

Research Paper

Geochronology and mantle origin of CO₂-rich fluid flow in a Cretaceous carbonate reservoir, offshore Angola

Nathan Rochelle-Bates^{a,1}, Stefan Schröder^{a,*}, Greg Holland^a, Nick M.W. Roberts^b, Cedric M. John^{c,2}, Ian Millar^b, Richard Dixon^a

^a Department of Earth and Environmental Sciences, University of Manchester, Manchester, UK

^b Geochronology and Tracers Facility, British Geological Survey, Nottingham, UK

^c Department of Earth Science and Engineering, Imperial College London, London, UK

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ABSTRACT

Drilling on the volcanic rifted margin of southern Angola has encountered high volumes of CO₂ and evidence for hydrothermal fluid flow, but the sources of CO₂, the timing of fluid flow and its impact on basin thermal structure, reservoir evolution and resource distribution have so far remained unresolved. This study integrates in-situ U-Pb geochronology, noble gas and clumped isotope geochemistry, and petrography to reconstruct the burial history and fluid-rock interaction in a CO₂-rich Aptian carbonate reservoir. The carbonates have not preserved depositional ages, but they were recrystallized at 111.2 ± 3.4 Ma and 87.7 ± 5.5 Ma, coincident with thermal pulses at temperatures of 114–138 °C and 145–149 °C (1SE), respectively. Evolved basinal fluids that had interacted with siliciclastics, volcanic and/or basement rocks, but also contained a significant mantle volatile component, were responsible for recrystallization. Decompaction analysis suggests that at least the older event can be considered hydrothermal. The occurrence of such a thermal and fluid pulse within c. 6–16 Ma of deposition will have significantly altered the thermal structure of the basin. The Albian age of fluid flow and calcite recrystallization complements age data from the conjugate Brazilian margin and suggests that this widespread but spatially variable event was genetically linked to the early stages of oceanic spreading. The second fluid pulse coincides with the age of the Peri-Atlantic Alkaline igneous Province (PAAP). This study highlights the importance of early diagenetic fluid flow involving mantle-derived volatiles for basins on the South Atlantic conjugate margins.

1. Introduction

Volcanic rifted margins are characterized by significant vertical and horizontal stratigraphic heterogeneity due to interactions between sedimentary, volcanic and volcanoclastic lithologies. The presence of volcanic units and deep-seated faults modifies the thermal regime of the evolving rift basin (e.g. Morgan, 1982; Senger et al., 2017) and facilitates the circulation of hydrothermal fluids, which can carry significant volumes of magmatic volatiles such as CO₂, SO₂, and CH₄ (Robb, 2005). These fluids can have significant impacts on diagenesis, pore networks and basin thermal structure, while the volatiles impact resource production strategies and constitute unwanted greenhouse gases (e.g. Davies and Smith Jr, 2006; Lima et al., 2020; Neilson and Oxtoby,

2008). It is thus crucial to constrain where and when such potentially volatile-rich hydrothermal fluids interacted with the basin fill, with the aim to reconstruct tectonostratigraphic and thermal basin evolution, which in turn determine the distribution of natural resources.

However, the identification of volcanic-derived volatiles such as CO₂ is not always straightforward, as most geochemical tracers normally used in diagenetic studies are not diagnostic for mantle-derived CO₂ (Hoefs, 1997). Geochemically inert noble gases are present in all crustal fluids (Ballentine et al., 2002) and have proven to be a useful fingerprint for fluid origins, fluid dynamics in the subsurface, and the identification of magmatic sources (e.g. Ballentine and O'Nions, 1993; Gilfillan et al., 2025; Holland and Gilfillan, 2013). Mineral geochronology provides a temporal framework for diagenesis, but U-Pb geochronology as a

* Corresponding author.

E-mail address: stefan.schroeder@manchester.ac.uk (S. Schröder).

¹ present address: School of Earth and Environmental Sciences, University of St Andrews, St Andrews, UK.

² present address: Digital Environment Research Institute, Queen Mary University of London, UK.

method of choice has been problematic in carbonate diagenesis due to low uranium concentrations in most sedimentary and diagenetic carbonates, and because of low spatial analytical resolution (Parnell and Swainbank, 1990; Roberts et al., 2017). The application of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has considerably advanced geochronology of carbonate diagenesis (e.g. Brito et al., 2024; Manguet et al., 2018; Roberts et al., 2017; Rochelle-Bates et al., 2021).

Basins in Angola and Brazil host important lacustrine carbonates ('Pre-Salt' carbonates) that were deposited in alkaline lakes influenced

by volcanic catchment areas (Wright, 2022; Wright and Barnett, 2015). Lithologies in these lakes include crystal shrub and spherulitic limestones, Mg clays, laminites, stromatolites, but also travertines forming where fluids reached the surface (Farias et al., 2019; Figueiredo et al., 2025; Wright and Barnett, 2015). On the Brazilian margin (Santos and Campos basins), a significant body of work has constrained the depositional framework and has determined depositional-diagenetic ages, many using LA-ICP-MS U-Pb geochronology (Alkmim et al., 2025; Brito et al., 2024; Figueiredo et al., 2025; Rochelle-Bates et al., 2022; Strugale et al., 2025). The importance of hydrothermal fluids is increasingly

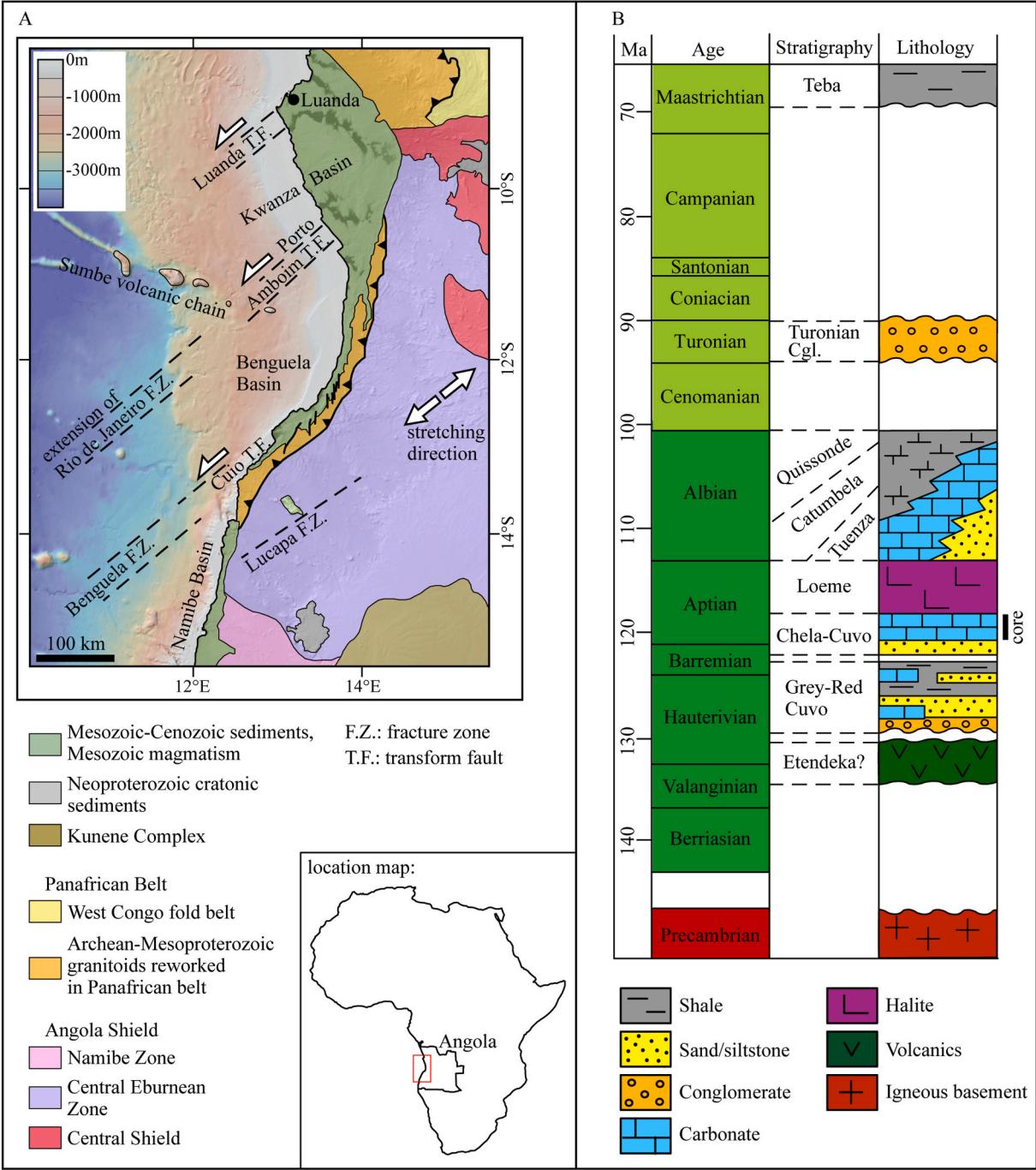


Fig. 1. (A) Onshore geology and offshore bathymetry of southwestern Angola. The main structural elements between the Namibe, Benguela and Kwanza basins are shown. The Benguela Basin represents a transform margin opening sub-parallel to the stretching direction. Map sources: BRGM (2007); de Carvalho et al. (2000); Ferreira et al. (2024); Guiraud et al. (2010). Bathymetry from Global Multi Resolution Topography (GMRT 4.4.0; Ryan et al., 2009), available at <https://www.gmrt.org>. (B) Stratigraphy of the onshore Benguela Basin after Guiraud et al. (2010). Chronostratigraphy after International Chronostratigraphic Chart, v2024/12 (Cohen et al., 2013). The position of the studied core is indicated.

being recognized in Angola and Brazil (Figueiredo et al., 2025; Girard et al., 2017; Godeau et al., 2021; Lima and De Ros, 2019; Loma et al., 2018). Although depositional and diagenetic processes were likely similar between Angola and Brazil, significantly less data are available in the public domain for Angola. Both margins have the added complication that many hydrocarbon exploration wells have encountered significant CO₂ volumes in potential reservoirs (Gilfillan et al., 2025; Liu et al., 2022, 2023; Santos Neto et al., 2012).

The novelty of this contribution is in combining petrography, LA-ICP-MS U-Pb geochronology, noble gas and clumped isotope analysis to reconstruct the diagenetic evolution of a core through a CO₂-bearing carbonate reservoir in the Benguela Basin of Angola. This integrated approach provides an absolute temporal framework for diagenetic carbonate phases and constrains fluid types and origins, ultimately deriving the regional geodynamic driving mechanisms for diagenesis and fluid flow.

2. Geological setting

The Benguela Basin in southern Angola developed as part of the Central South Atlantic rifting between Africa and South America. The southern limit to the Namibe Basin is formed by the Benguela Fracture Zone and Cuio Transform Fault with a 050° trend (Fig. 1A; Guiraud et al., 2010). Northwards the Benguela Basin transitions to the southern Kwanza Basin via the Sumbe volcanic seamount chain trending 110° (Fig. 1A; Guiraud et al., 2010). The Benguela Basin opened as a left-lateral transform margin parallel to the NE-SW stretching direction. Faults within the basin trend NNE-SSW to N-S, dip both seaward and landward, and define short syn-rift half graben (Fig. 1A; Guiraud et al., 2010).

Initial rifting coincided with volcanism of the Paraná-Etendeka large igneous province (LIP) at c. 132 Ma (Fig. 1B; Marzoli et al., 1999; Renne et al., 1996). Basalt and latite lava flows in syn-rift graben of the Namibe and Kwanza basin represent this LIP (Bero Volcanic Complex; Jacobs et al., 2024; Jerram et al., 2019; Marsh and Swart, 2018). This volcanism is not directly recorded in outcrops or cores of the Benguela Basin (Guiraud et al., 2010), but has been modelled below the Cretaceous sediments using geophysical data (Rey-Moral et al., 2026). Following rift onset, rifting propagated northwards (Kukla et al., 2018). Between the Hauterivian and Barremian/Aptian (c. 132–121 Ma), siliciclastic and carbonate sediments filled the syn-rift graben in alluvial, fluvial and lacustrine depositional environments (Fig. 1B; Brownfield and Charpentier, 2006; Guiraud et al., 2010; Saller et al., 2016). The syn-rift graben transitioned to regionally extensive sag basins, where lacustrine carbonate sedimentation occurred during the Barremian–Aptian. Afterwards, the onset of a marine incursion led to precipitation of thick Aptian evaporites (Fig. 1B; Sabato Ceraldi and Green, 2017). Oceanic spreading between Angola and Brazil initiated by the early Albian (c. 110 Ma; Chaboureaud et al., 2013; Davison, 1999; Kukla et al., 2018; Torsvik et al., 2009), followed by a major phase of later Albian salt translation in the subsurface, due to differential post-rift thermal subsidence (Heine et al., 2013; Jackson et al., 2005). Younger volcanism in the Benguela Basin is represented by the Sumbe volcanics (c. 100 Ma), the Serra de Neve alkaline complex (93–91 Ma), and the Bentiaba basanite (88–81 Ma; Peri-Atlantic Alkaline Province, PAAP) (Comin-Chiaromonti et al., 2011; Jerram et al., 2019; Matton and Jébrak, 2009).

