Testing clumped isotopes as a reservoir characterisation tool: a comparison with fluid inclusions in a dolomitised sedimentary carbonate reservoir buried to 2-4 km

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Abstract

Constraining basin thermal history is a key part of reservoir characterisation in carbonate rocks. Conventional palaeothermometric approaches cannot always be used: fluid inclusions may be reset or not present while $\delta^{18}O$ palaeothermometry requires an assumption on the parent fluid composition. The clumped isotope palaeothermometer, however, is a promising technique for constraining the thermal history of basins. In this study we test if clumped isotopes record temperatures of recrystallisation in deeply-buried dolomitic reservoirs, through comparison with fluid inclusion data. The studied reservoir is the Cretaceous Pinda Formation, offshore Angola, a deeply-buried dolomitised sedimentary carbonate hydrocarbon reservoir. It provides an ideal test case as samples from industry wells are available over a relatively wide burial depth range of ~2000-4000 metres below sea floor (mbsf) and the constituent dolomites are relatively homogeneous.

Across this depth range, fluid inclusion homogenisation temperatures for the Pinda Formation record a range of temperatures from ~110-170 °C, increasing with depth. These closely match present-day ambient well temperatures, indicating recent resetting of the fluid inclusions. Clumped isotopes, however, record temperatures significantly (~20-60 °C) below fluid inclusion and well temperatures for the seven samples analysed. The deepest five samples (~2800-3700 mbsf) record clumped isotope temperatures around 100-120 °C, interpreted to represent a deep burial recrystallisation event responsible for a massive (re)dolomitisation of the reservoir. The lower clumped isotope temperatures (65 and 82 °C) of the shallower (2055 and 2740 mbsf) samples are interpreted to represent physical mixing of two dolomite generations due to incomplete burial recrystallisation of an early shallow dolomite. Determination of temperature through clumped isotopes allows calculation of the parent fluid $\delta^{18}O$ values. In the five deepest samples, the fluid $\delta^{18}O$ values of 3.7-6.5 ‰ cluster around the modern-day porewater composition (5 ‰) suggesting burial dolomitisation occurred in the presence of evolved brine. Mineral $\delta^{18}O$ values of ~-4.5 to -7 ‰ are lower than pristine Cretaceous marine dolomite and are in accordance with burial recrystallisation. Clumped isotopes are therefore interpreted to record temperatures corresponding to open-system burial recrystallisation events. This study shows that clumped isotopes are a valuable tool in characterising the thermal history of deeply-buried (>2000 m) carbonate hydrocarbon reservoirs.

Keywords: clumped isotopes; dolomite; recrystallisation; $\delta^{18}O$; palaeothermometry

Introduction

A key aspect in understanding the history of hydrocarbon reservoirs is to characterise their thermal history. Indeed, thermal exposure is known to be a prime factor in the degradation of hydrocarbon reservoirs (e.g. Nadeau, 2011). Changing temperature, for example during burial, can cause diagenetic recrystallisation which may affect physical reservoir characteristics such as porosity and permeability, and impact hydrocarbon recovery rates. The thermal history also affects hydrocarbon maturation. In basins containing carbonate rocks, the two main approaches to characterising thermal history in rocks of all ages are fluid inclusion (e.g. McLimans, 1987; Barker & Goldstein, 1990; Goldstein, 2001) and $\delta^{18}O$ (McCrea, 1950; Epstein*, et al.*, 1951) palaeothermometry. These techniques are well-established but have some drawbacks which may limit their application. Fluid inclusion palaeothermometry can be used to infer burial temperatures, and hence potentially burial recrystallisation, by measuring homogenisation temperature (T_h). This is obtained by heating a two-phase inclusion until the vapour bubble disappears and all that remains is a single-phase liquid (e.g. Goldstein & Reynolds, 1994). However, two-phase fluid inclusions are not always present or may not be large enough to reliably measure. This severely limits their use as a palaeothermometer in fine-grained carbonates. In addition, in the context of basin evolution, perhaps the most significant drawback is that they may stretch during subsequent burial, resulting in a resetting of T_h temperatures at present-day temperatures (e.g. Goldstein & Reynolds, 1994). This leads to fluid inclusions recording maximum burial temperatures, i.e. a temperature higher than the temperature at which the host mineral precipitated or recrystallized.

The $\delta^{18}O$ palaeothermometer is based on the relationship between mineral $\delta^{18}O$, temperature and the $\delta^{18}O$ of the parent fluid from which the mineral formed (McCrea, 1950; Epstein, et al., 1951). Measuring $\delta^{18}O$ in carbonates has been routine for many decades (e.g. Urey*, et al.*, 1951; Emiliani, 1955; Shackleton, 1967) but in order to calculate temperature, the $\delta^{18}O$ of the parent fluid must be known. In most cases this value is unconstrained and an assumption must be made. An incorrect assumption by only 1 ‰ may lead to a temperature estimate greater than ten degrees away from the true mineral formation temperature.

Clumped isotopes is a promising method which avoids the pitfalls in these other palaeothermometers. This technique is based on the thermodynamic relationship between carbonate mineral growth temperature and the abundance of chemical bonding ("clumping") between ^{13}C and ^{18}O isotopes (expressed as Δ_{47}) within single carbonate ions (e.g. Ghosh*, et al.*, 2006a; Schauble*, et al.*, 2006; Eiler, 2007). This relationship has led to the application of the carbonate clumped isotope palaeothermometer to address a range of geological questions. Most studies have focussed on surface and near-surface applications where the temperatures involved are in the ~0-35 °C range, including palaeoclimate (e.g. Affek*, et al.*, 2008; Passey*, et al.*, 2010; Thiagarajan*, et al.*, 2014) and palaeoaltimetry (e.g. Ghosh*, et al.*, 2006b; Huntington*, et al.*, 2010; Lechler*, et al.*, 2013; Carrapa*, et al.*, 2014) studies. The carbonate clumped isotope palaeothermometer can also be applied in the ~50-300 °C range, relevant to processes such as diagenesis and dolomitisation (Ferry*, et al.*, 2011; Passey & Henkes, 2012; MacDonald*, et al.*, 2013; Dale*, et al.*, 2014; Henkes*, et al.*, 2014; Sena*, et al.*, 2014; Vandeginste*, et al.*, 2014; Geske*, et al.*, 2015; John, 2015; Kluge & John, 2015; Kluge*, et al.*, 2015; MacDonald*, et al.*, 2015; Shenton*, et al.*, 2015; Stolper & Eiler, 2016).

