



Using the $^{87}\text{Sr}/^{86}\text{Sr}$ of modern and paleoseep carbonates from northern Cascadia to link modern fluid flow to the past

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ABSTRACT

Most authigenic carbonates previously recovered from the Cascadia slope have $^{87}\text{Sr}/^{86}\text{Sr}$ signatures that reflect shallow precipitation in equilibrium with coeval seawater. There is also evidence for carbonate formation supported by fluids that have been modified by reactions with the incoming Juan de Fuca plate ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7071$; Teichert et al., 2005) or with terrigenous turbidites ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70975$ to 0.71279; Sample et al., 1993). We report on the strontium isotopic composition of carbonates and fluids from IODP Site U1329 and nearby Barkley Canyon (offshore Vancouver Island), which have strontium isotope ratios as low as 0.70539. Whereas the strontium and oxygen isotopic compositions of carbonates from paleoseeps in the uplifted Coast Range forearc indicate formation in ambient bottom seawater, several samples from the Pysht/Sooke Fm. show a ^{87}Sr -depleted signal ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70494$ and 0.70511) similar to that of the anomalous Site U1329 and Barkley Canyon carbonates.

Our data, when analyzed in the context of published elemental and isotopic composition of these carbonates (Joseph et al., 2012), point to two formation mechanisms: 1) shallow precipitation driven by the anaerobic oxidation of methane (AOM) with $\delta^{13}\text{C}$ values as low as -50% and contemporaneous $^{87}\text{Sr}/^{86}\text{Sr}$ seawater ratios, and 2) carbonate precipitation driven by fluids that have circulated through the oceanic crust, which are depleted in ^{87}Sr . Carbonates formed from the second mechanism precipitate both at depth and at sites of deep-sourced fluid seepage on the seafloor. The ^{87}Sr -depleted carbonates and pore fluids found at Barkley Canyon represent migration of a deep, exotic fluid similar to that found in high permeability conglomerate layers at 188 mbsf of Site U1329, and which may have fed paleoseeps in the Pysht/Sooke Fm. These exotic fluids likely reflect interaction with the 52–57 Ma igneous Crescent Terrane, which supplies fluids with high calcium, manganese and strontium enriched in the non-radiogenic nucleide. Tectonic compression and dehydration reactions then force these fluids updip, where they pick up the thermogenic hydrocarbons and ^{13}C -enriched dissolved inorganic carbon that are manifested in fluids and carbonates sampled at Barkley Canyon and at Site U1329. The Crescent Terrane may have sourced cold seeps in this margin since at least the late Oligocene.

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1. Introduction

The deep hydrosphere, which includes pore waters of marine sediments and fluids circulating within the underlying oceanic crust, comprises the largest continuous aquifer system on Earth (Davis and Elderfield, 2004). Characterizing the temporal and spatial characteristics of this aquifer is the topic of active research, as fluid flow plays a critical role in modulating the mechanical, chemical, and biological processes in the lithosphere (Kastner et al., 1991; Torres et al., 2004; Fisher, 2005; Screaton, 2010; Saffer and Tobin, 2011). The most

important processes that modulate fluid composition in convergent margins include: biogenic and thermogenic degradation of organic matter with subsequent hydrocarbon formation; gas hydrate formation or dissociation; microbially mediated anoxic oxidation of methane (AOM) and associated carbonate mineral precipitation; dehydration reactions of hydrous clay minerals and opal; and alteration of the oceanic crust (e.g. Han and Suess, 1989; Kastner et al., 1991; Sample, 1996; Elderfield et al., 1999; Torres et al., 2004; Screaton, 2010). Through these reactions, fluids acquire geochemical and isotopic characteristics that allow us to trace their origin and flow pathways.