The studied core represents 25 m of carbonates in the Cuvo/Chela formations directly underlying the Aptian Loeme salt (Fig. 1B; Brownfield and Charpentier, 2006; Guiraud et al., 2010). The core itself contains no biostratigraphic information, but it is located above a well section with ostracods assigned to Aptian biozones AS11–12, indicating a depositional age slightly younger than 121.4 Ma for the cored section (following international chronostratigraphic chart, version 2024/12; Bate, 1999; Buratti and Dupont, 2026; Cohen et al., 2013). Salt deposition in the Kwanza Basin is estimated to have started at c. 124–121 Ma

(Karner and Gamboa, 2007). Age of the cored section is here estimated at c. 124–121 Ma, which compares well with the most recent depositional to eodiagenetic calcite U-Pb age data from Santos and Campos basin sag carbonates (124.8 ± 2.6 – 120 ± 1.6 Ma and 126.2 to 120 Ma; Alkmim et al., 2025; Figueiredo et al., 2025), although some diachroneity between the margins is likely.

3. Materials and methods

Samples were taken along the entire length of the core and are representative of all encountered lithofacies. Petrography and mineral paragenesis in the studied core were established using polarized light, ultraviolet light (UV), cathodoluminescence (CL), and scanning electron (SEM) microscopy on 32 thin sections and sample chips. Transmitted light analysis was done with a Nikon Eclipse LV100N Pol polarizing microscope fitted with a CoolLED pE-300-W UV source. Cathodoluminescence analysis of uncovered thin sections was carried out on a Nikon Eclipse Ci Pol microscope attached to a CITL Mk 5.2 controller. The operating conditions for the electron beam were 10–15 kV, c. 500 µA and a vacuum of c. 0.08 torr. A subset of sample chips were gold coated and mounted for SEM analysis on a Quanta 650 ESEM under low vacuum with a 15 kV accelerating voltage.

Seven samples containing calcite shrubs (samples B1–7) and three samples with calcite spherulites (samples B8–10) were analyzed by LA-ICP-MS U-Pb geochronology at the Geochronology and Tracers Facility, British Geological Survey, following the method of Roberts et al. (2017). All results represent lower intercept ²⁰⁶Pb/²³⁸U dates from Tera-Wasserburg plots; systematic uncertainties have been propagated to derive 2σ errors (see Data Repository 1).

Eleven powder samples (B1–B5, B6.1, B6.2, B7, B8.1, B9, B10) were extracted by micro-drill for stable isotopic analysis (Table 1). The Δ₄₇ analysis (which incorporated δ¹³C and δ¹⁸O analysis) of 6 samples (B1, B5, B6.1, B7, B8.1, B10) was performed in the Qatar Stable Isotope Laboratory at Imperial College London. One of these (B8.1) was not dated via LA-ICP-MS. Typical sample sizes were in the range of 3–4 mg per replicate. Samples were treated for 20 min by low-temperature plasma ashing to remove organic contaminants. Reaction with 105% orthophosphoric acid at 90°C liberated CO₂ that was purified using a manual line (Davies and John, 2018) before being loaded into a Thermo 253 mass spectrometer. The results were analyzed using the software package Easotope (John and Bowen, 2016). Standards used for data correction included ETH2 and ETH3 carbonates (Bernasconi et al., 2021) as well as CO₂ heated at 1000°C (heated gas) and equilibrated at 30°C based on Dennis et al. (2011). For non-linearity correction, the Pressure Baseline Correction method of Bernasconi et al. (2013) was used. Analytical precision (1σ) of Δ₄₇ varied between 0.02 and 0.25 (Table 1).

For 5 powdered samples (B2–4, B9, and B6.2 for inter-laboratory comparison), δ¹³C and δ¹⁸O analysis was performed at the University of Liverpool using an automated on-line-system attached to a Thermo-Elemental Delta Plus XL mass spectrometer. Samples were reacted with phosphoric acid at 25°C for 30 min. Estimated analytical precision (1σ), based on replicate analysis of laboratory calcite quality control materials, is better than ±0.2‰ for both carbon and oxygen delta values (Table 1). All δ¹³C and δ¹⁸O results are expressed in the standard delta notation as per mil differences to the V-PDB (‰ V-PDB) or V-SMOW (‰ V-SMOW) standards. Oxygen isotope fractionation between calcite and water was assessed using the equations (O'Neil et al., 1969):

$$\delta^{18}\text{O}_{\text{calcite}}(\text{SMOW}) = 1.03086 \times \delta^{18}\text{O}_{\text{calcite}}(\text{PDB}) + 30.86 \quad (\text{Eq. 1})$$

$$\delta^{18}\text{O}_{\text{calcite}}(\text{SMOW}) - \delta^{18}\text{O}_{\text{water}}(\text{SMOW}) = 2.78 \times \left(\frac{10^6}{T^2} \right) - 2.89 \quad (\text{Eq. 2})$$

where T = temperature from Δ₄₇ analysis in Kelvin (Table 1).

Thirteen micro drilled samples (B1–4, B5.1, B5.2, B7, B9–15) were

Table 1
Stable isotope data.

Sample ID	ICL	Liverpool	$\delta^{13}\text{C}$	$\delta^{13}\text{C}$ error ($\pm 1\sigma$)	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$ error ($\pm 1\sigma$)	Δ_{47}	Δ_{47} error ($\pm 1\sigma$)	Age cluster	Fabric			
	(No of replicates)		(‰ V-PDB)	(‰ V-PDB)	(‰ V-PDB)	(‰ V-PDB)	(‰ C-DES)	(‰ C-DES)					
B1	x (5)		1.00	0.03	−14.95	0.24	0.48	0.01	generation 1	shrub			
B2		x	1.10	0.20	−15.59	0.20	n.d.	n.d.	generation 2	shrub			
B3		x	0.86	0.20	−13.48	0.20	n.d.	n.d.	generation 1	shrub			
B4		x	0.87	0.20	−13.99	0.20	n.d.	n.d.	generation 1	shrub			
B5	x (5)		0.96	0.02	−14.66	0.15	0.50	0.02	generation 1	shrub			
B6.1	x (1)		1.30	n/a	−13.13	n/a	0.48	n/a	generation 1	shrub			
B6.2		x	1.38	0.20	−13.66	0.20	n.d.	n.d.	generation 1	shrub			
B7	x (5)		1.17	0.05	−13.82	0.13	0.46	0.01	generation 2	shrub			
B8.1	x (6)		1.20	0.05	−16.54	0.25	0.46	0.02	not dated	spherulite			
B9		x	0.91	0.20	−18.22	0.20	n.d.	n.d.	generation 1	spherulite			
B10	x (2)		0.82	0.04	−15.27	0.06	0.49	0.02	generation 2? ^a	spherulite			
Sample ID	Replicates	Δ_{47} temperature	Min temperature (1SE)	Max temperature (1SE)	Min temperature (95% CL)	Max temperature (95% CL)	Fluid $\delta^{18}\text{O}$	Min fluid $\delta^{18}\text{O}$ (1SE)	Max fluid $\delta^{18}\text{O}$ (1SE)	Min fluid $\delta^{18}\text{O}$ (95% CL)	Max fluid $\delta^{18}\text{O}$ (95% CL)	Age cluster	Fabric
		(°C)	(°C)	(°C)	(°C)	(°C)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)		
B1	5	134.5	131.4	137.6	126.1	143.3	2.10	1.59	2.60	1.14	3.05	generation 1	shrub
B5	5	119.4	113.7	125.5	104.0	136.9	1.08	0.39	1.79	−0.58	2.75	generation 1	shrub
B6.1	1	129.8	n.c.	n.c.	n.c.	n.c.	3.58	n.c.	n.c.	n.c.	n.c.	generation 1	shrub
B7	5	147.0	145.1	149.0	141.7	152.6	4.24	3.97	4.53	3.70	4.79	generation 2	shrub
B8.1	6	149.8	143.2	156.8	133.4	168.4	1.65	0.89	2.41	0.11	3.19	not dated	spherulite
B10	2	126.7	114.1	140.5	21.9	714.9	1.11	−0.11	2.31	−13.52	15.72	generation 2? ^a	spherulite

1 σ : 1 standard deviation.

n/a: small number of replicates does not allow error calculation.

n.d.: not determined (only d13C and d18O in Liverpool laboratory).

1SE: 1 standard error; 95% CL: 95% confidence level.

n.c.: not calculated, absent error in isotope measurement.

^a age (89.4 $\pm$ 8.2 Ma) fits generation 2, but removed from age pool due to high MSWD (=4).

analyzed for radiogenic Sr isotopes at the Geochronology and Tracers Facility, British Geological Survey. Analysis was conducted using a Thermo-Finnigan Triton TIMS instrument in static collection mode. An internal NBS 987 standard was used for calibration with a reproducibility of $\pm 0.1\%$ (2σ). Data were corrected to an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at c. 121 Ma using Sr and Rb concentrations measured together with Sr isotopes via inductively-coupled plasma mass spectrometry (ICP-MS) (Table 2). Determination of trace element concentrations by ICP-MS was carried out at the Williamson Research Centre, University of Manchester. Prior to analysis, 0.03–0.1 mg samples were drilled from carbonate phases and digested in 6M HCl which was progressively diluted to 1.5M over 3 days. The samples were centrifuged and then analyzed on an Agilent 7700x ICP-MS.

Noble gas analysis (He, Ar, Kr, and Xe) was conducted on 6 core samples (samples B1.1, B1.2, B3, B8, B13, B15) in calcite, quartz and sphalerite phases. In addition, calcite and hematite phases in two samples from onshore travertines in the Namibe Basin of southern Angola (samples N1, N2; Rochelle-Bates et al., 2021) were equally analyzed for comparison (Table 3). Analysis used a VG5400 mass spectrometer in the noble gas laboratories at the University of Manchester following standard noble gas extraction and separation procedures (Barry et al., 2016). Gas was extracted by manual crushing of 50–80 mg samples under ultra-high vacuum ($<2 \times 10^{-8}$ mbar) using modified Swagelok valves with rounded steel tips. Samples were fully crushed in one step when the valve tip was fully extended. Samples were purified and analyzed following standard procedures that use activated charcoal at liquid nitrogen temperature to separate He from Ar, Kr and Xe. A line/crusher blank and an air standard were analyzed for each sample.

4. Results

4.1. Petrography and mineral paragenesis

The core contains carbonate, sulfate, sulfide and silicate mineral phases (Figs. 2–4). Their relative paragenetic succession is summarized in Fig. 5. Depositional textures are spherulite and shrub framestones and laminites, stromatolites, as well as breccias with intraclasts. Spherulites and shrubs are radial-fibrous calcite structures. Shrubs consist of highly asymmetric and bifurcating crystal bundles a few mm long (Fig. 2A), whereas spherulites are symmetrical to slightly asymmetrical and usually <2 mm in diameter (Fig. 2B–D). There is a notable absence of Mg-phyllsilicates, which are typically associated with spherulites and some shrub fabrics in other Pre-Salt successions (Wright and Barnett, 2015). All primary calcite fabrics have recrystallized to micro-rhombs aligned along their c-axes and with homogenous luminescence (phase C1; Fig. 2E). The result is a pseudo-fibrous structure with sweeping extinction under cross-polarized light that includes both fascicular-optical (divergent fibers) and radial-fibrous (straight fibers)

Table 2
Strontium isotope data.

Sample	Sr (ppm)	Rb (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{ini}}$	error (2σ)
B1	1423.45	0.08	0.713229	0.713229	0.000012
B3	2100.84	0.11	0.713285	0.713285	0.000012
B4	1877.06	n.d.	0.713286	n.d.	0.000012
B5.1	1725.76	0.08	0.713186	0.713186	0.000015
B5.2	1761.19	0.02	0.713230	0.713230	0.000009
B7	1714.19	n.d.	0.713591	n.d.	0.000008
B9	1492.45	0.17	0.713206	0.713205	0.000007
B10	2126.39	0.11	0.713056	0.713056	0.000011
B11	1684.84	0.13	0.713243	0.713243	0.000013
B12	1703.94	0.07	0.713317	0.713317	0.000012
B13	1393.81	0.11	0.713292	0.713292	0.000008
B14	1456.92	n.d.	0.713247	n.d.	0.000012
B15	1401.56	n.d.	0.713647	n.d.	0.000012

n.d.: not determined.

calcite (Fig. 2A; Kendall, 1985; Kendall and Tucker, 1973; Richter et al., 2011). Inside a given shrub, spherulite or thin section, micro-rhombs can vary in size between 5 and 100 μm , and their long physical (not optical) axes can change by 90° relative to the fiber axis. Micro-rhomb amalgamation and calcite overgrowths are common (Fig. 2E). This recrystallized calcite phase C1 was analyzed for noble gases.

Depositional fabrics are cemented by isopachous circumgranular calcite with blocky-rhombic and slightly dogtooth morphology (phase C2; Fig. 2C–F). These cements are locally spalled, with pseudo-fibrous spherulites and shrubs partly dissolved below the cement (Fig. 2F). Early diagenesis further includes isolated dolomite rhombs in pore space and as matrix replacement (Fig. 3A–B). Dolomite rhombs are 25–300 μm in size and typically consist of a cloudy inclusion-rich core and clear overgrowths (phase D1). Under cathodoluminescence the rhombs show moderately bright cores with dull overgrowths and an outer moderately bright rim (Fig. 3B). Rhombs locally form stringers and bands of planar-e to planar-s mosaics (Fig. 3A–B).

