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Geochronology of volcanically associated hydrocarbon charge in the pre-salt carbonates of the Namibe Basin, Angola

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ABSTRACT
In volcanic rifted margins, the timing of hydrocarbon charge is difficult to predict, but is important in understanding fluid genesis. We investigated whether igneous activity was linked to hydrocarbon charge in the prolific South Atlantic pre-salt petroleum system. To do this, we applied in situ carbonate U-Pb geochronology, a relatively novel tool for dating hydrocarbon migration, to bituminous veins in pre-salt travertines from the rifted onshore Namibe Basin (Angola). To test if fluid flow was synchronous with known volcanic pulses, we also obtained new ⁴⁰Ar/³⁹Ar geochronology from a nearby volcanic complex. Bitumen is associated with calcite in a first generation of veins and vugs, and with dolomite in younger veins. The dated calcite veins yielded a pooled U-Pb age of 86.2 ± 2.4 Ma, which overlaps the volcanism ⁴⁰Ar/³⁹Ar age of 89.9 ± 1.8 Ma. The overlapping dates and the localized bitumen occurrence around the dated volcanic center show a clear genetic relationship between Late Cretaceous igneous activity and hydrocarbon charge. The dolomite was dated at 56.8 ± 4.8 Ma, revealing a previously unknown Paleocene/Eocene fluid-flow phase in the basin.

INTRODUCTION
The nature and timing of fluid flow can be difficult to predict in ancient volcanic rifted margins due to their highly (albeit locally) perturbed geothermal regimes (e.g., Morgan, 1982). Despite the ubiquity of carbonate minerals in a wide range of hydrological and diagenetic settings, carbonate U-Pb geochronology has only recently been applied to date fluid-flow events (see Roberts et al., 2020), and the technique has rarely been applied to bituminous carbonates. Traditional bulk dissolution methods are hindered by low spatial resolution and the potential presence of organic inclusions as sources of common Pb and open-system U (Parnell and Swainbank, 1990). Recent advances in the application of laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) to U-Pb carbonate geochronology have demonstrated its efficacy for dating vein-filling and diagenetic low-U carbonates (e.g., Li et al., 2014; Roberts and Walker, 2016; Nuriel et al., 2017; Mangenot et al., 2018; Holdsworth et al., 2019). High-spatial-resolution sampling can mitigate the impact of diagenetically altered zones and generate a large spread in U/Pb ratios (Roberts et al., 2020). Here, we show that it also greatly improves the utility of U-Pb geochronology in providing the timing of bitumen-related mineral authigenesis.

This study applied LA-ICP-MS U-Pb geochronology to date bituminous carbonate veins from the Cretaceous Angolan volcanic rifted margin. A lack of absolute age data means that both the stratigraphy and complex diagenetic history of the Namibe Basin were hitherto poorly constrained. We also present new ⁴⁰Ar/³⁹Ar dates from a nearby volcanic center. The data revealed a genetic relationship between hydrocarbon charge and volcanism. These results were used to explore controls on fluid flow at different times in the basin’s evolution.

GEOLOGICAL SETTING
The Namibe Basin lies in the Mesozoic orthogonal- to oblique-rifted margin segment of southwestern Angola. It is a frontier petroleum province in Angola with no offshore wells and few onshore studies. Onshore bitumen seeps occur along the margin, but published information on the timing of generation and charge is scarce. The local basement is a Precambrian polyorogenic belt, and the Mesozoic rift geometry was influenced by inherited northeast-southwest Pan-African structural trends (e.g., at transfer zones; Figs. 1A and 1B). The sedimentary fill includes Hauterivian–Aptian “pre-salt” and Upper Cretaceous “post-salt” successions, separated by Aptian evaporites (Fig. 1C). The basin is a volcanic rifted margin that records two major igneous pulses. The Bero Volcanics (ca. 134 Ma) formed during rift initiation and are equivalent to those of the Etendeka-Paraná large igneous province (Marsh and Swart, 2018). The Bentiaba Basanite (ca. 88–81 Ma) formed during the postrift Peri-Atlantic alkaline pulse (PAAP; Matton and Jébrak, 2009), and it gets younger toward the south, reflecting the final “unzipping” of Africa and South America (Jerram et al., 2018).