The ability of carbonate clumped isotopes to retain temperatures of original precipitation or fluid-driven recrystallisation at burial temperatures of 50-300 °C is not well established yet. Burial of carbonate rocks may lead to open-system recrystallisation, whereby pre-existing carbonate minerals dissolve on contact with a fluid and reprecipitate. Assuming complete open-system recrystallisation,

the Δ_{47} value should reflect the ambient temperature during recrystallisation. However, recent work (Dennis & Schrag, 2010; Passey & Henkes, 2012; Henkes, et al., 2014) has suggested that temperatures attained during burial may lead to closed-system resetting of clumped isotopes, where intra-crystal diffusion of O and C occurs and Δ_{47} does not necessarily record the temperature at which open-system recrystallisation occurred but is locked at a temperature between formation temperature and the maximum temperature of burial. Clumped isotope measurements of pristine carbonatites have given a wide range of temperatures, many around ~150-250 °C, which are interpreted as blocking temperatures during cooling (Dennis & Schrag, 2010). Without recrystallisation during burial diagenesis, the mechanism proposed for attaining the cooling temperatures is solid-state closed-system bond reordering of C-O bonds in the carbonate lattice (Dennis & Schrag, 2010; Passey & Henkes, 2012). If calcite is exposed to temperatures greater than ~100 °C for millions of years, bond reordering may occur (Dennis & Schrag, 2010; Passey & Henkes, 2012; Henkes, et al., 2014; Stolper & Eiler, 2015), bringing the clumped isotope temperatures to the ambient temperature.

The fact that bond reordering can occur in calcite held at >100 °C for millions of years indicates that it is a key process to consider when investigating the utility of clumped isotopes in the characterisation of deeply-buried reservoirs. Studies on bond reordering have concentrated on calcite while in this study we focus on a dolomitic reservoir. The only available kinetics data on bond reordering in dolomite is from a published conference abstract by Bonifacie et al., (2013); this suggested unpublished experimental data indicated dolomite was resistant to solid-state bond reordering up to ~300 °C. This suggests that bond reordering will have a lesser effect, if any, on the preservation of temperature signatures recorded by clumped isotopes in dolomite. In this study, we compare clumped isotope temperatures with an extensive suite of previously acquired fluid inclusion and ambient well temperatures (Walgenwitz*, et al.*, 1990; Eichenseer*, et al.*, 1999) to investigate if clumped isotopes in dolomite are affected by bond reordering, or whether they are recording temperatures of geologically meaningful events such as burial recrystallisation.

Sample Characterisation

Geological Setting

The dolostone samples investigated in this study are from the Cretaceous Pinda dolomite Formation from offshore Angola (Fig. 1a). The tectonic framework of the Pinda Formation begins with the breakup of southwestern Gondwana during the Early Cretaceous (Reyre, 1984). The initial rifting phase and associated sedimentary deposition was dominated by lacustrine sediments (Eichenseer, et al., 1999), followed by evaporite formation (e.g. Coajou & Ribeiro, 1994). As continental rifting continued northwards, marine transgression took place and marine carbonates of the Pinda Formation were deposited during Albian time (Koutsoukos*, et al.*, 1991). Halokinesis during the Albian resulted in turtle-back and raft structures which created hydrocarbon traps (Bremner*, et al.*, 1993; Eichenseer, et al., 1999).

Modelling of the burial history of the Pinda Formation by TOTAL indicates that after deposition of the thick Pinda sequence, there was little or no burial until the Oligocene (Fig. 1b). This is supported by Walgenwitz et al., (1990) who indicated that diagenesis mainly took place in the late Oligocene following reactivated subsidence. Initial dolomitisation of the Pinda carbonates is interpreted to have occurred during early diagenesis , producing dolomite microrhombs (Eichenseer, et al., 1999). Early dolomitisation was amplified by later shallow burial recrystallisation, producing cloudy dolosparites with a clear outer rim (Eichenseer, et al., 1999). It was proposed that this later

recrystallisation was triggered by mixed saline-meteoric fluid circulations at shallow depth (mixing-zone dolomitisation) and resulted in a significant modification of the original geochemical signature of the dolostone (Eichenseer, et al., 1999). Eichenseer et al., (1999) indicated no evidence in support of a late deep burial (high temperature) dolomitisation event, and considered that the bulk of the dolomitisation was of early shallow origin. The current model of dolomitisation for the Pinda Formation therefore relies solely on a mixing-zone dolomitisation mechanism, which took place during early diagenetic stages in relation with sea level fall and prior to any significant burial.

Fluid Inclusions

Fluid inclusion thermometry was conducted by TOTAL and details of the microthermometric procedures and measurements are given in Walgenwitz et al., (1990). Fluid inclusion measurements were conducted on two-phase fluid inclusions located in crystals of dolosparite and in recrystallized feldspar grains. A large suite of homogenisation temperatures was obtained from ~40 samples across the Pinda Formation in the study area (13 wells). Homogenisation temperatures (T_h) range from ~110 to 170 °C (Fig. 2). The fluid inclusion assemblage exhibits a roughly linear temperature-depth relationship, coincident with a suite of downhole ambient well temperature readings (Fig. 2). This was interpreted by Eichenseer et al., (1999) as reflecting progressive resetting of fluid inclusion T_h values during burial down to present-day depths. However, the error bars on many of these are large and make confident interpretation difficult (see further discussion below). Homogenisation temperatures (sample averages) corresponding to the specific core plug samples selected for clumped isotope analysis range from 111 to 152 °C (Table 1).

Clumped Isotopes

Methodology

Carbonate clumped isotope measurements were carried out in the Qatar Stable Isotope Laboratory at Imperial College London. Samples were powdered using a dental drill. In order to remove hydrocarbons and other organic matter, the powders were treated with 4 to 8 washes in a cold cleaning solution of 3 % H_2O_2 and 0.9 wt% sodium hexametaphosphate. Subsequently the treated powders were washed with ethanol and DI water before being dried in an oven at 50 °C to evaporate any remaining water. Where this treatment was not sufficient, sample powders were treated in a TePla 400 oxygen plasma asher at the London Centre for Nanotechnology at University College London. Powders were placed in petri dishes and heated at ~40 °C for 5 minutes in an oxygen plasma. The method resulted in the complete combustion of all organic matter under vacuum after a 5 minute treatment. Given the short treatment time, the temperature in the oxygen plasma asher only reaches ~40 °C, well below the temperature threshold for initiating closed-system bond reordering. Additionally, this method was tested on a Carrara Marble standard and was not found to have any effect on clumped isotope systematics. For clumped isotope analysis, 5-6 mg of sample powder was reacted under vacuum with 104 % phosphoric acid at 90 °C for 20 minutes. Water generated during the reaction was separated from the produced CO_2 by first trapping in liquid nitrogen then swapping the liquid nitrogen for an ethanol-liquid nitrogen mixture held at ~-90 °C. The water remained frozen while the CO_2 was passed through a Poropak Q chromatography trap held at -35 °C. Full details on the purification procedure are described in Dale et al., (2014).

