of authigenic ferroan dolomite accompanied by pyrite. Samples with >80% dolomite, have stable isotope compositions in two groups. The more indurated concretions have $\delta^{18}\text{O}$ around +4‰ and $\delta^{13}\text{C}$ values between -8 and -29‰ indicating dolomite forming from anaerobic oxidation of thermogenic methane (hydrocarbon seep), in the sulphate-methane transition zone. The outer surfaces of some concretions, and the less-cemented concretions, typically have slightly heavier isotopic compositions and may indicate that concretion growth progressed from the outer margin in the ambient microbially-modified marine pore fluids, inward toward the central conduit where the isotopic compositions were more heavily influenced by the seep fluid. Sr isotope data suggest the concretions are fossil features, possibly of Pliocene age and represent an exhumed hydrocarbon seep plumbing system. Exposure on the modern seabed in the shallow subtidal zone has caused confusion, as concretion morphology resembles archaeological stonework of the Hellenic period.

Keywords: Dolomite, Concretions, Stable isotopes, Hydrocarbon-seep, Marine archaeology, Zakynthos

1. Introduction

This study discusses concretion-like structures found in shallow subtidal waters of the Ionian island of Zakynthos (Fig. 1). These structures were discovered by snorkelers and divers and sparked interest as they bear superficial resemblance to archaeological stonework, as the labelling on Google Earth v7.1 (2014) amateur photographs attests (see also Fig. 2). While archaeological sites are ubiquitous in Greece, they are not well documented in the shallow offshore. Such discoveries are therefore carefully examined *in situ* by the Ephorate of Underwater Antiquities of Greece, in this case assisted by one of the authors (M.G. Stamatakis). However, these investigations did not reveal any further supporting evidence for antiquities at this site. A geological origin is therefore explored here as the structures look like concretions formed by localised authigenic cementation of sediment (cf. Angeletti et al., 2015; Nyman et al., 2010; Wirsig et al., 2012). Our interpretations and conclusions while of obvious interest to geologists also have significance for archaeologists and even tourists who enjoy snorkelling. We summarise our findings with the maxim ‘all that glistens is not gold’ or in this case ‘columns and pavements in the sea, not always antiquities will be’.

2. Study site, concretion morphology and geological setting

The study site is in the modern subtidal (2-5 m water depth) zone of Alikanas Bay on the E coast of Zakynthos (37° 50' 50.80" N; 20°46' 46.54" E; Fig. 1). The concretions are found on, and in, the modern seabed sediments (Fig. 2) in a zone 20-30 m wide and about 180 m long, on two sub-parallel WSE –ENE arrays. Within this zone concretion density is patchy, with local areas 15-20 m² containing up to 5 large structures (dimensions given below), interspersed with apparently barren areas. The larger concretions are detached from the sediment and appear to have slumped from a low ridge structure (P. Tsampourakis, diver & member of the Ephorate of Underwater Antiquities, pers. comm. 2014).

The concretions are mostly: (1) pipe-like structures up to 70 cm long, with external diameters 5-30 cm, and central hole diameters of 1-2 cm (Fig. 3); or (2), disk or doughnut-shaped (Figs 2 and 4) up to 60 cm thick with external diameters 30-100 cm, and with an central hole, 1 to 30 cm diameter. The central holes in the pipes and doughnuts are usually open, although one pipe had a cavity filling of off-white sparry carbonate cement of coarser crystallinity than the chimney wall (Fig 5a). A few rectilinear ‘slab-like’ concretions were also observed (Fig. 2b). Pipe-like concretions are mostly heavily lithified with outer surfaces bored and encrusted by

modern marine organisms (Fig. 5b), whereas some doughnuts/disks are less-heavily cemented and clearly display laminae inherited from the host sediment.

