Tubular carbonate concretions as hydrocarbon migration pathways? Examples from North Island, New Zealand

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Abstract
Cold seep carbonate deposits are associated with the development on the sea floor of distinctive chemosynthetic animal communities and carbonate mineralisation as a consequence of microbially mediated anaerobic oxidation of methane. Several possible sources of the methane exist, identifiable from the carbon isotope values of the carbonate precipitates. In the modern, seep carbonates can occur on the sea floor above petroleum reservoirs where an important origin can be from ascending thermogenic hydrocarbons. The character of geological structures marking the ascent pathways from deep in the subsurface to shallow subsurface levels are poorly understood, but one such structure resulting from focused fluid flow may be tubular carbonate concretions.

Several mudrock-dominated Cenozoic (especially Miocene) sedimentary formations in the North Island of New Zealand include carbonate concretions having a wide range of tubular morphologies. The concretions are typically oriented at high angles to bedding, and often have a central conduit that is either empty or filled with late stage cements. Stable isotope analyses (δ13C, δ18O) suggest that the carbonate cements in the concretions precipitated mainly from ascending methane, likely sourced from a mixture of deep thermogenic and shallow biogenic sources. A clear link between the tubular concretions and overlying paleo-sea floor seep-carbonate deposits exists at some sites.

We suggest that the tubular carbonate concretions mark the subsurface plumbing network of cold seep systems. When exposed and accessible in outcrop, they afford an opportunity to investigate the geochemical evolution of cold seeps, and possibly also the nature of linkages between subsurface and surface portions of such a system. Seep field development has implications for the characterisation of fluid flow in sedimentary basins, for the global carbon cycle, for exerting a biogeochemical influence on the development of marine communities, and for the evaluation of future hydrocarbon resources, recovery, and drilling and production hazards. These matters remain to be fully assessed within a petroleum systems framework for New Zealand's Cenozoic sedimentary basins.

Keywords: Tubular concretions, cold seeps, methane, carbonate, New Zealand

Introduction
Cold seep systems are typically sourced from the subsurface migration of hydrocarbons to the seafloor, the most common fluids and gases being methane-rich (Roberts and Aharon 1994; Peckmann et al. 2001; Campbell et al. 2002). Anaerobic oxidation of methane (AOM) in the shallow subsurface and at the seafloor is the biogeochemical driving mechanism for carbonate precipitation within these systems. At modern sea bed expulsion sites, carbonate features such as chimneys, slabs and mounds are widely identified (Roberts and Aharon 1994; Orpin 1997; Cavagna et al. 1999; Díaz-del-Río et al. 2003). However, any subsurface expression of the plumbing system of cold seeps is presently poorly understood and logistically difficult to investigate. Many examples of tubular carbonate concretions are known from sedimentary successions in the North Island of New Zealand. These concretions have diverse morphologies and mineralogical compositions that allow for their field categorisation (Table 1). We suggest that the tubular concretions may be "fossilized fluid conduits" that mark focussed subsurface fluid pathways feeding ancient cold seep systems. If so, they provide valuable insight into the three-dimensional shallow subsurface geometry of seep fields, as well as the connection with surface fluid expulsion. This short paper records aspects of the occurrence of tubular concretions in some North Island locations, how they relate to seep fields, and their implications for petroleum systems.