The purified CO_2 was measured in one of two Thermo Fisher MAT 253 isotope ratio mass spectrometers (Pinta and Nina, see Supplementary Data) in dual inlet mode with a measurement time of ~2.5 hours. Masses 44-49 were measured, with 48 and 49 used to test for potential

contamination as CO_2 with those molecular masses is extremely rare relative to mass 47 (e.g. Eiler, 2007). Only samples with δ_{48} and Δ_{48} values that fall within 2 ‰ of the heated gas line (Δ_{48} Offset) and had a 49 Parameter of <0.2 were accepted (Dale, et al., 2014). Mass spectrometer non-linearity was corrected based on methods described in Huntington et al., (2009) using a 30-day moving average of heated gases as this provided a suitable number of heated gases and carbonate standards to correct against. All Δ_{47} values reported are in the Carbon Dioxide Equilibrated Scale (CDES) (Dennis*, et al.*, 2011) using a secondary transfer function based on Carrara Marble, ETH-3 (an externally verified carbonate standard (Iso C in Meckler*, et al.*, 2014)) and heated gases. Following correction to the absolute reference frame, the empirical acid fractionation factor of +0.069 ‰ calculated in Guo et al., (2009) and experimentally derived by Wacker et al., (2013) was added to the Δ_{47} value to bring the data into the 25 °C scale used in calibrations. This acid fractionation factor is consistent with internal laboratory tests at Imperial College London, and with the values used for the Imperial College calibration (Kluge et al, 2015). The Carrara Marble standard gave a linearity- and acid-corrected average Δ_{47} value of 0.382±0.020 ‰ across both mass spectrometers while the ETH-3 value was 0.700±0.016 ‰; these compare well with published values of 0.395 ‰ (Dennis, et al., 2011) and 0.705 ‰ (Meckler, et al., 2014) respectively. All standard and sample data are given in the Supplementary Data Table. For $\delta^{18}O_{dolomite}$, the acid fractionation factor of Rosenbaum and Sheppard (1986) was applied. The calibration of Kluge et al., (2015) was used to convert Δ_{47} into temperature as this is the only experimental calibration that extends over the 25-250˚C range, and it was derived using the same methods and instruments as in this study. $\delta^{18}O_{porewater}$ values were calculated with the carbonate-water equilibrium fractionation factors from Land (1980). The calculated $\delta^{18}O_{porewater}$ are reported in the Vienna Standard Mean Ocean Water (VSMOW) scale, whilst measured $\delta^{18}O$ and $\delta^{13}C$ values are reported in the Vienna PeeDee Belemnite (VPDB) scale.

Results

Seven dolostone bulk samples from six different wells were selected for clumped isotope analysis. The samples were taken from depths ranging from 2055 to 3705 metres below sea floor (mbsf). They are generally unimodal planar-S (Sibley & Gregg, 1987) dolosparites (Fig. 3a); one sample contains very minor calcite (Fig. 3b) and most have isolated quartz grains (Fig. 3a). Crystal size range is ~50-500 µm and shape is anhedral to euhedral. The smallest, most euhedral dolomite rhombs are found lining moldic pores (Fig. 3c) after dissolution of ooids – a fabric commonly preserved (Fig. 3b). Dolomitized shelly fragments are also occasionally observed (Fig. 3d).

The $\delta^{13}C$ values of the seven samples are all within a narrow range of ~3-3.5 ‰ and do not correlate with depth (Fig. 4a, Table 1). $\delta^{18}O$ values range from ~-3.5 to -7 ‰ (Fig. 4b, Table 1) and do not correlate with depth or $\delta^{13}C$, although the shallowest sample has the least depleted $\delta^{18}O$ value. Δ_{47} values range from 0.495 to 0.592 ‰, which translates to temperatures of 65 to 122 °C, with temperature errors in the range of ±1 to ±7 °C. Temperatures increase with burial depth in the two shallower samples before clustering around 100-120 °C in the five deeper samples (Fig. 4c, Table 1). The shallowest sample (JM2055) has a calculated parent fluid $\delta^{18}O$ value of 1.7 ‰, rising to 2.7 ‰ in the next deepest sample (JM2740) (Fig. 4d, Table 1). The five deeper samples, which record clumped isotope temperatures of ~100-120 °C (average = 111 °C), exhibit calculated fluid $\delta^{18}O$ values of 3.7-6.5 ‰ (average = 4.9 ‰), with no depth trend. These five samples plot within or close to the modern-day porewater $\delta^{18}O$ of ~5 ‰ (Walgenwitz, 1989).

Discussion

Interpretation of the fluid inclusion homogenisation temperatures is complicated by the fact that they have large error bars and record a spread of temperatures of ~110-170 °C, which likely reflects thermal re-equilibration during burial subsequent to fluid inclusion trapping. It is well known that not all fluid inclusions are affected in the same way by thermal resetting, some fluid inclusions being more resistant than others depending on their size and shape (Goldstein, 2001). The lowest T_h values recorded in the fluid inclusions are at ~110 °C (Fig. 2) and would therefore represent the most conservative temperature for any burial dolomitisation episode. Eichenseer et al. (1999) did not interpret any such late burial dolomitisation. The higher T_h values recorded by fluid inclusions up to 170 °C in the Pinda Formation reflect a subsequent increase in the ambient temperature and thermal resetting of fluid inclusions without dolomite recrystallisation. Where ambient temperatures were available (five of the seven samples), homogenisation temperatures are within 10 °C of the present-day ambient temperature (Fig. 4c, Table 1).

Clumped isotope temperatures, however, fall well below present-day ambient well temperatures and average fluid inclusion temperatures at all investigated depths by about 20 to 60 °C (Table 1, Fig. 4c). The clumped isotope temperature of ~100-120 °C recorded by the five deeper samples is consistent over a ~1000 m depth range (~2800-3700 mbsf; Fig. 4c) and close to the lower end of the range of fluid inclusion T_h values (~110 °C, Fig. 2). This strongly suggests that the clumped isotopes in these five samples are recording a single open-system recrystallisation event, interpreted to represent a deep burial recrystallisation episode responsible for the blocky planar-s texture observed in the studied samples. The fluid $\delta^{18}O$ values (~3.5-6.5 ‰) calculated for these samples are clustered around modern-day porewater composition (5 ‰) and suggest consistent brine $\delta^{18}O$ values with the time of burial diagenesis. The similarity between present- and palaeo-fluid compositions is suggestive of open-system recrystallisation (dissolution-reprecipitation). With open-system recrystallisation, the $\delta^{18}O$ value of the carbonate will reflect the ambient temperature and $\delta^{18}O$ value of the fluid that enabled recrystallisation to occur. Therefore, if either of these two parameters (ambient temperature or fluid $\delta^{18}O$) did vary during the open-recrystallisation process then the mineral $\delta^{18}O$ values should also vary over a depth range in a single formation/basin. This is the case of the five deeper samples of the Pinda Formation investigated in this study which have undergone complete burial recrystallisation and show a 2 ‰ range in their bulk $\delta^{18}O$ values, reflecting a variation of ~20 °C in temperature and ~2.8 ‰ in fluid $\delta^{18}O$. Eichenseer et al., (1999) interpreted measured bulk $\delta^{18}O$ values of these sediments to record isotopic resetting during burial of early seafloor dolomite. Indeed, the mineral $\delta^{18}O$ values reported by Eichenseer et al., (1999) and in our study are more depleted than typical marine carbonate values from the Cretaceous (Veizer*, et al.*, 1999), and cannot reflect early seafloor conditions.

After deposition of the ~1-1.5 km-thick Pinda Formation in the Albian, there was little or no burial until the Oligocene (Fig. 1b) when the Pinda sediments were buried under a thick sequence of Oilgocene and Miocene sediments, with a steady subsidence continuing to the present day. The base of the Pinda Formation was buried from ~1.4 km at the beginning of the Oligocene to ~2.7 km at the end of the Oligocene, reaching a burial temperature of ~100 °C, based on the present-day geothermal gradient of 40-45 °C/km (Walgenwitz, et al., 1990). According to (Walgenwitz, et al., 1990) a major diagenetic event occurred at ca. 25 Ma, towards the end of the episode of Oligocene subsidence. It therefore seems highly plausible that bulk and clumped isotopes record burial recrystallisation of dolomite during a major diagenetic event at about 100-120°C and at ca. 25 Ma (Fig. 1b).

