## Evolution of Pore Size and Structure in Siliceous Sediments and The Influence of Discontinuous Burial or Uplift on Cementation and Formation of Secondary Porosity

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## **ABSTRACT**

Biosiliceous sediments undergo a unique diagenetic evolution with dramatic, and in some cases, abrupt transformations in porosity, density, and other rock properties, such as sonic velocity and rock strength. Given enough time or increased temperature, the original biosiliceous sediments undergo two distinct transitions in silica phase that are either stratigraphically sharp or gradational depending on the compositional range of the primary deposits and the local burial history. The resulting highly siliceous diagenetic rocks (porcelanite or chert) develop a number of different microfabrics of intercrystalline micro- and nanoporosity with distinct pore morphologies and pore-size distributions. Although bulk-rock porosity and permeability trends have been studied by previous workers, we present a quantitative petrographic microfabric analysis of argon ion milled surfaces of the 2-dimensional pore shape, size and structures of different siliceous rocks. We also present evidence for how discontinuous burial/uplift history influences the evolution of porosity, including pore-filling cementation or development of vugular secondary porosity in different rocks and diagenetic settings.

Diatomaceous or radiolarian sediments are composed of frustules or tests of microfossils formed of hydrous, X-ray-amorphous opal-A. These microfossil skeletons are highly complex and form both intra- and interparticle porosity, commonly within the range of 55-80% of the sedimentary rock volume.

Although opal-A is highly soluble, once pore fluids are saturated with silica, compaction is primarily mechanical and high porosity is preserved until the first phase change due to skeletal rigidity and interlocked contacts between tests. At the first silica-phase transition, precipitation of nuclei of lower solubility opai-CT creates a new silica sink that increases dissolution of biogenic opal-A, weakening the rock framework that collapses under the lithostatic load. Simultaneous with this weakening, opai-CT crystallites grow in radial clusters termed "lepispheres". Bulk porosity generally decreases to -20-45 % except for in cherts that form by pore-occluding cementation and typically have porosities < 5 %. The new nano- to micropores in the opal-CT stage are entirely intercrystalline with morphologies defined by the equant to bladed crystal shapes and their angular intersections. Mean "circular-equivalent" diameter of pores in opal-CT phase rocks is approximately 100 nm, with all pores generally less than 300 nm in equivalent diameter. In relatively pure porcelanites (low-detritus, >75% silica), porosity consists of separated zones of nanopores and micropores associated with the radial growth of opai-CT crystallites in the Iepispheres. Lepisphere cores are formed of highly porous granular opai-CT, but this porosity is mostly isolated by a dense, virtually pore-free, surrounding impermeable mantle. The larger and better- connected interlepispheric pores are formed by larger, crosscutting and radiating bladed crystals. In less pure porcelanites (<75% silica), the pore shapes are more irregular and pore distribution may be patchy or homogeneous but does not display the lepispheric zonal pore structure and pores are generally less interconnected.

With continued burial, opal-CT converts to quartz by another dissolution-reprecipitation step and porosity in porcelanite generally decreases to 10-30% of rock volume. Although bulk porosity is decreased, the mean pore sizes in quartz-phase porcelanites are approximately 1 0 times larger than in the opal-CT-phase rocks that they were derived from. This means that while total porosity was lost, remaining pores coalesced into fewer, larger and better connected pores. Mean "circular-equivalent" diameter ranges from 0.5-2.0 micrometers in different rocks, with some measured pores up to 7.0 microns in equivalent diameter.

The original sedimentary fabric of the diatomite continues to influence the spatial distribution of pores even through one or two diagenetic steps in which the biogenic silica skeletal fragments were entirely dissolved and reprecipitated as opal-CT and then quartz. Laminated diatomites produce diagenetic porcelanites that retain a highly heterogenous, laminated pore distribution. Greater connectivity in porous laminations produce an anisotopic fabric that likely controls directional permeability. Similarly, diatomaceous gravity flow deposits with a heterogeneous composition (so-called "speckled beds") produce porcelanites with isolated, patchy distribution of more porous lenses that are largely isolated by surrounding less-porous matrix.

Diagenetic changes in silica phase, lithology, and porosity are usually considered under conditions of simple progressive burial in which phase transformation kinetics are driven by continuous increases in temperature and overburden. However, a history of discontinuous burial or tectonic inversion has important implications for localized loss or gain of porosity in highly siliceous sediments. Many successions experience pauses in burial or are reversed by tectonic uplift. When burial is halted, the transformation zone between opal-A and opal-CT or opal-CT and quartz phase rocks becomes a site of enhanced, localized diffusional transport of silica from higher to lower solubility phases between and along strata and across larger stratigraphic intervals. Horizons can be sufficiently silicified to create seismically resolvable reflections that are unrelated to the current burial depth of active prograde diagenetic transformation. These horizons can become "fossilized" reaction fronts that have been uplifted above the zone of active transformation, or 'paleo" reaction fronts that continued to be buried and no longer separate silica phase zones but are still discernible by excess silicification during pauses in burial. Uplifted successions that had barely reached the initial transformation of opal-CT to quartz can develop substantial secondary porosity by scavenging of opal-CT for precipitation of quartz in "lateformed" cherts. Silica derived from opal-CT dissolution is reprecipitated as pore- and fracture-filling quartz to form thickened beds or nodules of chert and cemented chert breccias. Diagenetically enhanced porosity from dissolution in associated pure opal-CT donor rocks can reach 65% -typical of much more shallowly buried opal-A diatomite. Porosity in these rocks is not intercrystalline, but instead consists of large, 1-10 micrometer-scale, interconnected dissolution vugs.