Geologic setting
In North Island, tubular concretions are known from

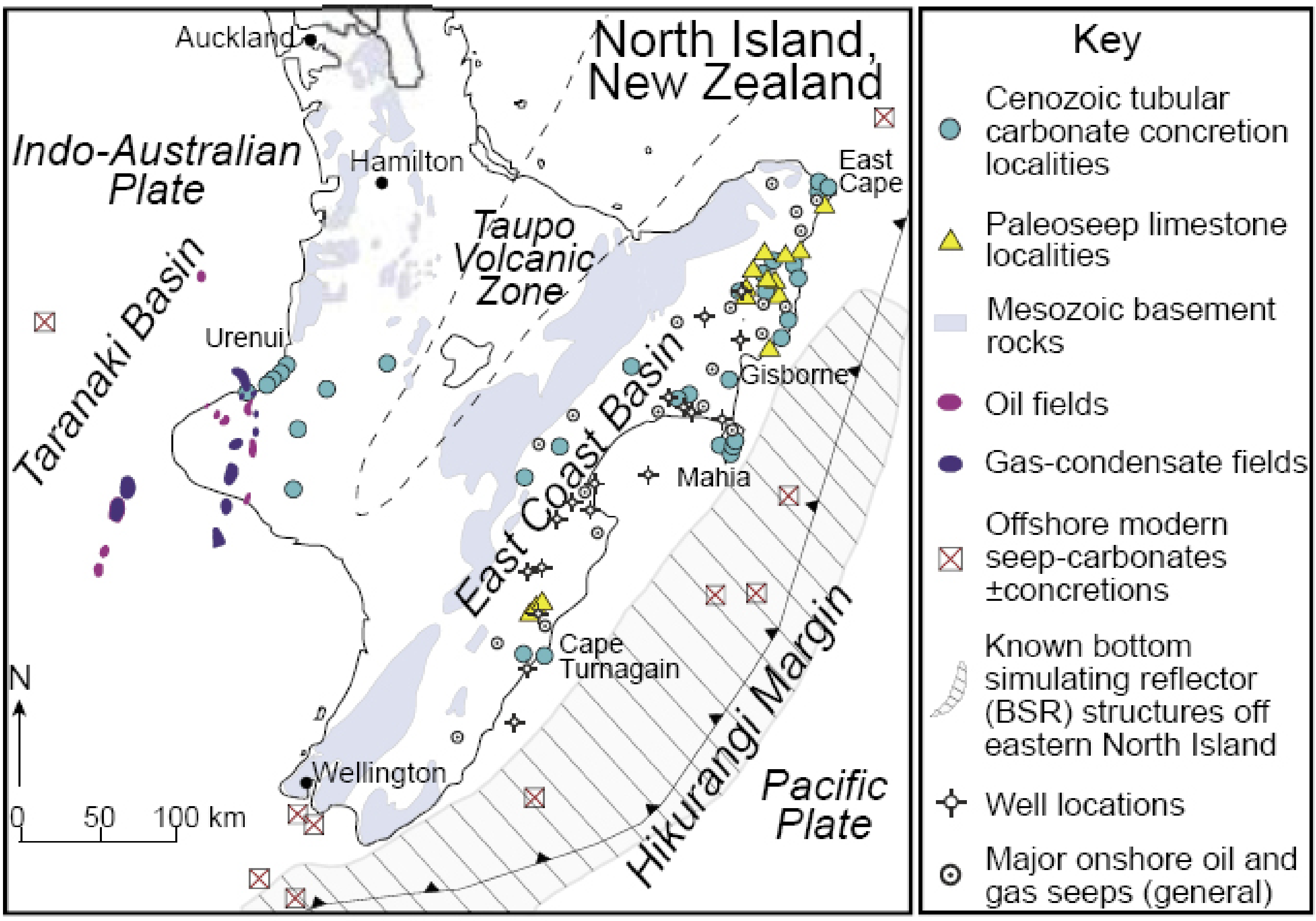

Figure 1: *Generalised locality map of some tubular concretion sites in Cenozoic rocks of North Island, New Zealand. The two main study regions are onshore eastern Taranaki Basin (passive margin) and onshore East Coast Basin (active margin). Also shown are thelocations of some paleoseep limestones, offshore modern seep carbonates, known bottom simulating refl ector (due to gas hydrate), oil fi elds, gas fields, well locations, and major onshore oil and gas seeps. Locality information comes mainly from personal knowledge of the authors, from Francis (1995), Francis and Murray (1997) and Lewis and Marshall (1996), from personal communication with Dave Francis (Geological Research Ltd, Lower Hutt), and from the Crown Minerals website http://www.crownminerals.govt.nz/petroleum/index.asp.*

the tectonically passive eastern margin of Taranaki Basin, along the coastline near Urenui and inland, and throughout the tectonically active East Coast Basin from East Cape in the north, to inland Gisborne and Mahia, and south at Cape Turnagain (Fig1). The concretions are hosted mainly in Miocene and Pliocene outer shelf and upper slope marine mudrocks, often involving turbidite and other redeposited facies. At some of the East Coast Basin localities the tubular concretions stratigraphically underlie ancient cold-seep limestones (Campbell and Francis 1998), supportive of a genetic connection between the concretions and the limestones. Oil and gas seeps are widespread today throughout the basin (Fig. 1; Francis 1995) and modern seep carbonates dot the offshore Hikurangi Margin (Fig. 1).

Concretion morphology and composition

Tubular concretions are a well cemented body of rock within an otherwise less cemented host rock, typically siliciclastic mudstone. They are mainly cylindrical, tubular, or pipe-like in shape (Fig. 2a), and often include a conspicuous central hole or conduit that runs the length of the concretion (Fig. 2b). Conduits range from millimetres to decimetres in diameter and may be empty (Fig. 2b), or filled with later generation cements and/or foreign sediments (Fig. 2c). Some concretions have multiple conduits, while others appear to lack a conduit, which can only be discerned by slight variations in colour depending on cement composition or abundance. The concretions usually lie at high angles to sedimentary bedding, they can be straight, tortuous, or sinuous, they may branch, anastomose, and coalesce, and they can curve downward, producing slabs, or taper up- or downwards (Table 1).