The two shallowest samples (2055 & 2739 mbsf) have clumped isotope temperatures of 65 and 82 °C, somewhat lower than the deeper samples. The present-day well temperatures at these shallower depths, 111 °C and 141 °C respectively, are also lower than that of the deeper samples (147-161 °C), and close to the hotter end of the temperature of the later burial dolomitisation episode (~120°C). The clumped isotope temperatures of these samples are therefore best explained as reflecting incomplete dolomite recrystallisation and physical mixing of the two generations of dolomite, i.e. early shallow dolomite (~35 °C) and burial dolomite (~100-120 °C).

In all samples, fluid inclusions have been reset to near present-day temperatures while clumped isotopes have not and are instead interpreted to record open-system recrystallisation. This is in accord with previous studies of subsurface carbonates which have suggested recrystallisation temperatures are recorded in clumped isotope systematics. John (2015) found that clumped isotopes were recording deposition and recrystallisation in a suite of Cretaceous oysters from Oman. One well-preserved individual recorded a primary precipitation temperature of 37±4 °C and a fluid $\delta^{18}O$ value typical of slightly-evaporated Cretaceous seawater in a restricted platform basin. Other oysters from the suite, however, record clumped isotope temperatures of ~60-70 °C indicating at least partial burial recrystallisation. Ferry et al., (2011) calculated clumped isotope temperatures of ~40-80 °C in the Latemar Platform which they attributed to initial dolomitisation while Sena et al., (2014) used clumped isotopes to show that early dolomite re-equilibrated through neomorphism from proto-dolomite to well-ordered dolomite with fluids at 60-70 °C in a shallow burial setting in a Tethyan carbonate platform in Oman.

It is however important to address the potential for closed-system bond reordering (Passey & Henkes, 2012; Henkes, et al., 2014; Stolper & Eiler, 2015) to have occurred. Assuming open-system behaviour, the Δ_{47} value should reflect the ambient temperature during recrystallisation. However, recent work has indicated that closed-system resetting of clumped isotope systematics can occur at high temperatures, thus resetting the Δ_{47} value recorded earlier during deposition or after open-system recrystallisation. If calcite is exposed to temperatures of greater than ~100 °C for tens to hundreds of millions of years, this bond reordering may occur (Dennis & Schrag, 2010; Passey & Henkes, 2012; Henkes, et al., 2014). The reordering process is interpreted to be a two-stage process with initial rapid isotope diffusion resulting in a change of ~1-40 °C at ambient temperatures of ~75-120 °C sustained for ~100 Myr. Following this, slow isotope exchange reactions between adjacent carbonate groups at >~150 °C sustained for >~100 Myr could bring the clumped isotope temperatures to the ambient temperature (Henkes, et al., 2014; Stolper & Eiler, 2015). Such bond reordering in calcite has been documented in natural samples. Dennis and Schrag (2010) hypothesised that some form of closed-system reordering must be occurring during slow cooling of rocks as they found that carbonatites with no petrographic or geochemical evidence for diagenesis were recording clumped isotope temperatures well below those expected for carbonatite crystallisation temperatures. This study led to the initial development of the bond reordering hypothesis, showing that the clumped isotope composition of calcite and phosphate did change in laboratory experiment when these minerals were exposed for several weeks at temperatures in excess of 200 ˚C (Passey & Henkes, 2012; Henkes, et al., 2014; Stolper & Eiler, 2015). Shenton et al., (2015) further confirmed with natural samples that different components (brachiopods, crinoids etc) of calcite limestones from the Palmarito Formation, Venezuela, and the Bird Springs Formation, Nevada, were affected by bond reordering during burial (to ~4-5 km, 150-175 °C) and exhumation.

The only available constraints on the kinetics of bond reordering in dolomite are from the published conference abstract of Bonifacie et al., (2013) which indicated dolomite was resistant to

solid-state bond reordering up to ~300 °C. Until the full results of these experiments - and hence the parameters required for modelling closed-system bond reordering in dolomite - are published, the exact effects of bond reordering on the Pinda Formation dolostones cannot be determined. We note that 300 ˚C is well above the well temperature offshore Angola, where our samples come from but how would the Pinda dolomite behave, if we assumed dolomite had similar Arrhenius parameters to calcite? In the absence of dolomite-specific modelling parameters, we used the bond reordering model for calcite of Passey and Henkes (2012) to investigate a 'worst-case' scenario for bond reordering in the Pinda dolostones. This was conducted using the input parameters for optical calcite MGB-CC-1 (Passey & Henkes, 2012) using their Equation 13 (first-order kinetics) and the evolution of Δ_{47} through time is modelled in the style of the Thermal History Reordering Models of Shenton et al. (2015).

Four scenarios were modelled. Three of these use a 'representative' Pinda burial curve, based on the dashed line on Figure 1b from thermal modelling by TOTAL for sample JM2923. These scenarios vary in their diagenetic histories: no post-deposition recrystallisation (scenario 1); shallow dolomitisation only (scenario 2); shallow dolomitisation and burial recrystallisation at ca. 25 Ma at a burial temperature of 115 ˚C (scenario 3) (Walgenwitz, et al., 1990). Scenario 4 is specific to the base of the Pinda Formation (sample JM3705), using an extrapolation of the representative Pinda curve to the present-day depth of ~3.7 km and ambient temperature inferred to be 170 °C from the geothermal gradient (dotted line in Figure 1b). For all 4 scenarios, deposition is assumed to be at 25 °C with shallow dolomitisation at 35 °C and burial recrystallisation at 25 Ma, if applicable (Walgenwitz, et al., 1990). For each of the (re)crystallisation events (deposition, early dolomitisation, recrystallisation during burial), the Δ_{47} is controlled by the temperature of the respective process, regardless of whether any change on Δ_{47} due to bond reordering has occurred before, as each represents an open-system (re)precipitation. Modelling results are shown in Figure 5.

In all four scenarios, no closed-system bond reordering occurs before the end of the Oligocene burial despite the ambient temperature reaching ~130 °C in the base Pinda scenario. In scenario 4 (base Pinda), the burial curve indicates that the open-system burial recrystallisation will occur at ~130 °C, i.e. towards the end of the Oligocene. As the ambient temperature increases from 130 °C to 170 °C in the 25 Myr between recrystallisation and the present-day, the temperature would be high enough to drive the Δ_{47} values in calcite to the ambient temperature resulting in 100 % bond reordering (Fig. 5a) and a recorded temperature of 170˚C. With the 'representative' Pinda burial history (sample JM2923, scenario 3), the burial curve indicates that the open-system burial recrystallisation will occur at ~115 °C towards the end of the Oligocene (Fig. 5b). As the ambient temperature increases from 115 °C to 147 °C (sample JM2923, Table 1 & Fig. 4c) in the 25 Myr between recrystallisation and the present-day, modelling indicates partial reordering of the Δ_{47} value would occur in calcite to a present-day clumped isotope temperature of 120 °C. Open-system burial recrystallisation at is important in facilitating post-recrystallisation closed-system bond reordering in calcite as in the scenarios where no burial recrystallisation is assumed (scenarios 1 and 2), there is very limited bond reordering. With shallow dolomitisation only (scenario 2), bond reordering would modify the observed temperature from 35 to 47 °C and with no post-deposition recrystallisation at all, bond reordering would modify the temperature from 25 to 37 °C (Fig. 5b).