The local bedrock is Plio-Pleistocene marl, claystone and sandstone (Papanikolaou et al., 2010) resting unconformably on the Paxos Unit, the tectonic foreland of the Hellenic Orogen, here comprising Mesozoic to Paleogene aged limestones, dolostones, cherts, porcelanites and evaporites (Dermitzakis 1978, Perry and Temple 1980, Brooks and Ferentinos 1984, Nikolaou 1986, Stamatakis et al., 1988, Triantaphyllou et al., 1997, Papanikolaou et al., 2010, Kokkalas et al., 2012). The Zakynthos Canyon, E of the island (Fig. 1), occupies a broad structural depression trending parallel to the local tectonic zones of the External Hellenides. The canyon contains the local NW-SE trending Zakynthos Basin, its geometry controlled by reverse faults or thrusts with associated diapirism in Triassic evaporites (Brooks and Ferentinos 1984). The area is seismically active, a 7.2 magnitude (Richter scale) event in 1953 destroying most buildings on the island.

3. Methods

Petrography was done using polished thin sections under normal light and cathodoluminescence (CL) and by scanning electron microscopy (SEM). Mineralogy was determined by powder X-ray diffraction with a Bruker 5005 X-ray diffractometer, using Rietveld Quantitative Analysis to calculate mineral percentages. Mineralogical determinations were augmented with SEM energy dispersive microanalysis using a JEOL JSM-5600 LINK ISIS. For stable isotopes an aliquot between 10 and 30 mg (depending on sample composition) of fine powder was reacted at 25°C with 1.5 ml of 102% orthophosphoric acid. The evolved CO₂ after 1 hour's reaction was taken to represent calcite, while continued reaction for a further week represented CO₂ from slower reacting ferroan dolomite (see Walters et al., 1972). Isotopic measurements were made on MIRA (Multi Isotope Ratio Analyser), the laboratory standard (UEACMST) giving a precision of 0.05‰ for both δ¹⁸O and δ¹³C. The carbonate-carbon dioxide acid fractionation factors for calculating δ¹⁸O_{calcite} and δ¹⁸O_{dolomite} were 1.01025 and 1.01182 respectively (Rosenbaum and Sheppard 1986). Results are in delta notation on the VPDB scale unless stated otherwise.

The phosphoric acid separation technique is imperfect (Walters et al., 1972) as reaction rates vary with grain size, proportions of phases and degree of mineral stoichiometry such that some cross-contamination of evolved gases is unavoidable. We thus only attempted calcite

separations on four samples where the percentage calcite was >10% (Table 1). Precision for co-existing mineral pairs is probably no better than $\pm 1\%$.

Sr isotope analysis of four representative samples began with a 10% acetic acid leach to dissolve mainly calcite, followed by a 6M HCl leach to characterise dolomite. Sr was separated using Sr-SPEC resin and loaded on single Re filaments using a TaO activator. Samples were analysed using a Thermo-Electron Triton mass spectrometer in multidynamic mode. Six analyses of the NBS987 standard gave a value of 0.710252 ± 0.000006 (8.1ppm, 1-sigma) at the time of analysis.

4. Results

4.1 Mineralogy and microstructure

The seafloor sediment is a mixed siliciclastic-carbonate (~5-20% calcite; table 1) silty-mud with fine-sand laminae (mm scale) with abundant foraminifera. Clay-minerals are mostly illite and chlorite (Table 1) while silt and sand grains are quartz, albite, mica and calcite mineralogies (Table 1). Concretion mineralogy differs from the host sediment mainly by the presence of between 43-89% of calcium-magnesium-iron carbonates (Mg-calcite, and ferroan dolomite, Table 1) depending on the degree of cementation. There is no systematic difference between the carbonate mineralogy of the more- and less-cemented concretions. The ferroan dolomite identification was confirmed by the presence of XRD ordering reflections (Fig. 6) as discussed in Gregg et al. (2015).

In thin sections the main body of the concretions comprise orange luminescing micrite to microspar (Fig. 7a) with coeval pyrite aggregates. In the less-cemented concretions the main body preserves host sediment laminae, typically either denser micrite with peloids and intraclasts or variously silty to fine-sand rich (50-200 μm grains) with abundant benthic foraminifers (Fig. 7b) and micritic patches with pyrite. SEM shows that coccolith plates and foraminifer tests and are well-preserved (Fig. 8) and open space in foraminifer chambers is partially cemented by (1) brightly orange luminescing micritic-microspar (Fig. 9) and then (2) dull-brown luminescing euhedral microspar (Fig 9) succeeded by pyrite framboids (Fig. 10a). In a few instances foraminifer chambers are completely filled by pyrite. The carbonate cement sequence in foraminifer chambers is also present in small fractures of the concretion body (Fig. 10b) and the brightly orange luminescing micritic-microspar is also present as

coronas (10-20 μm wide; Fig. 10b) around many siliciclastic grains and pyrite aggregates. No pyrite has been observed in the fractures.

