Brine silcrete: An expansion of the definition of silcrete and a unique early diagenetic feature of basin-basement interaction

Lowe, David G. [1,2], DeSantis, E.[1,3], Arnott, R.W.C.[1], and Conliffe, J.[4]

1: Department of Earth and Environmental Sciences, University of Ottawa. dlowe@mun.ca.

2: Present affiliation: Earth Sciences Department, Memorial University of Newfoundland.

3: Present affiliation: Fisheries and Oceans Canada.

4: Geological Survey of Newfoundland and Labrador.

Summary

Silcretes are indurated layers of silica-cemented soil, sediment, or rock formed by near-surface silica precipitation related to weathering processes, groundwater flow, and diagenesis (Summerfield, 1983; Milnes and Thiry, 1992; Nash and Ulyott, 2007). Silcretes have long been recognized as modern and ancient duricrusts, termed pedogenic silcretes, but more recently also as layers precipitated at groundwater tables, termed groundwater silcrete. The origin of pedogenic silcrete is relatively well understood. However, groundwater silcrete are not well understood, with proposed silica sources, transport mechanisms, and precipitation processes confined to the near-surface groundwater environment where silica saturation is low.

Here, an example of a groundwater silcrete from Upper Cambrian strata of the Potsdam Group is described and interpreted to be formed in a rift where Cambrian fault reactivation coincided with silcrete formation. Field relationships strongly support a connection between fault activity and silicification, including a systematic thickening and development of massive silcrete horizons above shear zones, brecciated silcrete near where faults intersect shear zones, and nodules along the margins of shear zones. Petrographic and cathodeluminesce microscopy of silcrete reveal early pre-compaction overgrowth cements with abundant primary fluid inclusions. Fluid inclusion microthermometry indicate that these fluids were high salinity (~22 – 25 eq. wt% NaCl+CaCl2) brines with homogenization temperatures of ~120º C – 150º C, implying silica precipitated from a hot, silica-saturated crustal brine from underlying Grenville Province basement. A combination of weathering reactions and direct quartz dissolution explains the chemical evolution of the source fluid, which likely originated as infiltrated meteoric water that had chemically equilibrated with Grenville crust at depth. Later, this brine was mobilized upward along reactivated faults during the Late Cambrian, and ultimately to the water table, where a combination of reduced pH and temperature promoted quartz supersaturation and quartz overgrowths on detrital quartz. This case example, therefore, expands the definition of silcrete to include near-surface silicification from externally-sourced crustal fluids, and provides a basis for interpreting silcrete as a feature of deformation and fluid migration along shear zones in fault-bounded continental basins.

Background and Geologic Setting

Here we test near-surface groundwater silcrete models with field- and laboratory-based observations of a ~ 8 – 142 cm-thick silicified horizon in Cambrian strata of the Potsdam Group, deposited over the St. Lawrence Rift system. This silcrete shows a progressive thickening, silicification, and brecciation toward numerous intrabasinal faults underlain by Mesoproterozoic shear zones in the Grenville Province (Fig. 1), suggesting the role of faults as conduits for silicifying fluids. To test this hypothesis, the paragenesis of silica cements and thermometry and petrography of their fluid inclusions are documented to constrain the potential sources and migration pathways of the silica-bearing fluids.

