**Climate controlled, fabric destructive, reflux dolomitization and stabilization via marine-
and synorogenic mixed fluids: an example from a large Mesozoic, calcite-sea platform,
Croatia**

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ABSTRACT

The Jurassic-Cretaceous dolomites, Adriatic platform, Croatia resulted from climate-influenced *post-depositional* reflux dolomitization (as opposed to syndimentary peritidal- and deeper burial dolomitization), and subsequent stabilization within a Mesozoic, “calcite sea” isolated platform. The dolomites are stratiform (10 to 200 m thick), fabric destructive (20 to over 500 μm crystals), nonluminescent, and zoned with respect to Ca. Bulk dolomites have low Mn (10 to 30 ppm), moderate Sr (60 to over 200 ppm), positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, only moderate ordering (0.25 to 0.6) and single-phase fluid inclusions (temperatures $<50^\circ\text{C}$). High-Ca dolomite (HCD; ~ 53 to ~ 59 mol% Ca; $\delta^{18}\text{O} +1$ to $>+3\text{‰}$ VPDB and $\text{Sr} > 100$ ppm) composes most Jurassic and 40% of Cretaceous dolomites, making up turbid dolomite cores and initial clear dolomite rims. A first generation of low-Ca dolomite (LCD-1; 50 to 53 mol% Ca; $\delta^{18}\text{O} +1$ to $>+3\text{‰}$ VPDB; 100-180 ppm Sr) forms cement and variably replaces (stabilizes) earlier HCD cores. HCD and LCD-1 formed in refluxing marine-dominated pore waters under semi-arid climate ($<300\text{m}$ depth, 30 to $\sim 40^\circ\text{C}$). $^{87/86}\text{Sr}$ values of the HCD and LCD-1 dominantly were controlled by the refluxing seawater $^{87/86}\text{Sr}$ with minor addition of $^{87/86}\text{Sr}$ from ascending cooling fluids. During maturation of HCD, Sr loss was greatest from least stable, more calcic HCD (>55 mol%) phases. A second generation of much younger, low-Ca dolomite (LCD-2; fracture-associated, more negative $\delta^{18}\text{O}$ from -1.4 to $+1\text{‰}$ VPDB, $\text{Sr} < 100$ ppm, enriched in radiogenic ^{87}Sr) overgrows and variably replaces earlier Cretaceous dolomites. It formed during Eocene-Oligocene deformation and uplift to <1 km burial depths ($<50^\circ\text{C}$) from synorogenic, mixed marine-meteoric pore fluids, circulating via faults, fractures and local permeable zones. Porosity loss by dolomite cementation coupled with localized, rapid Cenozoic uplift, variably arrested stabilization to LCD.

Keywords: isolated platform, post-depositional dolomite, geochemistry, mesohaline reflux, stabilization

1. Introduction

Budd (1997) used the term *post-depositional dolomites* for dolomites generated by reflux of normal to slightly evaporative waters on isolated platforms, to differentiate them from typical peritidal fine-grained dolomites formed at or near the sediment-water interface, and from dolomites that form in the deeper subsurface at elevated temperatures. Such post-depositional dolomites can form in marine phreatic zones of active reflux down to 200 m subsurface, and perhaps down to 300 m in marine-dominated mixing zones (Budd, 1997; Cander, 1994; Gaswirth et al., 2007). Little altered, post-depositional dolomites have been widely documented from Late Cenozoic isolated platforms that formed in aragonite seas (Supko, 1977; Saller, 1984; Aharon et al., 1987; Hein et al., 1992; Vahrenkamp and Swart, 1994; Budd, 1997; Stanley and Hardie, 1999; Wheeler et al., 1999; Suzuki et al., 2006; Zhao and Jones, 2012b). Post-depositional dolomites can be partly stabilized in marine fluids via overgrowth of more stoichiometric dolomite rims (Wheeler et al., 1999; Suzuki et al., 2006; Zhao and Jones, 2012b) or in mixing zones in which less stable, early marine dolomite phases are converted into more stable dolomites via replacement and growth of dolomite cements (Cander, 1994; Gaswirth et al., 2007; Li et al., 2015).

Few studies have documented post-depositional dolomites from Mesozoic isolated platforms from calcite seas (Galluccio, 2009; Stanley and Hardie, 1999). Most have focused on syndepositional peritidal, hydrothermal and burial dolomites (e.g., Frisia and Wenk, 1993; Balog et al., 1999; Iannace et al., 2011; Ronchi et al., 2011; Meister et al., 2013). The massive,

stratiform to discontinuous, coarse fabric-destructive dolomite units within the Upper Jurassic to Lower Cretaceous carbonates of the Adriatic platform, Croatia (Figs 1, 2) provide an opportunity to fill this knowledge gap. These were referred to as “late diagenetic dolomites” based mainly on field relations and petrography (Tišljarić et al., 1983, 2002; Vlahović et al., 2005). However, during our chemostratigraphic sampling of the platform succession, these typically coarse dolomites turned out to have surprisingly positive $\delta^{18}\text{O}$ values quite unlike most late diagenetic dolomites, overlapping the range of Mesozoic tidal flat- (Frisia and Wenk; 1993; Balog et al., 1999; Meister et al., 2013) and early, post-depositional dolomites (cf., Galluccio, 2009; Iannace et al. 2011). In this paper we document the major- and trace element, C-O isotope and Sr isotope makeup of the dolomites, and show that the dolomites are in fact reflux *post-depositional* dolomites that have been variably reset and coarsened by subsequent diagenesis during shallow burial and much later synorogenic uplift. Back-scattered electron (BSE) images were critical in defining the diagenetic history of these non-luminescent dolomites (Suzuki et al., 2006; Jones, 2007). Integrating field data with chemostratigraphic C-O isotope data and geochemistry helped document effects of variable overprinting by synorogenic, fracture-associated warm fluids. Analogous post-depositional porous and permeable dolomites in the region (cf. Galluccio, 2009) are potential oil and gas exploration targets in the Adriatic offshore (Croatian Hydrocarbon Agency, 2016).

2. Geologic setting

The Adriatic Platform (Figs 1, 2) was a large intraoceanic, Mesozoic carbonate platform 5 to 7 km thick, several hundred kilometers long, with a present width of ~200 km within the external fold thrust belt of the Dinarides (Tišljarić et al., 2002; Vlahović et al., 2005; Husinec and

Jelaska, 2006). The autochthonous western part of the platform (Dalmatian Zone) is over-ridden by the allochthonous eastern part (High Karst Zone). The platform was bordered on the west and east by steep margins with up to 3 km relief above the basin floor by the end Cretaceous (Dragičević and Velić, 2002; Grandić et al., 2010). The southeastern platform margin in Montenegro southeast of Dubrovnik, has a long-lived, pelagic re-entrant (Vlahović et al., 2005; Črne and Goričan, 2008; Bega, 2015) preserved within a NW to SE trending thrust-bounded slice (Budva Zone, Fig. 1B) between the allochthonous and autochthonous parts of the platform.

Subsidence rates were relatively rapid in the Late Jurassic (12 to 15 cm/kyr; Fig. 1D), with ophiolite emplacement on the distal eastern Adriatic plate margin (Schmid et al., 2008). Subsidence slowed through the Barremian, and was the lowest in the Aptian. Compression, initial folding and slumping started in the Late Cretaceous Late Santonian-Campanian and Maastrichtian, accompanied by renewed subsidence (Husinec and Jelaska, 2006; Prtoljan et al., 2007), terminating in end-Cretaceous warping and emergence, and uplift of the northeastern margin (Vlahović et al., 2005). Transgressive, dominantly Lower to Middle Eocene carbonates were deposited on the platform prior to later Eocene drowning. Deformation peaked during the Eocene-Oligocene to Early Miocene to form the present day imbricate thrust and fold belt, which underwent ~50% shortening (Fig. 1D; Matičec et al., 1996; Vlahović et al., 2005; Prtoljan et al., 2007; Ustaszewski et al., 2008). Neogene ramp carbonates and “flysch” were deposited in downwarping basins within the fold-thrust belt. Regional highs and islands on which the present day offshore outcrops are located remained positive features, bounded to the north and south by thrust- and reverse faults of opposite vergence, and underwent exhumation (Fig. 1C, D; Prtoljan et al., 2007). Counter clockwise rotation, right lateral strike-slip faulting and N-S compression overprinted the region from the Miocene on, resulting in flower structures associated with E-W

trending anticlines that form the present day islands (Prtoljan et al., 2007; Bega, 2015). Cenozoic uplift (Prtoljan et al., 2007) and exhumation over islands and on the mainland was relatively rapid (~ 30-60 m/Myr; Fig. 1D).

In the Late Jurassic the platform was in the tropics at 15° to 20° N and migrated to 20° to 25° N by the Early Cretaceous (Fig. 1E; Golonka, 2002). The Late Jurassic climate of the region was relatively hot and arid which persisted into the Early Cretaceous Berriasian (Fig. 2C; Ruffel and Rawson, 1994; Husinec and Read, 2006). The climate cooled (and became increasingly humid) in the Valanginian, warmed into the Hauterivian, returning to hot-arid conditions by the Barremian (with intermittent arid-humid cycles in the Hauterivian-Barremian), then cooling in the Aptian-basal Albian, to become hot and arid later in the Albian (Fig. 2C; Ruffel and Rawson, 1994; Scotese, 2002; Wilkinson and Riding, 2007; Husinec and Read, 2011; Föllmi, 2012).