Although the temperature generated through partial bond reordering of sample JM2923 (scenario 3) is close to the recorded clumped isotope temperature, it must be emphasised that these reordering models are based on the kinetics of calcite. Dolomite is perceived to have much slower

reordering kinetics (Bonifacie, et al., 2013). This is emphasised by the fact that modelling of bond reordering using the kinetics for calcite and the burial curve for the base of the Pinda Formation indicates that sample JM3705 would record the present-day ambient temperature of ~170 °C in its clumped isotope systematics. This is not the case – the clumped isotope temperature for this sample is 118 °C, well below ambient temperature (Table 1, Fig. 4c) reflecting the interpreted recrystallisation event at ca. 110 ˚C. We also note that we used the same Arrhenius parameters for bond reordering in the early dolomite and the recrystallised burial dolomite. This is unlikely to be the case, and recrystallised dolomite could be more resistant to bond reordering as it was equilibrated at higher temperature. The degree of stoichiometry of (proto-)dolomite is also likely to complicate bond reordering models. We acknowledge that while the kinetics of dolomite reordering are unpublished, our interpretation that the Pinda Formation dolostones are recording the temperature of diagenetic events cannot be proven beyond doubt. However, if the conclusions of Bonifacie et al., (2013) are valid, the temperature conditions (~300 °C) thought to be required for solid-state bond reordering in dolomite were not reached in the studied samples. This is supported by the results of our modelling simulations, that shows that the temperature recorded are compatible with a 110˚C recrystallization. Therefore our interpretation that the clumped isotopes are recording burial recrystallisation is well-founded.

The specificity of our study in the Pinda formation of offshore Angola is that samples are from deep cores and are at their maximum burial depth in the present day. This enables insight into clumped isotope systematics during deep burial without the complication of any potential closed-system resetting during slow geological exhumation as was encountered by Shenton et al., (2015). We suggest that in the Pinda Formation clumped isotopes are recording the palaeotemperatures of an open-system recrystallisation event that resulted in massive burial dolomitisation of an already dolomitic reservoir. Hence, reasonable fluid $\delta^{18}O$ values are calculated when using the clumped isotope data, while they appear rather high when using the fluid inclusion homogenisation temperatures. This illustrates that clumped isotope analysis can be a valuable tool in investigating the thermal history of deeply-buried carbonate reservoirs, and that it is of particular interest for distinguishing early-shallow from late-burial dolomitisation processes. In the Pinda Formation dolostones, the clumped isotopes recorded open-system burial recrystallisation at a temperature of ~100-120 °C. Our data further indicate that the clumped isotope signal was preserved during subsequent burial to conditions ~1600 m deeper (~3700 mbsf) and ~50 °C hotter (up to 161 °C). While the clumped isotope geothermometer does not yet have the spatial resolution to interrogate zonation within individual crystals or distinguish between multiple generations of thin cement layers, this study does show that its application to bulk samples has the ability to record diagenetic information in relatively homogeneous monophasic dolostones. It has indicated that the massive blocky planar-s dolosparite in the Pinda Formation formed during late burial recrystallisation at ~100-120 °C, a process that could not be documented from petrography and $\delta^{18}O$ (Eichenseer, et al., 1999). Advances in methodology (e.g. Hu*, et al.*, 2014; Petersen & Schrag, 2014) to increase spatial resolution to the millimetre and sub-millimetre scale will enable much wider usage of the clumped isotope palaeothermometer in reservoir characterization.

Conclusions

This study examined if carbonate clumped isotope palaeothermometry could be applied to characterise the thermal history of dolomitised sedimentary carbonate hydrocarbon reservoirs. It was performed on a set of seven dolostone samples from the Pinda Formation of offshore Angola

presently lying at their maximum burial depth, ~2000-3700 mbsf. Clumped isotope data suggest that temperatures derived from a well-established palaeothermometric technique – fluid inclusions – have been reset to current ambient well temperatures. Clumped isotope temperatures, however, record lower temperatures corresponding to open-system burial recrystallisation occurring prior to present-day maximum burial. Fluid $\delta^{18}O$ values calculated for the five deepest samples overlap with present-day porewater $\delta^{18}O$ while mineral $\delta^{18}O$ supports the conclusion that clumped isotopes are recording burial recrystallisation conditions. Closed-system isotopic bond reordering is not believed to have affected the Pinda Formation samples, therefore we contend that clumped isotope analysis can be a valuable tool in characterising the thermal history of dolomite hydrocarbon reservoirs. It may be particularly useful to help distinguish early-shallow from deep-burial origin of dolomite formations.

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Figure Captions

Figure 1: (a) map showing the general location of the studied samples, offshore Angola, after Eichenseer et al., (1999); (b) burial history of the Pinda Formation.

Figure 2: Fluid inclusion temperatures for the Pinda Formation (data reproduced from Eichenseer et al., 1999). Fluid inclusion homogenisation temperatures shown as red squares represent sample averages, while horizontal black bars represent the range of individual T_h values. Current ambient well temperatures are shown as blue diamonds, and are in close concordance with T_h average values (with one exception at ~3 km depth).

Figure 3: Plane polarized light photomicrographs showing typical petrographic textures of samples from the Pinda Formation. (a) blocky planar-s dolosparite texture typical of many of the samples, arrow denotes example of a sand grain; (b) red staining indicating minor calcite component, arrow denotes example of preserved ooid fabric typical of many of the samples; (c) moldic pore after ooid, lined with small euhedral dolomite rhombs; (d) rare preserved shell fabric.

Figure 4: Isotope data and Δ_{47}-derived temperatures for the seven samples from the Pinda Formation analysed for clumped isotopes, plotted against sample depth. (a) $\delta^{13}C$; (b) $\delta^{18}O$; (c) clumped isotope, fluid inclusion and ambient well temperatures; (d) parent fluid $\delta^{18}O$, shaded areas represent typical source fluid values.