The earliest quartz phases are clotted and laminated botryoidal-fibrous quartz and microquartz (phase Q1). They contain ghost structures of spherulites and shrubs, spherical microporosity, and locally corroded early dolomite rhombs of phase D1 as well as possible remnants of Mg-phyllsilicates (Fig. 2C–D, Fig. 3C–D). This quartz phase locally occurs in reworked breccia intraclasts where quartz fabrics are cut at the clast edge.

Dogtooth quartz cement (phase Q2a, crystal size $<200\ \mu\text{m}$) lines vugs and dissolution-enhanced fractures and develops on top of botryoidal-fibrous quartz and microquartz (Fig. 3E–F). It is locally followed by chalcedony quartz cement (phase Q2b; Fig. 3E–F). A coarse-crystalline dolomite cement fills vugs inside the dogtooth quartz (phase D2; Fig. 3A–B). The dolomite is rich in hydrocarbon inclusions and has dull red/orange luminescence. After the dolomite, multiple bands of diffuse hydrocarbon inclusions formed within the quartz Q2a (Fig. 3E–F). The frequency of hydrocarbon inclusions correlates with quartz crystal size. Hydrocarbons mostly show no or weak fluorescence, although locally red-blue fluorescent inclusions were observed (Fig. 4A–D).

Stylolites cut across all the above diagenetic phases, but stylolite formation both pre-dates and post-dates a blocky megaquartz (phase Q3). The megaquartz partly occludes remaining pore space (Fig. 2F and 3E) and contains mostly single-phase fluid inclusions, with only rare 2-phase inclusions. Blocky megaquartz was analyzed for noble gases. Later diagenetic phases are fluorite, sulfate and sulfide minerals. Celestine forms acicular to prismatic cement crystals (phase S1). Barite has a blocky habit and occurs within quartz-lined vugs, in pores in the depositional calcite fabric, or as a local replacement of celestine (phase S2). Fluorite occurs as replacive and euhedral cement crystals (phase F1) and is commonly associated with dissolution-enhanced fractures or vugs. The earlier replacive phase has rhombic cleavage reminiscent of calcite and locally contains corroded remnants of calcite (Fig. 4E). Calcite C1 micro-rhombs are locally cemented by fluorite (Fig. 4E). Pyrite and galena were only observed in association with one fracture (phases S3, 4), but sphalerite is the most widespread sulfide in the core. It occurs as both diffuse microcrystals and as coarse, fracture filling cements (phase S5; Fig. 4F). It is normally associated with some quartz and with dissolution features. Fracture-filling sphalerite was analyzed for noble gases.

4.2. Geochronology

The U-Pb age data have a low scatter, as indicated by mean square weighted deviates (MSWD) between 1.5 and 2.5 (Fig. 6A–B, Data Repository 1 and 2). Analyses of B1 and B3–6 shrub calcites gave ages between 112.3 ± 8.2 and 100.0 ± 37.1 Ma (Fig. S5). Spherulitic calcites in B8 and B9 have ages of 95.0 ± 12.3 Ma and 115.0 ± 10.5 Ma, respectively (Fig. S5). Data were pooled to define ages for shrubs (110.6 ± 3.5 Ma), spherulites (108.3 ± 8.3 Ma) and all calcite (111.2 ± 3.4 Ma) (Fig. 6C and S6; age generation 1). The samples are

Table 3
Noble gas data.

sample	mineralogy	⁴ He (cm ³ /cm ³)	total error	⁴⁰ Ar (cm ³ /cm ³)	total error	³⁶ Ar (cm ³ /cm ³)	total error	⁴⁰ Ar* (cm ³ /cm ³)	total error	⁸⁴ Kr (cm ³ /cm ³)	total error	¹³² Xe (cm ³ /cm ³)	total error
B1.1	calcite	3.31E-08	2.09E-11	7.15E-09	3.35E-12	6.98E-12	4.22E-14	5.07E-09	1.30E-11	2.27E-13	2.54E-15	4.46E-14	8.46E-16
B1.2	calcite	2.91E-08	3.27E-11	6.28E-09	8.79E-13	6.56E-12	4.65E-14	4.32E-09	1.39E-11	2.02E-13	2.03E-15	4.52E-14	8.25E-16
B3	calcite	5.16E-08	1.42E-11	7.27E-09	2.38E-12	4.77E-12	4.32E-14	5.85E-09	1.31E-11	1.20E-13	1.34E-15	1.78E-14	5.44E-16
B8	quartz	1.39E-09	7.35E-13	9.84E-09	1.83E-12	2.96E-11	4.14E-14	1.03E-09	1.25E-11	7.43E-13	4.24E-15	3.94E-14	6.23E-16
B13	quartz	1.93E-08	1.01E-10	1.15E-07	6.79E-12	3.40E-10	6.85E-14	1.40E-08	2.16E-11	1.32E-11	6.09E-15	9.30E-13	1.52E-15
B15	sphalerite	1.76E-08	4.03E-12	3.50E-09	9.83E-13	1.76E-12	4.21E-14	2.97E-09	1.26E-11	5.54E-14	1.28E-15	9.45E-15	4.26E-16
N1	calcite	5.85E-11	4.15E-13	2.17E-09	4.18E-12	7.26E-12	3.37E-14	3.96E-12	1.09E-11	1.55E-13	2.09E-15	1.03E-14	3.70E-16
N2	hematite	2.85E-11	9.88E-13	5.70E-09	1.37E-12	1.89E-11	8.12E-14	6.73E-11	2.43E-11	4.06E-13	4.93E-15	2.34E-14	9.58E-16
sample	mineralogy	³ He/ ⁴ He	total error	³ He/ ⁴ He (R/Ra)	total error	⁴⁰ Ar/ ³⁶ Ar	total error	⁴⁰ Ar*/ ⁴ He	total error	⁸⁴ Kr/ ³⁶ Ar	total error	¹³² Xe/ ³⁶ Ar	total error
B1.1	calcite	2.23E-06	1.81E-08	3.62	0.02	1024.20	0.48	0.1531	0.0004	0.03248	0.00040	0.00638	0.00015
B1.2	calcite	2.25E-06	2.03E-08	3.66	0.02	956.70	0.13	0.1488	0.0005	0.03085	0.00037	0.00689	0.00015
B3	calcite	2.27E-06	1.67E-08	3.69	0.02	1523.86	0.50	0.1133	0.0003	0.02507	0.00035	0.00373	0.00014
B8	quartz	2.41E-06	9.88E-08	3.93	0.11	332.79	0.06	0.7419	0.0085	0.02511	0.00014	0.00133	0.00002
B13	quartz	2.32E-06	3.57E-08	3.77	0.04	339.22	0.02	0.7267	0.0040	0.03886	0.00002	0.00273	0.00001
B15	sphalerite	2.00E-06	2.81E-08	3.26	0.03	1986.28	0.56	0.1686	0.0007	0.03148	0.00102	0.00536	0.00031
N1	calcite	8.62E-07	4.08E-07	1.40	0.46	298.55	0.58	0.0676	0.0429	0.02135	0.00029	0.00142	0.00005
N2	hematite	n.d.	n.d.	0.00	n.c.	301.56	0.07	2.3607	0.5667	0.02145	0.00027	0.00124	0.00006

n.d.: below detection limit.

n.c.: not calculated.

from a narrow depth range in the core, the recrystallized fabrics are petrographically similar, and the U-Pb age data are compatible (resulting in low pooled MSWDs, Fig. 6C), which justifies treating the recrystallized calcite as a single age phase. One recrystallized shrub sample (B7) gave a notably younger age of 87.7 ± 5.5 Ma (Fig. 6B–C). Although only measured in a single sample, this age is derived from 57 ablations and therefore considered reliable (Table S2; age generation 2). The age obtained in sample B8 (95.0 ± 12.3 Ma) overlaps with both generations due to a high content in common Pb. The initial $^{207}\text{Pb}/^{206}\text{Pb}$ in this sample is however well constrained and compares well with that obtained for other generation 1 samples, justifying the grouping of sample B8 with the older generation (Fig. S4). Results for samples B2 and B10 were rejected due to their high MSWD (Data Repository 1 and 2).

4.3. Stable and radiogenic isotopes

Recrystallized pseudo-fibrous calcite displays very negative $\delta^{18}\text{O}$ values from -13.13 to -18.22 ‰ V-PDB and slightly positive but relatively invariant $\delta^{13}\text{C}$ values from 0.82 to 1.38 ‰ V-PDB (Fig. 7, Table 1). Paleotemperatures calculated from Δ_{47} range from 119 to 150°C (Table 1) and group according to geochronology results: Samples from age generation 1 show paleotemperatures of 119 – 135°C (114 – 138°C at 1SE , $n = 2$) and age generation 2 has a paleotemperature of $147 \pm 2^\circ\text{C}$ (1SE , $n = 1$) (Fig. 8A). Sample B8.1 (not dated) gives a paleotemperature of $150 \pm 7^\circ\text{C}$. Samples B6 and B10 have high temperature error margins due to low number of replicates (Table 1); sample B6 was therefore

omitted from Fig. 8. Sample B6 groups with age generation 1, whereas B10 falls into age generation 2, although its MSWD from U-Pb analysis is high (see section 4.2 and Data Repository 1) (Fig. 8A). The minimum temperature (104°C at 95% confidence level; Fig. 8A–Table 1) is $> 10^\circ\text{C}$ higher than the current well temperature at the depth of the cored interval. All $^{87}\text{Sr}/^{86}\text{Sr}$ ratios fall within a narrow band from 0.713056 to 0.713647 (Fig. 9, Table 2). Fluid $\delta^{18}\text{O}$ values calculated from these results range from 1.08 to 4.24 ‰ V-SMOW, using the isotope fractionation of O'Neil et al., (1969) applicable to higher-temperature calcites (Fig. 8, Table 1).

4.4. Noble gas concentrations

The ratio of $^3\text{He}/^4\text{He}$ expressed relative to the atmospheric ratio (R/Ra) in the subsurface samples ranges from 3.261 to 3.927 (± 0.019 – 0.040), increasing from sphalerite through calcite to quartz (Fig. 10, Table 3). An absence of ^{20}Ne data precludes minor correction for air-derived He. However, all measured $^3\text{He}/^4\text{He}$ ratios are elevated relative to air, so results presented here can be considered lower limits for the true (air-corrected) $^3\text{He}/^4\text{He}$ ratios. The calcite surface sample has R/Ra of 1.403 (± 0.462 ; Fig. 10), whereas the hematite surface sample contained no detectable ^3He and has R/Ra of 0 (Table 3). The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios vary between 332.79 and 1986.28 (± 0.02 – 0.56) for the subsurface samples, whereas they are 298.55 ± 0.58 and 301.56 ± 0.07 for the two surface samples (Fig. 10B and Table 3). The ratios of $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{132}\text{Xe}/^{36}\text{Ar}$ form linear arrays suggesting two component mixing,