3. Methods

About one hundred and fifty dolomite samples were collected from a composite total of over three hundred meters section from the Adriatic Platform (Figs 2, 3). Dolomites were from the Upper Jurassic Tithonian near Dubrovnik (BK section) and Lower Cretaceous Valanginian to Barremian on Korčula Island (C sections); Tithonian and Valanginian-Barremian lime mudstones were obtained from Mljet and Lastovo islands (Fig. 1B, C; Appendix Table A1). Dolomite billets and thin sections were partly stained with Alizarin Red S (AR-S, Dickson, 1966). Only relatively pure dolomite bulk samples (75% of samples) including those with less than 2% calcite (25% of samples; based on image analysis of AR-S stained sliced dolomite billets) eliminated samples too contaminated by calcite (inclusions, cement, dedolomite and rare fracture fills). Slight contamination of about 25% of remaining samples by calcite would

potentially overestimate bulk Ca contents determined by INAA (discussed below) by 0-2 mol%. Dolomite crystal sizes are petrophysical classes of fine (<20 μm), medium (20 to 100 μm) and coarse (>100 μm) of Lucia (1995). Samples were initially examined using cathodoluminescence (CL) microscopy (Technosyn system; 10 kV and 16 μA) but all were nonluminescent. Bulk Ca, Mg, Sr and Mn analyses were done by INAA (Instrumental Neutron Activation Analysis) by Elemental Analysis, Inc., Lexington, Kentucky, USA on ~10 g crushed samples; relative standard deviation was +/- 0.6 wt.% for Ca and Mg; Ca and Mg contents were converted from wt.% to mol% and corrected to sum to 100%. Relative standard deviation for Sr analyses was +/- ~8 ppm and for Mn analyses was ~1 ppm. A Cameca SX-50 Electron Probe Microanalyzer (40° takeoff angle, beam of 15 keV and 20 nA and diameter 1.9 μm ; analytical error less than +/- 0.9 mol%) was used to define Ca and Mg content along traverses of about 35 dolomite crystals from seven dolomites. Chemical maps of Ca and Mg within crystals also were made. SEM back-scattered electron (BSE) images of 16 samples (including the microprobed samples) were done with a CamScan Series II Scanning Electron Microscope (20 kV and a working distance of 35 mm); abundance of high-Ca dolomite and low-Ca dolomite phases were estimated with ImageJ software. X-ray diffraction analysis using a Rigaku Miniflex-II X-ray diffractometer ($\text{CuK}\alpha$ radiation at 30kV and 15 mA) was done on twelve dolomites to define degree of lattice ordering using intensity ratio $I(015)/I(110)$ (Füchtbauer and Goldschmidt, 1965; Tucker and Wright, 1990; Andreeva et al., 2011; Jones *et al.*, 2001).

Carbon- and oxygen isotope analyses (reported as VPDB) of 150 bulk dolomite samples, along with about 100 undolomitized lime mudstones (Saltzman, 2002; Immenhauser et al., 2002) were obtained with a bench-mounted dental drill, and analyzed by H. Spero's Stable Isotope Laboratory, University of California Davis, U.S.A. (uncertainties of +/-0.04 ‰ for $\delta^{13}\text{C}$ and +/-

0.06 ‰ for $\delta^{18}\text{O}$). Individual dolomite crystal zones were too small to be micro-sampled. Given its uncertainty (Crowley et al., 2008), no dolomite-phosphoric acid correction was applied. Strontium isotope analyses were done on 5 Jurassic and 11 Cretaceous dolomite samples by Kreuger Geochemistry Laboratories, Billerica, Massachusetts, USA (uncertainties of ± 0.000008). Fluid inclusions from two typical dolomite samples containing rare late calcite veins were examined by Fluid Inclusion Technologies, Inc. staff, Broken Arrow, Oklahoma, USA. Correlation coefficients (R values) were computed for geochemical cross-plots with a qualitative scale of R < 0.3 being poor, 0.3 to 0.5 fair, 0.5 to 0.7 good, 0.7 to 0.9 very good and > 0.9 excellent. The student's t-test for two-sided distribution was used to compute significance, and confidence levels are only mentioned in the text where they were below 95%. Trend lines are least squares regression lines.

The $\delta^{18}\text{O}$ water values of the Late Jurassic lime muds were calculated using temperature dependent calcite-water fractionation equation of Friedman and O'Neil, (1977). The $\delta^{18}\text{O}$ water values of the dolomites were calculated using: $1000 \ln \alpha_{\text{Dolomite-water}} = 2.78 \times 10^6 T^{-2} + 0.91$, where T is temperature in degrees K; the constant includes addition of 0.8‰ to offset the dolomite-phosphoric acid fractionation factor (Fritz and Smith, 1970; Land, 1983; Suzuki et al., 2006). The equation of Vasconcelos et al. (2005) was not used as the bulk of the dolomites were not bacterially mediated protodolomites. Before plotting on the dolomite-temperature water graph, dolomite $\delta^{18}\text{O}$ was corrected for stoichiometric effects using: $(\text{Ca mol}\%) \times 0.17 - 8.5$, to account for the decrease of $\sim 0.17\%$ /mol% Ca relative to stoichiometric dolomite, the 0.17 being a conservative average value (~ 0.1 to perhaps ~ 0.2 , Vahrenkamp and Swart, 1994; ~ 0.2 , Wheeler et al., 1999; ~ 0.15 , Suzuki et al., 2006; ~ 0.26 , Zhao and Jones, 2012b). No stoichiometric correction was applied for dolomite-phosphoric acid fractionation (Zhao and Jones, 2012b) as it

is relatively small. Sr/Ca ratios of fluids were estimated using a $D_{\text{Sr}}^{\text{dol}}$ of 0.012 for a stoichiometric dolomite, with the coefficient increasing 0.0039/mol% Ca in the dolomite (Vahrenkamp and Swart, 1994). A concentration of 0.0003 ppm Mn in modern surface seawater and K_{Mn} of dolomite between 6 and 35 (Veizer, 1983; Donat and Bruland, 1995) was used to estimate Mn concentration in dolomite from seawater, adjusted for higher Ca contents of calcite seas (Stanley and Hardie, 1999).

4. Results

4.1 Field occurrence of the dolomites

The Upper Jurassic dolomites from the BK section near Dubrovnik occur on the lower thrust sheet of the High Karst Zone of the platform within about 50 km of the up-dip terminus of the pelagic Budva Basin re-entrant (Fig. 1B, 3A). Given the estimated 200 km of shortening between the offshore Dalmatian Zone (with its western platform edge) and the mainland High Karst Zone (de Leeuw et al., 2012), the section could have been at least this far from the main southwestern margin. The Lower Cretaceous Hauterivian, Valanginian and Barremian dolomites from C sections on Korčula I., occupy an anticlinal high bounded by thrust and oppositely vergent reverse faults, within the autochthonous Dalmatian Zone of the platform; it lay about 50 km from the southwestern platform margin (Figs 1B, 3B-D). Biostratigraphic control for both Upper Jurassic Tithonian and Lower Cretaceous Hauterivian-Barremian strata is based on well-described dasycladacean and bethic foraminifera biozones (e.g., Velić, 1977, 2007; Velić and Sokač, 1978; Husinec et al., 2000; Husinec and Sokač, 2006, Cvetko et al., 2011).

Some of the fabric destructive dolomites are from cyclic laminate-capped peritidal units (Upper Jurassic BKI section, Lower Cretaceous CSI section, Fig. 3A, C) whereas others are from

197 poorly cyclic subtidal carbonates (Lower Cretaceous CI and CAI sections; Fig. 3B, D), the facies
198 of which are described in Tišljär et al. (2002), Vlahović et al. (2005), Husinec and Read (2006,
199 2007, 2011), and Husinec et al. (2012). Parasequences occur in bundles of 4 to 6 parasequences,
200 suggestive of weak precession-eccentricity forcing and make up 3rd-order sequences bounded by
201 subaerial exposure breccias (Husinec and Read, 2007; Husinec et al., 2012). Most of these
202 dolomitized interior platform carbonates appear to have been low energy, interior platform
203 mudstone-wackestone, with only a few packstone-grainstone interbeds (Fig. 3), although
204 recognition of protoliths of the fabric destructive dolomites is commonly difficult. Evaporites are
205 absent from the Jurassic-Cretaceous of the study area, although Early Cretaceous sabkha cycles
206 occur in onshore and offshore wells 200 km to the northwest of the study area (Tišljär et al.,
207 2002). Rip-ups of dolomite are not observed above parasequence boundaries. Exposure breccias
208 are common near 3rd-order sequence boundaries (Fig. 3) and typically rest on irregular erosion
209 surfaces of underlying carbonates, are up to 10 cm thick, and generally consist of angular to
210 rounded, 0.5 to 10 cm diameter lithoclasts of subjacent limestones, commonly in a green gray,
211 argillaceous dolomite matrix (Tišljär et al., 2002).

212 The studied dolomites (Figs 2B, 3) occur as discontinuous to continuous units from a
213 meter to 100 meters or more thick, some of which are mappable over tens of kilometers, and
214 typically are medium to coarse grained (20 to 500 µm). Contacts with underlying or overlying
215 host limestone range from sharp to gradational (over a few centimeters). Dolomite units are
216 grossly conformable to bedding, and a few can be seen in the field to pass laterally along strike
217 into limestone. Dolomite- and calcite veins are relatively rare in the dolomites, except adjacent to
218 reverse faults or associated with thin zones of late dolomitization. Coarse grained *non-saddle*
219 dolomite line and fill some fractures; late burial saddle dolomite has not been observed. Coarse

clear calcite occur as poikilitic intercrystal cement in some dolomites, and post-date dolomite in fractures; the calcite vein fills have rare secondary(?) inclusions of yellow fluorescent oil. Calcite as dedolomite generally is a rare and volumetrically minor phase.

4.2 Petrography, major element geochemistry and ordering of the dolomites

Fine-grained (<20 μm) dolomites are rare (5% of all samples; Tišljär et al., 2002) and make up only 8% of the microbially laminated dolomites. Most dololaminites (92%) faintly preserve sedimentary layering, and consist of alternating faint layers of medium-grained (20 to 100 μm) and coarse euhedral to anhedral dolomite (Fig. 4A). They are petrographically and geochemically similar to the other medium and coarse grained dolomites, described below.