Figure 5: 'Worst case' scenario of post-depositional evolution of Δ_{47} values in the Pinda Formation, assuming the samples were calcite not dolomite. Modelled in the style of Shenton et al., (2015) using the calcite reordering kinetics of Passey and Henkes (2012) for optical calcite MGB-CC-1. (a)

449 the base Pinda, based on an extrapolation of the 'representative' Pinda burial history modelled by
450 TOTAL shown in (b).
451
452 Table Captions
453
454 Table 1: Summary table of sample details, isotopic values and temperatures. CDES denotes Carbon
455 Dioxide Equilibration Scale (Dennis, et al., 2011); T_h denotes fluid inclusion homogenisation
456 temperature (sample average); T_{well} denotes current ambient well temperature; T_{cl} denotes
457 clumped isotope temperature.
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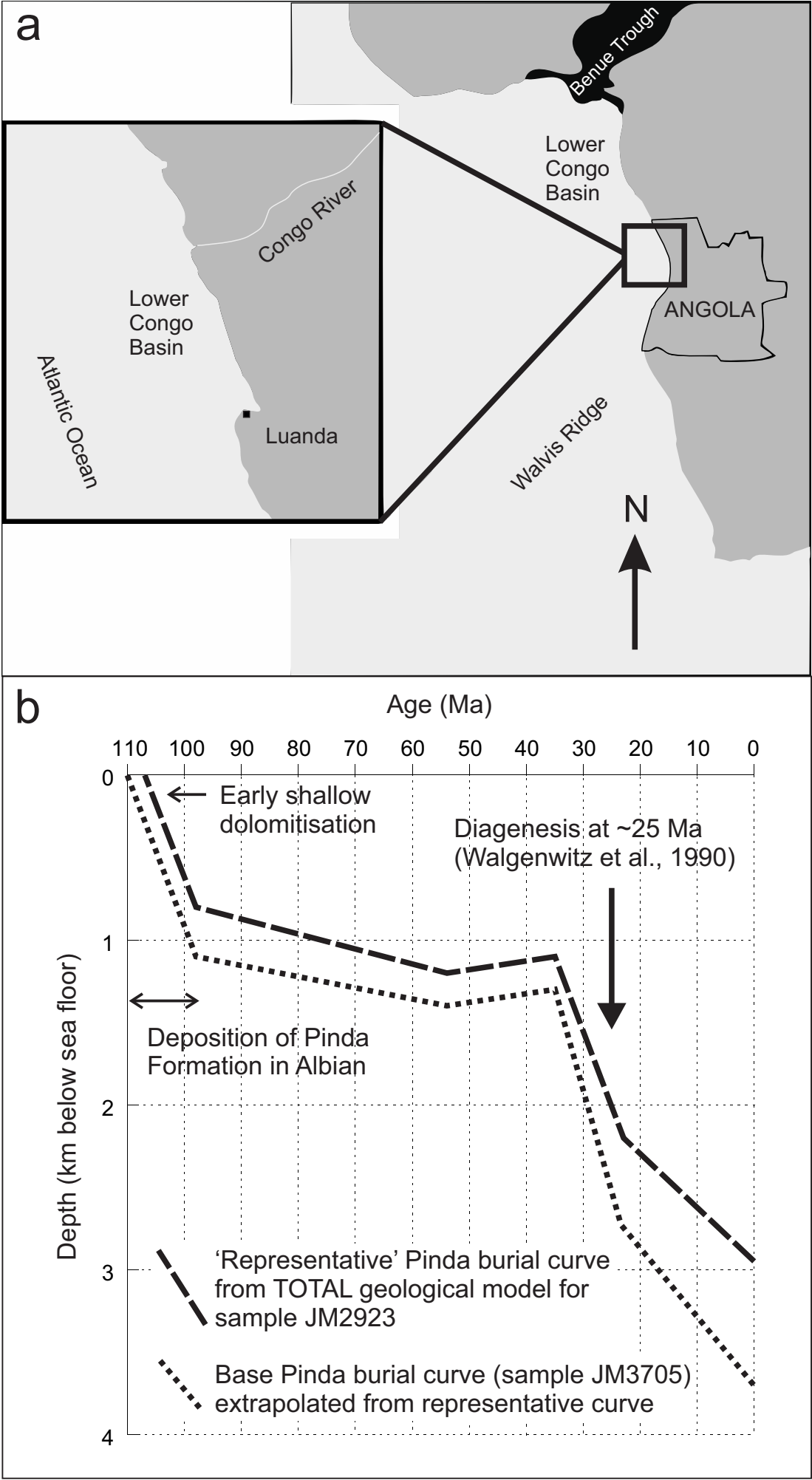