The tubular concretions at Taranaki Basin localities exhibit three main morphologies: pipe, bulbous, and layered. Pipe concretions are typically very straight, cylindrical, and equal in diameter throughout their length, with long axes vertical to bedding (Fig 3a).

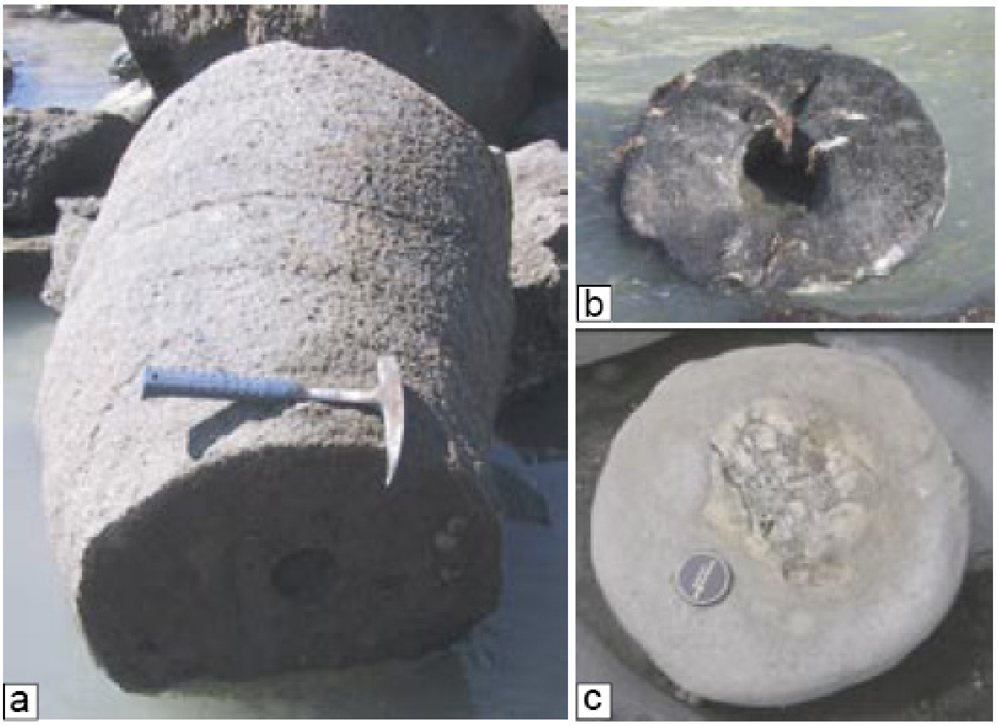

Figure 2: *Outcrop examples from onshore Taranaki Basin of a broken tubular concretion (a), and others illustrating an open (b) and cement filled (c) central conduit. The concretion in (b) is 75 cm across.*

Exposed examples measure 2-3 m long and 5-20 cm across. They are cemented by low- to high-magnesium calcite, as determined by X-ray diffraction.

Bulbous concretions, while also having their long axes vertical to bedding, are much more irregular in long profile (Fig 3b,c) and tend to taper inwards and outwards along their length (Fig 3b), at times "twisting" through the stratigraphy (Fig 3c). They can be up to 10 m long and up to 0.5 m across. The largest of the bulbous concretions observed extends the full height of the coastal cliff outcrop (10 m), suggesting that these features likely extend much further up and down through the stratigraphy. In contrast to the pipe concretions, X-ray diffraction shows that the bulbous concretions are cemented by dolomite.

Table 1: *Table describes the different tubular concretion morphologies found in New Zealand to date.*

Morphology	Description	Location	Possible fluid flow regime	Figure
Pipes	W: 0.1-1 m H: up to many metres	Taranaki and East Coast Basins	Directed fluid flow along an easy pathway	2a,b,c; 3a,e; 7c
Bulbous	W: up to 0.5 m H: 0.1-10 m	Taranaki Basin	Fluid flow along differentially permeable zones	3b,c
Layered	W: up to 2 m H: up to 2 m	Taranaki Basin	Fluid flow along zones of higher permeability	3d
Corkscrews	W: 0.1-0.5 m H: up to 1 m	East Coast Basin	More tortuous permeability zones	3f
Doughnuts	W: 2 - 4 m H: 0.5 - 1.5 m	East Coast Basin	Zone of higher permeability directly overlying a lower permeability zone	3g,h; 7a
Flowerpots	W: av. 1.5 m H: up to 1.5 m	East Coast Basin	Fluid flow along less compacted sediments; near surface	3i,j

