Marine and Petroleum Geology 80 (2017) 394–411

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo

Research paper

# Volcanic rock alterations of the Kwanza Basin, offshore Angola - Insights from an integrated petrological, geochemical and numerical approach

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ARTICLE INFO

*Article history:*
Received 4 October 2016
Received in revised form
15 December 2016
Accepted 20 December 2016
Available online 22 December 2016

*Keywords:*
Kwanza
Volcanism
Presalt
Continental carbonates
Numerical modelling
Hydrothermal fluids
$CO_2$
PHREEQC

ABSTRACT

The Lower Cretaceous presalt section of the Kwanza Basin (Angola) is in the spotlight following the discoveries of petroleum systems in this basin, and more generally in the South Atlantic. These systems are mostly composed of continental carbonates in close association with volcanic rocks. This work is focused on the study of an offshore Kwanza presalt volcanic sequence characterized as Valanginian trachytic subaerial lava flows. A detailed petrological analysis of the altered trachyte in association with fluid inclusion microthermometry was conducted in order to depict the initial mineralogy (albite, sanidine, titanomagnetite) and obtain a paragenetic sequence (quartz, siderite, kaolinite, calcite). Thermodynamic equilibrium modelling of the trachytes alteration by meteoric fluids, over a range of temperatures (25 °C–200 °C) and $CO_2$ partial pressure ($pCO_2$: 0.01 mbar to 100 bar), were performed with PHREEQC, and compared to the observed paragenetic sequence. Some numerical simulations reflect the observed paragenesis. As a result, the $pCO_2$ is constrained by the occurrence of siderite (from 0.1 bar at 50 °C to 30 bar at 125 °C) and kaolinite (from 0.2 bar at 50 °C to 1.2 bar at 125 °C). The simulations emphasize the need for a high $pCO_2$ in the hydrothermal system, to achieve the observed trachyte transformation. After reaching equilibrium with the trachytes, the simulated fluids highlight a mid-alkaline to near neutral pH with high Fe, $HCO_3$+$CO_3$, and alkali concentrations. The palaeofluids could have evolved from Ca- and Mg-rich to Ca- and Mg-poor with increasing temperature. Inversely, Si concentrations are positively correlated with increasing temperatures. This methodology, integrating a petrological approach and numerical simulations, proves to be a powerful tool leading to better understanding of the proxies ($pCO_2$, temperature, redox conditions) controlling paragenesis. To push further, these simulations are also a step toward improved understanding of palaeofluid evolutions in presalt systems and better prediction of reservoir quality.



## 1. Introduction

The presalt formations in the Southern Atlantic have been of major interest to petroleum companies for many years. The recent offshore oil discoveries in Brazil (Carminatti et al., 2008) have increased interest in the exploration of the West African rift systems (Greenhalg et al., 2012; Cazier et al., 2014), considered as valuable analogues of the Brazilian basins (Saller et al., 2016). Recent research into the global geodynamic evolution of the South Atlantic margins (Moulin et al., 2010; Unternehr et al., 2010; Chaboureau et al., 2013; Péron-Pinvidic et al., 2015) has shown that the Kwanza Basin is more influenced by volcanism than the conjugate Brazilian margin. The hydrothermal fluids (and especially $CO_2$) associated with volcanism during different rifting phases are thought to contribute significantly to the precipitation of carbonates, but also to the alteration of the volcanic rocks.

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http://dx.doi.org/10.1016/j.marpetgeo.2016.12.020

In this context, it is difficult to describe and predict the diagenetic state of buried presalt continental carbonates, but this task is essential for hydrocarbon prospectivity and reservoir quality prediction. Porosity in presalt carbonates depends in part on the nature of the fluids that participate successively in carbonate precipitation and in porosity evolution, during early to late diagenesis. Furthermore, defining the nature of the basement and the associated fluids is essential to feed numerical models simulating sediment diagenesis. By "associated", we mean the hydrothermal or meteoric fluids, enriched or not in $CO_2$, that have interacted with the basement.

From a sedimentological point of view, many studies have emphasized the influence of volcanic catchment areas on the carbonate factory of lacustrine environments developing on rifted margins (Renaut et al., 2002; Gierlowski-Kordesch, 2010; Tosca and Wright, 2015; Szatmari and Milani, 2016; Saller et al., 2016). Cerling (1994) highlighted the major impact of these volcanic catchment areas in influencing lake chemistry, using data from the East African Rift. Wright and Barnett (2015) evoke lacustrine environments fed by rivers draining basic volcanic terrains, coupled with thermal to ambient spring inflow and an arid climate for the presalt synrift lacustrine deposits (e.g. laid down before the extensive upper Aptian salt formation of the South Atlantic). In this context, high $CO_2$ input, high carbonate alkalinity, and high dissolved Si, Mg, and Ca concentrations, could have contributed to rapid mineralization. All these conditions favour the precipitation of the Mg-rich clays and carbonates (hydrated or not) that constitute the primary rock of the targeted presalt reservoirs.