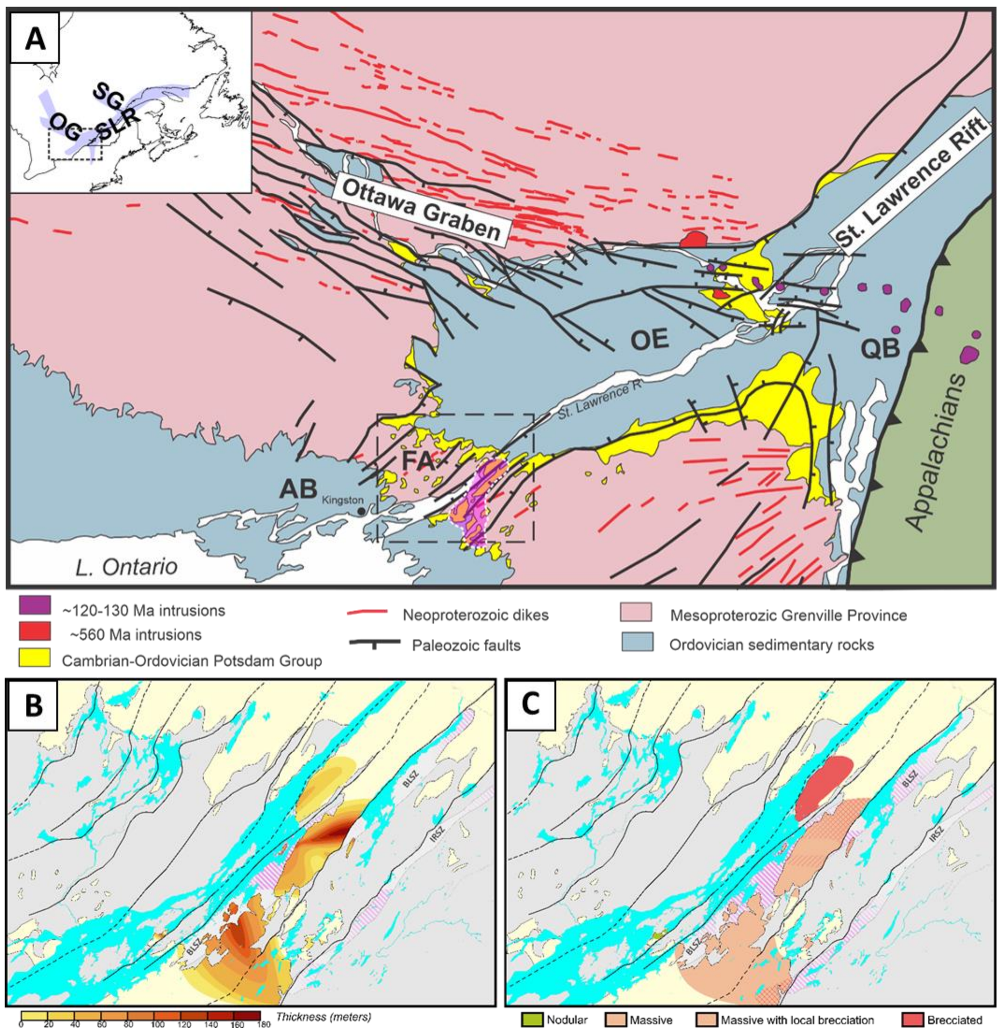

Figure 1: A) Map of the Potsdam Group cropping out along the margins of the Ottawa Graben and associated parts of the St. Lawrence rift system (shown in inset map – SLR=Saint Lawrence Rift, OG=Ottawa Graben, SG= Saguenay Graben). The current study area is shown by the black dashed box. This area is part of the southwest-striking extension of the St. Lawrence rift system outlined by Paleozoic faults transected orthogonally by a later structural high termed the Frontenac Arch (FA). Paleozoic basins that cover this segment of the St. Lawrence rift are termed the Ottawa Embayment (OE), Quebec Basin (QB) and Appalachian Basin (AB). The silcrete distribution across the Frontenac Arch is shown under the purple polygon. B) Map showing the distribution of Allounit 2 strata (pale yellow), Paleozoic faults, underlying Grenville Province rocks and Mesoproterozoic shear zones (pink and grey dashed polygons: BLSZ=Black lake Shear Zone; IRSZ=Indian River Shear Zone). Silcrete thickness contours from outcrop sections. (B) Map highlighting the distribution of the different textures displayed in the silcrete horizon.

Recent stratigraphic investigations of the Potsdam Group across the southern St. Lawrence Rift system reveal a complex internal stratigraphy comprising three unconformity-bound allounits. Provenance and paleoflow data suggest unconformity development coincided with local fault reactivation that modified basin morphology and sediment routing throughout this part of the St. Lawrence Rift system (Sanford and Arnott, 2010; Lowe et al., 2018). The silcrete horizon documented here caps strata of the middle allounit, and thus coincides with the timing of Late Cambrian fault reactivation.

Optical petrography was undertaken to determine silcrete compositions and textures. Optical photomicrographs of silcrete samples were then used to determine the apparent intergranular volume (IGV) and %-cement using ImageJ, an open-source image editing software. Framework grains were traced and filled-in black and color thresholds were adjusted to eliminate grains using the Global Threshold function and residual IGV was calculated using the Analyze Particle function. Backscattered electron (BSE) imaging of thin sections was undertaken using a JEOL JSM 7100 F SEM at Memorial University equipped with a Deben Centaurus Cathodoluminescence detector for CL imaging to determine silcrete zoning and paragenesis.