Note: Measurements (W: width, H: height) are generalised

Figure 3: *Examples of different tubular concretion morphologies: from onshore Taranaki Basin - (a) pipe; (b) tapered bulbous; (c) twisted bulbous; (d) layered; from onshore East Coast Basin - (e) pipe; (f) corkscrew; (g) doughnut - front view; (h) doughnut - side view; (i) flowerpot – taper down; (j) flowerpot – taper up.*

Layered concretions appear to be associated with bedding horizons formerly having higher permeability (i.e. siltier beds). They exhibit a slab-like morphology, often with a more pipe-like or bulbous concretion at the bottom and/or top of the slabby horizons (Fig. 3d).

East Coast Basin includes several tubular concretion morphologies (Table 1). Again, the pipe concretions like those found in Taranaki Basin are present (Fig 3e), but in general are less elongate (<1 m). Corkscrew concretions are similar to the pipes, being more or less equal in diameter throughout, but they twist through stratigraphy like some of the bulbous concretions in Taranaki Basin, and are much smaller (<1 m long) and more tortuous in profile (Fig 3f). The two most distinctive and different morphologies are doughnuts and flowerpots. Doughnut concretions superficially appear like “standard” spherical to subspherical concretions, but the occurrence of a clear central conduit indicates otherwise (Fig 3g, h). Doughnut concretions on average are 3.5 m across and 1.5 m thick, with a conduit diameter up to 0.6 m. Flowerpot concretions are very large, thick, with cement filled conduits and tend to taper downwards (Fig 3i) or upwards (Fig 3j) through the stratigraphy. Their widest point averages 1 m, tapering to about 0.5 m, and they stand up to 1.5 m tall.

The carbonate composition of the tubular concretions in East Coast Basin is primarily dolomite. However, the conduits, if cemented, are a mixture of calcite and dolomite. In the northern part of the basin (e.g., at East Cape) the conduits are cemented by up to 90% dolomite. The calcite content in the conduits increases southwards in the basin, averaging 50% dolomite/50% calcite in the fills at Cape Turnagain.

Origin of tubular concretions

As for all concretions, the origin of tubular concretions relates to the precipitation of mineral cement (in our case calcite or dolomite) from pore waters within the sediment interstices. However, for most "standard" (sub)spherical concretions, cement precipitation begins at some nucleation centre (e.g., about a shell fragment or organic material) and continues to develop outwards in a concentric growth pattern (Fig 4a). As a consequence, formation of horizons of spherical concretions can affect the fluid flow dynamics within a sedimentary body by retarding fluid movement in both horizontal and vertical directions (Lee et al. in press).

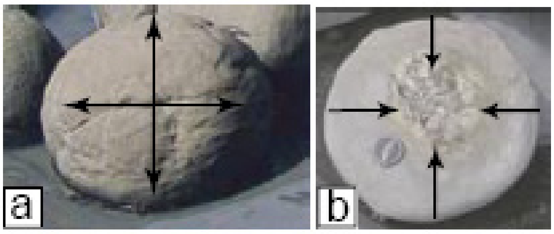

Figure 4: *Contrasting suggested growth directions for "standard" spherical concretions (1.25 m across) versus tubular concretions. Arrows indicate directions of cement precipitation.*

This contrasts with tubular concretions which have open central conduits, so that cement growth cannot have occurred outwards from some central nucleus. We favour a formative mechanism proposed by Clari et al. (2004) who documented pipe-like carbonate concretions associated with a Miocene mud volcano in Italy. They demonstrated for these concretions that cement was first precipitated at the outer margins of the structures, and continued to precipitate inwards towards the conduit, at times cementing the entire conduit. The precipitation sequence is the opposite of that for spherical concretions (Fig 4b). Consequently, tubular concretions actually encase dominant fluid passageways with an impervious crust, creating a barrier to lateral fluid flow but encouraging vertical fluid movement. Assuming ongoing similar rates of fluid movement through a sediment body, the cemented crusts will create a higher fluid pressure and the conduits will remain open and free of sediment clogging, allowing unrestricted and direct pathways upwards through the stratigraphy. The pathways may eventually become closed, congested, or cut-off if fluid volumes or pressures become reduced (allowing more carbonate precipitation), if the injected fluids become too sediment laden, or if some overlying barrier is reached.