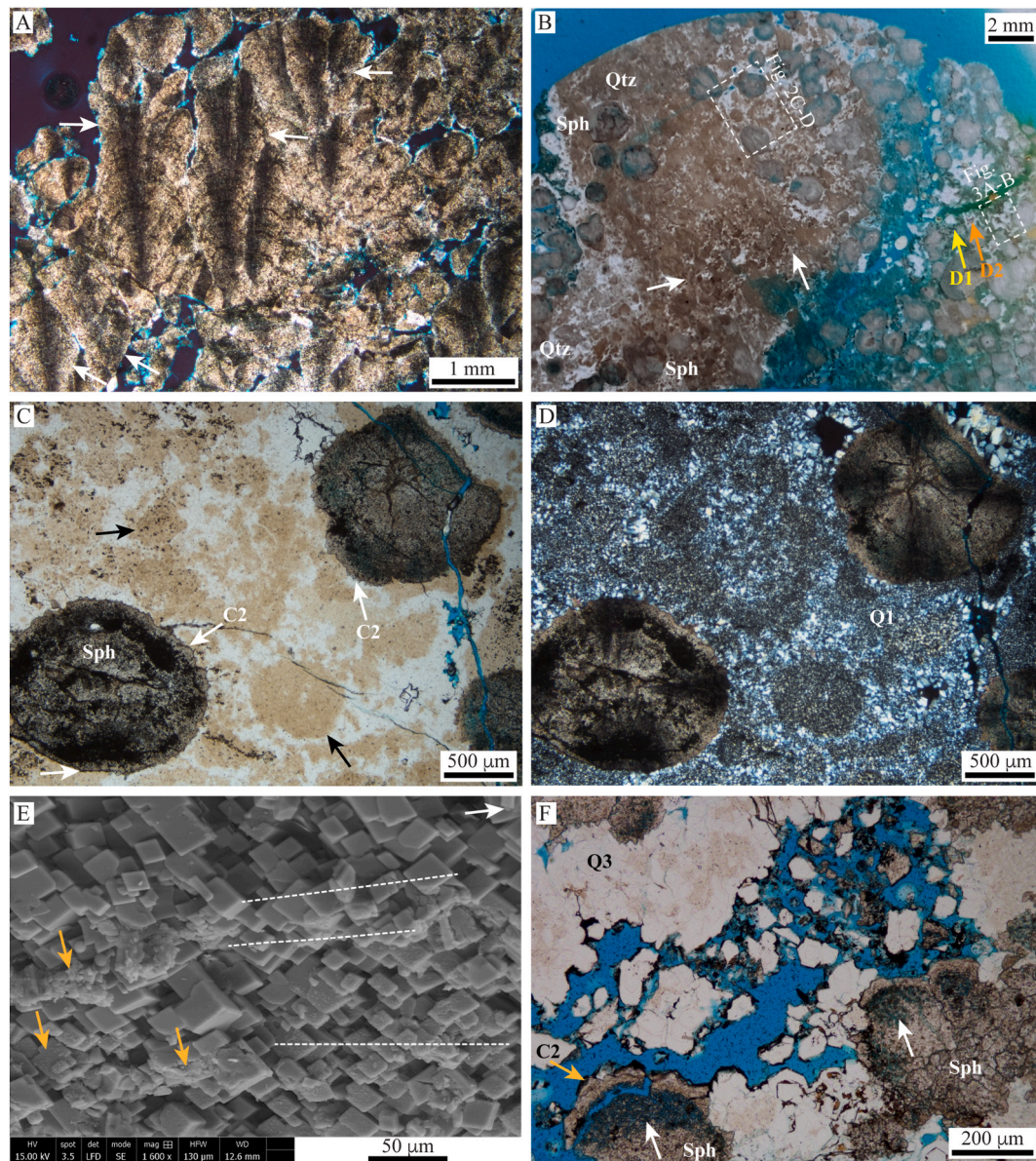


Fig. 2. (A) Cluster of shrubs (arrowed) with distinct sweeping extinction of divergent crystal fibers. Porosity in blue. Thin section photomicrograph under cross polarized light. Sample B3. (B) Millimetric calcitic spherulites (Sph) embedded in quartz (Qtz). Note the abundance of spherulite ghost structures in quartz (arrows, compare photo 2C). The yellow and orange arrows indicate dolomite phases D1 and D2, respectively (see Fig. 3A for details). The location of photos 2C-D and 3A-B is indicated by white rectangles. Full thin section image. Sample B9. (C-D) Paired thin section photomicrographs under plain and cross polarized light of spherulites (Sph) in microcrystalline quartz (phase Q1). Spherulite ghosts are visible in quartz (black arrows). Isopachous cements (phase C2) occur on some spherulites (white arrows). Sample B9. (E) Calcite micro-rhombs (phase C1) in a shrub sample chip under the scanning electron microscope. Alignment of these rhombs is indicated by the white dotted lines and the white arrow. This alignment creates the pseudo-fibrous fabric characteristic of shrub and spherulite recrystallization. Yellow arrows indicate calcite overgrowths on micro-rhombs. Sample B10. (F) Spherulites (Sph) with partially spalled circumgranular cement (phase C2, orange arrow), in turn cemented by megaquartz (phase Q3). Note diffuse dissolution of the spherulite beneath the calcite cement (white arrows). Porosity in blue. Thin section photomicrograph, sample B8.

although the quartz samples have a different endmember to the spherulite and calcite samples (Fig. 11).

5. Data analysis

5.1. Paragenetic sequence and depositional-diagenetic environments

The observed shrubs and spherulite depositional fabrics are equivalent to those described from other Pre-Salt carbonate deposits in Brazil and Angola (Sabato Ceraldi and Green, 2017; Saller et al., 2016; Wright and Barnett, 2015). On that basis, deposition of the studied limestones occurred in spatially extensive alkaline lake systems. The most profound

diagenetic alteration affecting this depositional fabric was recrystallization of fibrous calcite to a pseudo-fibrous structure with aligned calcite micro-rhombs (phase C1; Fig. 2E). Variability in micro-rhomb size, physical orientation, amalgamation and overgrowths suggests the recrystallization – while ubiquitous in the studied samples – was spatially heterogeneous. A similar, although mimetic recrystallization of shrub fibers, was reported from the Brazilian margin (Herlinger Jr. et al., 2017).

Although some of the clotted and laminated early quartz (phase Q1) is similar to quartz found in siliceous buildups from these lakes (Saller et al., 2016), most of the observed early quartz contains remnants of carbonates and Mg phyllosilicates and is therefore interpreted as

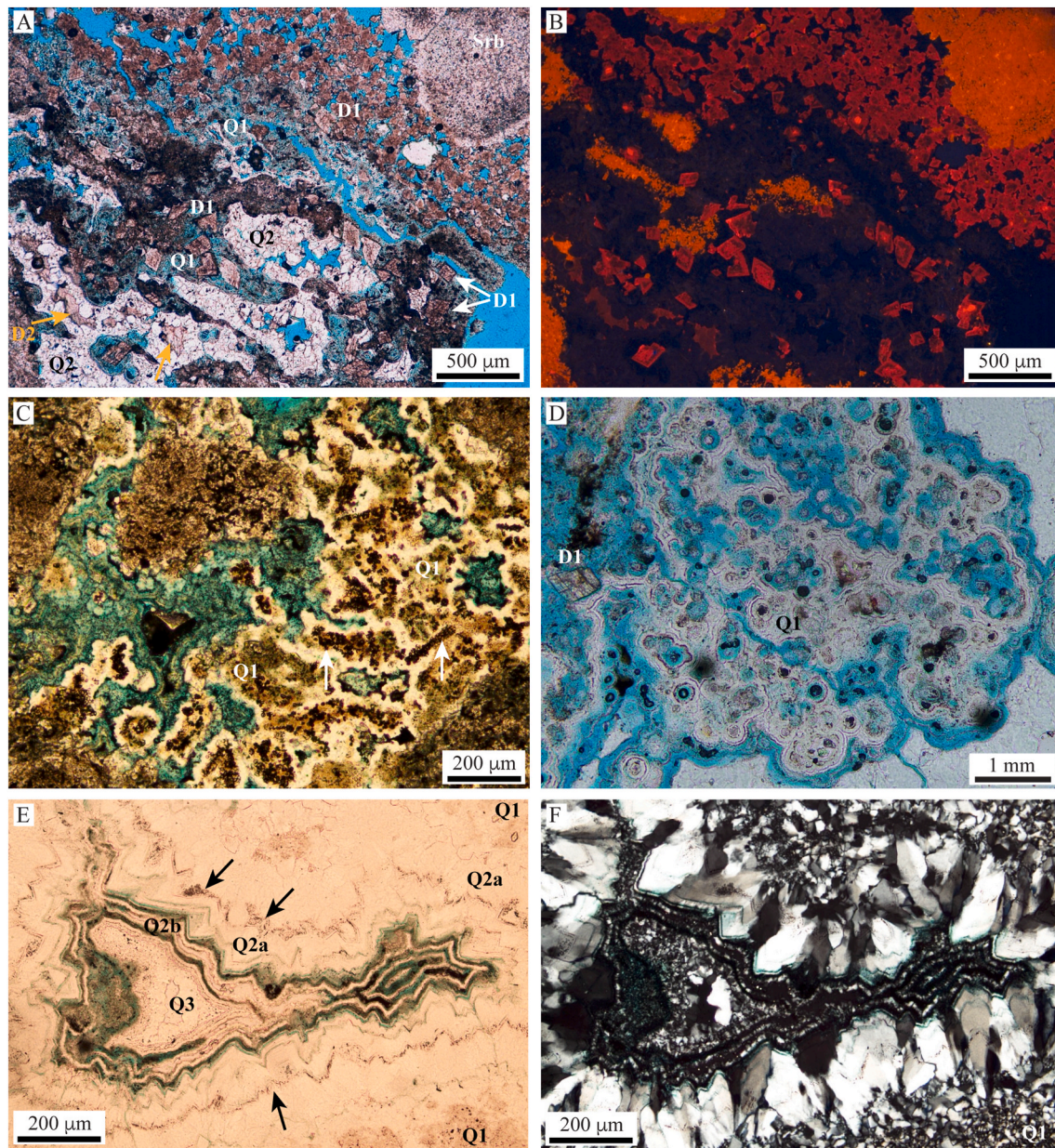


Fig. 3. (A–B) Paired transmitted light and cathodoluminescence light photomicrographs of isolated dolomite rhombs (phase D1, white arrows) now enclosed by microquartz to laminar-fibrous quartz (phase Q1) and quartz cement (Q2). A dolomite stringer forms a dense mosaic at the edge of the silicified zone (top right of photo). Vug-filling dolomite (phase D2, orange arrows) is present locally between quartz Q2. Calcite of framework shrubs (Srb) has orange luminescence, whereas dolomite shows red luminescence with some zonation. Quartz is non-luminescent. Porosity in blue. Sample B9. (C) Thin section photomicrograph of botryoidal-fibrous quartz and microquartz (phase Q1) with clotted dark brown, possibly microbial structures (arrows). Sample B16. (D) Fibrous to pseudo-fibrous laminated microquartz (phase Q1) with micro-porosity and local organic blobs. Note corroded dolomite rhomb (D1). Porosity in blue. Sample B8. (E–F) Paired thin section photomicrographs under plain and cross polarized light showing a vug-filling sequence from microquartz (phase Q1) via dogtooth (phase Q2a) to chalcedony (phase Q2b) and minor blocky megaquartz (phase Q3) in the center. Hydrocarbons (arrows) occur as inclusions along growth faces of dogtooth quartz. Sample B9.

replacive. Silicified shrubs and spherulites are visible as ghost fabrics in Q1 microquartz (Fig. 2C–D). Adjacent to these, partially dissolved ‘floating’ dolomite rhombs (phase D1) within pseudo-chalcedonic quartz fabrics suggest dissolution and silicification of labile Mg-phyllsilicates, which could have provided a source of silica (Fig. 3A–D; Tosca and Wright, 2018). The observed dolomite rhomb chain fabrics may result from clay removal and physical concentration of rhombs into layers interlaminated with microcrystalline quartz, further supporting replacement of primary Mg-phyllsilicates. Silicification likely was a syn-depositional to eodiagenetic process, with clotted quartz and early diagenetic quartz cements found in reworked intraclasts (comparable to Saller et al., 2016, their Fig. 9F). Isopachous

calcite cement (phase C2; Fig. 2C–F) was the earliest cement phase and stabilized the depositional framework.

Dogtooth quartz (phase Q2a) is interlaminated with bituminous quartz laminae; the associated vug-filling dolomite (phase D2) equally contains hydrocarbon inclusions (Fig. 3E–F). Hydrocarbons are likely pyrobitumen, because they mostly show no fluorescence, whereas the locally observed red-blue fluorescence is an indicator of hydrocarbon cracking (Fig. 4A–D; Khorasani, 1987; Ping et al., 2017). Mineral formation thus overlapped with a phase of hydrocarbon emplacement in the core (Fig. 5). Bitumen formation and CO₂ flushing affected the studied core, and studies from nearby wells indicate these processes may have been genetically related and in close temporal succession (Liu

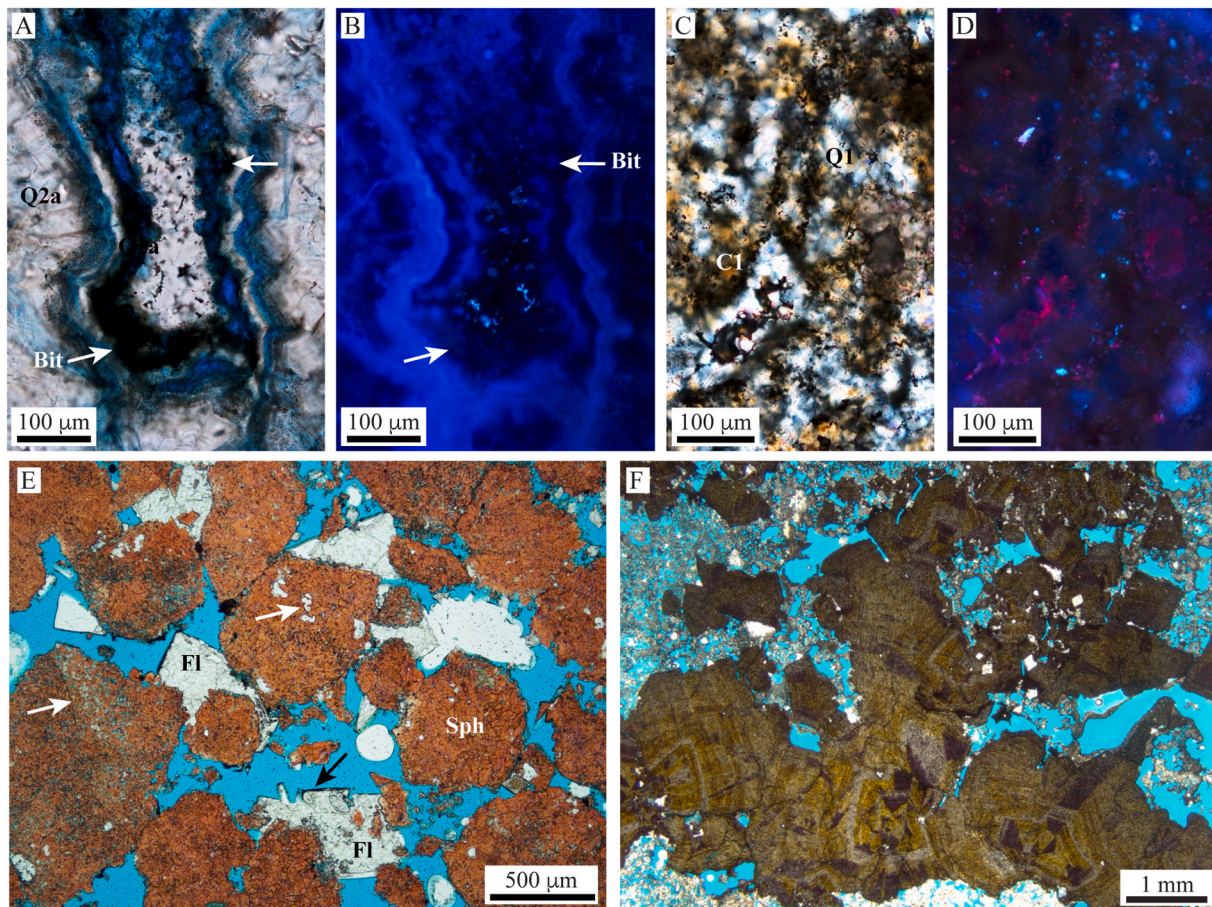


Fig. 4. (A-B) Paired transmitted and fluorescent light photomicrographs of dogtooth quartz (phase Q2a) with bituminous laminae (Bit). Hydrocarbons are non-to poorly fluorescent. Sample B8. (C-D) Paired transmitted and fluorescent light photomicrographs of micro-rhombic calcite (phase C1) with microquartz (phase Q1). Hydrocarbon inclusions are blue-red fluorescent. Sample B8. (E) Thin section photomicrograph of fluorite (Fl) between spherulites (Sph). Some fluorite crystals have a rhombic habit (black arrow) and fluorite locally cements calcite micro-rhombs (phase C1, white arrows). Porosity in blue. Sample B10. (F) Thin section photomicrograph of yellow-brown sphalerite in a vein. Porosity in blue. Sample B15.

et al., 2022). Stylolites cut across all diagenetic phases discussed above and these phases must therefore have formed before deeper burial (Fig. 5; Choquette and James, 1987).