Marine cold seeps, where pore fluids with exotic composition discharge at the seafloor, serve as a window into different depth levels of the deep hydrosphere and as a localized foci for the introduction of

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methane carbon to the ocean and potentially to the atmosphere (e.g. Torres et al., 2002; Riedel et al., 2006; Kim et al., 2011). Authigenic carbonates are a common feature at cold seeps (e.g. Han and Suess, 1989; Campbell et al., 2002; Greinert et al., 2002). Because these deposits remain in the geologic record, they provide valuable information to reconstruct the history of methane discharge, the processes transforming methane–carbon to carbonate, and the sources and pathways of the fluid transporting carbon. As such, authigenic carbonate analysis provides a history of evolving fluid processes in the deep hydrosphere (Sample and Reid, 1998).

Among the various geochemical tracers commonly used to fingerprint authigenic carbonates, $^{87}\text{Sr}/^{86}\text{Sr}$ is particularly valuable in tracing fluid–rock reactions, sources, and fluid mixing (e.g. Torres et al., 2004; Teichert et al., 2005; Solomon et al., 2009) because of the distinct composition of the various end-member fluids. Potential source materials responsible for the $^{87}\text{Sr}/^{86}\text{Sr}$ of interstitial waters are: continental detritus from the area bordering the Cascadia margin ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7119\text{--}0.7133$), biogenic calcite ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7068\text{--}0.7092$), and the oceanic crust ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7030$) (Veizer, 1989). The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ has varied through geologic time due to varying inputs of continental detritus and hydrothermal circulation within the oceanic crust (Burke et al., 1982; Veizer, 1989). Carbonates precipitate in equilibrium with the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the fluids from which they form (Hess et al., 1986). Therefore, the strontium isotopic composition of authigenic carbonate provides a spatially resolved context for evaluating ancient fluid flow.

Previous studies have documented extensive carbonate formation at cold seeps on the Cascadia slope, where precipitation is driven by the anaerobic oxidation of methane (AOM). AOM-derived carbonates are characterized by very negative $\delta^{13}\text{C}$ values and seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Sample and Reid, 1998). Carbonates sampled along a vertical fault zone at the deformation front of the accretionary wedge show extreme ^{18}O depletion and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70975–0.71279), indicative of deep dewatering and flow through terrigenous turbidites (Sample et al., 1993). Here we report on the $^{87}\text{Sr}/^{86}\text{Sr}$ of authigenic carbonates and pore fluids from the Integrated Ocean Drilling Program (IODP) Site U1329 and the nearby Barkley Canyon (Fig. 1), a known thermogenic gas-rich province south of Vancouver Island (Pohlman et al., 2005; Pohlman et al., 2009; Riedel et al., 2010). We compare these results with pore water data and with paleoseep authigenic carbonates from Oligocene and Pliocene sedimentary formations of the uplifted Coast Range forearc in Washington State (Martin, 2010; Joseph et al., 2012; Nesbitt et al., 2012) to identify sources and pathways of fluid flow in the modern and ancient Cascadia margin.

2. Site descriptions

The Cascadia margin off the coast of Vancouver Island forms in response to nearly orthogonal convergence of the Juan de Fuca plate with North America, at a present rate of about 45 mm/year (Riddihough, 1984). Seaward of the deformation front, the Cascadia basin consists of pre-Pleistocene hemipelagic sediments overlain by rapidly accumulating Pleistocene deposits. Most of the incoming sediment is scraped off the oceanic crust and folded and thrust upward to form a thick accretionary prism. Depositional coarse-grained turbidite layers and tectonically driven fractures and thrust faults act as high permeability migration pathways for deep-sourced fluids (Tréhu et al., 1994; Hyndman, 1995). As fluids ascend through the sediment column, pressure drops resulting in carbonate precipitation (e.g. Sample, 1996) (Table 1).

