

## Structural characterization of marine nano-quartz in chalk and flint from North Sea Tertiary chalk reservoirs for oil and gas

VICTOR A. DRITS<sup>1,\*</sup>, JØRGEN SKIBSTED<sup>2</sup>, OLGA V. DORZHIEVA<sup>1,3</sup>, ANTHONY E. FALLICK<sup>4</sup>, AND HOLGER LINDGREEN<sup>5</sup>

<sup>1</sup>Geological Institute, Russian Academy of Science, Pyzhevsky per 7, 119017, Moscow, Russia

<sup>2</sup>Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, DK-8000, Aarhus C, Denmark

<sup>3</sup>Institute of Ore Geology, Petrography, Mineralogy and Geochemistry, Russian Academy of Science, Staromonetny per 35, 119017, Moscow, Russia

<sup>4</sup>Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride, Glasgow G75 0QF, Scotland

<sup>5</sup>Geological Survey of Denmark and Greenland, Øster Voldgade 10, DK-1350, Copenhagen K, Denmark

### ABSTRACT

A new type of quartz, a nano-quartz consisting of spherical particles, is assumed to have formed by crystallization in the sea during sedimentation of the chalk in the North Sea and to have remained largely intact during burial diagenesis. The presence and nature of this nano-quartz have not been identified until recently, despite the fact that this quartz is the type present in the Upper Cretaceous-Danian chalk reservoir for oil and gas in the North Sea, both in the flint and as dispersed particles. In the present work detailed structural analysis of the nano-quartz has been carried out by X-ray diffraction, solid-state <sup>29</sup>Si and <sup>27</sup>Al MAS NMR, thermal analysis including water release, IR-absorption spectroscopy, and elemental analysis supplemented with analysis of oxygen isotope composition. It is found that <sup>IV</sup>Al substitutes for Si and that <sup>VI</sup>Al probably is bonded to hydroxyls on the particle surface of the nano-quartz structures. The charge compensation of tetrahedral Al<sup>3+</sup>, in addition to its conventional way of compensation by formation of the local structural arrangement [AlO<sub>4</sub>/M<sup>+</sup>]<sup>o</sup> defects (M<sup>+</sup> = H<sup>+</sup>, Na, K, Li), can occur at the expense of the OH<sup>-</sup> group coordinating one of the four tetrahedral Si<sup>4+</sup> nearest to the Al<sup>3+</sup> tetrahedron. The most significant feature of the North Sea nano-quartz deduced in the present investigation is the presence of [4H]<sub>Si</sub> defects, also known as hydrogarnet defects. This defect is present in up to 5% of the tetrahedral sites, whereas Al<sup>3+</sup> occupies less than 1% of the tetrahedral sites. Two types of distribution of the [4H]<sub>Si</sub> defects were determined. In one of them the [4H]<sub>Si</sub> defects aggregates parallel to the (0001) plane to form platelets as cracks with hydroxylated surfaces on both sides. The second type of [4H]<sub>Si</sub> defect occurs in the form of isolated tetrahedral vacant sites. The formation of the aggregated [4H]<sub>Si</sub> platelets lying in the (0001) plane mostly increases the *c* parameters of the structure, whereas the isolated [4H]<sub>Si</sub> defects and K+Na impurities contribute to increasing the *a* parameters.

The remarkable correlation of the positional distribution of the samples revealed from the relationships between *a* and *c* parameters and between amount of OH<sup>-</sup> groups responsible for formation of [4H]<sub>Si</sub> defects and *a* and *c* parameters can be considered as evidence for the validity of the structural formulas and, in general, of the main structural features of the studied samples. The unusually high content of [4H]<sub>Si</sub> defects in the nano-quartz samples may be related to their formation by precipitation in waters of the Danish North Sea.

**Keywords:** Nano-quartz structure, nano-quartz formation, hydrogarnet defects, X-ray diffraction, <sup>27</sup>Al and <sup>29</sup>Si MAS NMR, IR spectroscopy, thermal water release, δ<sup>18</sup>O isotope chemistry, elemental analysis