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Silica diagenesis in Eocene carbonates of the Okçular Formation, Turkey: inferences from field observations and petrography – discussion

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Yeşilot Kaplan (2025) provided important insights into the typology and petrography of Eocene cherts in Turkey. But, several aspects of his study need critical assessment and some important details have been undervalued or omitted, this in turn resulting in incomplete, or in some instances erroneous, interpretation of the observations made. This discussion covers the following questions raised by Yeşilot Kaplan (2025): (1) Why is the Eocene Epoch characterized by widespread chert formation? (2) What are the origins of bedded and nodular cherts? (3) What are the silica forms relevant to silica diagenesis (i.e., the opaline group)? (4) What is the relationship between porosity and displacive vs. replacive growth of secondary silica?

WIDESPREAD CHERT FORMATION DURING THE EOCENE

Eocene cherts frequently appear as substantial bedded cherts, brown to grey nodular layers, or discrete stratigraphic marker horizons within limestones and chalks (e.g., Henchiri, 2022), mostly comprising weathering-resistant quartz, chalcedony, or opal precursors. Significant global climate events and hydrochemical changes that brought silica-rich fluids into marine carbonate environments are associated with widespread lower Eocene chert deposits. The extensive occurrence of chert during the Eocene has been interpreted as resulting from hydrochemical interfaces caused by volcanogenic and hydrothermal venting activities supplying silica-rich diagenetic fluids (Muttoni and Kent, 2007; Henchiri, 2007, 2022; Varkouhi et al., 2024) into marine basins during tectonic and volcanic events. Yeşilot Kaplan (2025), however, ruled out a volcano-hydrothermal silica source for Eocene chert formation in Turkey. Eocene volcanism in Turkey is represented by an extensive, roughly 1,000-kilometre-long, east-west trending magmatic belt across northern and central Anatolia (Keskin et al., 2008). It formed following the closure of the northern Neo-Tethys Ocean and the collision of the Pontides with Gondwana-derived microcontinents. Volcanic rocks and volcano-hydrothermal emanations were once considered as the primary source of silica for chert and porcelanite, regardless of whether evidence for biogenic silica dominates, as in relatively recent cherts, or does not, as in most older cherts. Yeşilot Kaplan (2025) is unconvincing in postulating that a volcano-hydrothermal source for silica is not necessary for the Eocene cherts, for many authors have indicated a widespread association between volcanic rocks and diatomaceous/radiolarian deposits, and argued that this association is not coincidental but genetic (e.g., Racki and Cordey, 2000). High sea levels, intense weathering, and a surge in the biological productivity of silica-secreting animals such as diatoms, radiolarians and sponges were all consequences of the early Eocene global warming peaks (Varkouhi et al., 2024).

ORIGINS OF BEDDED AND NODULAR CHERTS

BEDDED CHERTS

Regardless of whether evidence for biogenic silica still predominates, as in Cenozoic formations, or not, as in the majority of older cherts, volcanic rocks and volcanic emanations were originally thought to be the main source of silica for chert. For example, Behl (2011) proposed that the source of silica for both Franciscan and Monterey cherts and porcelanites was volcanic emanations that accumulated silica in sea water and then precipitated silica gel. He proposed that the silica gel trapped the numerous, well-preserved radiolarian and diatom tests found in these formations. Volcanic rocks and diatomaceous deposits are commonly associated, according to Calvo (2012). Wise and Weaver (1974) examined ash layers from DSDP Leg 6 and found that opal-CT or quartz could only be detected in the presence of siliceous organisms. Similarly, Lancelot (1973) documented many tuffaceous intervals from DSDP Leg 17 that showed no signs of porcelanite or chert. Montmorillonite, zeolites, palygorskite, and potentially trace amounts of opal-CT are the principal alteration prod-

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ucts of deep-sea ash beds. Cook and Zemmels (1972) identified opal-C as the sole deep-sea porcellanite that is directly linked to volcanogenic material. Lava flows are usually linked to opal-C (Jones and Segnit, 1971). Deep-sea cherts and porcellanites form beneath belts of high plankton productivity, as demonstrated by a recent compilation by Keene (1975) of the distribution of Lower Eocene to Pliocene cherts and porcellanites recovered by the DSDP from the Pacific.