The carbonate content in the concretions ranges from 30-75% and consists of very finely crystalline calcite and/or dolomite micrite/microsparite cement. Interstitial precipitation of this cement within the host mudstone indicates that precipitation occurred within buried sediment, and not as free-standing pipes or tubes upon the sea floor. Variations in the contents of calcite and dolomite amongst the concretions within and between locations suggest an origin in different sub-seafloor geochemical environments, in time of formation, or in the availability of magnesium, matters requiring further study.

Stable isotope analyses ($\delta^{13}C$, $\delta^{18}O$) for the carbonate cements are presently available only for the eastern Taranaki Basin concretions (Nelson et al. 2004), and remain to be more fully investigated for all occurrences. Despite some scatter on a $\delta^{13}C$-$\delta^{18}O$ plot, three clusters are apparent (Fig 5). Cluster 1 involves spherical concretions contained in the same strata as associated tubular concretions, as well as conduit-filling late cements within the tubular concretions, and has isotope values ($\delta^{13}C$ -5 to +5 ‰, $\delta^{18}O$ -8 to -3 ‰) suggesting a post-methanic origin from subsurface connate waters with possibly a freshwater influence. Cluster 2 corresponds mainly to bulbous concretions with isotope signatures ($\delta^{13}C$ -10 to +10 ‰, $\delta^{18}O$ +2 to +4 ‰) suggestive of carbonate precipitation below the sulphate reduction zone from pore water and methane-derived CO_2. Cluster 3 is associated with pipe concretions in which the isotope values ($\delta^{13}C$ -40 to -30 ‰, $\delta^{18}O$ -2 to 0 ‰) show very depleted carbon values, supportive of thermogenically derived methane and precipitation within the sulphate reduction zone from methane–derived CO_2.

In summary, a combination of the elongated concretion morphologies, their outcrop disposition, the existence of central conduits, and the stable isotope data strongly suggest that precipitation of the tubular concretionary carbonate cements was closely linked to the oxidation of ascending methane-rich gases and fluids (e.g. Peckmann et al. 2001, 2002; Campbell et al. 2002) and that, unlike central nucleation, which is typical for most standard concretions, the tubular concretions developed around fluid migration pathways involving increasingly focused fluids pumping their way towards the surface.