Blocky megaquartz (phase Q3) formed both before and after stylolite formation. Dominance of single-phase fluid inclusions suggests that megaquartz precipitation started at temperatures below c. 50°C (Goldstein and Reynolds, 1994), but then continued into deeper burial (Fig. 5). On the other hand, fluorite (phase F1), sulfates and sulfides (phases S1-5) all postdate stylolite formation and thus formed in a deeper burial (mesodiagenetic) environment (Fig. 5). This is supported by their preferential occurrence in fractures that allowed circulation of burial fluids.

Spatial relationships between the burial diagenetic phases and the C1 micro-rhombs put some constraints on the timing of recrystallization (Fig. 5). Dissolution below isopachous cements C2 affected only micro-rhombs (Fig. 2F), thus micro-rhombs must have been present during dissolution. The presence of fluorite (phase F1) cement in corroded micro-rhombic frameworks (Fig. 4E) places a younger age constraint on recrystallization, although some recrystallization could have been also associated with sulfide precipitation.

5.2. Fluid and temperature characterization

Calcite stable isotope data presented here likely reflect the condition of recrystallization to a pseudo-fibrous fabric, an interpretation supported by the pervasive formation of calcite micro-rhombs with

homogeneous luminescence. Alteration was buffered for carbon, as the $\delta^{13}\text{C}$ values (0.82 to 1.30 ‰ V-PDB) are broadly consistent with $\delta^{13}\text{C}$ values from other sag deposits in Brazil and Angola interpreted as an original depositional signal (Fig. 7; Sabato Ceraldi and Green, 2017). This suggests relatively high rock/fluid ratios during recrystallization. The 1–2 ‰ drop in $\delta^{13}\text{C}$ relative to Kwanza values, if these are taken as depositional, can reflect a small contribution from organic carbon or CO_2 ($\delta^{13}\text{C}$ of CO_2 -4 ‰ in nearby well; Liu et al., 2023). Linear mixing modeling suggests that c. 10% CO_2 or c. 1% organic carbon would be required in the gas phase for this shift. On the other hand, the very negative $\delta^{18}\text{O}$ values (-13.13 to -18.22 ‰ V-PDB) indicate precipitation from warm and/or isotopically light fluids during diagenesis (Katz et al., 2006; Swart, 2015). Previously published $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data from the Kwanza and Campos basins define a population of largely invariant $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ between -6 and +5 ‰, regarded as evidence of precipitation from shallow evaporative lakes and local diagenetic overprint (Fig. 7; Sabato Ceraldi and Green, 2017). The very light $\delta^{18}\text{O}$ values measured in this study (-13 to -18 ‰) suggest that the oxygen isotope system may in fact reflect a mix between evaporative surface and burial diagenetic processes.

Clumped isotope data constrain the temperature of these fluids to between 104 and 169°C at 95% confidence (119–157°C at 1SE; Fig. 8A). These values are >10°C above current temperatures at the base of the core. To test if fluid temperatures exceeded normal burial temperatures at c. 111 Ma, a simple decompacted burial analysis was carried out (cf. Angevine et al., 1990; van Hinte, 1978). The present thickness of the

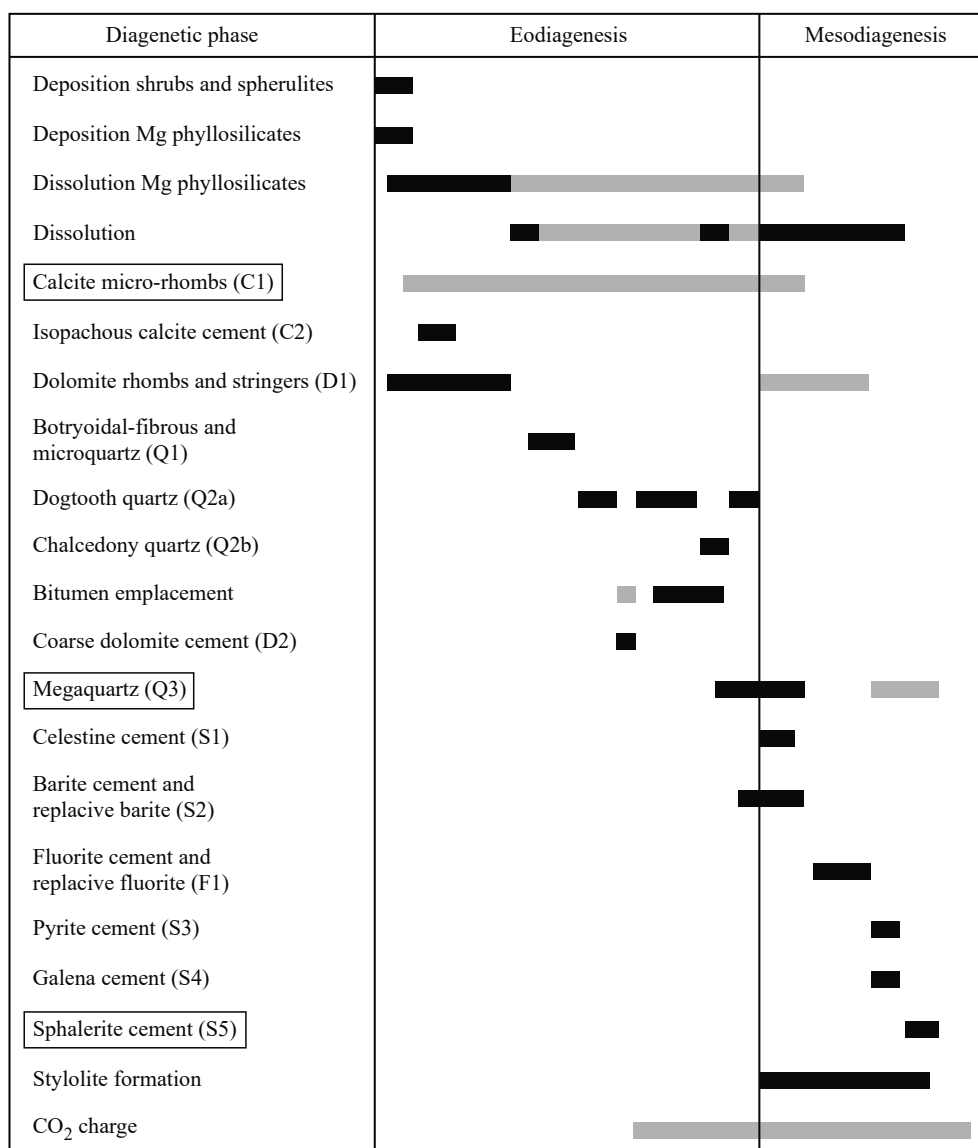


Fig. 5. Relative paragenesis of observed phases. Boxed phases were analyzed for noble gases. Grey bars represent uncertain timing. Note that petrographically, recrystallization and formation of C1 calcite micro-rhombs cannot be placed relative to the other phases with certainty.

Grey Cuvo Fm. between the base of the cored section and the base salt is 86 m. The well was drilled on a salt dome, so the depositional thickness of salt can only be estimated from relatively undeformed zones adjacent to the salt structure, where it reaches 500–750 m. No Albian is present on top of the salt, either due to non-deposition or erosion. The Pacassa Mb. (broadly lower-middle Albian) reaches a thickness of 300–500 m in the onshore Kwanza Basin (Tillement, 1987). Seismic lines off the studied structure allow an estimation of 300 m for the Albian succession, although it is unknown how much was deposited until c. 111 Ma. Assuming a conservative value of 300 m for the Albian, the total compacted overburden thickness at well location is then 886–1136 m. For decompaction, original porosity of bioclastic and oolitic Albian grainstones was estimated at 40% (e.g. Halley and Harris, 1979), whereas 15% was taken as the present-day average porosity (Eichenseer et al., 1999). No compaction was assumed for the salt, as any primary porosity is reduced to close to zero within few meters below the surface (Hardie et al., 1985). Decompaction of the Grey Cuvo Fm. assumed an original porosity of 40%, based on porosities in young tufa and travertines as a close fabric analog (Schröder et al., 2024; Soete et al., 2015), and a present-day average porosity of 16% in the studied core. A compaction coefficient of 2498 is assumed for both Albian and Grey

Cuvo Fm. (Schmoker and Halley, 1982). The decompacted thickness of this succession at c. 111 Ma was 1049–1296 m. Assuming mean geothermal gradients for a warm rift basin of 40–56 °C/km (Kolawole and Evenick, 2023; MacGregor, 2020), normal burial temperatures of 47–78 °C would have been reached at the base of the cored section by c. 111 Ma. Fluid temperatures exceeded these burial temperatures by ≥ 26 °C (at 95% confidence) or ≥ 41 °C (at 1SE), thus the fluids can be considered hydrothermal fluids (Machel and Lonnee, 2002). The presence of fracture-bound metal sulfides and fluorite further supports the repeated circulation of hydrothermal metal-rich fluids during diagenesis (e.g. Leach et al., 2005; Neilson and Oxtoby, 2008).

Extending the above analysis to the second age generation at c. 88 Ma needs to consider the Cenomanian-Coniacian succession. Although not present in the core, its current thickness off structure based on seismic interpretation is 520 m for the Cenomanian and 480 m for the Turonian-Coniacian. Lithologies will likely be dominated by shales and marls (Brownfield and Charpentier, 2006), for which a present-day porosity of 1%, a depositional porosity of 70% and a compaction coefficient of 1961 were assumed (data from Lee et al., 2019). The total decompacted overburden at c. 88 Ma was 3239–3489 m, which translates into 135–166 °C burial temperature using a 40 °C/km gradient after

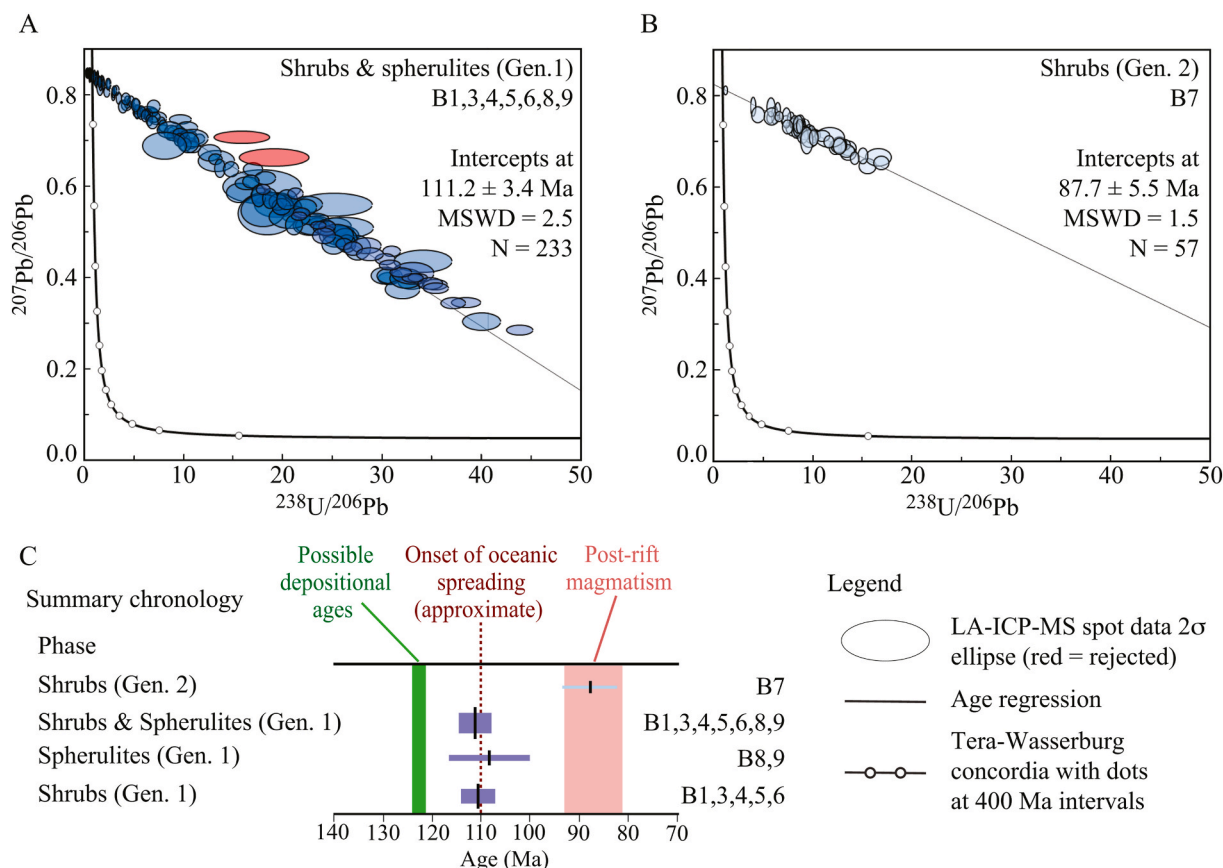


Fig. 6. (A-B) Tera-Wasserburg concordia plots showing collated carbonate $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ data. (C) Age splits for identified phases. Bar thickness is scaled according to the number of pooled samples. Sample numbers are listed next to the corresponding results. MSWD = mean squared weighted deviates.