NODULAR CHERTS

Lancelot (1973) came to the conclusion that "there appears to be a consistent relationship between the mineralogical nature of the chert and the composition of the host sediments in which it is found" based on a thorough analysis of the stratigraphic occurrence of chert and porcellanite from DSDP boreholes. Quartz makes up the majority of chert found in clayey strata. Danelian et al. (2007) and Varkouhi et al. (2024) made similar observations. The source of silica is thought to be biogenic silica for both bedded porcellanite in clayey layers and nodular chert in carbonates. According to Lancelot (1973), the authigenic silica phase characteristics are determined by the ratio of silica to metallic cations. When the ratio is high: e.g., in clayey sediments, opal-CT will precipitate; but when the ratio is low; e.g., in carbonate sediments, chalcedony and quartz will precipitate. He described the opal-CT rims surrounding chert nodules as follows: the silica/metallic cations ratio gradually drops as the quartz nodule grows outward due to an accretion front, pushing clays and metallic cations along the accretion front. Finally, opal-CT will precipitate when this ratio has drastically dropped and is closer to the ratio in clayey sediments.

SILICA FORMS RELEVANT TO SILICA DIAGENESIS

The differentiation between silica phases or varieties in cherts, particularly the presence of the opaline subgroup, which encompasses opal-A, opal-C, and opal-CT (the diagenetic sequence of silica), is not always clear-cut since these mineral phases (characterized by short-range order in cherts) can be challenging to identify or diagnose with standard methods such as powder X-ray diffraction (which is suited for phases with long-range order). These mineral phases are primarily present in trace quantities beneath the detection limits of this equipment. Evidence of the expected occurrence of these silica types in cherts is seen in SEM observations through clusters of lepispheres (von Rad and Rosch, 1974) while XRD analysis, when above detection limits, shows a wide peak at 19.5–24.5°A and at 35.9º 2θ for opal-CT, along with a distinct peak at 4.0°A for opal-A. Moreover, infrared (FTIR) spectroscopy is more effective than and superior to XRD in identifying silica forms (Henchiri and Fattah, 2012; Awadh and Yasenn, 2019; Ben Fadhel and Henchiri, 2023), though it still has detection limits tied to the quantity of silica forms present.

POROSITY AND DISPLACIVE VS. REPLACIVE GROWTH OF SECONDARY SILICA

Yeşilot Kaplan (2025) did not discuss possible porosity enhancement in the limestone and silica (orthosilicic acid) supply studied, as regards subsequent secondary silica formation. The diagenetic dissolution of calcareous and opaline skeletons of planktonic organisms such as radiolarians or diatoms in a permeable carbonate matrix releases dissolved silica, as monomeric silicic acid. The subsequently created secondary porosity is likely to be the preferential site for subsequent stable and resistant secondary (euhedral) precipitation of quartz that forms owing to its crystallinity index (Murata and Norman, 1976) and its low specific surface area and ultramicroporosity (Bustillo et al., 1993) that make it the most mineralogically competent and the most chemically resistant mineral in such environments.

Freely occurring authigenic euhedral forms of silica as perfect minute crystals (some doubly terminated) in Okçular Formation limestone implies displacive silica growth in available pore space and not replacive growth since the secondary silica does not show entrapped calcareous material, this rather being pushed aside. Displacive growth of secondary silica is a well-studied diagenetic phenomenon in the geological record (e.g., Henchiri et al., 2015 ; Dowey and Taylor, 2019).

Silica diagenesis is considered as a major factor that influences reservoir characteristics as well as petroleum migration and accumulation (Carothers and Kharaka, 1978; Surdam et al., 1984; Gao et al., 2022). The silica phase transformation from opal-A to opal-CT to (authigenic) quartz results in a major decrease in the porosity and significant increases in density, cohesiveness, and brittleness of siliceous rocks (Snyder et al., 1983; Thyberg et al., 2010).

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