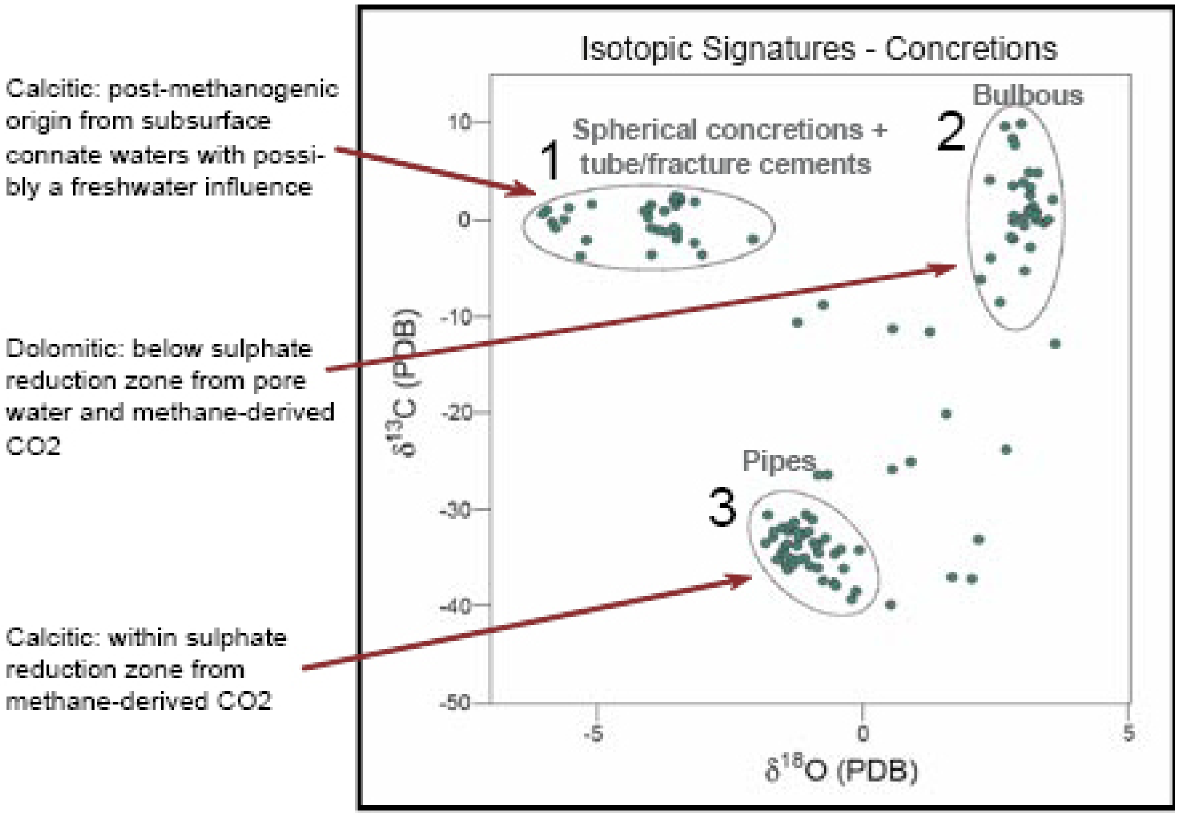

Figure 5: *Stable oxygen and carbon isotope values for tubular (pipe and bulbous) concretions from onshore Taranaki Basin (from Nelson et al. 2004). Note the tendency to cluster within three areas of the plot.*

Overview of cold seep systems

A schematic diagram of a complete subsurface to surface cold seep system is depicted in Figure 6. The system is initiated by the upwards migration of methane-bearing fluids and gases at depth, in this example from a hydrocarbon reservoir, preferentially focused along pathways like faults, fractures, or more permeable sediment layers, and potentially eventually escaping at the sea floor.

Fault and joint control on fluid migration is well demonstrated in many of the East Coast Basin occurrences where the tubular concretions are strung out along the strike of linear fractures, which do not necessarily pass directly into and through the concretions themselves (Fig 7a,b,c). The influence of a sedimentary control from enhanced permeability is best evident at several Taranaki sites where stacked slabs of preferentially cemented carbonate develop within slightly coarser textured layers (siltier) compared to the intervening layers (Fig. 7d). The associated low permeability mudrock supports tubular concretions (Fig 7d), both below and above the layered concretions, and it appears that these have acted as the principal fluid feeders for the layered concretions.

Anaerobic oxidation of methane (AOM) is the driving force behind carbonate precipitation in cold seep systems (Cavagna et al. 1999; Hinrichs et al. 1999; Orphan et al. 2001). As methane rich fluids migrate towards the surface, reverse working methanogenic archea and sulfate reducing bacteria convert methane and sulphate to water, bicarbonate, and sulphide (Reitner et al. 2005). AOM increases alkalinity in the system (Reitner et al. 2005), and with free bicarbonate present, carbonate cement then precipitates. In the shallow burial environment, tubular concretions form around any focussed fluid pathways as a result of AOM (Fig. 6).

Fluids reaching the sea floor either dissipate through the surficial sediments or may vent out at high flow rates and precipitate carbonate chimneys and other sea-floor seep carbonate features, well known from both modern and ancient cold seep deposits (Campbell and Bottjer 1993; Roberts and Aharon 1994; Orpin 1997; Cavagna et al. 1999; Aiello et al. 2001; Conti and Fontana 2002; Clari et al. 2004). AOM and sulphate reduction of fluids reaching the sea floor provide the appropriate habitat for colonisation by chemosymbiotic biota, like tube worms and lucinid and vesicomyid bivalves (Cavagna, Clari et al. 1999; Campbell et al. 2002) (Fig. 6), known from some of