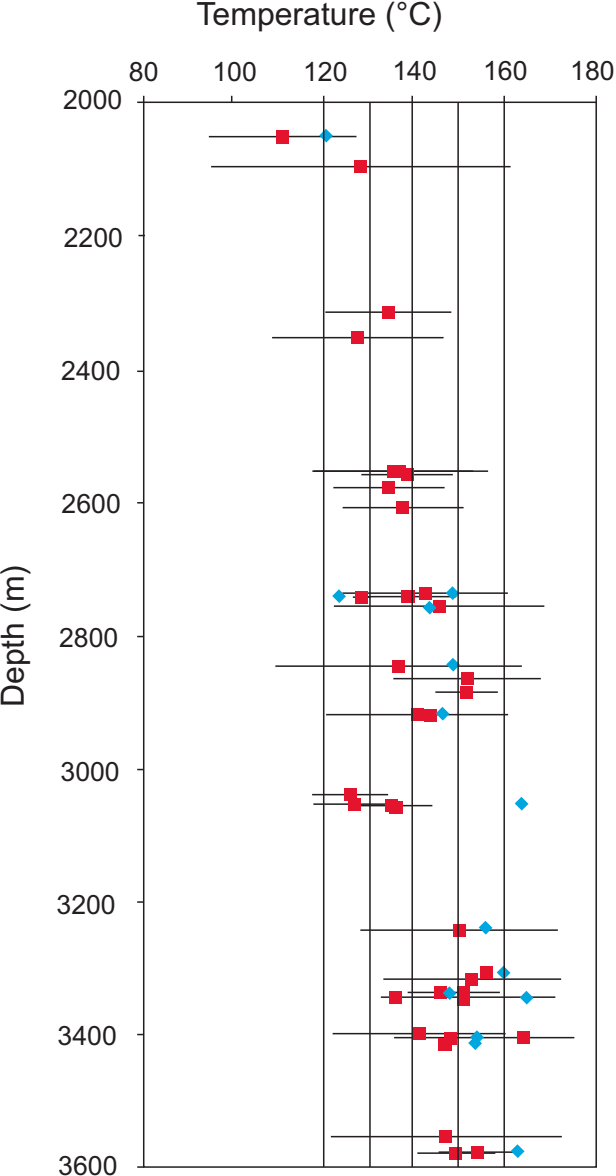
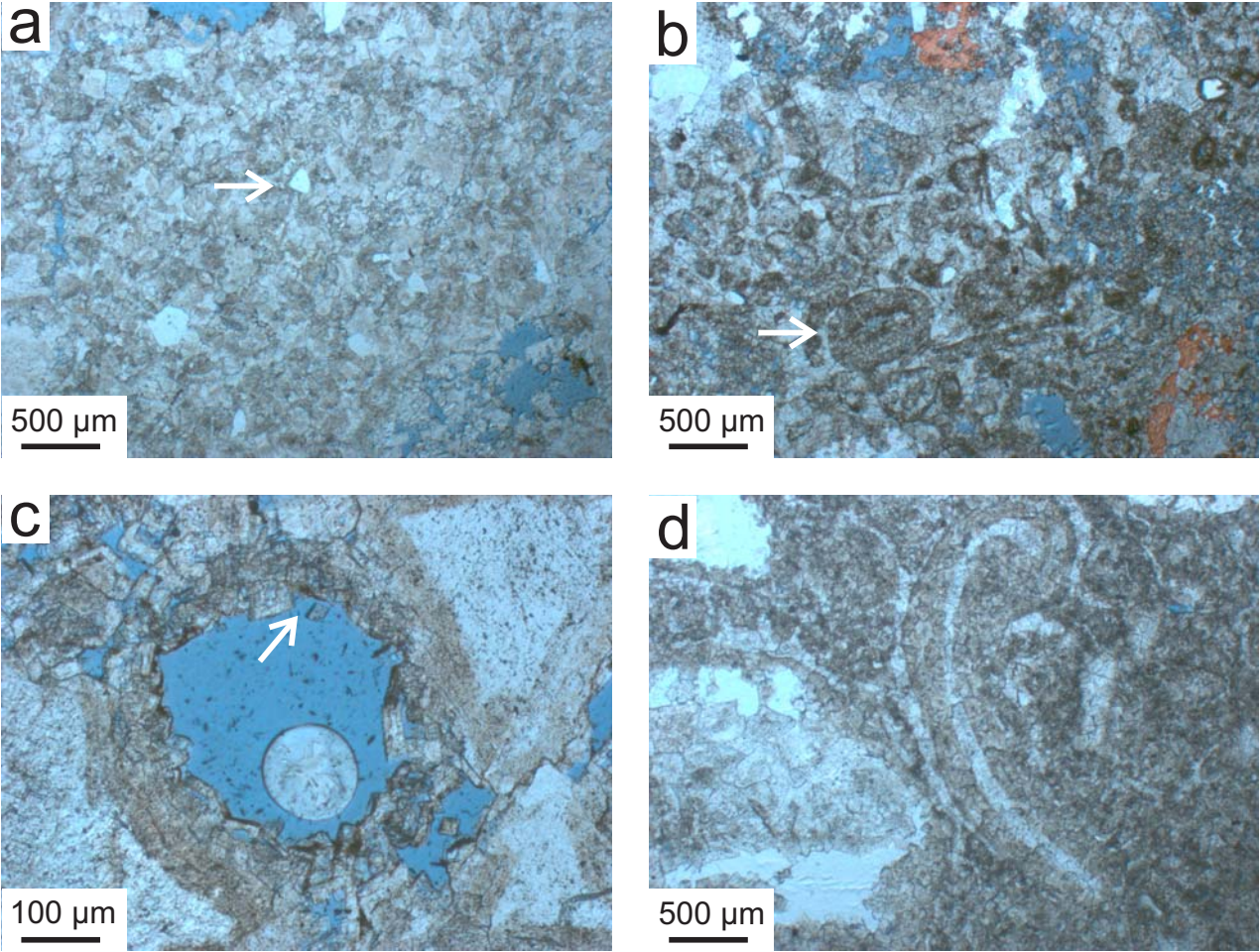
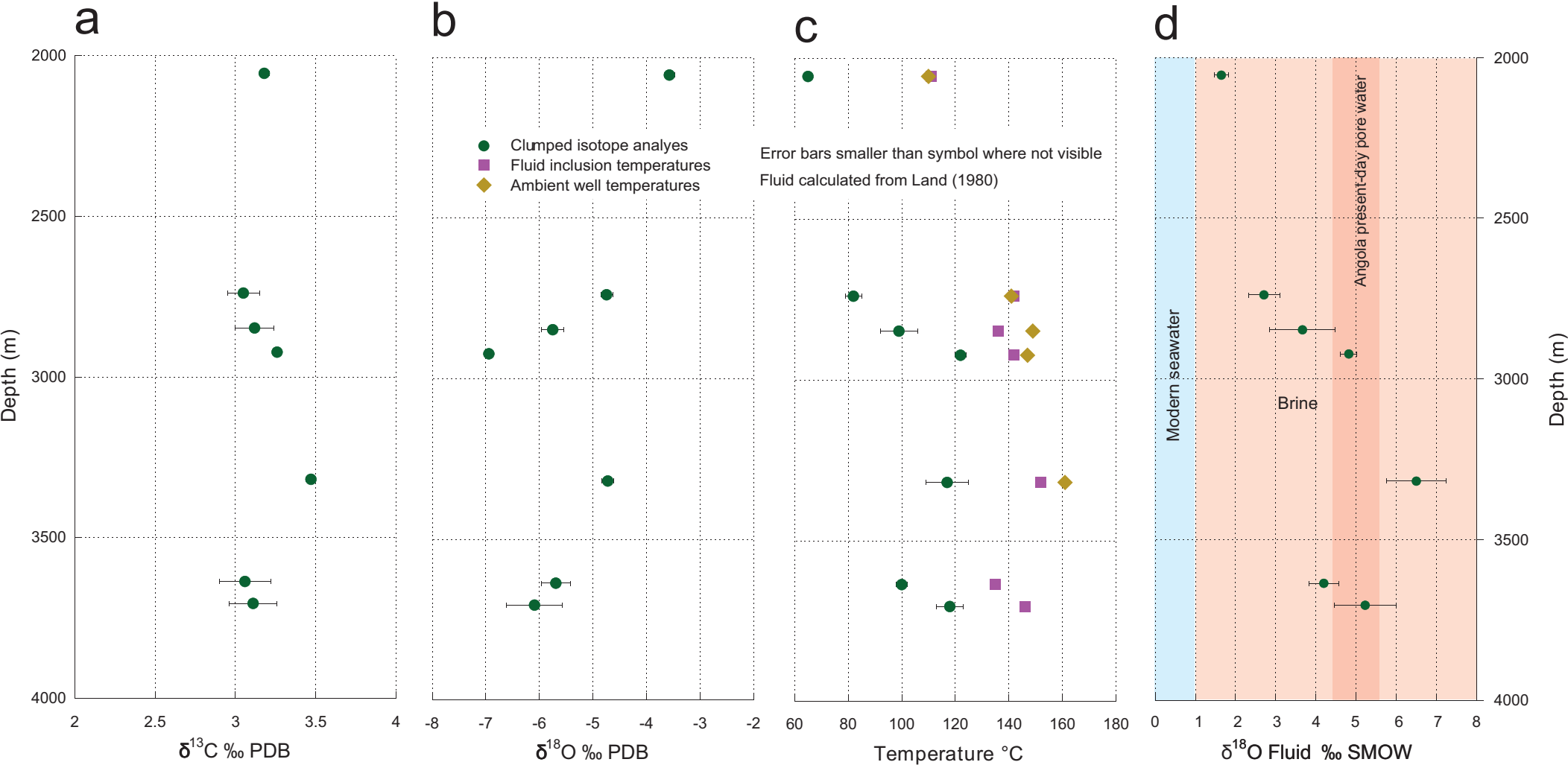
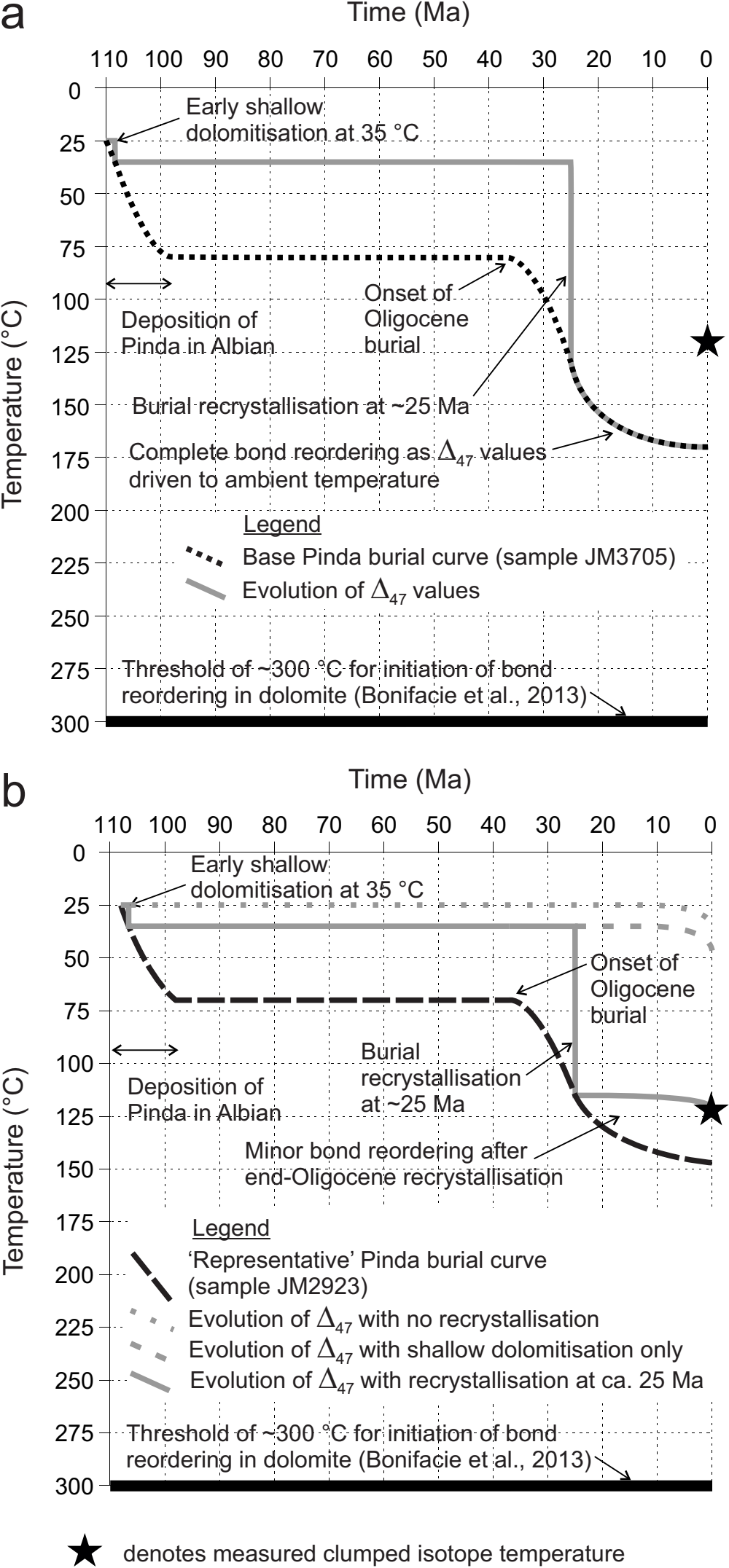
Sample	Depth (m)	No. of Analyses	Mineral $\delta^{13}C$ (‰) PDB	StDev (‰)	Mineral $\delta^{18}O$ (‰) PDB	StDev (‰)	Δ_{47} CDES (‰)	StErr (‰)	T_h (°C)	T_{well} (°C)	T(Δ_{47}) (°C)	StErr (°C)	Fluid $\delta^{18}O$ (‰) SMOW	StErr (‰)
JM2055	2055	3	3.18	0.03	-3.57	0.10	0.592	0.001	111	110	65	1	1.7	0.2
JM2740	2740	3	3.05	0.10	-4.74	0.11	0.560	0.005	142	141	82	3	2.7	0.4
JM2848	2848	5	3.12	0.12	-5.75	0.21	0.530	0.011	136	149	99	5	3.7	0.8
JM2923	2923	3	3.26	0.01	-6.94	0.03	0.495	0.003	142	147	122	1	4.8	0.2
JM3319	3319	3	3.47	0.03	-4.72	0.11	0.503	0.010	152	161	117	6	6.5	0.8
JM3637	3637	5	3.06	0.16	-5.69	0.27	0.528	0.004	135	n/a	100	2	4.2	0.4
JM3705	3705	3	3.11	0.15	-6.09	0.52	0.502	0.008	146	n/a	118	7	5.2	0.8