Medium (20 to 100 μm) to coarse (>100 μm), massive, dominantly *fabric destructive* dolomites (Tišljär et al., 2002) are the main dolomite type (88% of samples) and consist of euhedral to subhedral dolomite crystals with turbid cores overgrown by inclusion free, clear dolomite rims (Fig. 4B). A few samples (7%) consist of fine to coarse dolomite with faint ghosts of original grains such as ooids or peloids, or leached grains outlined with fine dolomite and filled with a coarse grained dolomite (Fig. 4C). Most dolomites typically have little porosity; the apparent abundance of intercrystal pores illustrated in Figure 7 reflects selective sampling for microprobe traverses into pores.

SEM back-scattered electron (BSE) images when tied to the microprobe data and Ca-Mg element maps of dolomites, show the dolomites are composed of high-Ca dolomite (HCD; light colored under BSE; ~ 53 to $\sim 58 \pm 0.9$ mol% Ca), and a later low-Ca dolomite (LCD; darker under BSE; from 48 to ~ 53 mol% Ca) (Figs 5, 6). The $\sim 53 \pm 0.9$ mol% boundary (defined by electron microprobe) between HCD and LCD under BSE is similar to that determined by Drits et

al. (2005), but is lower than that determined by Jones (2007). The cutoff between HCD-rich and LCD-rich *bulk dolomites* was also made at 53 mol% Ca.

There are possibly 4 dolomite phases under BSE; *HCD turbid crystal cores*, less calcic *HCD rims*, and LCD which overgrows earlier crystals and variably replaces cores; LCD can be separated geochemically (discussed later) into *LCD-1* and a late stage *LCD-2* that also fills microfractures, and is associated with faults and fractures in the field (Fig. 6C, D). Intensity ratios of X-ray peaks I(015)/(110) (Füchtbauer and Goldschmidt, 1965; Andreeva et al., 2011) for twelve dolomites show that they are moderately ordered (Fig. 7A; average 0.5, range 0.25 to 0.62).

4.2.1 High Ca-dolomite (HCD)

HCD-rich dolomites (>53 mol% Ca) show order ratios of 0.25 to 0.5 (Fig. 7A). HCD with Ca contents of 55 to 58 mol% makes up turbid dolomite cores (Figs 4A, B, 6A, C, F) which commonly contain micropores, and some have micron sized calcite inclusions (Fig. 6A, C). Turbid cores are overgrown with a limpid, inclusion-free HCD (Fig. 6A-F) that tends to have slightly lower Ca content (mean of ~54 mol% Ca) than cores. Away from pores, HCD rims form compromise crystal boundaries within subhedral to anhedral mosaics (Figs 4A, 6A, C). Manganese for the bulk dolomites is very low with a mean of 9 ppm and generally ranges from 3 to 15 ppm (Table 1).

Most (82%) Upper Jurassic dolomites are dominantly HCD with Ca >53 mol% (Fig. 5A, C). This is supported by BSE images, in which HCD makes up on average 80% by volume of Upper Jurassic samples. Sr in Jurassic bulk samples (dominantly HCD), ranges from 90 to 206 ppm (Fig. 7A). Upper Jurassic HCD rich samples have $\delta^{13}\text{C}$ values of 0 to +1.5‰ VPDB, and

$\delta^{18}\text{O}$ values of +1 to +3.2‰ VPDB (Fig. 8A) with a mode around 2.5‰ VPDB (Fig. 8C). The $\delta^{18}\text{O}$ values of the Jurassic dolomites on chemostratigraphic profiles tend to fluctuate within a limited range of +1 to +3‰ VPDB (Fig. 3A). The $^{87/86}\text{Sr}$ values of Upper Jurassic HCD-rich samples range from 0.707061 to 0.707323 (Fig. 10; Table 1) which span the range of $^{87/86}\text{Sr}$ values from coeval seawater to slightly elevated values (Figs 10, 11A).

Only about 36% of Lower Cretaceous dolomites are HCD-rich with $\text{Ca} > 53$ mol% (Fig. 5B, D). This is supported by BSE images, in which HCD averages only ~50% by volume of Lower Cretaceous dolomites. Sr in the Cretaceous HCD-rich bulk samples ranges from 90 to 190 ppm (Fig. 7C). Lower Cretaceous HCD-rich samples have $\delta^{13}\text{C}$ values of -0.3 to +2‰ VPDB. Cretaceous HCD and LCD have similar $\delta^{18}\text{O}$ modal values around +2‰ VPDB (Fig. 8D) with most Cretaceous HCD having $\delta^{18}\text{O}$ values from +1 to 2.6‰ VPDB. The $\delta^{18}\text{O}$ values of the Cretaceous bulk dolomites on chemostratigraphic profiles tend to fluctuate between +1 to +2.6‰ VPDB; except where there is evidence of significant later alteration associated with dolomite veins, boxworks, or faults, which are marked by $\delta^{18}\text{O}$ excursions from below +1 to -1.3‰ VPDB (25% of Cretaceous HCD samples; Fig. 3B, C, D). The $^{87/86}\text{Sr}$ values of Lower Cretaceous bulk HCD-rich samples ($n=2$) range from 0.707385 to 0.707721 spanning the range from coeval seawater to elevated values (Fig. 10; Table 1).

4.2.2 Low-Ca dolomite (LCD)

LCD-rich bulk dolomites (48 to 53 mol% Ca) have order ratios of 0.4 to 0.6 (Fig. 7A). LCD forms clear dolomite overgrowths on the earlier HCD rims, especially in Lower Cretaceous samples (Fig. 6). Contacts between overgrowths of earlier HCD and later LCD are commonly sharp and less commonly gradational (Fig. 6A-E), or rarely interbanded (Fig. 6B).

LCD variably replaces earlier HCD cores (Fig. 6B, C) particularly in Lower Cretaceous samples and less commonly in Upper Jurassic samples. Replacement LCD ranges from small patches (few μm) that commonly interconnect via microfractures to form arborescent areas within the HCD to relatively continuous masses comprising the bulk of the cores, in which small blebs of original HCD occur (Fig. 6B, C). Some rhomboidal cores of LCD are encased within HCD rims with ragged interior boundaries (Fig. 6E, F; cf., Fouke, 1994; Jones and Luth, 2003). In HCD-rich samples, LCD also forms rare thin irregular replacement (?) zones along compromise crystal boundaries. Rarely, the latest phase of LCD replaces parts of some HCD rims (Fig. 7D) and also fills microfractures (Fig. 6C, D).

Mn in LCD-rich samples is low (4-15 ppm), with three samples with slightly higher values (20-33 ppm). Fluid inclusions in the Croatian dolomite cement overgrowths were too small to be measured but they are all single phase. They could not be artificially stretched with heating, thus they did not yield melting temperatures. Based on the geochemistry (Figs 7-11), LCD is subdivided into LCD-1 and LCD-2. LCD-1 generally has 51 to 53 mol% Ca, $\delta^{18}\text{O} > +1\text{‰}$ VPDB, Sr > 100 ppm, and $^{87/86}\text{Sr}$ near-marine values. LCD-2 typically has Ca between 48 and 51 mol% Ca, more negative $\delta^{18}\text{O}$ values ($< +1$, but up to $+2$ in the most Mg-rich samples), Sr typically < 100 ppm, and $^{87/86}\text{Sr}$ elevated relative to seawater values. Ordering ratios for LCD-1 and LCD-2 are similar and on average slightly higher than HCD (Fig. 7A).

Only a few (18%) Upper Jurassic samples are LCD-rich < 53 mol%Ca (Fig. 5A, C) and this is LCD-1. Sr in Upper Jurassic LCD-1 samples ranges from 100 to 190 ppm (similar to HCD; Fig. 7B). Jurassic LCD-1 rich samples have $\delta^{13}\text{C}$ values of $+0.5$ to $+1.5\text{‰}$ VPDB, and $\delta^{18}\text{O}$ values $+1.25$ to $+3\text{‰}$ VPDB (Fig. 8A). The two Jurassic LCD-1 samples analyzed for $^{87/86}\text{Sr}$ had slightly elevated $^{87/86}\text{Sr}$ values relative to roughly contemporaneous seawater (Fig.

11C).

A majority (64%) of Lower Cretaceous samples are LCD-rich <53 mol% Ca (Fig. 5B, D). Lower Cretaceous dolomites average ~50% LCD by volume (determined by BSE images and XRD) and in a few samples LCD is over 90%. Statistics for Cretaceous LCD on crossplots (Figs. 7-11) are based on LCD-1 and LCD-2 grouped together unless otherwise stated. Lower Cretaceous LCD-rich samples commonly are variable mixes of LCD-1 and LCD-2 and lesser HCD. Cretaceous LCD-1 has similar composition to Jurassic LCD-1, with 51 to 53 mol% Ca, Sr from 100 to 175 ppm (Fig. 7C, 9D), $\delta^{18}\text{O}$ +1 to +3.5‰ VPDB (Fig. 8B; 9B, D), and near-marine $^{87/86}\text{Sr}$ values (Fig. 11B, D, F). LCD-2 has between 48 and 52 mol% Ca and Sr from 60 to 100 ppm (rarely reaching 150 ppm in some more Ca-rich LCD-2; Figs 7C, 9D). LCD-2 $\delta^{18}\text{O}$ values generally are from -0.6 to +1‰ VPDB (Fig. 8B, D), but reaching +2‰ VPDB in the most Mg-rich samples (Fig. 9C). LCD-2 has $^{87/86}\text{Sr}$ values elevated relative to seawater values (Fig. 11B, D, F). In the field, ^{18}O -depleted, near stoichiometric LCD-2 rich samples are commonly associated with narrow zones (1 to 3m) with fracturing, brecciation and boxworks, which on chemostratigraphic profiles show negative excursions of $\delta^{18}\text{O}$ below +1‰ VPDB (LCD-2 rich zones) whereas $\delta^{13}\text{C}$ values are variable across the zones (Fig. 3C, D). Vein filling dolomite from a small reverse fault (Fig. 3D, middle of CAI section) had average $\delta^{13}\text{C}$ values of +1.4‰ VPDB, and average $\delta^{18}\text{O}$ values near 0‰ VPDB typical of LCD-2 (Fig. 9B).