Results and Discussion

The silcrete horizon that caps quartz arenite strata of Allounit 2 crops out over an area of approximately 0.3 km^2 in northwestern New York State (Fig.1). The horizon is 8 - 142 cm thick with the thickest parts located north of two prominent northeast-trending faults (Fig.1). Moreover, most of the exposed silcrete overlies two major shear zones in Grenville Province basement (Fig. 1). Silcrete texture varies across this area, and includes nodular and massive forms consisting internally of medium- to coarse-grained quartz grains cemented by 10 – 50 µm thick syntaxial quartz overgrowths preserving 30-32% IGV. Compared to the average of 22% IGV in baseline Potsdam strata, this suggest that the silcrete formed prior to significant compaction. Notably, primary stratification is preserved in both nodular and massive silcrete, and features like vertical zonation and jointing are absent, consistent with a groundwater silcrete origin.

Massive silcrete is the most widespread form and is characterized by an 8 - 105 cm-thick silicified horizon with a sharp, undulating base (Fig. 2A). Nodular forms are generally limited to the northwestern edge of the silcrete horizon. Silcrete nodules are 4 - 14 cm in diameter and rounded with either a spherical or bedding-parallel elliptical shape (Fig. 2B). The outer surfaces of nodules are commonly highlighted by a 0.1-10 mm rind of poorly-indurated iron oxide and clay-cemented sand. The rind commonly thickens near the top of nodules and consists of sand grains dispersed in a pore-filling matrix of kaolinite, iron oxide and quartz silt. These interstitial fines are interpreted as infiltrated (illuvial) clays that were transported downward (i.e. translocation) through the vadose zone following nodule formation.

Brecciation of silcrete, post-dating silcrete formation, occurs within ~ 1 km of faults that overlie Grenville basement shear zones. Here, vertical fractures extend upward into the base of the massive silcrete, forming a complex network of fractures and intraclast breccia with intraformational clasts. The outer boundaries of the silcrete clasts tend to be broken along grain boundaries, but some sharply truncate grains and overgrowths in silcrete. The matrix consists of medium-grained sandstone with a moderately well-sorted framework of angular quartz grains surrounded by ~ 10 – 30% clay sized iron oxide, kaolinite and admixed quartz silt.

Figure 2: A) Massive silcrete horizon, base outlined by yellow dashed line. B) Nodular silcrete horizon.

Cathodoluminescence (CL) imaging of samples from silcrete nodules and the massive silcrete reveal three generations of quartz overgrowths termed C1, C1.5, and C2. C1 is a grain-coating cement consisting of ~ 10 – 40 μm-thick, euhedral or subhedral quartz overgrowths, and exhibits concentric luminosity zoning (Fig. 3). C1.5 discordantly succeeds C1 in CL, filling most of the remaining interstices and occluding spaces up to 120 μm in diameter (Fig. 3), and exhibits euhedral sector zoning (Fig. 3). C2 is a non-luminescing euhedral quartz overgrowth cement that postdates C1 and C1.5, filling any remaining void space (Fig. 3). Several samples of matrix from breccia were also imaged using CL, revealing that disaggregated subangular quartz grains were rimmed or partly rimmed by C1 commonly truncated by corroded margins, suggesting silica dissolution occurred during or after brecciation (Fig. 3).

Fluid inclusions are common in C1 quartz overgrowths, and have remarkably similar petrographic and microthermometric characteristics in all samples, representing a single fluid event. At room temperature, fluid inclusions in C1 cements are two-phase (liquid + vapor) and are liquid rich (~5-15% vapor). They are generally small (< 5μm) but rarely up to 20μm. Fluid inclusion microthermometry results from C1 overgrowths constrain silica precipitation to temperatures of ~ 120.2 to 151.6°C, and therefore well in excess of near-surface meteoric water. Moreover, these fluids were saline, containing 22.7 to 25.8 eq. wt% $NaCl+CaCl_2$, and were enriched with Ca relative to Na (Na/(Na + Ca) of 0.11 to 0.15).