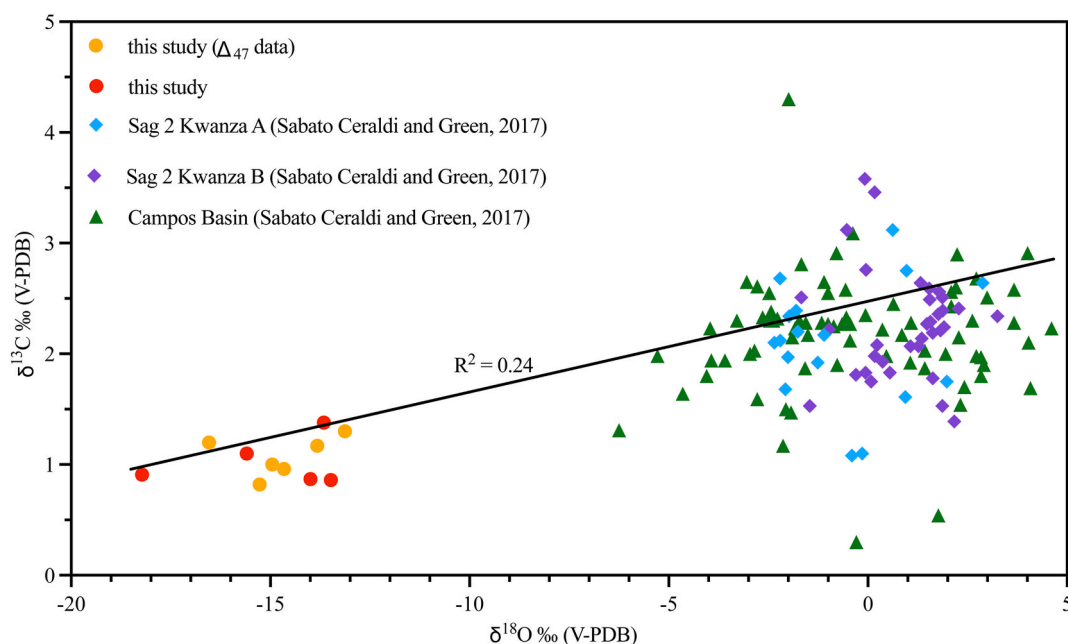


Fig. 7. Calcite C and O stable isotope data from this study (Δ_{47} samples shown), with equivalent data from three other Pre-Salt cores taken from Ceraldi and Green (2017). A trendline is fitted through all data.

111 Ma, or 113–144°C using a 30 °C/km gradient after 111 Ma, which is transitional to modern lower gradients on the passive Angola margin (MacGregor, 2020). At this time, most measured fluid temperatures

remain indistinguishable from estimated burial temperatures and only the highest fluid temperatures can be considered hydrothermal.

The measured $\delta^{18}\text{O}_{\text{calcite}}$ are consistent with $\delta^{18}\text{O}_{\text{fluid}}$ between 1.08

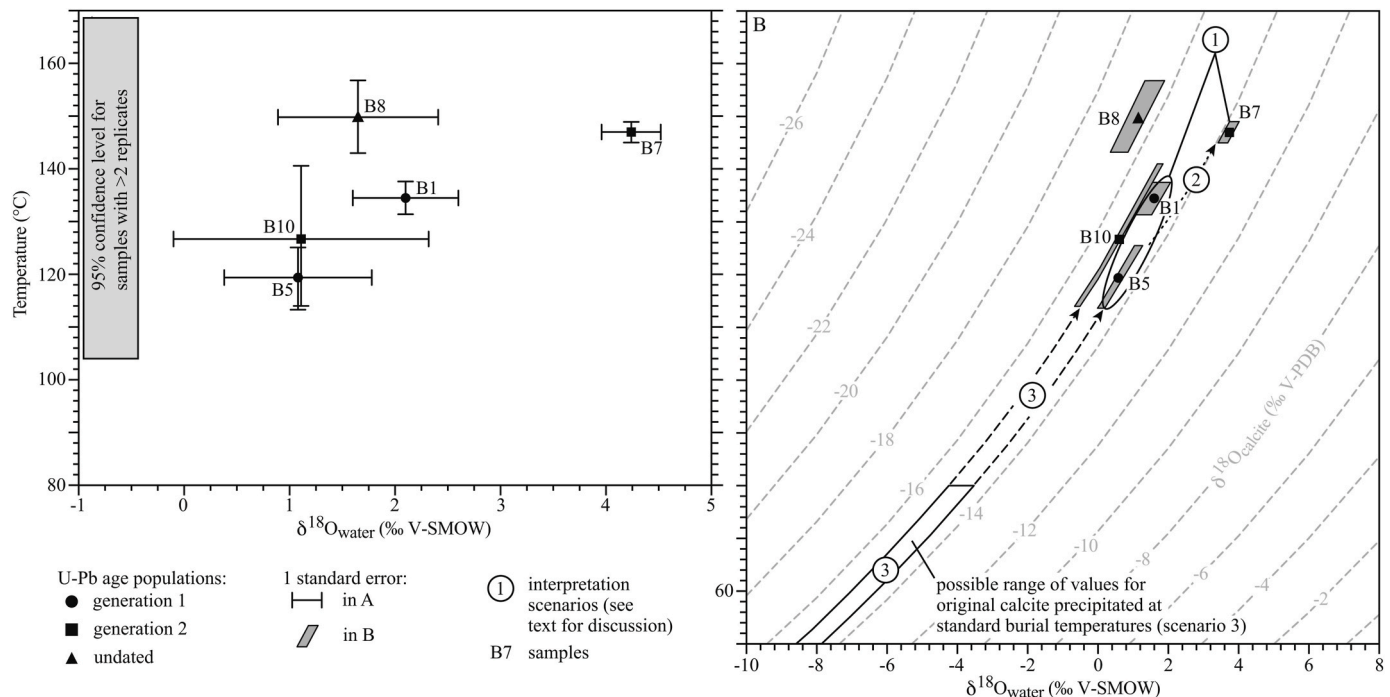


Fig. 8. (A) Δ_{47} paleotemperatures vs. calculated fluid $\delta^{18}\text{O}$ compositions. Error bars represent 1 standard error for Δ_{47} paleotemperatures and mineral $\delta^{18}\text{O}$. Temperature range at 95% confidence interval (for samples with at least 2 replicates) is indicated. (B) Δ_{47} paleotemperatures vs. calculated fluid $\delta^{18}\text{O}$ compositions superimposed onto measured mineral isotope data (grey dashed lines). Grey fields represent 1 standard error for mineral $\delta^{18}\text{O}$ and temperature. Circled numbers and arrows indicate interpretation scenarios discussed in section 6.1.

and 4.24‰ V-SMOW (Fig. 8B), which are typical of evolved saline formation waters in sedimentary basins that reflect variable contributions of marine, meteoric, sedimentary and crustal fluid sources (Hanor, 1994; Hoefs, 1997). A crustal fluid source and interaction with radiogenic sedimentary and basement lithologies are further supported by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.71306–0.71365) that exceed Barremian–Aptian seawater (0.70723–0.70746; Prokoph et al., 2008) and Aptian evaporite (0.70750–0.70770; Loma et al., 2018) values (Fig. 9; Elderfield, 1986). Although no published $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the basement in the Benguela Basin (belonging to the central Eburnean zone and the Pan-African belt, Fig. 1A; de Carvalho et al., 2000; Guiraud et al., 2010) are available, data can be compared with igneous units in the Namibe and Kwanza basins (Fig. 9; Loma et al., 2018; Marsh and Swart, 2018; Marzoli et al., 1999). Calcite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are more radiogenic than those from mafic lithologies of the syn-rift Bero Volcanic Complex, but they match their intermediate counterparts (0.71230–0.71422, Fig. 9; Marsh and Swart, 2018). The ratios measured here likely reflect mixing of various radiogenic sources, including granitoids making up a large portion of the local basement (de Carvalho et al., 2000), but hydrothermal fluid circulation through mafic and intermediate volcanics of the Bero Volcanic Complex would provide the necessary radiogenic ^{87}Sr and Ca for calcite precipitation (Figueiredo et al., 2025).

In combination with the magmatic origin of CO_2 established in nearby reservoirs (Gilfillan et al., 2025; Liu et al., 2022, 2023), the above argument points towards a magmatic contribution to the evolved basinal fluids. Although the stable isotope data are broadly compatible with a magmatic contribution, they alone are not diagnostic, as magmatic fluids typically fall in the $\delta^{18}\text{O}_{\text{fluid}}$ range of 6 to 10‰ V-SMOW (Hoefs, 1997).

5.3. Noble gas data: evidence for a mantle/magmatic contribution to fluid flow

Noble gases are chemically inert tracers that allow identification of atmospheric, crustal and mantle contributions to reservoir fluids

(Ballentine et al., 2002; Byrne et al., 2018). The $^3\text{He}/^4\text{He}$ ratio of the two surface samples is within range of typical atmospheric values (1 R/Ra; Ballentine et al., 2002) (Fig. 10), and it is thus dominated by an atmospheric signature. In contrast, the high $^3\text{He}/^4\text{He}$ ratios in subsurface samples (3.261 to 3.927; Fig. 10) far exceed crustal values (~ 0.02 R/Ra; Ballentine and Burnard, 2002). Although below mid-oceanic ridge basalt (MORB) values (8 ± 1 R/Ra; Graham, 2002), they are close to typical values for the subcontinental lithospheric mantle (6.1 ± 2.1 R/Ra; Day et al., 2015) (Fig. 10A), thus indicating a significant mantle volatile contribution to He (Ballentine et al., 2002; Oxburgh et al., 1986) mixed with a minor atmosphere-derived component. Whilst He isotopes are dominated by a mantle component in all subsurface samples, elemental ratios of heavy noble gases (Ar, Kr, Xe) reflect either an air saturated water (ASW) component (quartz samples) or a component enriched in heavy noble gases that is typical of sedimentary basins (calcite samples) (Fig. 11). Heavy noble gas enrichment is likely from hydrocarbon reservoir fluids and/or organic matter (Ballentine et al., 2002), which could relate to the CO_2 flushing and bitumen generation observed in this well (cf. Liu et al., 2022).