4.2 Isotopes

The calcite has $\delta^{18}\text{O}$ values between +0.3 and +3.8‰ (Table 1), although the total amount of calcite in most cemented samples is <12% which means the gases derived for isotopes are almost certainly contaminated with gas from fast reacting fine-grained ferroan dolomite. In the sample with the most calcite (ZC40_C) $\delta^{18}\text{O}_{\text{calcite}}$ is 0.3‰ (Table 1) which may be the best indicator of the actual calcite values. Similarly the calcite in ZC40_C has the least negative $\delta^{13}\text{C}$ value of -1.7‰, whereas samples with <12% calcite have $\delta^{13}\text{C}$ values between -5 and -17‰ (Table 1). Samples with dolomite mostly contain >80% dolomite, such that their isotopic values should be indicative of actual compositions. Dolomite isotope values fall into two clear isotopic groups: group 1 (Figs 11 and 12), mainly the less indurated doughnut concretions, with $\delta^{18}\text{O}$ between +2 and +3‰ and with $\delta^{13}\text{C}$ values >0‰; and group 2 (Table 1; Figs 11 and 12), with $\delta^{18}\text{O}$ mostly around +4‰ (ZO is an exception) and $\delta^{13}\text{C}$ values between -8 and -29‰. The four samples selected for $^{87}\text{Sr}/^{86}\text{Sr}$ analysis, two from less cemented concretions and two from more indurated material have 10% acetic acid leach values between 0.708867-0.708966 and 6M HCl leach values between 0.709038-0.709091 (Table 1). ZSR has an anomalously radiogenic 6M HCl leach value: this sample contained 57% non-carbonate minerals such that the 6M HCl probably leached radiogenic Sr from clay minerals and because of this it is discarded from further interpretation.

5. Interpretation of sedimentary, morphological and isotopic data

The shallow shelf location determines that if these concretions are marine, they must have formed during sea-level highstand when the shelf sediments were submerged. Moreover, the linear distribution of the concretions, and their association with a low sea-bed ridge suggests the possible presence of a blind fault below the recent sea bed muds, which might be related to fluid flow. The pipe-like, disk and doughnut morphology and the size of the concretions is typical of authigenic carbonates associated with hydrocarbon-seeps seen both in modern seafloor and palaeo-settings (e.g., Angeletti et al., 2015; Kocherla et al. 2015; Reitner et al., 2015). Pipe-like concretions, are considered by Reitner et al. (2015) to be formed by micro

seepage of hydrocarbon-rich fluids and slab-like morphologies have been related to more diffuse flows (Naehr et al., 2007; Suess 2014).

The petrography suggests that authigenic carbonates mainly cemented open-space in the host sediment as micritic to microsparitic cements to form the body of the concretions. The mainly orange CL colours suggest that ferroan dolomite cementation occurred while pore water Fe^{2+} concentrations were below 3.0 wt% FeCO_3 (Fairchild 1983) with Mn^{2+} concentrations probably >0.03 wt% MnCO_3 (Fairchild 1983). As pore water $\text{Mn}^{2+}/\text{Fe}^{2+}$ ratio is thought to control dolomite CL colour intensity (higher ratio causing brighter CL; Miller 1988) it is likely that the bright orange luminescing cements formed when the pore water $\text{Mn}^{2+}/\text{Fe}^{2+}$ ratio was at its highest, perhaps when rapid pyrite precipitation reduced dissolved Fe^{2+} concentrations, followed by duller CL colour in the later euhedral microspars as Mn^{2+} concentrations became limiting.