C1 Fluid inclusion temperature and chemistry are similar to documented crustal brines formed by equilibration of externally-sourced fluids with crystalline basement adjacent to or underlying continental basin sediments (Carpenter et al 1974; Bodnar et al. 2014; Yardley and Bodnar, 2014). In this case, the most likely origin of crustal brines is meteoric water that infiltrated along faults and underlying basement shear zones following Neoproterozoic and/or Early Cambrian rifting. The evolution from mildly acidic meteoric water to high-salinity, silica-saturated brines can be explained by the equilibration with local Grenville basement, consisting of marble, metapelite, quartzite, and granite (Wong et al., 2011). Albite and calcite dissolution resulted in increased salinity (addition of Na+ and Ca2+) and pH (addition of bicarbonate). As fluid salinity, pH and temperature increased, so too did the solubility of silica, leading to the direct dissolution of quartz from associated granite, quartzose metapelites, and quartzite. Following upward migration silica-bearing fluids entered the water table, where a coinciding decrease in silica solubility and precipitation occurred due to a decrease in temperature and pH with re-equilibration with near-surface conditions (e.g., Selleck, 1978). Local brecciation of the silcrete then occurred during later fluid migration along faults, coinciding with high fluid pressure and localized strain.

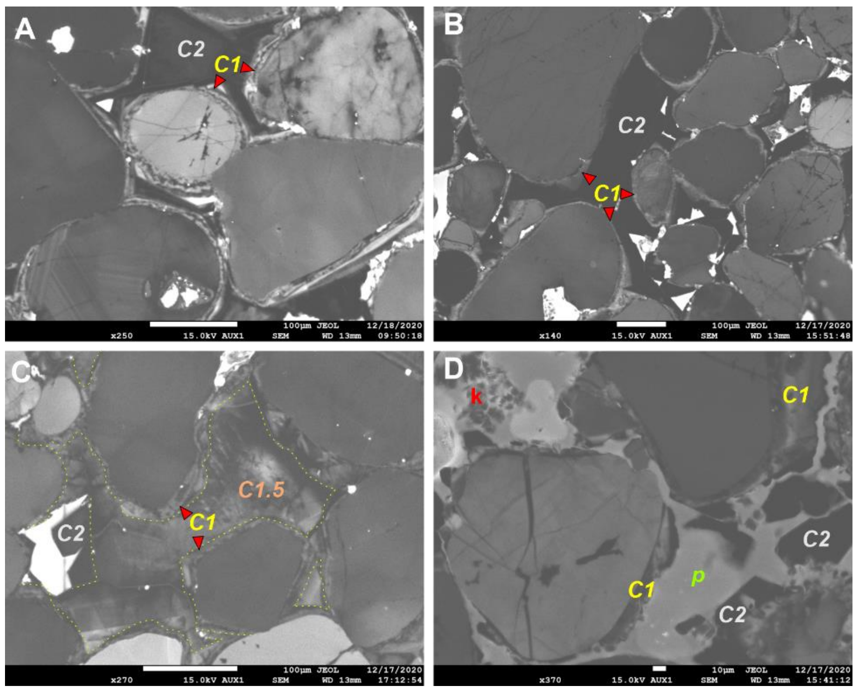

Figure 3: False-color panchromatic cathodoluminescence (CL) images of the silcrete. (A) Image from the interior of a silcrete nodule showing early generation grain-coating cement, C1, characterized by oscillating zones of alternating luminosity. A later generation of optically-continuous, non-luminescing quartz overgrowths, termed C2, fills most of the remaining void space. (B) Sample from the massive horizon showing early C1 and later C2 quartz overgrowth cement. (C) Some silcrete samples, like this example from a massive horizon, exhibit three generations of overgrowth, including C1, C2, and an intermediate zoned and luminous C1.5. (D) CL image from the breccia matrix showing corroded C1 overgrowths, void-filling C2, and remnant porosity (p).

Much of Allounit 2 strata were eroded during the Late Cambrian (Lowe et al., 2018). The silcrete horizon acted as a local well-indurated cap that locally prevented the erosion of Allounit 2. Succeeding Ordovician seaway transgression and sedimentation Potsdam strata were buried to a depth of at least ~ 1 km (Sanford and Arnott, 2010; Bédard et al., 2018). During this time, dissolved silica from pressure solution of detrital quartz was transported by pore fluids to the relatively porous uncompacted silcrete horizon, where C2 quartz overgrowths precipitated over earlier C1 ± C1.5 cements and occluded most of the remaining porosity.

Novel/Additive Information

This example of groundwater silcrete highlights a unique case example with crustal silica sources and fluid migration along faults. The possibility that many such groundwater silcretes precipitated from crustal brines thus expands the model of groundwater silcrete to include a new type – here termed brine silcrete– and could provide a basis to identify evidence of syn-sedimentary deformation in similar tectonically active basins. It also highlights unexpected complexity in a basal Cambrian sandstone, with the development of an early diagenetic reservoir barrier caused by reactivation of underlying basement.

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