



## Primary silica precipitate at the Precambrian/Cambrian boundary in the South Oman Salt Basin, Sultanate of Oman

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### ABSTRACT

An organic-rich laminated chert (silicilyte) consisting of up to 90% microcrystalline quartz that formed at the Precambrian–Cambrian boundary acts as a light-oil reservoir in the subsurface of the South Oman Salt Basin, Sultanate of Oman. Fully encased in salt domes, it was first discovered during the 1990's hydrocarbon exploration activities of Petroleum Development Oman. Because of the economic significance and the unconventional reservoir characteristics, there is great interest in understanding the origin of the laminated chert, its source of silica and mode of precipitation in an anoxic, sulphur-rich, stagnant and highly saline basin.

The homogeneous distribution and high values of stable Si isotope composition (avg.  $\delta^{30}\text{Si} = 0.83 \pm 0.28$ ) coupled with a low molar Ge/Si ratio ( $< 0.25 \times 10^{-6}$ ) of the microcrystalline matrix quartz clearly reveal dissolved silica in the seawater as the Si source, whereas hydrothermal or biogenic (e.g. sponge-derived) silica can be excluded.

Silica precipitation from seawater was likely the result of a dramatic increase in salinity in response to salt dissolution atop and adjacent to the edges of transtensional depressions on the deep basin floor, thus markedly reducing the solubility of amorphous silica in these brine-filled seawater depressions. This saturation triggered the formation of silica-gel, which accumulated at the basin floor forming a soft silica-rich layer on bacterial mats giving rise to a laminated sediment. The mean number of laminae is ca. 32 per year suggesting that layering is non-annual and controlled by processes such as fluctuations in nutrient supply, lunar driven re-mixing or diagenetic segregation.

The transformation of the silica-gel to microcrystalline quartz occurred below 45 °C indicating a less than  $-4.5\text{‰}$   $\delta^{18}\text{O}$  composition of the pore-water during microcrystalline quartz formation.

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### 1. Introduction

An organic-rich finely laminated chert (locally named Al Shomou Silicilyte) acts as a hydrocarbon reservoir in the subsurface of the South Oman Salt Basin, Sultanate of Oman. Up to 400 m thick and several kilometres wide slabs of this laminated chert are entrapped in salt domes at depths of 4–5 km. The silicilyte is

a prolific source rock mature for light oil and it produces light and sour oil (using massive fracturing technology) from a high-porosity, low-permeability microcrystalline silica matrix, deposited around the Neoproterozoic–Cambrian boundary. The economic significance and the unconventional reservoir characteristics have triggered numerous studies to elucidate the origin and distribution of this rather unusual reservoir since its discovery in the early 1990s (e.g. Al Siyabi, 2005).

Comparing the silicilyte with other siliceous deposits (Amthor et al., 2005) highlights its unique nature, because all of the possible known analogues (e.g. Precambrian banded iron formation type chert; or Phanerozoic biogenic cherts e.g. Monterey Fm.; lacustrine Magadi-type chert; or hydrothermal sinters) differ either in their source of silica, i.e. biogenic, or mode of formation,

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i.e. solid crust, or transformation characteristics, i.e. replacing amorphous silica.

Despite recent progress concerning the depositional framework and origin of the silicilyte (Al Rajaibi, 2011; Amthor et al., 2005; Grosjean et al., 2009; Kowalewski et al., 2009; Schröder and Grotzinger, 2007; Wille et al., 2008) the source of silica and its mode of precipitation have generally remained unresolved. Grosjean et al. (2009) point out that a specific biomarker discovered in the silicilyte was described from demospongiae (McCaffrey et al., 1994), in which case the quartz crystals might have formed diagenetically by precipitation from dissolved biogenic silica (Schieber et al., 2000). Other potential sources of silica are from volcanic activity along mid-oceanic ridges, weathering and riverine input, inorganic precipitation from seawater as proposed for Precambrian cherts (Maliva et al., 2005) or sorption on organic molecules (Mukhopadhyay et al., 2004).

In this paper we apply state-of-the-art Si and O stable isotope investigations together with trace element analyses and fluid inclusion microthermometry to further constrain the source of silica and the mode of microcrystalline quartz formation.

## 2. Tectonic setting, stratigraphy and depositional environment

The present-day outlines of the NE-elongated salt basin in south Oman (Fig. 1) are interpreted as regional structural trends created by NW/SE-oriented transtension during Ara depositional times (e.g. Allen, 2007). Uplifted blocks became sites of carbonate deposition, whereas basinal transtensional depressions were overlain with black shale and silicilyte (Amthor et al., 2005). Evaporites blanketed both basinal areas and uplifted blocks.