The presence of pyrite indicates active sulphate reduction in the sediment throughout the cementation history. The ferroan dolomite mineralogy points to ‘in-sediment’ cementation where sulphate-reduction has lowered dissolved sulphate concentrations favouring dolomite precipitation (Baker and Kastner 1981), rather than the commonly observed aragonite or calcite seafloor cementation described in many hydrocarbon seep settings (e.g. Aloisi et al., 2000; Gontharet et al., 2007).

Authigenic carbonate concretions with $\delta^{13}\text{C}$ below -20‰ suggest strongly the influence of bacterial methane oxidation (see e.g. Hovland et al., 1987). Anaerobic oxidation of methane (AOM) is thought to be mediated by a consortium of methanotrophic archaea and sulphate reducing bacteria (e.g. Boetius 2000; Joye, 2012; Miluka et al. 2012) at the base of the sulphate reduction zone (sulphate-methane transition zone). The simplified reaction,



increases pore water alkalinity (Reeburgh 1983; Raiswell 1987, 1988) and reduces dissolved sulphate concentrations, both features that facilitate formation of authigenic dolomite (Baker and Kastner 1981; Magalhães et al., 2012; Wirsig et al., 2012). The availability of iron for incorporation into the dolomite is also consistent with concretion formation in the sulphate-methane transition zone (Rodriguez et al. 1999), as iron in the overlying sulphate reduction zone is preferentially precipitated as iron sulphide. The Zakynthos $\delta^{13}\text{C}$ values between -8

and -29‰, are consistent with authigenic carbonates forming in hydrocarbon seep environments, overlapping for example (Fig. 12), with dolomite data from Monterey Bay, the Santa Barbara and Eel River Basins (Naehr et al., 2007) the Gulf of Cadiz (Magalhães et al., 2012) and the south eastern Adriatic (Angeletti et al., 2015). The most negative $\delta^{13}\text{C}$ values, are not below -30‰ which suggests oxidation of thermogenic methane rather than biogenic methane (Naehr et al. 2007), consistent with the findings of Etiope et al. (2013) from nearby Katakolon Bay (Fig. 1). Dolomite $\delta^{13}\text{C}$ values between -8 and -20‰ probably indicate a component of bicarbonate from methane oxidation mixed with pore water dissolved inorganic carbon (DIC) modified by sulphate reduction, or methanogenesis-impacted pore water bicarbonate (see below).

The 6M HCl leaches (representing dolomite) have Sr isotope values, which if interpreted as marine precipitates, suggest a Pliocene Age of ~3-4 Ma (McArthur et al., 2001) for concretion growth, which is consistent with the local bedrock sediment age. This age is not tightly constrained as the 10% acetic acid leach ‘calcite’ treatment will have altered the bulk value somewhat, as will potential leaching of radiogenic Sr from siliciclastic detritus in the samples. However, it is also possible that the Sr isotope values represent a mixture of seawater and a basinal fluid that had equilibrated with Mesozoic basement carbonates or Neogene carbonate sediments with $^{87}\text{Sr}/^{86}\text{Sr}$ values between ~0.7072 and 0.7088 (McArthur et al., 2001). In a mixing scenario the data would allow the seawater to be of any age from Pliocene to Modern, dependent on the degree of mixing with basinal fluid. The range of $^{87}\text{Sr}/^{86}\text{Sr}$ values for these dolomite-bearing sediments (Table 1) is similar to other hydrocarbon seep fluids and authigenic dolomites for which the interpretation is either ambiguous (e.g. Naehr et al, 2007) or indicative of basinal fluids equilibrated with deeper seated sediments (Martin et al., 1996).

If the authigenic carbonates formed ‘in-sediment’ in the marine sulphate-methane transition zone then the stable isotope compositions should be indicative of the early diagenetic conditions. Regardless of the precise age for authigenic carbonate growth, i.e., Late Pliocene sea-level highstand or younger, modern seawater isotopic compositions serve as a robust starting point for interpretation, as interglacial (highstand) seawater stable isotopic composition has not changed more than ~ 0.3‰ over the last 4 Ma (Rohling 2007). Modern Ionian Sea surface water has $\delta^{18}\text{O}$ values around +1.3‰VSMOW (based on data in Stenni et al., 1995; López Correa et al., 2010). We cannot be sure of the temperatures at which the concretions formed, but the sulphate-methane transition zone is typically at least -5 m below