5. Interpretation

Most of the data is from the analysis of bulk dolomites, and so reflects a component of *physical mixing* of dolomites. Mixing of HCD and LCD populations is less a problem in the Upper Jurassic samples (dominantly HCD with lesser LCD-1), but is important in the Lower

Cretaceous samples that commonly are admixtures of HCD and LCD-1, while others also are admixed with LCD-2.

5.1 Precursor sediments and their C-O isotopic compositions

The Croatian precursor sediments likely were low-Mg calcite reflecting low molar Mg/Ca ratios below 2 for Late Jurassic to mid-Cretaceous ocean water (Stanley and Hardie, 1999). Primary calcite mineralogy is supported by lack of moldic fabrics and vugs (Husinec and Read, 2007), and dominance of fabric-destructive as opposed to fabric retentive dolomite (Sibley 1982; Dawans and Swart, 1988; Budd, 1997; Wheeler et al., 1999; Zhao and Jones 2012a).

Published $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data show that Upper Jurassic *open-marine* calcites (hemipelagic limestones and belemnites) have similar ranges to the Lower Cretaceous (Fig. 8; Veizer *et al.*, 1999; Weissert and Erba, 2004; McArthur et al., 2007; Malkoc and Mutterlose, 2010). Most (85%) of the C- and O-isotope values for Croatian *Upper Jurassic platform* lime mudstones lie within the published open marine calcite field (Fig. 8A), suggesting that they compacted and lithified in marine phreatic pore waters. Using tropical surface seawater temperatures during the greenhouse Late Jurassic-Early Cretaceous of about 25 to 33°C, ~3°C above the seasonal range of Bahama seawater (Cloud, 1962, p. 14; Frakes et al. 1992; Golonka, 2002; Royer et al. 2004; their Figure 4), would suggest Upper Jurassic lime mudstones formed from ~-0.4 to +4‰ SMOW waters. Comparison to modern Bahamian platform waters suggests that the Upper Jurassic marine waters were normal to mesohaline (to perhaps hypersaline) concentrated by evaporation but below gypsum precipitation (Lloyd, 1966; Swart et al. 2009) under semi-arid climate (Fig. 2C; Ruffel and Rawson, 1994; Scotese, 2002; Wilkinson and Riding, 2007). The few ^{13}C - and ^{18}O -depleted Jurassic lime mudstones likely were modified by

late stage synorogenic fluids (discussed later), whereas most Jurassic lime mudstones by this stage were impermeable.

Most Croatian *Lower Cretaceous* lime mudstones have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values outside the coeval open marine calcite field (Fig. 8B). If they had ~40% average microporosity after initial compaction-dewatering (Scholle and Halley, 1985), this could have been partly filled by ^{13}C - and ^{18}O -depleted meteoric cement deposited during intermittently humid climates of the Lower Cretaceous (Lohmann, 1988; Ruffel and Rawson, 1994; Scotese, 2002), with common exposure breccias (Fig. 2A) acting as meteoric recharge surfaces. If Cretaceous lime mudstones retained up to 20% remnant microporosity at maximum burial of 2 km (Scholle and Halley, 1985), this could have been subsequently filled by synorogenic late calcite cement ($\delta^{18}\text{O} \sim -6\text{‰}$ VPDB; Galluccio, 2009; Ronchi et al., 2011). The small negative shift in $\delta^{13}\text{C}$ values could reflect oxidation of small amounts of organic carbon, petroleum migration (Heydari, 1997), and/or a meteoric component of late stage fluids (Lohmann, 1988; Ronchi et al., 2011). The relatively heavy $\delta^{18}\text{O}$ values of the outcropping now impermeable lime mudstones reflects the relatively short time in the burial regime <2 km (Saltzman, 2002; Immenhauser et al., 2002; Machel, 2005; Vahrenkamp, 2010; Ronchi et al., 2011; Fig. 1D).

5.2 Laminated dolomites – peritidal vs. post-depositional overprint

Relatively few of the Jurassic-Cretaceous laminites were dolomitized in peritidal settings (Tišljarić et al., 2002) from microbially mediated, hypersaline waters with elevated Mg/Ca ratios (McKenzie, 1981; Vasconcelos et al., 2005; Bontognali et al., 2010). The positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the laminated dolomites are similar to Holocene and little modified ancient peritidal dolomites (McKenzie, 1981; Patterson and Kinsman, 1982; Balog et al., 1999; Rameil, 2008;

Bontognali et al., 2010) as well as post-depositional dolomites. Critically, grain size of laminated dolomites is generally much coarser than typical fine grained peritidal dolomite, their high Ca contents (53 to 58 mol% Ca) also are similar to the post-depositional dolomites, as are their Sr contents (50 to 250 ppm) which are much lower than Holocene microbial dolomites (500 to 1000 ppm or more Sr; Patterson and Kinsman, 1982; Bontognali et al., 2010; Sánchez-Román et al., 2011). Thus although a few dolomites may have started to form in peritidal settings, they coarsened during post-depositional dolomitization and their geochemistry reflects this. The remainder of the discussion thus will focus on the more abundant medium- and coarse-grained dolomites (20 to over 100 μm crystals).

5.3 Formation of the post-depositional high-Ca dolomites

The BSE images (Fig. 6) indicate that HCD formed earlier, at shallower depths and lower temperatures than LCD, given the relatively rapid subsidence rates (Fig. 1D). The high $\delta^{18}\text{O}$ values (Fig. 8) and Sr values (100 to ~ 200 ppm) of the Jurassic-Cretaceous HCD (Fig. 7) overlap the ranges of Neogene platform dolomites that generally have never been buried deeper than 500 m (Fig. 8; Aharon et al., 1987; Hein et al., 1992; Vahrenkamp and Swart, 1994; Budd, 1997; Wheeler et al., 1999; Suzuki et al., 2006; Zhao and Jones, 2012b). Their low to moderate ordering and single phase fluid inclusions all support Jurassic-Cretaceous HCD forming in near surface marine-dominated pore fluids (cf., Hird, 1985, in Tucker and Wright, 1990, p. 371; Galluccio, 2009; Ianace et al., 2011; Andreeva et al., 2011; Meister et al., 2013). Given that dolomite should be enriched in ^{13}C relative to co-existing calcites (Chacko et al., 2001), the similar ranges of $\delta^{13}\text{C}$ values of bulk dolomites with coeval lime mudstones suggest waters were only partly rock buffered by precursor sediment (Fig. 8A; cf., Budd, 1997). During HCD

formation, carbonate and Ca^{2+} ions were mainly sourced from dissolution of calcite, but Mg^{2+} ions were supplied by marine pore fluids (Kaczmarek and Sibley, 2011). As dolomitization slowed with increasing shallow burial, turbid HCD cores were variably overgrown by more stable clear HCD rims with slightly lower Ca contents, either as dolomite cement in grainstones or by replacement of lime mud in muddy carbonates (Choquette and Hiatt, 2008). The low Mn concentrations of all the Croatian dolomites (mean of 9 ppm) are consistent with their lack of cathodoluminescence, relatively near-surface oxidizing pore waters, low organic content of the predominantly light colored Croatian carbonates and limited Mn source on this isolated platform. The mean Mn value for the Croatian dolomites is slightly higher than calculated Mn contents (1 to 6 ppm) of a dolomite from seawater, and given the uncertainties (Kester and Pytkowicz, 1969; Byrne, 2002), suggests that dolomitizing marine pore waters had slightly elevated Mn/Ca ratios.

5.3.1 Jurassic high-Ca dolomites

The +1 and +3‰ difference in $\delta^{18}\text{O}$ between the Upper Jurassic dolomites and coeval marine calcites (Fig. 8A) is compatible with the $\Delta^{18}\text{O}_{\text{dol-cal}}$ of +3 to +4‰, (Tucker and Wright, 1990, p. 382-386; Budd, 1997; Vasconcelos et al. 2005) suggesting that they formed from similar marine waters and temperatures. Jurassic HCD-rich samples when corrected for stoichiometric effects (see methods) would require refluxing pore waters between +1 to about +4.5‰ SMOW at 25 to 33°C (Fig. 12) only slightly more enriched than those forming the Jurassic lime mudstones. This suggests marine to mesohaline waters formed by evaporation under relatively arid climate (Fig. 2C; cf. Sun and Estaban, 1994) and salinities from 35 to below 60 p.s.u., well below the onset of gypsum precipitation (cf., Lloyd, 1966; Li et al., 2015). Part of the negative shift in $\delta^{18}\text{O}$ of the Jurassic dolomites relative to the Neogene platform dolomite field (Fig. 9A) could be due

to scarcity of polar ice in the Late Jurassic and the higher temperatures of greenhouse seas (Price, 1999; Royer et al., 2004), along with a small burial diagenetic overprint. The relatively minor fluctuations of $\delta^{18}\text{O}$ on chemostratigraphic profiles of the Jurassic HCD (Fig. 9F) suggests that most have been little modified by later fluids.