a
Benue Trough
Lower
Congo
Basin
Congo River
Lower
Congo
Basin
ANGOLA
Atlantic Ocean
Luanda
Walvis Ridge
N
b
Age (Ma)
110
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
Depth (km below sea floor)
Early shallow
dolomitisation
Diagenesis at ~25 Ma
(Walgenwitz et al., 1990)
Deposition of Pinda
Formation in Albian
'Representative' Pinda burial curve
from TOTAL geological model for
sample JM2923
Base Pinda burial curve (sample JM3705)
extrapolated from representative curve


Temperature (°C)
80
100
120
140
160
180
Depth (m)
2000
2200
2400
2600
2800
3000
3200
3400
3600


a
500 µm
b
500 µm
c
100 µm
d
500 µm


a
b
c
d
Depth (m)
2000
2500
3000
3500
4000
Clumped isotope analyes
Fluid inclusion temperatures
Ambient well temperatures
Error bars smaller than symbol where not visible
Fluid calculated from Land (1980)
Modern seawater
Angola present-day pore water
Brine
δ13C ‰ PDB
δ18O ‰ PDB
Temperature °C
δ18O Fluid ‰ SMOW


a
Time (Ma)
110 100 90 80 70 60 50 40 30 20 10 0
0 25 50 75 100 125 150 175 200 225 250 275 300
Temperature (°C)
Early shallow dolomitisation at 35 °C
Deposition of Pinda in Albian
Onset of Oligocene burial
Burial recrystallisation at ~25 Ma
Complete bond reordering as Δ47 values driven to ambient temperature
Legend
Base Pinda burial curve (sample JM3705)
Evolution of Δ47 values
Threshold of ~300 °C for initiation of bond reordering in dolomite (Bonifacie et al., 2013)
b
Time (Ma)
110 100 90 80 70 60 50 40 30 20 10 0
0 25 50 75 100 125 150 175 200 225 250 275 300
Temperature (°C)
Early shallow dolomitisation at 35 °C
Onset of Oligocene burial
Deposition of Pinda in Albian
Burial recrystallisation at ~25 Ma
Minor bond reordering after end-Oligocene recrystallisation
Legend
'Representative' Pinda burial curve (sample JM2923)
Evolution of Δ47 with no recrystallisation
Evolution of Δ47 with shallow dolomitisation only
Evolution of Δ47 with recrystallisation at ca. 25 Ma
Threshold of ~300 °C for initiation of bond reordering in dolomite (Bonifacie et al., 2013)
denotes measured clumped isotope temperature