The Athel Formation is one of five formations comprising the subsurface Ara Group (Amthor et al., 2003, 2005; Forbes et al., 2010) (Fig. 2). The Athel Formation (Fig. 2) includes at the base the 375 m thick Al Shomou Silicilyte Member and at the top the 140 m thick Thuleilat Shale Member. This basinal sequence overlies the 115 m thick organic rich shales of the U Formation, which is correlated with the U Carbonate Member of the A4 cycle on the adjacent carbonate platform (Amthor et al., 2005; Schröder and Grotzinger, 2007; Forbes et al., 2010). A globally correlative negative carbon isotope excursion at the base of the U Formation together with the numerical age of an ash bed at the base of the U-Carbonate dated at  $541 \pm 0.13$  Ma (Bowring et al., 2007) reveal that the sequence was laid down just above the Ediacaran–Cambrian boundary (Amthor et al., 2003, 2005; Schröder and Grotzinger, 2007).

The available high-precision U–Pb age dates and their extrapolation bracket the deposition of the Ara Group between ca. 547 and 538 Ma (Bowring et al., 2007) and allow to estimate the average duration of carbonate/evaporite sequences to about 1.2–1.3 my. Using this average duration, the ages of the individual Ara sequences can be estimated quite precisely. Given the remaining uncertainties in terms of the stratigraphic correlation of the U and Athel Formations, a duration of 2 my (542–540 Ma) is considered to be the best estimate for the A4 sequence covering both the U and Athel Formations (Forbes et al., 2010).

The Al Shomou Silicilyte was deposited during a transgressive to highstand systems tract in the deepest depressions of a segmented basin with topographic lows and highs flanked by carbonate platforms (Fig. 1). Limited detrital input reached the basin from the flanks and the silicilyte formed mainly in a stratified water mass. Recent studies by Schröder and Grotzinger (2007) and Wille et al. (2008) on redox sensitive trace elements, and by Grosjean et al. (2009) and Kowalewski et al. (2009) on source rock characteristics corroborate earlier studies on organic biomarkers in the silicilyte

(e.g. Terken et al., 2001; Nederlof et al., 1997) and indicate an anoxic, sulphur-rich, stagnant and highly saline water body during the deposition of the silicilyte. In addition, the presence of X-branched compounds and Dinorhopane in the saturated hydrocarbons, in both source rocks and oils, is attributed to an origin from extinct heterotrophic bacteria and chemotrophic bacteria, respectively (Kowalewski et al., 2009; Terken et al., 2001; Höld et al., 1999; Thiel et al., 1999; Nederlof et al., 1997).

## 3. Methods

The study is based on core material provided by Petroleum Development Oman from 10 wells in two oil fields, a well in the central deep basin, and one on the eastern flank (Fig. 1). A total of 8 shale samples are from the Thuleilat Member and 25 silicilyte samples from the Al Shomou Member.

A series of optical, isotope, geochemical and physical methods were applied to unravel the source(s) of silica and the physico-chemical conditions of quartz precipitation. The detailed descriptions of the methods are given in Appendix A.

## 4. Results

### 4.1. Matrix description

Microscopy, SEM, TEM and XRD investigations (Amthor et al., 2005; Al Rajaibi, 2011) reveal the finely laminated and porous aspect of the silicilyte with a mean lamina thickness of ca. 20  $\mu\text{m}$ , consisting of predominantly organic matter-rich and microcrystalline quartz-rich layers, respectively (Fig. 3A). The laminae are generally continuous on a thin-section scale but pinching-out was also observed. Moreover, they show compactional features and syn-depositional deformation (Fig. 3B) indicative of soft sediment conditions during deposition and early stage diagenesis. Petrographic evidence suggests that compaction has reduced the initial sediment thickness by at least 50% of which ca. 30% is mechanical compaction (Fig. 3C).

The silicilyte comprises a small quantity (<5%) of detrital components such as silt- and fine-sand sized quartz, K-feldspar, rock fragments and white mica or illite. The origin of the latter is unknown but a combined detrital/authigenic source is likely. Thin-section analyses by Amthor et al. (2005) document abundant amorphous organic matter dispersed in the silicilyte. Authigenic idiomorphic quartz crystals are the main component of the silicilyte (Fig. 3D,E). Other diagenetic phases are pyrite, apatite, dolomite, magnesite and barite. Moreover, the low crystallinity index of quartz ( $\text{CI} = 1\text{--}4$ ; Amthor et al., 2005) in the silicilyte is comparable to chert ( $\text{CI} = <1\text{--}4$ , Murata and Norman, 1976) indicating a similar small size of the coherent diffraction domain, which is often related to the crystallite size (Amthor et al., 2005; Murata and Norman, 1976).

### 4.2. Geochemistry

In order to determine the effect of aluminosilicates on the  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  values in quartz and indications of the source of silica, the element concentrations were analysed by XRF, LA–ICP–MS and ICP–OES. However, the micrometre crystal size of quartz and white mica and their intimate intergrowth precluded an in-situ determination of Al and Ge in individual quartz crystals.

#### 4.2.1. Trace elements in bulk silicilyte

Semi-quantitative XRF-analyses (Table 1) of eight bulk silicilyte samples show a clear covariant relationship of Al and K ( $r^2 = 0.996$ ) indicating a dominant common source of both elements. Possible

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