Sr content (100 to ~200 ppm) of Jurassic HCD with 53 to about 55 mol% Ca lies within the Neogene platform dolomite field (Fig. 7B), indicating retention of Sr. Using 150 ppm average Sr value for 53 mol% HCD, and 200 ppm Sr for a typical maximum value (Fig. 7A, B) gives fluid Sr/Ca ratios of ~7 to 17 mmol/mol, which exceed the 3 to 9 mmol/mol Sr/Ca for Jurassic open-ocean water (Steuber and Veizer, 2002; Holmden and Hudson, 2003; Coggon et al., 2010). The elevated Sr/Ca ratios reflect the D_{Sr} for dolomite and calcite $\ll 1$, evaporative concentration of waters that had precipitated low Sr calcite muds prior to reflux (cf. Cloud, 1962), Sr from small amounts of algal or molluscan aragonite and increase in Sr/Ca ratios with shallow burial depth (Swart, 2015). These HCD-rich samples (53 and 55 mol% Ca) that retained their Sr values also have more positive $\delta^{18}\text{O}$ (Fig. 9B, D) supporting formation and stabilization in marine fluids (with high effective Sr/Ca and enriched in ^{18}O).

The more Ca-rich phases of HCD (55 to 58 mol% Ca) likely had higher initial Sr due to increase in $D_{\text{Sr}}^{\text{dol}}$ with increasing mol% Ca (Vahrenkamp and Swart, 1994; Fig. 7B), but because they were less stable than more stoichiometric dolomites, they lost Sr during maturation. This converted any original *positive* correlation between Ca and Sr (Vahrenkamp and Swart, 1994) into the negative correlation for HCD (Fig. 7). Sr loss likely occurred in pore fluids with lowered effective Sr/Ca ratios, perhaps due to addition of Ca^{2+} (from replacement dolomitization or calcite dissolution) or due to slightly increased temperatures (Banner, 1995) that decreased Sr uptake by dolomite (due to increased SrHCO_3^+ ion pairing, while CaHCO_3^+ ion pairing remained

unaffected; Banner, 1995). Sr removal from microporous HCD crystal cores also could have been aided by Sr diffusion via pore fluids (Pingatore, 1982; Richter and Liang, 1993). The loss of Sr from HCD-rich samples with Ca >55mol% (Fig. 7A) also destroyed any original *negative* correlation between Sr and $\delta^{18}\text{O}$ (cf., Zhao and Jones, 2012a), the more negative $\delta^{18}\text{O}$ values of the low Sr HCD reflecting slightly higher temperatures.

The $^{87/86}\text{Sr}$ data on the bulk dolomites compared to the Sr-isotope sea-level curve (Fig. 10) supports the earlier age for the Upper Jurassic dolomites compared to the Lower Cretaceous dolomites. Two of the three Jurassic HCD samples have Tithonian seawater $^{87/86}\text{Sr}$ values (Figs 10, 11A; cf., Paull et al., 1995; Swart et al., 2001), along with the expected high $\delta^{18}\text{O}$ but only the one with the lowest $^{87/86}\text{Sr}$ (Tithonian seawater) has the expected high Sr (low 1/Sr; Fig. 11 C, E). The Jurassic HCD trend of decreasing Ca, Sr and $\delta^{18}\text{O}$ with increasing $^{87/86}\text{Sr}$ (Fig. 11A, C, E) strongly suggests that the “altered” HCD with more radiogenic $^{87/86}\text{Sr}$ has undergone greater recrystallization in ^{87}Sr -enriched waters without being converted to LCD. This most likely occurred during late stage synorogenic fluid migration, discussed later. The lower effective Sr/Ca ratios of these later fluids probably reflect the warmer temperatures and slower rates of dolomitization (Katz and Matthews, 1977; Banner, 1995), the higher temperature also giving more negative $\delta^{18}\text{O}$ dolomite.

5.3.2 Lower Cretaceous high-Ca dolomites

The relatively little altered Jurassic dolomites provide a baseline against which the more heavily altered Cretaceous dolomites can be compared (Figs 8, 9). The relatively high $\delta^{18}\text{O}$ (+1 to +3‰ VPDB) and $\delta^{13}\text{C}$ (0 to +2‰ VPDB) values of ~75% of the preserved Cretaceous HCD resemble the Jurassic HCD (Figs 7-10), thus they likely formed from similar marine-dominated

pore fluids (Fig. 12A, B). Sabkha-type evaporites some 200 km to the northwest attest to periods of aridity and evaporatively concentrated waters on the Early Cretaceous platform (Tišljär et al., 2002; Fig. 2C). The more negative $\delta^{18}\text{O}$ values of the remaining 25% of Cretaceous HCD (“altered” HCD) could be due to the more humid climate and lower salinity of refluxing platform waters, or recrystallization in lower mixing zone waters (Cander, 1994; Gaswirth et al., 2007). However the common association of these samples with faulting and fracturing, and the good negative correlation ($R = -0.6$) between Ca and $\delta^{18}\text{O}$ of “altered” HCD and LCD-2 (Fig. 9C) suggests that they formed by recrystallization in Cenozoic synorogenic fluids, which also deposited ^{18}O -depleted dolomite (LCD-2; discussed later). The $^{87/86}\text{Sr}$ values of Cretaceous HCD (only 2 samples) again suggest, while some HCD retained marine $^{87/86}\text{Sr}$ values, the “altered” HCD (Fig. 11B, D, E) retained their high Ca compositions but recrystallized in synorogenic(?) pore fluids that were more radiogenic than coeval seawater. Low to moderate ordering of Cretaceous HCD, typical of near surface to shallow subsurface dolomites (cf., Hird, 1985, in Tucker and Wright, 1990, p.371; Andreeva et al., 2011), was maintained, indicating that the ordering of most HCD was not much modified by later burial warm fluids.

5.4 Formation of the low-Ca dolomites

The BSE images show that LCD formed after HCD, at slightly greater depths and temperatures given the relatively rapid subsidence rates (Fig. 1D). However the local fine interbanding of HCD with LCD suggests that their depth and temperature ranges overlapped. That many LCD-rich samples formed at relatively shallow subsurface depths from a few hundred meters to 1km, between ~ 30 to 50°C is suggested by abundant single phase fluid inclusions in the dolomites (Goldstein, 2001), lack of high temperature saddle dolomites, generally positive

$\delta^{18}\text{O}$ (cf., Galluccio, 2009; Ianace et al., 2011; Meister et al., 2013), and moderate degree of ordering (0.4 to 0.6) below the range of late diagenetic dolomites (Hird, 1966, in Tucker and Wright, 1990, p. 371; Andreeva et al., 2011). Given that the LCD formed at greater subsurface depths (and hence perhaps slightly more reducing conditions) than HCD, the low Mn contents (and nonluminescent character) of the LCD-rich samples reflects a limited Mn reservoir typical of an isolated platform. Microscale replacement of earlier HCD by LCD was not controlled by bulk solution (S. Kaczmarek, pers. comm., 2014) and required addition of only small amounts of Mg^{2+} ions; the bulk of the Mg and carbonate ions being supplied by HCD dissolution (cf., Kaczmarek and Sibley, 2007; 2011). In contrast, the common Cretaceous LCD *cements* required addition of substantial amounts of Ca^{2+} , Mg^{2+} and carbonate ions and thus these sediments needed to be permeable prior to porosity loss by “overdolomitization” (Choquette and Hiatt, 2008).

5.4.1 Jurassic low-Ca dolomite LCD-1

Given the $\delta^{18}\text{O}$ range of +1 to +3‰ VPDB for the Jurassic LCD-1-rich samples (Fig. 9A), corrected for stoichiometric effects (see methods), and assumed temperatures between 30 to about 40 °C or so, then it could have formed from evaporated marine waters of +2 to >+5‰ SMOW (Fig. 12A), compatible with the arid climate, coupled with water-rock reaction with isotopically heavier carbonates (Lloyd, 1966; Heydari, 1997). The $^{87/86}\text{Sr}$ values of the two Jurassic LCD-1 rich samples are only slightly elevated relative to coeval Tithonian seawater values (Figs 10, 11A, C, E), supporting formation from modified marine fluids that gained some ^{87}Sr perhaps from slowly convecting deeper pore fluids (Fig. 9B). Nevertheless, their high Ca composition, high Sr >100 ppm, positive $\delta^{18}\text{O}$ values, in conjunction with only slightly elevated

^{87/86}Sr are suggestive of Jurassic LCD-1 having mainly formed in refluxing modified marine fluids at shallow depths (<300 m), with effective Sr in the LCD decreasing with increasing temperature, the ~2‰ range in $\delta^{18}\text{O}$ reflecting differences in temperature and/or $\delta^{18}\text{O}$ of fluids. The overall scarcity of Jurassic LCD-1 and absence of LCD-2 probably reflects the semi-arid climate that promoted early porosity occlusion by HCD resulting in Jurassic dolomites that were impermeable to later fluids.

5.4.2 Cretaceous Low-Ca Dolomite LCD-1

Cretaceous LCD-1 which generally has Sr, $\delta^{18}\text{O}$ and ^{87/86}Sr values compatible with marine-derived pore fluids (Figs. 7-11), likely formed at burial depths of <0.3 km with temperatures between ~30 to 40 °C (Cander, 1994; Budd, 1997; Jones et al., 2004; Gaswirth et al., 2007). At these temperatures, Cretaceous LCD-1 samples ($\delta^{18}\text{O}$ ranges between +1 to +3‰ VPDB; Fig. 8B), if corrected for stoichiometric effects (see methods), could have formed from marine-dominated pore waters of +1 to >+5‰ SMOW (Fig. 11A, B), compatible with periods of reflux dolomitization during intermittent arid phases (Fig. 2C), and with refluxing fluids having reacted with isotopically heavier carbonates (Lloyd, 1966; Heydari, 1997). The positive correlation between $\delta^{18}\text{O}$ vs. mol% Ca for Cretaceous LCD ungrouped data (Fig. 9C) is consistent with the more *Ca-rich* LCD-1 forming at lower temperatures than *Ca-poor* phases of LCD-2 (cf., Dawans and Swart, 1988; Zhao and Jones, 2012b).