the sea bed. At this depth temperatures should be slightly above (~ 0.2 °C) sea bottom water temperatures (inferred from data in Erickson and Von Herzen 1978; Feseker et al., 2009). The mean annual modern seawater temperature at the site is ~ 20 °C (www.seatemperature.org/europe/greece, using NOAA data). Calcite in equilibrium with seawater-derived pore water of this composition at ~ 20 °C would have $\delta^{18}\text{O} \sim +0.4\text{‰}$ and dolomite $\sim +3.5$ to $+4.5\text{‰}$ (using a $\Delta\delta^{18}\text{O}_{\text{dol-cal}}$ of $\sim +3$ to $+4\text{‰}$ from Horita (2014), based on a review of experimental and theoretical data). The calcite in ZC40c (outer edge of concretion) has a $\delta^{18}\text{O}$ of $+0.3\text{‰}$, (Fig. 11), and the Group 1 less cemented dolomitic concretions have $\delta^{18}\text{O}$ between $+2$ and $+3\text{‰}$. These are near-equilibrium (~ 20 °C) values based on modern seawater, indicating that the pore-waters were marine-derived.

The crust calcite (ZC_{40c}) with a $\delta^{13}\text{C}$ of -1.7‰ (Fig. 11) is the only calcite sample where contamination from isotopically-negative fast reacting dolomite is not possible, because the co-existing dolomite in the sample has a more positive $\delta^{13}\text{C}$ composition. It should therefore be representative of the heaviest likely $\delta^{13}\text{C}$ composition for calcite. While the other three calcite values are potentially compromised by isotopically negative carbon from fast reacting dolomite during sample preparation (see Results), taken together with ZC_{40c} they constrain calcite $\delta^{13}\text{C}$ between approximately -2 and -8‰ . This is much more negative than an equilibrium seawater value (Fig. 11) but consistent with modified marine pore-water DIC in the sulphate reduction zone (Raiswell and Fisher 2000), or with a small component of isotopically negative carbon from methane oxidation.

Sample ZI (Group 1 dolomites) has a $\delta^{13}\text{C}$ of $+4.9\text{‰}$ which is probably indicative of methanic environments where isotopically enriched pore water DIC results from partially closed system methanogenesis. For example, Naehr et al. (2007) interpret $\delta^{13}\text{C}$ values $> +5\text{‰}$ from the Eel River Basin dolomites as methanic-related. The other Group 1 dolomites have $\delta^{13}\text{C}$ between $+1.9$ and $+2.5\text{‰}$ which may similarly indicate influence of methanic-conditions, albeit mixed with isotopically more negative DIC, e.g. from sulphate reduction. While the Group 1 dolomite values plot close to marine equilibrium values (Fig. 11), this is probably coincidental, given their likely early diagenetic formation in the sulphate-methane transition zone.

Three of five Group 2 ferroan dolomite samples with $\delta^{13}\text{C}$ below -8‰ have $\delta^{18}\text{O}$ up to 1‰ enriched relative to the Group 1 dolomites. One source of ^{18}O -rich fluids in hydrocarbon-seep settings is oxygen from gas hydrate dissociation at depth in formation waters (Martin et

al., 1996), although this not likely in water depths less than 400 m where such hydrates are unstable (Foucher et al., 2009). Another possible source is from upward-migrating formation waters where fluid-rock interactions at burial temperatures above 50 °C can produce fluids with $\delta^{18}\text{O} > +8\text{‰}$ (e.g. Land and Prezbindowski 1981; Moore 1989 p.265). Alternatively these slightly enriched $\delta^{18}\text{O}$ values may simply be evidence of cooler fluid temperatures as favoured by Angeletti et al. (2015) for their eastern Adriatic site.

The outer surfaces of some concretions (and the less-cemented concretions) typically have the heavier isotopic compositions. This may suggest that cementation in these outer horizons was the least influenced by methane oxidation of the ‘seep fluid’ isotopic composition. This may point to early concretion growth starting at the outer edge in the ambient modified marine pore fluids of the sulphate-methane transition zone, and constraining lateral spreading of the seep fluid (Nyman et al., 2010). The cementation then proceeded inward toward the central conduit where the isotopic compositions were more heavily influenced by the ‘seep fluid’ (see e.g., Clari et al., 2004; Nyman et al., 2010). Most concretion central conduits remain open, but the example with a coarser-grained sparry carbonate fill attests to some mineralization as a final stage in cementation.