Radiogenic Ar from ^{40}K decay ($^{40}\text{Ar}^*$) is present in all subsurface samples, generating $^{40}\text{Ar}/^{36}\text{Ar}$ higher than the atmospheric value of 298.6 (Fig. 10B and Table 3). This $^{40}\text{Ar}^*$ originates from the mantle and is also produced in-situ in the crust (Ballentine et al., 2002). Given that calcite and sphalerite data lie on a mixing line between air and mantle (Fig. 10A), the Ar in these samples is, like He, likely also mantle-derived. The quartz samples have a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio closer to air due to the dilution of a high $^{40}\text{Ar}/^{36}\text{Ar}$ component by a significant ASW component with $^{40}\text{Ar}/^{36}\text{Ar}$ identical to air, as observed in Kr/Ar vs. Xe/Ar space (Fig. 11). However, although the $^{40}\text{Ar}/^{36}\text{Ar}$ is only slightly elevated above atmosphere in the quartz samples (Fig. 10B), the $^{40}\text{Ar}^*/^4\text{He}$ in the quartz samples is the highest observed in any sample type (Fig. 10A). The quartz samples have both higher $^{40}\text{Ar}^*$ and lower ^4He concentrations (Table 3) compared to calcite, suggesting that the ASW component carried additional radiogenic ^{40}Ar and that the quartz, a mineral known for poor retention of He (e.g. Argunova et al., 2003), may have lost

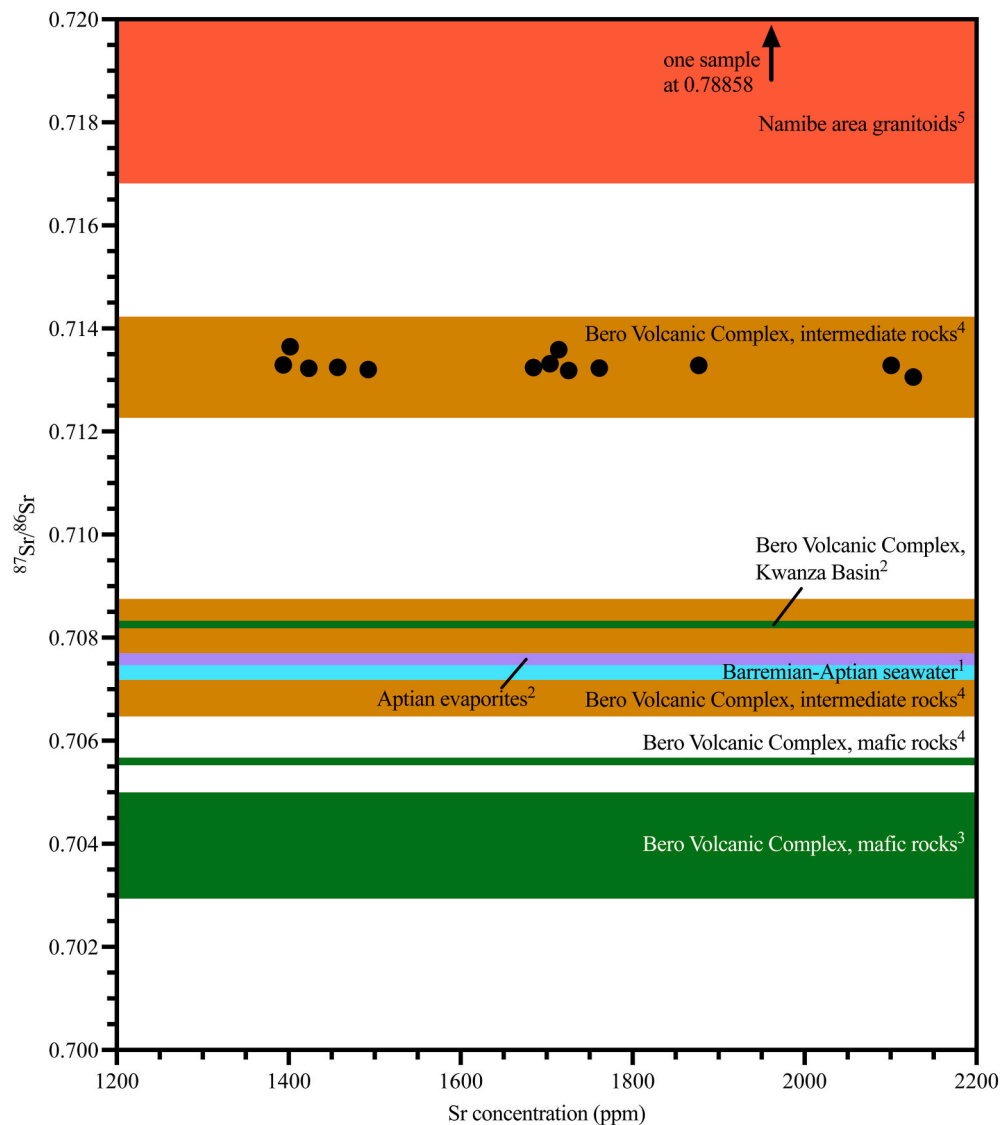


Fig. 9. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio plotted against Sr concentration for the Benguela pseudo-fibrous calcite samples. Strontium isotope ratios of contemporaneous seawater (blue bar) and of anhydrites (purple bar) in the regional Loeme evaporites are shown for comparison. Equally shown are $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of various igneous basement units from the Namibe Basin (red, green and brown bars); no published $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the Benguela area basement are available. Data sources: 1: Prokoph et al. (2008); 2: Loma et al. (2018); 3: Marzoli et al. (1999); 4: Marsh and Swart (2018); 5: de Carvalho and Tassinari (1992).

variable amounts of He. The igneous basement partly responsible for the radiogenic Sr isotopes (see discussion in section 5.2) may have also been a source of silica for mesodiagenetic quartz precipitation. Radioactive decay of ^{40}K in basement minerals like mica and amphiboles could be at least partly responsible for the elevated $^{40}\text{Ar}^*/^{4}\text{He}$ in quartz. Although the breakdown of Mg phyllosilicates equally supplies Si (Tosca and Wright, 2018), it is a less likely source of Ar, as these minerals are usually poor in K, although they can locally contain K from intermixed detrital clays (da Silva et al., 2021). Sphalerite appears to have retained its full complement of He and Ar but at lower concentrations than calcite. Many factors are potentially responsible for loss and gain of noble gases in minerals (Ballentine and Burnard, 2002), therefore a detailed discussion is beyond the scope of this paper. However, these processes, although they have the potential to modify noble gas elemental ratios, have minimal effect on isotope ratios, specifically $^3\text{He}/^4\text{He}$ - the discovery of mantle-derived fluids trapped within these samples is unequivocal. Together with the observed enrichment in heavy noble gases, this suggests neomorphic calcite and sphalerite

precipitated from fluids that contained both a crustal and a significant mantle component. The quartz samples have incorporated an additional groundwater (ASW) dominated component.

5.4. Calcite geochronology

Pooled calcite data from shrubs and spherulites yield latest Aptian–Albian ages (111.2 ± 3.4 Ma, age generation 1, Fig. 6A), which post-date the likely Barremian–early Aptian depositional age of c. 124–121 Ma. A smaller proportion of data record a Coniacian age (87.7 ± 5.5 Ma, age generation 2, Fig. 6B). Due to the widespread recrystallization of calcite observed in the core, the calcite ages are here interpreted to reflect diagenetic resetting of the U–Pb system during recrystallization. The process of recrystallization occurred during a major Albian event and a Coniacian event, the latter being relatively minor due to its more limited distribution in the dataset. While the ages are solid, they cannot be discriminated petrographically.

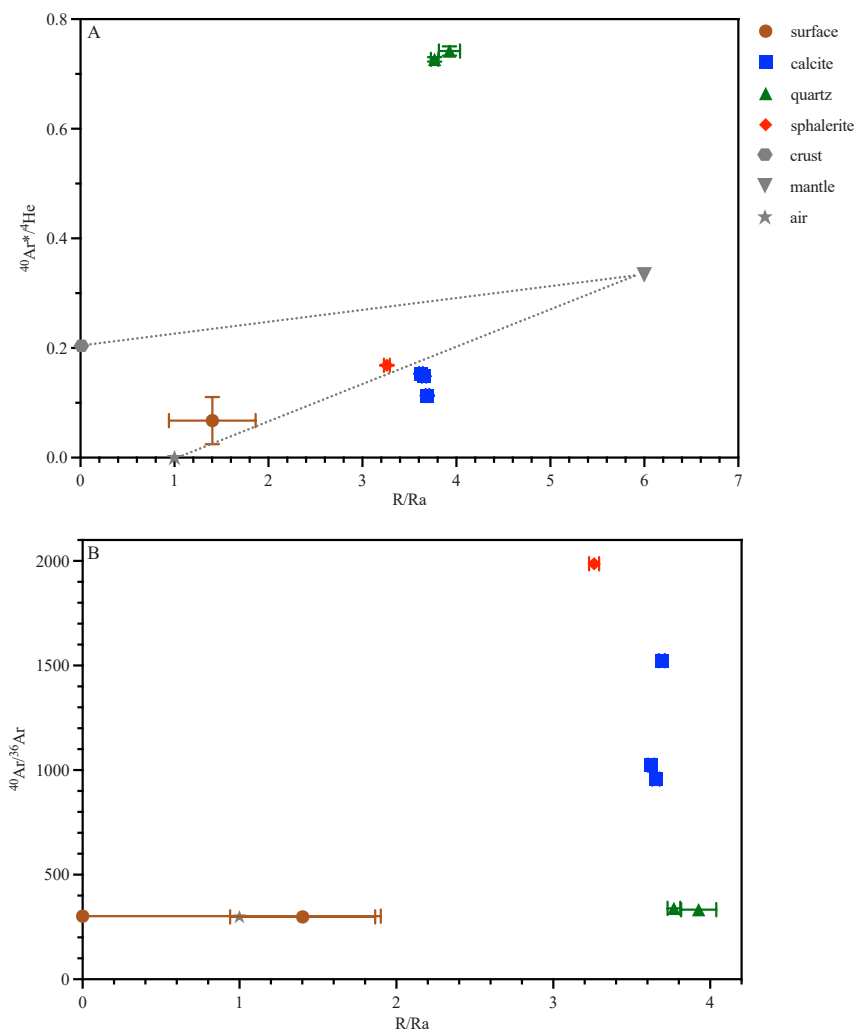


Fig. 10. $^3\text{He}/^4\text{He}$ ratio (normalized to the atmospheric ratio and shown as R/Ra) vs. $^{40}\text{Ar}^*/^4\text{He}$ ratio (A) and $^{40}\text{Ar}^*/^{36}\text{Ar}$ ratio (B) in the subsurface and surface samples. Error bars represent 1 σ uncertainty. In (A), one data point (surface sample N2) is located outside the plotted area ($\text{R}/\text{Ra} = 0$ and $^{40}\text{Ar}^*/^4\text{He} = 2.36$).

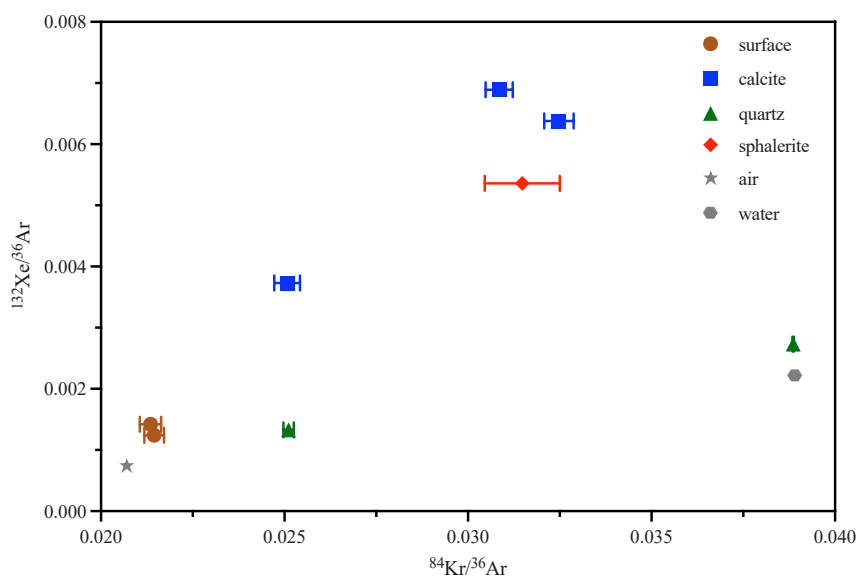


Fig. 11. $^{84}\text{Kr}/^{36}\text{Ar}$ ratio vs. $^{132}\text{Xe}/^{36}\text{Ar}$ ratio in the subsurface and surface samples. Error bars represent 1 σ uncertainty.

6. Discussion

6.1. Diagenetic evolution in the core

Following deposition at c. 124–121 Ma the studied rocks underwent diagenetic alteration via interaction with fluids of mixed basinal, crustal and mantle-derived origin. Fluid oxygen isotope values are broadly compatible with evolved basinal formation waters, Sr isotopes suggest interaction with crustal rocks, and noble gases provide evidence for a mantle volatile component during calcite recrystallization, quartz and sphalerite precipitation. Resetting of oxygen isotopes during calcite recrystallization suggests that at least the oxygen system was dominated by the fluid signature during fluid-rock interaction.

The combined petrographic, isotopic and geochronologic data of this study are most pertinent to the relationship between age and temperature of recrystallization. The data suggest a link between U–Pb age generations and Δ_{47} temperature. Age generation 1 (111.2 ± 3.4 Ma) corresponds to lower temperatures (114–138°C, 1SE) and fluids with $\delta^{18}\text{O}_{\text{water}}$ of c. 0–2‰ V-SMOW (Fig. 8B). This was followed by age generation 2 (87.7 ± 5.5 Ma) with temperatures of 145–149°C (1SE) and $\delta^{18}\text{O}_{\text{water}}$ of c. 3.5–4‰ V-SMOW (Fig. 8B). However, there is no unique relationship between temperature, age and recrystallization. Samples of the same age generation show spatial variability in recrystallization evident in micro-rhomb sizes, orientation, amalgamation and overgrowths. This style of recrystallization is however identical for calcites of both age generations, and warmer temperatures do not correspond to more fabric recrystallization. The spatial heterogeneity of recrystallization could relate to minor variations in fluid composition, fluid-rock interaction and susceptibility of fabrics to recrystallization. The recrystallization can be interpreted as one of 3 scenarios.