LCD retained much original Sr, as indicated by the good positive correlation between Sr and mol% Ca for ungrouped LCD ($R=0.77$; Fig. 7C), which is compatible with the increase in $D^{\text{Sr}}_{\text{dol}}$ with increasing mol% Ca (Vahrenkamp and Swart, 1990) and decrease in effective Sr/Ca ratios with increasing temperature from LCD-1 to LCD-2 deposition (Banner 1995). Similarly,

the fair positive correlation between total Sr and $\delta^{18}\text{O}$ in ungrouped LCD samples ($R=0.41$; Fig. 9D) is primary. The *Ca-rich* LCD-1 samples (51 to 53 mol% Ca, Sr contents >100 ppm; Fig. 7C) with their relatively positive $\delta^{18}\text{O}$ (Fig. 9C, D) are similar to little altered HCD (Ca between 53 and 55 mol%), and so likely formed from similar marine fluids, perhaps at slightly greater depths and slightly warmer temperatures, offset by increased Sr/Ca ratios and increased $\delta^{18}\text{O}$ values of the deeper pore fluids (Swart, 2015). The rare *Ca-poor* LCD-1 samples have Sr values <100 ppm more typical of burial dolomites (Fig. 7C; Veizer, 1983), and may have formed at slightly greater depths and temperatures than more Ca-rich LCD-1; the low Sr contents probably reflect a combination of decreasing $D^{\text{Sr}}_{\text{dol}}$ with decreasing mol% Ca, and lower *effective* Sr/Ca ratios in fluids with increasing temperature (Banner, 1995), while the positive $\delta^{18}\text{O}$ values (Fig. 9D) support relatively shallow depths and marine pore fluids.

Cretaceous LCD samples (ungrouped) show good negative correlation between $^{87/86}\text{Sr}$ vs. Ca mol%, $1/\text{Sr}$ and $\delta^{18}\text{O}$ (Fig. 11B, D, F) supporting formation of Cretaceous LCD-1 from slightly lower temperature undiluted marine pore fluids than later LCD-2. Thus much Cretaceous HCD was stabilized via replacement by and precipitation of LCD-1 in marine-dominated pore fluids (cf., Suzuki et al., 2006; Jones, 2007; Zhao and Jones, 2012a, b; Cander, 1993; Gaswirth et al., 2007).

5.4.3 Cretaceous Low-Ca Dolomite-2 (LCD-2) and “Altered” HCD

Cretaceous LCD-2 rich samples and “altered” HCD samples that commonly have more negative $\delta^{18}\text{O}$ values below +1 down to at least -0.5‰ VPDB (Figs 3B, 8B) associated with intervals of faulting, brecciation and boxwork veining, suggest that some earlier dolomites underwent additional much later, synorogenic dolomitization. This likely was done by ascending,

cooling fluids migrating upwards via faults and fractures during deformation (cf., Heydari, 1997). Single phase fluid inclusions suggest temperatures below 50 °C for LCD-2 overgrowth cements; relatively low temperatures also are supported by the similar ordering of LCD-2 rich samples to the earlier dolomites (<0.6) that is lower than typical late burial dolomites. However, this is not to discount the possibility that some LCD-2 might have formed above 50 °C, if on further study some LCD-2 samples are found to contain primary two-phase fluid inclusions.

The $\delta^{13}\text{C}$ ($\sim +1.4\text{‰}$ VPDB) of vein dolomite and the 0 to $+2\text{‰}$ VPDB range for Cretaceous LCD-2 indicates the fluids moving up through the fractures were rock buffered (Fig. 8B) and formed prior to oil migration, because oxidation of hydrocarbons would have provided light ^{12}C to the fluids (Heydari, 1997). The increase in $\delta^{18}\text{O}$ (reaching $+2\text{‰}$ VPDB) with decreasing Ca content of LCD-2 ($R=-0.6$; Fig. 9C) is due to stoichiometric effects (Vahrenkamp and Swart, 1994). The near zero $\delta^{18}\text{O}$ values of vein dolomite lie at the low end of the almost all of the LCD-2 (Fig. 8B). This suggests that both the LCD-2 and vein dolomites formed from 0 to $>+5\text{‰}$ SMOW evolved marine pore fluids below 50 °C (Fig. 12B). These fluids were slightly more ^{18}O -depleted than the LCD-1 fluids (Fig. 12B) even though they had probably undergone considerable rock water reaction that should have made them more enriched in ^{18}O . This suggests that the pore fluids had been slightly diluted by a meteoric component.

LCD-2 rich samples commonly have Sr values below 100 ppm (Fig. 9D) typical of burial dolomites (Veizer, 1983); this along with typically more negative $\delta^{18}\text{O}$ may reflect the slightly warmer waters of formation compared to LCD-1, resulting in lower effective Sr/Ca in the waters and slightly depleted ^{18}O values in the dolomites (Banner, 1995). Sr contents above 100 ppm occur in LCD-2 with Ca compositions near the LCD-HCD boundary, and in ^{18}O -depleted “altered” HCD, likely reflecting mixing of HCD and LCD-2, greater substitution sites and

perhaps slightly cooler temperatures compared to more stoichiometric LCD-2 (Banner 1995; Fig. 7C). The markedly elevated $^{87/86}\text{Sr}$ values of LCD-2 reflect synorogenic pore fluids contaminated with more radiogenic $^{87/86}\text{Sr}$ (Figs 10, 11B), with relatively low effective Sr/Ca ratios (high 1/Sr in LCD; Fig. 11D) and slightly higher temperatures than LCD-1 (yielding more negative $\delta^{18}\text{O}$ dolomite; Figs 11F, 12B). These ^{87}Sr -enriched fluids likely resulted from rock water-reactions with more radiogenic carbonates that could include older Jurassic or Upper Cretaceous carbonates (Fig. 11) and perhaps Cenozoic siliciclastics within the fold-thrust belt. The timing of LCD-2 precipitation can be tied to the timing of deformation of the carbonates coupled with exhumation, given that LCD-2 formed below 50 °C (single phase fluid inclusions). Major compression in the Eocene-Oligocene to Early Miocene formed the present structures and the bulk of the faults, and was accompanied by exhumation over structural highs. This suggests that this later stage dolomitization (LCD-2) of the studied outcrops (now associated with a structural high) likely was initiated in the *early* part of the major Eocene-Oligocene deformation when the Cretaceous carbonates on structural highs were partly exhumed to shallow depths <1km. Compressional deformation and uplift in the hinterland likely caused an initial flux of modified marine pore fluids diluted by a smaller upland-derived meteoric component (Galluccio, 2009; Ronchi et al., 2011), to be expelled from the platform carbonates within the fold-thrust belt, and move via fractures and faults up into the structural highs, resulting in deposition of ^{18}O -depleted LCD-2 within permeable dolomites and fractures, at the same time resetting some HCD to form the more negative $\delta^{18}\text{O}$ values of “altered” HCD.

6. Discussion

The Jurassic-Cretaceous Adriatic Platform dolomites provide a rare example of *early*

611 *post-depositional dolomitization* of an isolated platform within a calcite sea. Another (with
612 similar chemistry and detailed petrophysics) comes from the nearby Cretaceous Albian
613 succession of the Apennine Platform, Italy (Galluccio, 2009). Superficially resembling later
614 burial dolomites, the Croatian dolomites' initiation during semi-arid climate phases, positive
615 $\delta^{18}\text{O}$, single phase fluid inclusions and moderate ordering attest to their dominantly early post-
616 depositional origin.

617 The fabric destructive character is related to the precursor calcite mineralogy, which was
618 less susceptible to dolomitization than aragonite-high Mg calcite mineralogies of aragonite sea
619 platforms. Widespread dolomitization in low Mg/Ca calcite seas may have been driven by high
620 sea levels, elevated salinities, high alkalinity and hot and at least seasonally dry climate (Folk
621 and Land, 1975; Carpenter, 1980; Machel and Mountjoy, 1986; Sibley, 1991; Montanez and
622 Read, 1992; Arvidson and McKenzie, 1997; Burns et al., 2000). Hot, relatively dry climate
623 phases and long term shallowing events (Tithonian, Berriasian and Albian) promoted intense
624 post-depositional reflux dolomitization by HCD (cf., Sun and Estaban, 1994). Cooler humid
625 climates (e.g., Valanginian-Hauterivian-early Barremian) with intermittent hot dry phases,
626 produced much less *early* post-depositional dolomite and were more susceptible to later
627 dolomitization (LCD-2) forming very local, intensely dolomitized sections (Fig. 2C).

628 Reflux of mesohaline waters below gypsum precipitation field (cf., Simms, 1984; Machel
629 and Mountjoy, 1986; Shields and Brady, 1995; Goldstein, 1996; Budd, 1997; Jones et al., 2000;
630 Melim and Scholle, 2002; Jones and Xiao 2005) appears to be the most likely dolomitizing
631 mechanism forming HCD and LCD-1. These mesohaline waters probably penetrated to relatively
632 shallow depths (<300 m) given the muddy low permeability sediments and relatively low density
633 mesohaline waters (Jones et al., 2004). Where HCD matured in marine fluids by addition of

HCD overgrowth cements, they retained Ca-excess compositions. HCD-rich samples that lost Ca did so by replacement and cementation by LCD-1. The $^{87/86}\text{Sr}$ values of HCD and LCD-1 that lie within or slightly above the predicted coeval seawater ranges are compatible with little modified marine dolomitizing fluids. Thermal convection (Kohout, 1965) may have mixed a small component of ascending ^{87}Sr -enriched deeper fluids with the refluxing waters at the dolomitizing front (Jones et al., 2004). The subsidence rates (6 to 15 cm/kyr) would have kept the Adriatic Platform dolomites within the subsurface reflux zone (<200 m for active reflux; Budd, 1997; Wheeler et al., 1999; Swart and Melim, 2000; Suzuki et al., 2006) for 1 to 3 m.y. which provided ample time for local dolomitization by mesohaline waters (Kaufman, 1994).