6. Wider interpretation and discussion

Modern deep-sea sediments on the eastern margin of the Zakynthos Canyon and in the nearby Gulf of Patras show active fluid venting and thermogenic and biogenic gases associated with pockmarks (Fig. 1; Hasiotis et al., 1996, 2005). Seepage of natural gas was also documented by Etiope et al. (2013) from an oilfield offshore of the Katakolon peninsula, 50 km SE of the study site (Fig. 1). There is however, no clear evidence of active fluid venting at the site today. There are no reports from snorklers of shimmering water or thermal anomalies often encountered with submarine springs and no distinctive fauna as commonly observed at active hydrocarbon seeps (e.g., Olu-Le Roy et al., 2004). Overall the evidence suggests the concretions are fossil features, possibly of Pliocene age based on the simplest interpretation of the Sr isotope data. The ferroan dolomite mineralogy points to in-sediment concretion growth in the sulphate-methane transition zone, probably around -5 m below sea floor. The combined mineralogy and isotopic compositions of the concretions are therefore inconsistent with their current seafloor exposure (as outlined by Naehr et al. 2007), demonstrating that

they have been exhumed by seabed erosion. Upon exposure in the modern shallow subtidal the hard substrates were then bored and encrusted by modern marine organisms. We thus interpret these concretions as part of an extinct and partially exhumed hydrocarbon seep 'plumbing system' (cf. Angeletti et al., 2015; Magalhães et al., 2012; Wirsig et al., 2012; Nyman et al., 2010), the linear seabed distribution suggesting a genetic relationship to faulting. Hydrocarbon seepage elsewhere in the region has been linked to earthquake triggering (Hasiotis et al., 1996, 2002; Etiope et al., 2013).

The nearshore shallow shelf sea setting of these exhumed concretions contrasts with many published descriptions of hydrocarbon seep authigenic carbonates, both locally in the eastern Mediterranean and Adriatic (e.g. Aloisi et al., 2000; Angeletti et al., 2015; Gontharet et al., 2007; Zitter et al., 2008) and further afield. Most of these sites are in deep sea settings in many hundreds and often thousands of metres water depth. In deep sea settings the hydrocarbon-bearing fluid is always basinal or marine; however, in nearshore settings fluid pathways could also be affected by circulating groundwater sourced from an onshore hydrogeological head, such as coastal mountains, particularly where faulting is active.

In our study area there is evidence for active hydrogeological activity associated with hydrocarbons. An onshore borehole at Alikanas (Fig. 1) encountered asphalt and meteoric-sourced groundwater at -800 m, driven by a hydrological head in the Vrachiona Mountains to the west (K. Nikolaou pers. comm. 2014) and water supply drilling has also encountered liquid and gaseous hydrocarbons in the faulted zone between the Mesozoic limestones and Neogene sediments. Four km N of the study site at Xygia Bay, H₂S-rich meteoric water-sourced springs emanate in shallow seawater, forming a turbid yellow-brown sea-surface plume with sulphur efflorescence of several km² extent. Tar seeps, known since antiquity, also occur at Limni Keri (Tar Lake) beach (Fig. 1) 18 km S of Alikanas Bay.

As meteoric water is clearly a component of some onshore hydrocarbon-bearing fluids that could be routed through faults in the shallow offshore, we here consider its possible involvement in the fluids that formed the concretions, again using stable isotope compositions as a tracer. Modern Zakynthos meteoric water recharge has $\delta^{18}\text{O}$ of -5.2‰ (mean annual) to -5.7‰ VSMOW (mean winter; calculated from OIPC v.2.2 (Bowen and Wilkinson 2002; Bowen and Revenaugh 2003; see also Dotsika et al., 2010). Meteoric-sourced shallow groundwater in this part of Greece has a temperature $\sim 15^\circ\text{C}$ (based on data in Brasier et al., 2010). Carbonate minerals in equilibrium with such a groundwater would