- (1) The two age and temperature groups reflect two distinct fluid pulses that independently caused calcite recrystallization (scenario 1 in Fig. 8B). These are however petrographically indistinguishable. Both involved a mantle volatile component and reset the oxygen isotope composition, but they did not or only minimally alter the carbon isotope signal in calcites as the carbon isotope system remained rock-buffered. The higher $\delta^{18}\text{O}_{\text{water}}$ of the younger pulse could reflect a higher contribution of a mantle component, possibly directly related to coeval volcanism in the Benguela Basin (Jerram et al., 2019; Matton and Jébrak, 2009; Rochelle-Bates et al., 2021).
- (2) Given that recrystallization in the studied samples is highly variable and cannot be assigned unambiguously to one age generation, the discussion should consider external heat pulses causing closed system solid-state re-ordering of C–O bonds in the calcite crystal lattice (Henkes et al., 2014). This process can modify Δ_{47} temperatures, but it is unlikely to reset the U–Pb clock. Consequently, it is conceivable that the first, lower temperature fluid pulse at 111.2 ± 3.4 Ma was followed by a second pulse at 87.7 ± 5.5 Ma that did not involve further recrystallization, but instead was accompanied by re-ordering of C–O bonds. This could have shifted Δ_{47} temperature without a change in $\delta^{18}\text{O}_{\text{calcite}}$. This change is graphically represented by the dotted arrow in Fig. 8B (scenario 2), illustrating that sample B7 could represent a modified sample from the earlier recrystallization event. This sample however belongs to age generation 2, which would require simultaneous resetting of the U–Pb system. This is considered unlikely.
- (3) With an analogous argument as for scenario 2, age generation 1 calcites could reflect solid-state reordering rather than a fluid pulse, leaving only the younger event as a distinct fluid flow event. In this scenario, generation 1 calcite recrystallized at 111.2 ± 3.4 Ma under normal burial conditions (c. 50–80°C, see calculation in section 5.2). A distinct fluid flow pulse at 87.7 ± 5.5 Ma was responsible for generation 2 ages, but it

equally caused solid-state reordering in calcites from age generation 1, shifting them to a higher temperature. Consequently, these samples originally would have plotted in the area marked ‘3’ in Fig. 8B, followed by translation along the dashed arrows to their measured position. The relatively lower temperature of the original calcite and its $\delta^{18}\text{O}_{\text{water}}$ of –8 to –4‰ V-SMOW (Fig. 8B) suggest calcite formation from meteoric waters (Choquette and James, 1987). Given an estimated burial depth of c. 1050–1300 m at 111.2 ± 3.4 Ma and stratigraphic position below the Loeme evaporites, this seems unlikely.

The data presented here thus favor a model of two independent fluid and temperature pulses at 111.2 ± 3.4 Ma and 87.7 ± 5.5 Ma, each causing calcite recrystallization of a similar nature. The 111.2 ± 3.4 Ma recrystallization age determined here overlaps with a bitumen Re–Os age of 116 ± 29 Ma established in a neighboring well (Liu et al., 2022). The present study found bitumen in association with pre-compaction quartz (phase Q2a) and dolomite (phase D2), although the temporal relationship between these phases and calcite recrystallization cannot be determined.

6.2. Mantle-derived volatiles in the core

The influence of magmatism on deposition, diagenesis and its links to geodynamic models involving mantle exhumation are increasingly being recognized for the Pre-Salt system on both conjugate margins (e.g. Péron-Pinvidic et al., 2013; Wright, 2022). The unique depositional system of the South Atlantic Pre-Salt consists of abiotic $\pm$ microbially influenced carbonate precipitates forming in highly alkaline lake waters (Mercedes-Martín et al., 2017; Saller et al., 2016; Wright, 2022; Wright and Barnett, 2015). The high alkalinity and enrichment in Ca and Mg ions are generally attributed to magmatic contributions – either as direct input of CO_2 -rich fluids into the lakes (e.g. along sub-lacustrine faults, Milesi et al., 2020; Pecoraino et al., 2015; Wright, 2022), via indirect input of hydrothermal fluids moving along deep-seated faults as evidenced by lake-margin travertines (e.g. Figueiredo et al., 2025), or via leaching of mafic basement rocks and ion transport to lakes in surface or subsurface waters (e.g. Pietzsch et al., 2018). Mantle-derived volatiles further affected inorganic diagenetic alteration of this succession (Girard et al., 2017; Pestilho et al., 2022). The current study provides noble gas evidence for mantle-derived volatiles within the fluids responsible for calcite, quartz and sphalerite precipitation. The mantle signature in calcite was unlikely preserved from carbonate deposition. Instead, resetting of oxygen isotopes during calcite recrystallization suggests that the noble gas system would have been equally dominated by the fluid signature during fluid-rock interaction. A mantle noble gas signature is also preserved in quartz (phase Q3) and in mesodiagenetic sphalerite (phase S5), but quartz equally shows a significant crustal noble gas component (Fig. 10).

Many hydrocarbon reservoirs on both margins, including the studied well, contain significant volumes of CO_2 that may have replaced an earlier hydrocarbon charge (Gamboa et al., 2019; Gilfillan et al., 2025; Santos Neto et al., 2012). A mantle origin of this CO_2 was postulated for several wells, including a neighboring well in the Benguela Basin (Gamboa et al., 2019; Gilfillan et al., 2025; Santos Neto et al., 2012). In the absence of direct CO_2 characterization, the present study cannot verify this hypothesis, but the close geographic proximity, identical basin context, and the very similar association between CO_2 and bitumen between the well studied here and the study of Gilfillan et al. (2025) point to a common diagenetic event involving hydrocarbon emplacement, mantle-derived CO_2 charge, bitumen formation and carbonate recrystallization that were temporally and genetically closely related. Having established a mantle signature in fluid-rock interaction, it is also necessary to consider its relation to the broader geodynamic context.

6.3. Regional drivers for mantle contribution to fluid flow

The southern Angola margin (Kwanza to Namibe basins) was affected by several episodes of volcanism as the potential source of CO₂: (1) syn-rift basaltic volcanism related to the Parana-Etendeka LIP (Marsh and Swart, 2018; Marzoli et al., 1999; Renne et al., 1996); (2) tholeiitic mid-ocean ridge basalt (MORB) volcanism linked with continental breakup at c. 112–110 Ma (Araujo et al., 2022; Karner and Gamboa, 2007; Kukla et al., 2018; Torsvik et al., 2009), although an older c. 123 Ma breakup age was suggested by (Quirk et al., 2013); (3) pillow basalts and hyaloclastites of the Sumbe submarine volcanics (c. 100 Ma; Jerram et al., 2019); (4) basic to evolved volcanism of the Serra de Neve alkaline complex at c. 93–91 Ma (Comin-Chiaromonte et al., 2011; Jerram et al., 2019); and (5) 88–81 Ma basic alkaline eruptive and intrusive volcanism of the Bentiaba basanite, belonging to the Peri-Atlantic Alkaline Province (PAAP; Jerram et al., 2019; Matton and Jébrak, 2009; Rochelle-Bates et al., 2021).

Generation of oceanic crust in the Central South Atlantic started c. 112–110 Ma and thus overlaps with the first calcite recrystallization event documented in the core (Generation 1, Fig. 6A). Crust hyperextension and possible mantle exhumation were postulated for the late stages of rifting (Péron-Pinvidic et al., 2017). A subsequent magmatic pulse could have facilitated final lithospheric break-up (Bronner et al., 2011; Cannat et al., 2009; Jagoutz et al., 2007). Such magmatism could trigger hydrothermal fluid circulation and/or a heat spike, possibly with some structural reactivation and exploitation of large detachment faults (e.g. Incerpi et al., 2020; Rochelle-Bates et al., 2022). A MORB noble gas signature was suggested for the reservoir CO₂ in a neighboring well (Gilfillan et al., 2025). In addition, any exhumed mantle material could provide a source of mantle CO₂ and Ca ions for carbonate recrystallization observed in the studied core.

The second generation of calcite recrystallization at 87.7 ± 5.5 Ma (Generation 2, Fig. 6B) is petrographically indistinct from generation 1. Data presented in this study suggest that it reflects a distinct fluid pulse, albeit not necessarily hydrothermal, as fluid temperatures were similar to standard burial temperatures at this time. Generation 2 coincides with the Bentiaba volcanism (88–81 Ma; Jerram et al., 2019), which related to “unzipping” between Angola and Brazil in the Late Cretaceous and structural reconfiguration on fractures zones (Jerram et al., 2019). Volcanism could have caused fault reactivation and triggered renewed fluid convection to drive the observed recrystallization.

6.4. Hydrothermal fluids in the Pre-Salt succession

This study highlights the importance of hydrothermal fluids in diagenesis of the Pre-Salt carbonates, which has consequences not only for recrystallization, cementation of matrix pores and fractures, and dissolution (Alvarenga et al., 2016; Herlinger Jr. et al., 2017), but also for modeling of the thermal basin evolution. It is significant that hydrothermal heat pulses, associated with source rock maturation and hydrocarbon charge, CO₂ charge, bitumen formation and calcite recrystallization, happened very early in the burial history, i.e. within 6–16 Ma of deposition. This was equally a time of significant geodynamic changes, such as the onset of oceanic crust formation. Such early burial heat pulses and the circulation of hot metalliferous fluids with mantle contribution are increasingly being recognized on both conjugate margins of the South Atlantic (e.g. Fiordalisi et al., 2024; Herlinger Jr. et al., 2017; Strugale et al., 2025). Stratiform copper, zinc and lead sulfide mineralization has been reported from the Cuvo Formation in the onshore Kwanza and Benguela basins (van Eden, 1978) for the Kwanza Basin, Girard et al. (2017) documented an early heat pulse involving saline and CO₂-rich fluids hotter than 150°C. Geochronology of associated carbonate and silica cements gave ages between 92 ± 3 Ma and 112.5 ± 2.8 Ma (Godeau et al., 2021). Basalt alteration ⁴⁰Ar/³⁹Ar ages of 106.9 ± 1.6 Ma to 114.5 ± 2.9 Ma were used to constrain a hydrothermal (c. 140°C) pulse in the Kwanza Basin (Loma et al., 2018). In the

Santos and Campos basins, carbonate diagenetic ages range from ~120 to ~80 Ma (Alkmim et al., 2025; Brito et al., 2024; Figueiredo et al., 2025), with distinct hydrothermal fluid pulses at 116 Ma, 110 Ma and 101 Ma (Figueiredo et al., 2025). Fluid inclusions in Santos Basin barite yielded homogenization temperatures between 110.5 and 174.6°C, average fluid salinities of 24.7%, and a mantle noble gas signature (Pestilho et al., 2022). Hydrothermal (90–170°C) activity was dated in the Campos Basin with adularia ⁴⁰Ar/³⁹Ar ages of 107.0 ± 1.0 – 104.3 ± 0.8 Ma (Tritilla et al., 2018). Collectively, the mineralogical and geochemical observations in this study (Pb–Zn sulfides, fluorite, barite, hosted in fractured carbonates, relatively hot fluids) resemble a Mississippi Valley type style of mineralization (Leach et al., 2010).

Magmatic heat pulses and hydrothermal fluid circulation were thus not isolated phenomena, but they occurred on both margins over a protracted period until at least 80 Ma, and likely up to c. 55 Ma (Rochelle-Bates et al., 2021). These processes would be most pronounced along deep-seated detachment or transfer faults, where crustal and/or magmatic components could be added. The Benguela Basin is located close to a rift transfer fault and volcanic centers (Guiraud et al., 2010; Jerram et al., 2019; Rey-Moral et al., 2026), and was a focal point for these processes.

7. Summary

The current study combines petrography, clumped isotopes, LA-ICP-MS U–Pb geochronology and noble gas analysis to reconstruct the diagenetic evolution of a Pre-Salt carbonate core in the Benguela Basin of Angola. As magmatic processes played an important role in the diagenesis of South Atlantic reservoirs, the study aims to verify if fluids and volatiles had a mantle origin and to provide a geochronological framework for diagenesis. The main results are:

- (1) A protracted diagenetic history involved carbonate precipitation, cementation, and recrystallization, as well as silica diagenesis, fluorite and metal sulfide cementation, in part similar to Mississippi Valley type mineralization.
- (2) Diagenetic fluids were evolved basinal formation waters with sedimentary and crustal sources. Noble gas signatures of calcite, quartz and sphalerite indicate a significant mantle volatile component in these fluids.
- (3) Calcite recrystallization occurred in two pulses at 111.2 ± 3.4 Ma and 87.7 ± 5.5 Ma from aqueous fluids with temperatures of c. 114–138°C and 145–149°C, respectively. Fluid temperatures exceeded standard burial at 111.2 ± 3.4 Ma and the fluids are interpreted as hydrothermal. Fluid temperatures during the younger event are largely indistinguishable from burial temperatures.
- (4) The influence of magmatism on sedimentary basins is known on the South Atlantic conjugate margins, but in Angola has received little study in the public domain so far. This work illustrates the importance of hydrothermal fluid flow with a mantle component. Such fluid flow affected sedimentary basins within 6–16 Ma of deposition and continued for a protracted period of burial, significantly altering the thermal structure of basins.

CRedit authorship contribution statement

Nathan Rochelle-Bates: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Stefan Schröder:** Conceptualization, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Greg Holland:** Formal analysis, Investigation, Methodology, Writing – review & editing. **Nick M.W. Roberts:** Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Cedric M. John:** Formal analysis, Investigation, Methodology, Writing – review & editing. **Ian Millar:** Formal analysis, Investigation, Methodology,

Writing – review & editing. **Richard Dixon:** Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Nathan Rochelle-Bates reports financial support was provided by UK Research and Innovation Natural Environment Research Council. Stefan Schroeder reports a relationship with BP Plc that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marger.2026.207858>.

Data availability

All data acquired for this study are contained within the article and supplementary material. Due to confidentiality reasons, background information cannot be shared.

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