Site U1329 was drilled within the modern accretionary prism during the IODP Expedition 311, 65 km offshore in a water depth of 946 mbsl (Riedel et al., 2006). The sediment section recovered at this site is divided into three lithostratigraphic units. Unit I (<37 mbsf) is characterized by clay and silty clay sediment locally interbedded with coarse-grained sediments. Unit II (37–135.6 mbsf) is characterized by a transition to

a diatom ooze. A layer of rounded conglomerate clasts that corresponds to an unconformity between upper Miocene and Pleistocene sediments marks the lithostratigraphic boundary between Units II and III. Unit III is characterized by clay to silty–clay detrital sediments with a few interlayered, coarse turbidite deposits. Another conglomerate layer sampled at 188 mbsf marks the base of Unit III and represents the deepest drilled section at Site U1329 (Riedel et al., 2006). This conglomerate consists of carbonate cemented sandstone/quartzite and mudstone clasts up to 4 cm in diameter (Fig. 2).

Barkley Canyon is a headless submarine canyon located about 100 km off the west coast of Vancouver Island at 850 mbsl. Previously recovered thermogenic gases and gas hydrates were used to suggest that Barkley Canyon acts as a focus for discharge of deep-sourced fluids within the Cascadia subduction zone (Pohlman et al., 2005). Authigenic carbonate samples and pore fluids from this site were collected from piston cores during a Pacific Geoscience Centre expedition in 2008 (samples BC1–BC4) and seafloor grabs and push cores collected using the remotely operated vehicle (ROV) Doc Ricketts during the MBARI Pacific Northwest Expeditions in 2009 (BC5–BC6) and 2011 (BC7–BC13) (Joseph et al., 2012).

Fossil cold seeps within the uplifted accretionary wedge sequences of the Olympic Mountains in Washington, USA were identified by the presence of fossilized chemosynthetic invertebrate communities and have been previously described by Martin (2010), Torres et al. (2010), and Nesbitt et al. (2012). Paleoseep carbonate petrology and geochemistry is reported in Joseph et al. (2012). We build on these results by analyzing the strontium isotopic composition of authigenic carbonates from the Pliocene Quinault Formation (southern Olympic Peninsula) and from the Oligocene–Miocene Sooke (southern Vancouver Island) and Pysht Formations (northern Olympic Peninsula).

The Pysht Formation is typified by 1 km thick pelagic and fine grained turbidite deposits. The Sooke Formation consists of inner neritic to supratidal sandstones and conglomerates. These two formations are part of the same submarine fan incised by the Strait of Juan de Fuca. We will refer to them jointly in this study. The Quinault Fm. is typified by 3 km of outer-shelf to estuarine storm-dominated deposits with a localized distribution of fossilized seep organisms (Campbell, 1992).

Underlying the paleoseep host formations is the Eocene Crescent Formation, which is known as the Siletz River Formation in Oregon and as the Metchosin Formation on Vancouver Island (Snaveley et al., 1968; Tréhu et al., 1994). The Crescent Formation is the most voluminous of all Coast Range volcanic sequences, consisting of pillowed and massive basaltic flows up to 15 km thick (Brandon et al., 1998). It may have originated as a result of the accretion of an oceanic island or seamount (e.g. Duncan, 1982; Johnston and Acton, 2003) or as an accreted oceanic plateau (Babcock et al., 1992). This 52–57 Ma igneous terrane comprises the basement unit of the Coast Range and Olympic Mountains throughout Washington and Oregon and forms the modern crystalline backstop to the northern Cascadia accretionary complex landward of Barkley Canyon and Site U1329 (Fig. 1).

3. Methods

The pore water strontium isotopic composition for Site U1329 was available from the literature (Riedel et al., 2010). The analytical techniques and the elemental and isotopic composition of carbon and oxygen for carbonate samples used in this study are presented in Joseph et al. (2012). We measured the strontium isotopic composition of authigenic carbonates and pore fluids from Barkley Canyon and of carbonates recovered from Site U1329 and from exposed paleoseep formations. The same Sr-separation technique was used for both carbonates and pore fluids.

Pore fluids from Barkley Canyon were collected from Core 23 during the PGC2008-007 expedition using pre-soaked Rhizone samplers to a maximum depth of 190 cmbsf. For $^{87}\text{Sr}/^{86}\text{Sr}$ analysis, 50 μl of pore

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