Burial below 300 m probably terminated reflux dolomitization as fluid flux rates decreased. The Upper Jurassic dolomites in Croatia underwent burial to at least 3.5 km by the end of the Mesozoic, while the Lower Cretaceous dolomites were buried to at least 2 km (Husinec and Jelaska, 2006). Low fluid flux and low permeabilities of the muddy carbonates inhibited burial diagenesis. Late dolomitization by much younger ^{18}O -depleted and ^{87}Sr -enriched LCD-2 and “altered” HCD in the Cretaceous dolomites was triggered by Eocene-Oligocene deformation causing marine-dominated pore fluids to migrate out from beneath the orogenic highlands via fracture networks to mix with variable amounts of upland-derived meteoric waters contaminated with radiogenic Sr. Dolomitization by LCD-2 ended with influx of synorogenic Ca-rich waters which moved up through the increasingly fractured zones (Prtoljan et al., 2007). This along with continued uplift of the hinterland and the resulting increased hydraulic head (Heydari, 1997) allowed deeply penetrating upland-sourced Ca-rich meteoric waters to mix with deeper, marine pore fluids; these warm marine to brackish Ca-rich waters invaded the Alpine-Dinaride belt (Galluccio, 2009; Ronchi et al., 2011) and deposited calcite in fractures and

remnant intercrystal pores. Secondary oil-inclusions in the Croatian vein calcites likely were emplaced at this time during the main Oligocene-Early Miocene oil migration (Caldarelli et al., 2013).

The similarity of the Adriatic Platform post-depositional dolomites to later burial dolomites (in terms of field relations and petrography, local slightly cross cutting relations, coarse grain size, fabric-destructive character; Tišljär et al., 2002), especially given the later overprinting by faulting that affected many of these Mesozoic platforms, suggests that early post-depositional dolomites could easily be misinterpreted as being totally of burial origin, in the absence of data showing positive $\delta^{18}\text{O}$ compositions and single-phase fluid inclusions. Similar coarse fabric-destructive dolomites of Mesozoic calcite sea platforms, assumed to be burial on the basis of petrography and field relations might be worth re-examining.

7. Conclusions

This study provides a rare documented example of early *post-depositional* fabric destructive dolomitization (vs. peritidal- and burial dolomitization) of a Mesozoic isolated platform within a calcite sea. The Adriatic Platform Upper Jurassic and Lower Cretaceous dolomites, Croatia are medium to coarse grained (>20 to 500 μm) high-Ca dolomite (HCD; 53 to 58 mol% Ca) comprising turbid cores and initial clear rims; later LCD (48 to 53 mol% Ca) variably replaced HCD cores and formed LCD rims plugging porosity. Most Jurassic dolomites and fewer Cretaceous dolomites are HCD-rich, have positive $\delta^{18}\text{O}$, and formed during semi-arid phases from refluxing mesohaline waters. Earlier HCD with >55 mol% Ca lost considerable Sr, whereas more stable HCD with Ca between 53 and 55 mol% tended to retain much original Sr.

A few Jurassic dolomites and most Cretaceous dolomites were converted into LCD-rich

dolomites. LCD-1 replaces HCD cores and forms cement (positive $\delta^{18}\text{O}$; moderate Sr and marine $^{87/86}\text{Sr}$) and formed from early post-depositional refluxing marine pore fluids (modified by rock-water interaction) below 50 °C and <300 m burial. The dolomites underwent little modification during short-lived burial to 2 to 3 km. Low fluid flux, generally low permeability due to near-surface over-dolomitization, and short residence time at depth due to subsequent rapid Cenozoic uplift limited burial alteration. Much later dolomitization (LCD-2) and stabilization occurred during Eocene-Oligocene deformation and uplift, within local zones of fracture-controlled, warm (<50°C, <1 km depth) synorogenic fluid circulation within rising anticlines. This LCD-2 and associated “altered” HCD is characterized by more negative $\delta^{18}\text{O}$, low Sr and elevated $^{87/86}\text{Sr}$, indicating modified marine pore waters variably contaminated with upland-derived meteoric fluids and radiogenic Sr. LCD-1 and -2, being relatively stable phases, retained original Sr and $\delta^{18}\text{O}$ compositions.

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FIGURE CAPTIONS

Figure 1. (A) Map showing location of the Adriatic Platform. (B) Enlarged map of study area in southern Croatia, showing location of sections from which samples were obtained. Faults from Prtoljan et al., (2007) and Črne and Goričan (2008). (C) Cross section of study area, modified from Croatian Hydrocarbon Agency (2016). (D) Subsidence history plot for study area. Modified from Husinec and Jelaska (2006). (E) Simplified latest Jurassic-earliest Cretaceous paleogeographic sketch map showing location of the Adriatic Platform (modified from Golonka, 2002).

Figure 2. (A) Chronostratigraphic chart showing the Mid-Jurassic to Late Cretaceous part of the Adriatic Platform succession showing the thicknesses, the stratigraphic position of major dolomites, unconformities and emergence breccia zones; thick vertical bars indicate stratigraphic position of the dolomites studied (Korčula sections – CSI, CAI, CI; Dubrovnik section BKI). (B) Cross sections showing occurrence of major coarse dolomites, modified from Vlahović et al. (2005). (C) Percent dolomite within each stage, calculated from data in Vlahović et al. (2005) and plotted against major climatic phases after Wilkinson and Riding (2007).

Figure 3. Detailed columnar sections along with $\delta^{18}\text{O}$ profiles of the dolomites (black dots linked by heavy line) with rectangle outlining +1 to +3‰ VPDB range typical of the least altered dolomites (only pure dolomites used). Solid red circles in (D) are late stage vein dolomites. (A) BKI (Jurassic, Lower Tithonian), (B) CI (Cretaceous, Valanginian to Early Hauterivian), (C) CSI (Cretaceous Barremian), and (D) CAI (Cretaceous Hauterivian). The detailed columns (unpublished data) show mineralogy on the left (dolomites shown with sloping brick pattern), sedimentary structures (central column) and Dunham textures and lithology (right column). Numbers alongside columns relate to field measured sections that include both limestones and dolomites, but only the dominantly dolomite portions are shown, and $\delta^{18}\text{O}$ values are only shown for pure dolomites uncontaminated by calcite.

Figure 4. Plain light photographs of dolomites. (A) Medium to coarse grained fabric destructive dolomite showing darker gray turbid cores and light clear dolomite rims (CSI 57, Barremian). (B) Typical coarse grained, fabric-destructive dolomite characterized by inclusion rich turbid cores and limpid, clear dolomite overgrowths (CI 24, Valanginian). (C) Poorly fabric retentive dolomite, a relatively minor dolomite type, composed of ghosts of leached peloids and oncoids outlined by finer-grained dolomite and filled with coarse dolomite cement (BKI 152, Lower Tithonian).

Figure 5. (A, B) Histograms of Ca (mol%) of the dolomites determined by INAA for the bulk dolomite samples from the Jurassic and the Cretaceous. (C, D) histograms of microprobe

data derived from probe traverses of single crystals of dolomite from the Jurassic and the Cretaceous. Ranges of LCD and HCD are marked with a line. Jurassic samples are dominated by HCD, whereas Cretaceous samples are a mix of HCD and LCD.

Figure 6. Back scattered electron (BSE) images of dolomite showing zones defined by atomic weight, and microprobe points with ranges of measured mol% Ca for the zones (white numerals). Under BSE, calcite is white (as are the microprobe spots), HCD is light gray, LCD is darker gray and pore space is black. Samples containing some porosity were selected in order to get a complete zonation of phases into open space. (A) Coarse grained dolomite with turbid, inclusion-rich HCD cores grading out into HCD rims, overgrown by LCD rims, typical of Jurassic and Cretaceous HCD-rich samples (BKI 143, Jurassic, Lower Tithonian). (B) Coarse grained HCD with turbid, inclusion rich, microporous cores with highly irregular, patchy replacement by late LCD. The cores pass out into a clear non-porous HCD rim overlain by an LCD rim, interlayered with a thin HCD zone at base (CAI 7, Cretaceous, Hauterivian). (C) Coarse grained dolomite, with HCD core with small amount of replacement LCD, overgrown with HCD rim, followed by possibly two generations of LCD rim cement; the earlier HCD- and LCD rim being cut by later LCD veins (white arrows), which do not appear to cut the latest LCD rim. (CI 25, Cretaceous Valanginian-Hauterivian). (D) Coarse grained dolomite adjacent to fault showing more intense replacement of HCD core and part of HCD rim (arrow) by highly irregular masses of LCD, and overgrown by LCD rim typical of Cretaceous LCD-rich samples (CAI 57, Cretaceous Hauterivian). (E) Coarse grained dolomite composed of rhombic cores of LCD with irregular boundaries (either complete replacement of HCD or filling of leached HCD core by LCD) overlain by rim of LCD; this is a relatively rare fabric (CSI 62, Cretaceous, Barremian). (F) Schematic illustration of the typical dolomite zonation. Most Jurassic fabrics are dominated by HCD cores (1) and HCD rims (2), with lesser LCD-2 (3) forming overgrowths and replacement fabrics. Many Cretaceous dolomites show a zonation of early HCD cores (1) and HCD rims (2), and LCD-1 rims (3) and locally late LCD-2 rims (4), with LCD (zone 3 or 4) replacing HCD cores. The two generations of LCD are defined geochemically and are not easily distinguished petrographically.