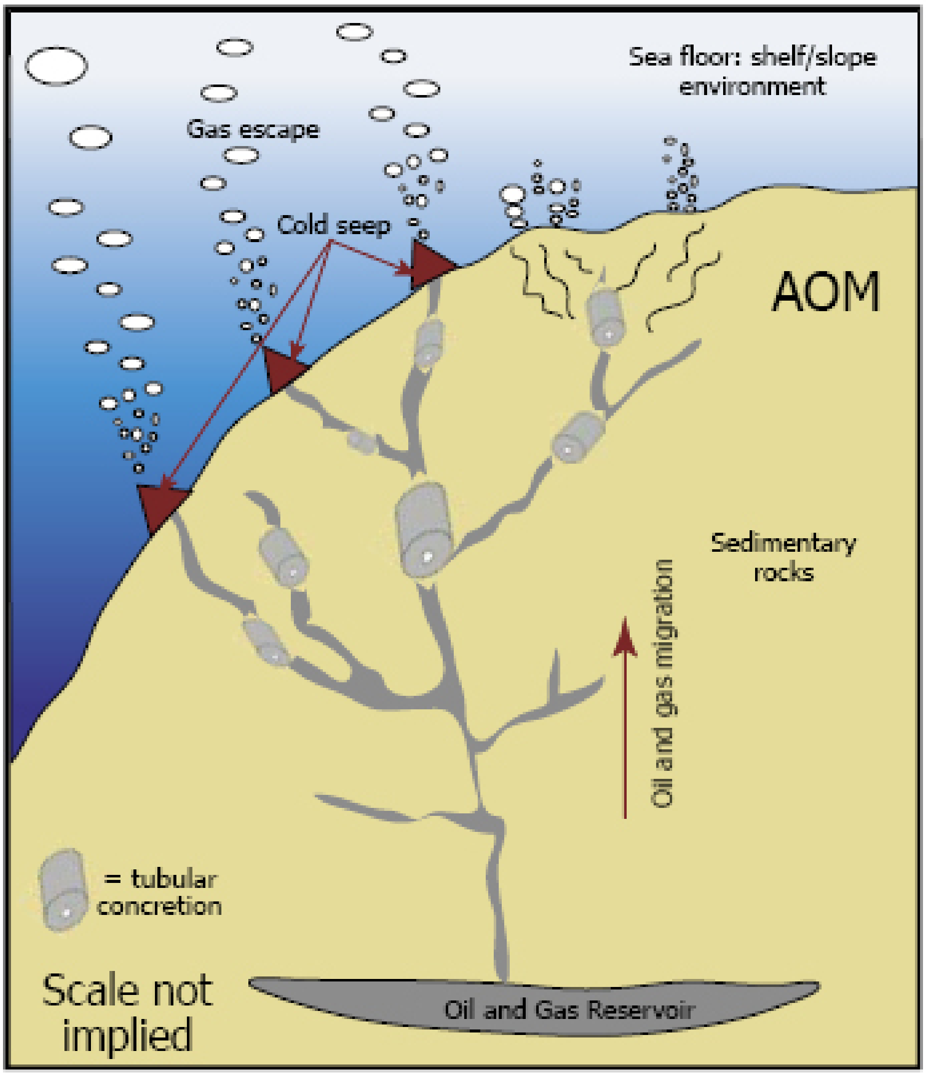

Figure 6: *Schematic diagram of a cold seep system and associated features in the context of a progradational shelf-slope continental margin. Methane rich fluids, from leaky oil and gas reservoirs and/or biogenic methane, migrate upwards along faults, joints, and permeable sedimentary layers. As the fluids enter the shallow burial environment, anerobic oxidation of methane (AOM) occurs from reverse working methanogenic archaea. The result is an increase in alkalinity, and with the appropriate pore water constituents available, carbonate minerals (calcite or dolomite) may preferentially precipitate around the fluid conduits, giving a "tubular" morphology to concretions (see Fig 4b). If the methanic fluids/gases reach the surface, cold seeps form. Carbonate precipitates upon the sea floor in the form of chimneys, mounds, and slabs, while chemosymbiotic communities develop due to the available energy source from the venting fluids.*

the East Coast Basin paleoseep localities (Campbell and Francis 1998) and offshore in the modern (Lewis and Marshall 1996).

Implications

It is our contention that the tubular concretions in the North Island sections studied (Fig. 1) mark the shallow subsurface plumbing system of cold seeps, where variable proportions of thermogenic methane have migrated upwards from reservoir rocks to the sea floor. At the time of their origin the tubular concretions indicate an active or recently active hydrocarbon system. In the Taranaki Basin, tubular concretions are located in Miocene sediments near producing oil and gas fields from Late Cretaceous to Eocene source and reservoir rocks (King et al. 1993; Nelson et al. 2004). In the East Coast Basin, tubular concretions and paleoseep limestones are located in Miocene-Pliocene sediments near oil and gas seeps from leaky reservoir rocks of Neogene age and source rocks of late Cretaceous and Paleocene age (Francis 1995; Francis and Murray 1997).

On a global scale, not all cold seeps are sourced from hydrocarbons. We plan to further investigate other occurrences of New Zealand tubular concretions, as well as the cold seep limestones where preserved, to determine whether the carbonate carbon sources can be distinguished, whether these have a thermogenic or biogenic origin, or both, and whether the geochemical characteristics of the carbonate features (e.g. isotopes, lipid biomarkers; Pearson and Nelson 2005) may be used as hydrocarbon indicators.