In the Kwanza Basin (Angola), presalt volcanic activity occurred from $145 \pm 9$ Ma to $124 \pm 10$ Ma, *i.e.* from the Berriasian to the Lower Aptian (Torquato and Amaral, 1973; Marzoli et al., 1999). This volcanism is bimodal, mafic, and felsic, with silica-saturated basalts and rhyolitic end-members. In this paper, we focus on the investigation of one core of volcanic material recovered during an early presalt oil exploration programme in the early 90s. The drilled material is mainly composed of an altered volcanic rock, which lies directly below the salt. Buried presalt volcanic rocks in offshore settings are rarely described in the literature. This material therefore provides an exceptional opportunity to investigate the physico-chemical parameters linked to offshore presalt volcanism, and their inferred palaeoenvironmental and diagenetic consequences.

In modern environment, geochemical simulations of volcanic rocks alteration usually include the use of sampled aqueous fluids (Aiuppa et al., 2000; Carvalho et al., 2015). In buried sequences, little information about the fluids involved during the alteration is available. In this study, we aim to establish the mechanisms and consequences of the alteration of these volcanic rocks. The first objective was to decipher their initial mineralogy, paragenetic sequence, and to characterize the type of fluids involved during the precipitation of secondary minerals in order to feed and constrain numerical models. A discussion of the type of magmatism is proposed, with regard to the well-known and well-constrained onshore volcanic series. The second objective was to compare the numerical models thus obtained with the mineralogical data. Van Pham et al. (2012) used batch- and 1D diffusion-reaction simulations using PHREEQC in order to investigate the potential for $CO_2$ mineral storage in basalts. Conversely, we use PHREEQC modelling in order to: (1) constrain the physico-chemical conditions leading to alteration, (2) evaluate the impact of $CO_2$ input in such systems, and (3) evaluate the palaeoenvironmental implications of alteration for the deeply buried presalt syn-rift sedimentary series.

## 2. Geological setting

### 2.1. Regional geology

The Kwanza Basin was formed during the Neocomian rifting related to the breakup of Pangea (Teisserenc and Villemin, 1990; Guiraud and Maurin, 1991; Jackson et al., 2005; Guiraud et al., 2010). The rifting was associated with the asynchronous separation of Gondwana that led to the South Atlantic opening (Von Nicolai et al., 2013). This asynchronous spatio-temporal process generated four segments (equatorial, central, southern, and "Falkland") bounded by major oceanic fracture zones (Torsvik et al., 2009; Moulin et al., 2010; Beglinger et al., 2012; Von Nicolai et al., 2013). The Kwanza Basin is located in the southern part of the central segment, bordered to the south by the Florianopolis Fracture Zone (Von Nicolai et al., 2013). This basin can be split into two sub-basins, known either as the Inner and Outer Kwanza basins, or the onshore Kwanza Basin and the offshore Kwanza Basin (Fig. 1A; Hudec and Jackson, 2002, 2004). A basement high located in the offshore Kwanza Basin and termed "Central Platform" or "Atlantic Hinge Zone" separated these two sub-basins (Fig. 2B; Marton et al., 2000; Jackson et al., 2005). According to Von Nicolai et al. (2013), the onshore Kwanza Basin coincides with present-day onshore Angola. The overall tectono-sedimentary history is reviewed in Guiraud et al. (2010).

Several recent papers have tried to establish a new vocabulary to describe the different stratigraphic events occurring between intracratonic rifting and seafloor spreading (Moulin et al., 2010; Unternehr et al., 2010; Chaboureau et al., 2013; Péron-Pinvidic et al., 2015). These studies characterize large-scale margin architecture, divided into five structural domains (proximal, necking, distal, outer, and oceanic), underlining the strong dissymmetry along the Angola-Gabon rifted margin. Crustal thinning may be favoured by the development of detachment faults creating upper and lower plate domains (Unternehr et al., 2010; Péron-Pinvidic et al., 2015). Ductile deformation could occur in the lower plate domain, where the accommodation space is mainly horizontal, leading to the formation of large basins with little subsidence. The upper plate could exhibit more brittle deformation, leading to narrow subsiding basins, with more abrupt margins. In these models, volcanic activity is mainly located where the thermal gradient is strong, generally in the upper plate domain. This high thermal gradient may also cause a strong vertical uplift, associated with strong erosion and hydrothermalism.

Volcanic activity is also associated with rift initiation at approximately 138 Ma, with the eruption of the Paraná flood basalts, onshore Brazil (White and McKenzie, 1989; Hawkesworth et al., 1992). Three major sequences after this rift initiation have been inferred from the tectono-stratigraphic evolution of the Kwanza Basin (Ala and Selley, 1997; Schollnberger, 2001; Serié et al., 2016): presalt (Late Proterozoic–Barremian), syn-salt (Aptian) and post-salt (Albian–Holocene). Brice et al. (1982) defined the presalt sequence as a series of intracratonic basins associated with continental deposits. Rifting is associated with fluvio-lacustrine siliciclastics and carbonate deposits (Uncini et al., 1998; Greenhalg et al., 2012; Serié et al., 2016). The end of the rifting (Late Barremian to Early Aptian) is associated with the filling of a syn-exhumation sag basin by massive salt deposits, inducing strong salt tectonic activity (see Marton et al., 2000; Guiraud et al., 2010; Unternehr et al., 2010). All these sequences are closely associated with active magmatism, as described in many studies (Cruz, 1960; Pereira, 1969; 1971; Marzoli et al., 1999; Comin-Chiaramonti et al., 2011). Marzoli et al. (1999) highlighted two