Figure 7. (A) Degree of dolomite ordering based on ratio of intensity of diffraction peaks (015) and (110) plotted against strontium content. (B) Ca (mol%) vs Sr (ppm) for Croatian Upper Jurassic HCD and lesser LCD-1 samples, (C) Ca (mol%) vs Sr (ppm) for Lower Cretaceous HCD-rich and LCD rich samples. Solid red dots are LCD-2, and have $\delta^{18}\text{O}$ below $\sim +2\text{‰}$ VPDB for LCD-2 with Ca < 50 mol% (to account for stoichiometric effects); LCD-2 with > 50 Ca mol%, along with associated “altered” HCD have $\delta^{18}\text{O}$ below $+1\text{‰}$ VPDB. Generalized field of Neogene isolated platform dolomites outlined; data from individual Cenozoic platforms show much narrower range and much better correlation than the generalized field shown (data from Vahrenkamp and Swart, 1990; Wheeler et al. 1999; Suzuki *et al* 2006; and Zhao and Jones, 2012 a, b). Gray arrows show likely path of diagenetic evolution of dolomites.

Figure 8. (A) Carbon vs oxygen isotope cross plot of Croatian Upper Jurassic dolomites (HCD and LCD-1) with field of coeval lime mudstone shown for reference. Only samples analyzed for major and trace elements are plotted. Gray outlined box in this figure and in (B) is estimated field of Late Jurassic and Early Cretaceous open marine calcites from data in Weissert and Erba (2004), McArthur et al. (2007) and Malkoc and Mutterlose (2010). Red outline defines generalized field of Neogene post-depositional dolomites (Dawans

and Swart, 1988; Vahrenkamp and Swart, 1994; Wheeler et al., 1999; Suzuki et al., 2006; Zhao and Jones, 2012b). (B) Carbon vs. oxygen cross plot for Croatian Lower Cretaceous post-depositional dolomites HCD and LCD-1 and late diagenetic LCD-2, with coeval lime mudstone field shown for reference. (C, D) Histograms of $\delta^{18}\text{O}$ compositions of Jurassic (dominantly HCD) and Cretaceous (dominantly LCD and lesser HCD) dolomites uncorrected for stoichiometric effects. Cretaceous HCD and LCD-1 have similar modes and make the ^{18}O enriched population, while LCD-2 makes up the smaller more ^{18}O depleted population. Vertical dashed line marks +1‰, the $\delta^{18}\text{O}$ upper limit of LCD-2.

Figure 9. (A) Cross plot of $\delta^{18}\text{O}$ vs. Ca for the Upper Jurassic HCD and LCD-1 rich samples. Generalized field for Neogene platform dolomites outlined (data from Dawans and Swart, 1988; Vahrenkamp and Swart, 1990; Wheeler et al. 1999; Suzuki et al. 2006; and Zhao and Jones, 2012 a, b). The Bahamas data has had the dolomite-phosphoric acid fractionation factor removed, to make it comparable to the other data. (B) Cross plot of $\delta^{18}\text{O}$ vs. Sr for Upper Jurassic dolomites. (C) Cross plot of $\delta^{18}\text{O}$ vs. Ca for the Lower Cretaceous dolomites. Cenozoic field same as in A. Gray solid arrow marks likely path of diagenetic evolution of the Cretaceous HCD and LCD-1 dolomites while the dashed gray arrow marks the diagenetic path due to late synorogenic diagenesis (D) Cross plot of $\delta^{18}\text{O}$ vs. Sr for the Lower Cretaceous dolomites. Field of late diagenetic LCD-2 rich samples (dashed line) and associated HCD samples affected by late alteration (dotted line) shown.

Figure 10. The $^{87/86}\text{Sr}$ values of the Upper Jurassic and Lower Cretaceous dolomites plotted against $^{87/86}\text{Sr}$ isotope curve for Jurassic-Cretaceous seawater of McArthur et al. (2001). Massive HCD-rich samples, LCD-1- and LCD-2-rich samples and laminated samples keyed to legend. Dashed parts of $^{87/86}\text{Sr}$ curve mark possible ranges of refluxing seawater.

Figure 11. (A) Plot of Ca vs. $^{87/86}\text{Sr}$ for the Upper Jurassic (Lower Tithonian) dolomites. Heavy horizontal bar in this and subsequent figures shows possible range of $^{87/86}\text{Sr}$ values for refluxing seawater. (B) Plot of Ca vs. $^{87/86}\text{Sr}$ for the Lower Cretaceous dolomites. (C) Plot of 1/Sr vs. $^{87/86}\text{Sr}$ for the Upper Jurassic dolomites. (D) 1/Sr vs. $^{87/86}\text{Sr}$ plot for the Lower Cretaceous dolomites. (E) $\delta^{18}\text{O}$ vs. $^{87/86}\text{Sr}$ plot for the Upper Jurassic dolomites. (F) $\delta^{18}\text{O}$ vs. $^{87/86}\text{Sr}$ plot for the Lower Cretaceous dolomites.

Figure 12. (A, B) Graphs of temperature vs $\delta^{18}\text{O}$ for dolomite (corrected for stoichiometric effects) contoured in $\delta^{18}\text{O}$ values of water (see methods). Light gray rectangles show fields of HCD-rich samples at 25 to 33°C. Green rectangle LCD-1-rich samples plotted for temperatures of ~30 to ~40°C. Green rectangle LCD-2-rich samples in (B) plotted for temperatures below 50 °C. (A) Upper Jurassic: fields suggest formation and maturation in mesohaline marine pore fluids of +1 to >+4.5‰ SMOW for HCD, with the slightly deeper fluids forming LCD-1 being slightly more ^{18}O enriched (+2 to +5‰ SMOW). (B) Early Cretaceous: HCD field suggests similar mesohaline marine fluids (+1 to +4‰ SMOW). LCD-1 field suggests mesohaline fluids (+2 to >+5‰ SMOW). Field of synorogenic late stage LCD-2-rich samples is more ^{18}O depleted (0 to +4‰ SMOW) than the fluids that formed Cretaceous LCD-1, which is compatible with mixed warm evolved marine fluids with variable amounts of upland sourced meteoric fluids.

Appendix

Table A1. Geographic coordinates of logged roadcut sections.

fig 1 de

A

fig 2a

fig 2bc

fig 4

A **fig 5**

Jurassic

B **Cretaceous**

C **Jurassic**

D **Cretaceous**

fig 6

fig 7

fig 8

$^{87}/^{86}\text{Sr}$

fig 10

Jurassic

B

C Jurassic

D Cretaceous

E Jurassic

F Cretaceous

Table 1. Summary of Croatian dolomite.

	Petrography and occurrence	BSE Image, Ordering	Sr and Mn [ppm]	$\delta^{13}\text{C}$ [‰ VPDB]	$\delta^{18}\text{O}$ [‰ VPDB]	$^{87/86}\text{Sr}$	Origin
Bulk dolomite	Mainly medium to coarse (20 to 100 μm); fabric destructive with minor poorly fabric retentive types; nonluminescent,	See below	Sr 62-206 Mn 3 to 15, rarely up to 33	Jurassic; Most 0 to +1.5 Cretaceous -0.4 to +2	Jurassic: +1 to +3; Cretaceous -1.4 to +3.5	U. Jurassic 0.707061 to 0.707323; Lower Cretaceous 0.707385-0.707721	See below
High Ca-dolomite (HCD; >53 mole% Ca)	Forms turbid cores and early clear rims. Bulk of Jurassic dolomites HCD rich (88%) and about 36% of Cretaceous dolomites HCD rich	Light gray, forms cores and early rims, the rims having slightly less Ca than cores. Ordering 0.25-0.53	Jurassic: Sr 90-206; Cretaceous: Sr 90-190	Jurassic: 0 to +1.5. Cretaceous -0.4 to +2	Jurassic: +1 to +3. Cretaceous: 0 to +2.5, with outlier at -1.4	Range from seawater values to slightly elevated values (Jurassic HCD) and marine values to elevated values (Cretaceous)	Mesohaline marine reflux at shallow depths and 25 to 33°C; stabilize in marine fluids, but some contaminated with radiogenic ^{87}Sr
Low Ca-Dolomite (LCD; <53 mole% Ca)	Dominant in 20% of Jurassic dolomites and 64% of Cretaceous dolomites. Forms clear LCD rims and variably replaces HCD cores. LCD-1 early generation. LCD-2 associated with fracturing.	Dark gray, forms patchy to arborescent replacement of HCD cores, and later LCD cement rims. Ordering of LCD-1 and LCD-2 similar, 0.4 to 0.6	Jurassic: Sr 100-190; Cretaceous Sr 60-180	Jurassic: 0.5 to +1.5 Cretaceous: LCD-1: <0 to +2; LCD-2: 0 to +2 Vein fill averages +1.4	Jurassic LCD-1: +1 to +3 Cretaceous LCD-1: +1 to +3.5 LCD-2: -1.3 to +1. Vein fill averages ~0	Jurassic LCD-1: seawater values to slightly elevated values Cretaceous LCD-1: mainly seawater values to slightly elevated values Cretaceous LCD-2: mainly elevated values Vein fill ~0.7076, midrange of observed Cretaceous values	Mesohaline marine reflux <300 m depths, 33 to 40 °C; some contaminated with radiogenic ^{87}Sr Mesohaline marine reflux <300 m depths, 33 to 40 °C; a few contaminated with radiogenic ^{87}Sr Cooling ascending mixed marine-meteoric pore fluids driven by deformation and uplift during Eocene-Oligocene main orogenic phase; contaminated with radiogenic ^{87}Sr
	Dolomites post-dated by poikilitic calcite and vein calcite						

Table A.1. Geographic coordinates of logged roadcut sections.

Section	Bottom		Top	
	Longitude	Longitude	Longitude	Longitude
BKI	6524263	4716904	6524366	4717336
CAI	6415037	4755591	6415187	4755766
CI	6414586	4755567	6414794	4755684
CSI	6415222	4755817	6415278	4756005

Note: Grid used is World Geodetic System (WGS) 84.