Early Eocene (ca. 55 Ma) igneous activity is well documented in Namibia, South Africa, and Brazil (Marsh, 1973; Jelsma et al., 2004; Guedes et al., 2005; Moore et al., 2008), but it is not yet recognized in Angola. Walgenwitz et al. (1990) also reported possible Paleocene–Eocene anomalously high-temperature (100–200 °C) diagenesis from K-Ar–dated alluvial clays in the Lower Congo Basin. In the Paleocene–Eocene, changing poles of plate rotation of the South American and African continents created...
changing stress regimes along fracture zones, with concomitant hotspot activity. Postrift igneous activity strongly influenced petroleum prospectivity in the Central South Atlantic (e.g., CO₂ flushing, changing source rock maturity; cf. the Supplemental Material).

In the distal sag basins, highly prolific pre-salt lacustrine carbonate reservoirs formed (Wright and Barnett, 2015). In similar but proximal stratigraphic positions, many pre-salt carbonates precipitated around springs and occurred at transstensional relay zones, where interacting structural fabrics created complex, high-permeability fault and fracture networks (Sharp et al., 2012). The studied pre-salt Cangulo Formation includes fissure- and fault-fed springs that sit on basement at the western edge of the paleovalley. Two dikes were sampled for ⁴⁰Ar/³⁹Ar geochronology to test whether they belong to the Bentiaba Basanite or a previously undocumented, more recent (Eocene?) event.

The Cangulo Formation outcrop is a karstified decameter-scale travertine complex that sits on basement at the western edge of the paleovalley. At the sample localities, a moderate to very dense array of dominantly stratabound veins and vugs cuts the travertine-complex host rock. Fibro-prismatic calcite with primary bitumen is included in the veins (as inclusions) and Dolomite fractures with intercrystalline bitumen. Minor amounts of bitumen have leaked locally into other phases, but bitumen is always associated with C₄ (as inclusions) and Dolomite as an intercrystalline coating. The paragenesis is summarized in Figure 3. The C₄ fills were used to infer an absolute age for the first hydrocarbon charge event. Veins of Dolomite were used to provide an upper estimate for a second (younger) charge event, as the bitumen is not trapped within crystals.

METHODS

Full data sets and detailed methodologies are provided in the Supplemental Material. Six carbonate samples were chosen for U-Pb analysis to investigate the timing of hydrocarbon charge. Eleven powder samples of host rock and C₄ were extracted by microdrill for stable isotopic analysis, which were performed at the University of Liverpool (UK); results are expressed in the standard delta notation as per mil differences relative to the Vienna Peedee belemnite standard (‰, VPDB). In situ LA-ICP-MS U-Pb geochronology was conducted on polished blocks following

Figure 1. Geology of the Namibe Basin (Angola) with published absolute age constraints (Strganac et al., 2014; Jerram et al., 2018; Marsh and Swart, 2018). (A) West Africa structure after Guiraud et al. (2010). Fault zones: Be—Benguela, Lu—Lucapa. WR—Walvis Ridge, MAR—Mid Atlantic Ridge. (B) Digital elevation model (NASA/METI/AIST/Japan Spac systems and U.S./Japan ASTER Science Team, 2009) with structural lineaments (red) and basin-bounding fault (dark red) remotely mapped in ArcMap 10.4.1 (https://www.arcgis.com). Published ages for Bentiaba Basanite (and equivalents) are shown where sampled. Yellow boxes enclose (n) lineaments for rose diagrams; note high density around Chapeu Armado–Ponte Negra–Plambo and Bero, where the Cangulo Formation carbonates occur. (C) Basin stratigraphy after Jerram et al. (2018). BB—Bentiaba Basanite Formation, Bero Volcs.—Bero volcanics. (D) Google Earth image of the Chapeu Armado locality with observed structural elements (black, gray—inferred), Cangulo Formation spring carbonates (blue), Cangulo Formation siliceous springs (pink), and sample localities (yellow), where white arrows indicate Cretaceous opening direction. B—basement, BB—Bentiaba Basanite, CA—Chapeu Armado nephelinite complex, M—Maastrichtian sediment.
the method of Roberts et al. (2017); all quoted ages are lower concordia intercept dates from Tera-Wasserburg plots, at 2σ. For one sample, LA-ICP-MS elemental maps were created using line rasters to characterize the style of U enrichment and potential zones of secondary alteration. Two nepheline samples were analyzed at The Open University’s (Milton Keynes, UK) Ar/Ar and Noble Gas Research Laboratory for 40Ar/39Ar geochronology (see Jerram et al., 2018).