have $\delta^{18}\text{O}_{\text{calcite}}$ of -5.5‰, and $\delta^{18}\text{O}_{\text{dolomite}}$ of -2.5 to -1.5‰ (using a $\Delta\delta^{18}\text{O}_{\text{dol-cal}}$ of $\sim+3$ to $+4$ ‰ from Horita, 2014). These values are ~ 5 -6‰ lower than those measured in the concretions. This probably means that local meteoric-water circulation is shallow and not involved in the fluids that formed these concretions. However, pending further research, we remain open to the possibility that meteoric-water influence in the plumbing system could have been mixed with isotopically enriched basinal fluids to generate low positive $\delta^{18}\text{O}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ values that resulted from equilibration of fluids with basement limestones (see above).

7. Conclusions

Although some of the earliest hydrocarbon seep authigenic carbonate discoveries were reported from relatively shallow shelf sea sediments (see overview in Hovland et al., 1987) their continued documentation in modern shallow water settings is not that common (but see Taviani et al., 2015; Viola et al., 2015), most discoveries being reported from many hundreds and often thousands of metres water. In this study we describe authigenic carbonates from the shallow subtidal of the Ionian Sea and show:

1. The concretions are fossil features possibly of Pliocene age based on Sr isotope data.
2. The dolomitic mineralogy and stable isotope geochemistry show these carbonates formed in anoxic marine sediments of the sulphate-methane transition zone, probably around -5 m below the sea floor. Anaerobic methane-oxidation is clearly identified by characteristically negative $\delta^{13}\text{C}$ values.
3. Given their ‘in-sediment’ formation the concretions have been exhumed by erosion to be exposed on the seabed today.
4. There is no clear evidence that either basinal fluids or meteoric water was involved in concretion formation.
5. Exhumed sediment-hosted concretions exposed in shallow marine settings can be readily confused with archaeological artefacts in countries like Greece which are rich in submerged antiquities, but the extent of which are still poorly known.
- 6.

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Figure captions

Fig. 1. Map locating the study site and other features mentioned in the text. The pecked line shows the axis of the fault bounded Zakynthos submarine canyon system where water depths are >400 m; the open circle marks the deep water pockmark field of Hasiotis et al. (2005). Arrow on inset map shows the position of the study site in Greece.

Fig. 2. Submarine site photographs: a) doughnut concretion with superficial resemblance to column shaft elements often found in classical ruins in Greece; black and white scale bar is 30 cm total length; red arrow marks sampled area; b) slabs of cemented sediment resembling paving seen in classical Greek ruins; black and white scale bar is 30 cm total length.

Fig. 3. Submarine field photographs of: a) hard pipe-like conical concretion, 30 cm high 30 cm diameter at base; b) pipe-like concretion, black and white scale bar is 30 cm total length.

Fig. 4. Submarine field photographs (a-c) of a 'less cemented' doughnut concretion; black and white scale bar is 30 cm total length. a) Shows clear differential cementation in the outer wall, (b and c) show an 'unbored' inner ring, 5 cm in diameter, amongst fragments of concretion which are bored. This image was taken 24 hours after a diver cleaned out the central hole (P. Tsampourakis pers. comm. 2014), perhaps uncovering the inner ring from overlying sediment for the first time. d) Laboratory photograph of a 'less cemented' disc concretion without borings; ruler is 8 cm long.

Fig. 5. Laboratory photographs showing (a) part of a 15 cm long well-cemented pipe, 5 cm external diameter with 1 cm diameter internal off-white sparry cement filling of near identical mineralogy as the chimney wall (Table 1). b) Upper surface of concretion in Fig. 2a showing

extensive boring and encrustation by marine organisms, showing it has been exposed on the seafloor for some considerable time. Field of view is 3.5 cm wide.

Fig. 6 X-ray diffraction pattern of sample ZCI showing dolomite (d) reflections including ordering peaks (arrowed; d 101, d 015 and d 021). The basal reflections for calcite (c) and quartz (q) are also marked.