If the tubular concretions represent the subsurface plumbing system of cold seeps, then they may shed light on the development and evolution of cold seep systems. Understanding the cold seep system as a whole will provide more information on the global carbon cycle, carbon budget, and climate change, as well as fluid migration pathways in sedimentary basins. Tubular concretions and cold seeps can be derived from hydrocarbon sources, so that modern examples may demonstrate that the hydrocarbon

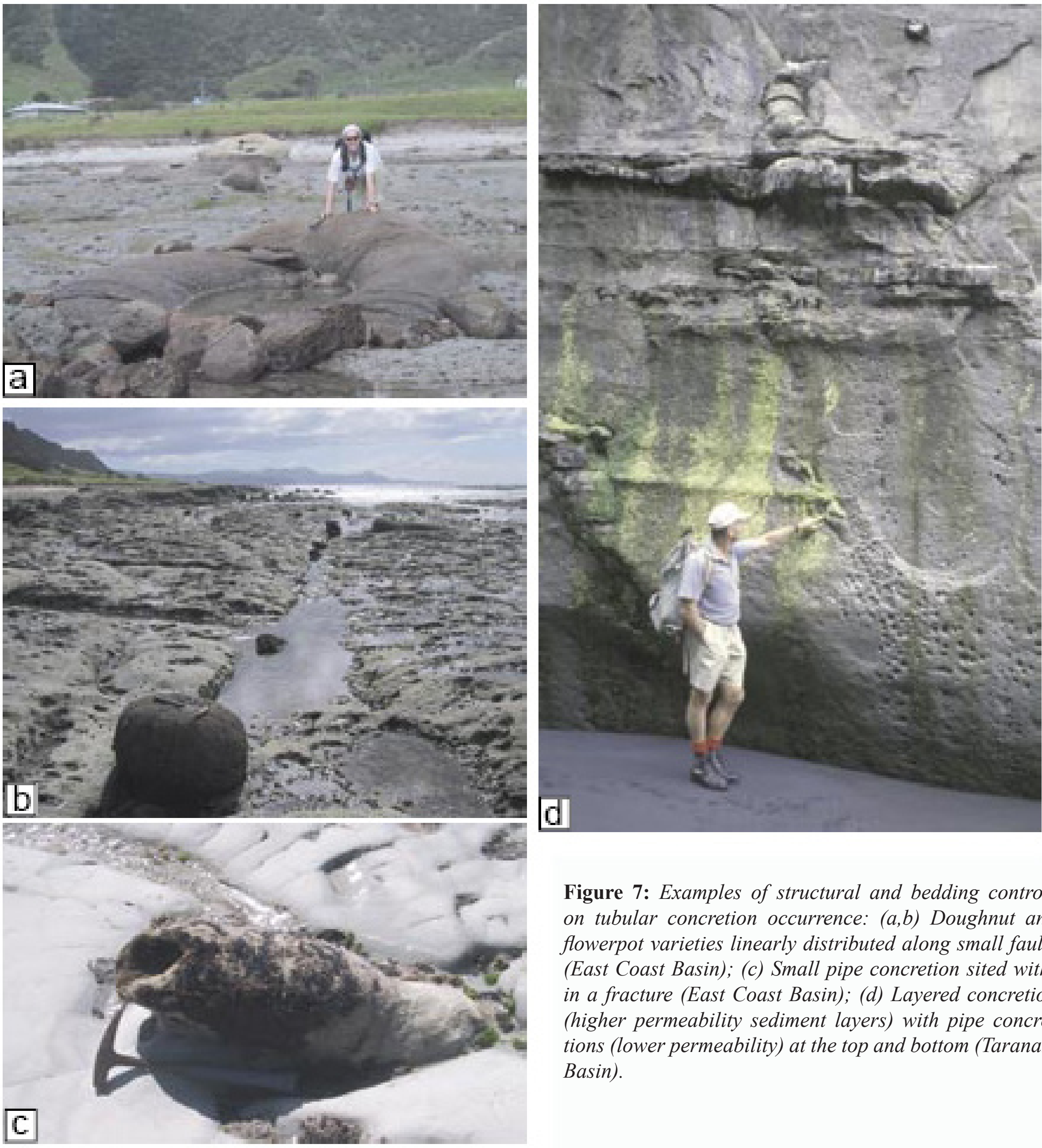

Figure 7: *Examples of structural and bedding controls on tubular concretion occurrence: (a,b) Doughnut and flowerpot varieties linearly distributed along small faults (East Coast Basin); (c) Small pipe concretion sited within a fracture (East Coast Basin); (d) Layered concretion (higher permeability sediment layers) with pipe concretions (lower permeability) at the top and bottom (Taranaki Basin).*

system has been active in recent times. If carbon sources can be differentiated, then tubular concretions and cold seeps may act as hydrocarbon migration indicators. Cold seeps are also known to be associated with gas hydrates. Gas hydrates cause many hazards in drilling and production of oil and gas (Milkov et al. 2002, 2004), and they are also a viable future energy source (Grauls 2001; Milkov et al., 2002, 2004). As such, cold seep systems may help identify gas hydrate hazards and resources in the future.

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