RESULTS
Carbonate (U-Pb)

Dates were determined for four samples (two others were lacking in radiogenic Pb). Elemental mapping and spot analyses revealed highly variable U and Pb contents; U and Pb contents across C1 sample areas ranged up to 33 ppm and to 520 ppm, respectively, whereas U and Pb contents across Dol, sample areas ranged from 0.22 to 3.7 ppm and from 0.1 to 120 ppm, respectively. Uranium, like most of the analyzed trace metals, follows crystal growth bands (Fig. 2), indicating that the preserved elemental distribution represents a primary (crystal growth) pattern. Analyses of C1 calcite (n = 5) yielded dates between 87.7 ± 4.6 Ma and 79 ± 12 Ma. Pooling C1 data (assuming contemporaneous formation) yielded a date of 86.2 ± 2.4 Ma. Dol, (n = 1) yielded a date of 56.8 ± 4.8 Ma (Fig. 4).

It was not possible to extract a reliable host-rock age due to low radiogenic/common Pb ratios, possibly reflecting detrital enrichment of common Pb. The youngest calcite (C4) phase did not yield sufficient data due to its small (<50 µm) size.

The level of precision and consistent age data imply that if bitumen has contributed to the U-Pb data via ablation of small inclusions, the contribution must be minor; alternatively, the U-Pb ratios of the bitumen could be similar to those of C1/Dol. Small bitumen inclusions may have contributed to outliers that were not used for regressions.

Volcanics (40Ar/36Ar)

Step-heating analysis produced a date of 89.9 ± 1.8 Ma for sample CA-1 (Fig. 4) based on 65% of the released 36Ar. The inverse isochron calculation, using the same steps, agreed with this plateau age, and the 40Ar/36Ar intercept was within error of the atmospheric ratio, suggesting this is a reliable age for CA-1. No statistically valid plateau age could be calculated for sample

Figure 2. Dated Cangulo Formation carbonates (Angola). H—host rock, Bi—bitumen. C1, C2, C3, C4, Dol1, and Dol2 indicate carbonate phases. (A) Outcrop with fracture generations and sample inset; note the contrasting orientations and fill. (B, C) Thin section with vein generations (Alizarin Red stained; plane-polarized light). Note the pervasive Dol2 bitumen coating and relative absence in earlier C3. (D, E) C1 nucleating on host rock. Note the primary bitumen inclusions that follow growth zonation (cross-polarized light). (F) Elemental maps of dated C1 vein. (G) δ13C vs. δ18O for microdrilled host calcite (H) and C1 veins. VPDB—Vienna Peedee belemnite.
CA-2, and although the inverse isochron correlation was poor, the age was within error of CA-1 (see the Supplemental Material).

Stable Isotopes (C-O)
Host rock and C1 displayed negative δ18O (down to −7.5‰ VPDB) and very negative δ13C (down to −19.9‰ VPDB; Fig. 2). The δ18O values of C1 are compatible with a variety of parent fluids. Fluid-rock interaction in active/recent volcanic terrains can lead to elevated δ18Owater values (∼3‰–10‰ standard mean ocean water [SMOW]), which would correspond to C1 precipitation temperatures of 70–140 °C (cf. Supplemental Material; Sheppard, 1986). The δ13C values of C1 indicate incorporation of organically derived, isotopically light carbon (Moore and Wade, 2013). Host rocks are similar but generally isotopically heavier than C1. This complements petrographic evidence (e.g., recrystallization around C1 walls) of host-rock recrystallization by C1 and possibly later vein fluids.