Fig. 7. Cementation in a weakly cemented doughnut concretion (ZPU). a) Cathodoluminescence (CL) photomicrograph showing bright orange luminescing concretion body composed mainly of ferroan dolomite (Table 1). Dark grains are of siliciclastic composition, mostly quartz. b) Plane polarized light photomicrograph showing micritic lamina with foraminifera toward base of image and silty lamina with micritic intraclast in middle to top of image.

Fig. 8. Backscattered electron SEM images from pipe-like concretions. (a) Muddy coccolith-rich detrital sediment from a chimney wall, showing intergrowth of euhedral authigenic dolomite crystals. b) Foraminifer test showing well-preserved chamber wall. Former open space in the chamber is filled with authigenic dolomite and pyrite (details in Figs 9a and 10a).

Fig. 9. a) Backscattered electron SEM image showing mainly euhedral authigenic dolomite crystals filling space in a foraminifer chamber (detail from pecked box on Fig 8b). b) CL photomicrograph showing cement stratigraphy filling a foraminifer chamber in sample ZI. The test wall (T) has orange CL colour which is overgrown by a bright orange luminescing dolomite cement fringe (CF), followed by dull orange luminescing, coarser dolomite crystals (DC). These dull orange crystals comprise most of the image shown in (a) while the bright orange luminescing cement fringe corresponds with the micritic crystals at bottom and top left in (a).

Fig. 10. a) Backscattered electron SEM image showing pyrite framboids forming in a foraminifer chamber (detail from pecked box on Fig 8b). These framboids postdate the euhedral dolomite cements also shown in Fig. 9. B) CL photomicrograph showing cement stratigraphy filling a fracture (F) in sample ZI. The cement CL stratigraphy is identical to that in the nearby foraminifer chamber (FC) and to that described in Fig. 9. Note also the bright orange luminescing coronas around quartz grains labelled Q.

Fig. 11. Carbon and oxygen isotopic data for the Zakynthos samples (Table 1): tie bars connect mineral isotopic compositions from a single sample. Samples ZPL, ZPM and ZPU are from the lower middle and upper part of a single ‘less cemented’ concretion. The dolomite data are separated into two groups, particularly for $\delta^{13}\text{C}$; group 1 mainly from the ‘less cemented’ concretions with $\delta^{13}\text{C}$ values $>0\text{‰}$, and group 2 with $\delta^{13}\text{C}$ values below -8‰ . Group 2 dolomite $\delta^{18}\text{O}$ is also around $+1\text{‰}$ higher than that in group 1. $\delta^{13}\text{C}$ values below -8‰ are inferred to contain some isotopically light carbon from oxidation of thermogenic methane (see also Fig. 12). The star symbols represent theoretical equilibrium calcite and dolomite compositions from modern seawater at 20°C (see text for discussion of $\delta^{18}\text{O}$). Modern seawater DIC $\delta^{13}\text{C}$ is probably $\sim +1.3\text{‰}$ (based on Pierre et al. 1986; 1999) yielding a carbonate $\delta^{13}\text{C} \sim +2.8\text{‰}$.

Fig. 12. Carbon and oxygen isotopic summary for dolomite-bearing seafloor carbonates associated with methane oxidation and methane, based on data in Stakes et al. (1999), Naehr et al. (2007) and Magalhães et al. (2012). Where A = aragonite, HMC = high magnesium calcite and D = dolomite. The dark fields labelled 1 and 2 show the Zakynthos ferroan dolomite fields. Note that the group 2 data overlap negative $\delta^{13}\text{C}$ fields for all sites except the Monterey Bay field with $\delta^{13}\text{C}$ values below -30‰ which are probably sourced by isotopically negative biogenic methane (Naehr et al. 2007). $\delta^{13}\text{C}$ values above -40‰ probably indicate oxidation of thermogenic methane, which, for the Zakynthos samples is consistent with the findings of Etiope et al. (2013) from nearby Katakolo Bay (W. Greece). Methanic dolomite fields have positive $\delta^{13}\text{C}$ values that just coincide $\sim +5\text{‰}$ with the most positive Zakynthos datum (Table 1).

Table 1. Mineralogy and isotope data for the concretions and surrounding seabed sediments. Mineral percentages are semi-quantitative estimates.