DISCUSSION
The ages of both the Chapeu Armado C1 veins and the nephelinite dikes fall within the Late Cretaceous PAAP. The overlapping ages of volcanism and nearby bituminous C1 vein formation suggest a genetic link between the two events. Data from C1 veins indicate formation from hydrocarbon-bearing, potentially hot fluids. Therefore, a likely scenario is that volcanism and associated reactivation of older synrift faults induced localized fluid flow and forced hydrocarbon maturation.

The ca. 57 Ma Dol2 veins give an upper age limit for a second hydrocarbon charge event. The pervasive bitumen in Dol2 veins, and its absence in adjacent fabrics, clearly indicates that hydrocarbon-bearing fluids exploited the same structures as the Dol2 fluids. The Dol2 fluid may have also borne hydrocarbons, but this is not possible to prove unequivocally with this data set. Petrographic and geochemical analyses did not show unambiguous differences between C1 and Dol2 bitumen (cf. Supplemental Material), suggesting that they shared similar or the same source rocks. The late Paleocene–early Eocene Dol2 veins cannot be tied to any dated volcanic event in Angola. We have shown that C1 hydrocarbon charge and Chapeu Armado volcanism are not equivalent to Eocene volcanic bodies observed in Namibia, South Africa, or Brazil. The Dol2 bitumen-associated event may, however, be a manifestation of an equivalent Cenozoic event in Angola.
Fracture generations at Chapeu Armado provide insight into the flow regimes of the hydrocarbon-bearing fluids in the Santonian and late Paleocene–early Eocene. The displacive stratabound C1 veins are indicative of "overpressure" (e.g., Cosgrove, 2001; Cobbold and Rodrigues, 2007; Meng et al., 2017). In contrast, the later crosscutting vertical/subvertical C3 and Dol2 veins suggest that effective tensile stress was roughly horizontal. These later veins are less occluded and show evidence of reactivation accompanied by further propagation, with local C3 fringes lining Dol2 veins. The younger (Eocene at the latest) fractures likely formed under a different flow regime, in which overpressure was not as significant as it was for the older C1 event.

Overpressure was likely generated by the Aptian evaporite that once capped the Early Cretaceous pre-salt sequence in the Namibe Basin. While the evaporite is no longer present in the paleovalley, Albian Binga Member marine sediments atop C1 calcite in some vugs indicate that full evaporite withdrawal occurred after C1 and before the Dol2 event. Additional overpressure structures, including "zebra"-type fabrics (Wallace et al., 1994; Davies and Smith, 2006) of barite, silica, and iron minerals, occur in the immediate pre-salt deposits at Chapeu Armado and similar localities. Baroque and "zebra" dolomite has also been documented in offshore Angolan pre-salt carbonates by Harris (2000). Neither stratabound veins (like C1) nor "zebra" fabrics were observed in any post-salt...
successions in the Namibe Basin. Thus, evidence of overpressured and potentially hot fluids is widespread in the immediate pre-salt successions but is notably absent in post-salt successions.

CONCLUSIONS

This study has shown the utility of in situ U-Pb carbonate geochronology in providing absolute age constraints for hydrocarbon charge events. The data reveal a genetic relationship between hydrocarbon charge and Late Cretaceous (and possibly also Eocene) igneous activity in the onshore Namibe Basin, where absolute age data were previously limited. Evaporite-associated overpressure fabrics may be a common feature of the immediate pre-salt successions in the South Atlantic. The events recorded in this study place constraints on the timing of evaporite removal, providing further insight into the exhumation history of the Angolan rifted margin. The South Atlantic petroleum system is thought to have been heavily influenced by post rift igneous activity. The results of this study show that post-rift igneous activity did indeed influence and likely helped to create an onshore petroleum system at a local scale.

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