Early quartz cements and evolution of paleohydraulic properties of basal sandstones in three Paleoproterozoic continental basins: Evidence from in situ $\delta^{18}$O analysis of quartz cements

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Abstract

Quartz cement microstratigraphy and high precision in situ $\delta^{18}$O values obtained by secondary ion mass spectrometry (SIMS) from $\mu$m-size quartz cement zones have been used here to determine the timing of cementation and to evaluate precipitation mechanisms within the basal sandstones of three economically significant Paleoproterozoic basins, the Athabasca and Thelon basins, Canada, and the McArthur Basin, Australia. In these examples, the earliest quartz cements have the highest $\delta^{18}$O values (up to 33‰; mean=26.0‰, V-SMOW) indicative of low temperature precipitation at depths of 0 to 1.1 km. Some paragenetically early cement phases, however, have lighter isotopic values that suggest either precipitation from isotopically depleted water or precipitation at higher temperatures. Subsequent generations of quartz cements have progressively lower $\delta^{18}$O values (mean=+16.1±3‰) consistent with precipitation at higher temperatures. These data combined with petrographic observations indicate quartz cementation began in near-surface vadose and phreatic zones; the next stage of cementation is characterized by syntaxial burial cement overgrowths. Regionally and stratigraphically, well-sorted sandstone facies that were initially aquifers preferentially experienced early quartz cementation, which resulted in cement-bridged pore throats at relatively shallow depths of 0–2 km and very early in their burial history transforming these units into diagenetic aquitards. As a result, these units did not experience mineralization. Compositionally and texturally immature braided fluvial facies did not experience early addition of quartz cement, but are instead marked by minor syntaxial overgrowth cement that make up <5% of the intergranular volume, formed at depths of 3–5 km, and were variably replaced by illite and chlorite during burial. These lithologies were still open to fluid movement at critical times in the basin when U and
1. Introduction

Proterozoic sedimentary basins are among the largest geological structures on Earth and contain vast amounts of economically important resources, including much of the world’s uranium and other metal resources (e.g., Williams, 1998; Kyser et al., 2000). Understanding the paleohydrology of Proterozoic basins is important because basin-hosted mineral deposits form in direct response to circulating burial brines associated with extensive mass transport (Bethke, 1986; Bethke et al., 1991; Kotzer and Kyser, 1995; Fayek and Kyser, 1997; Fishman, 1997; Kyser et al., 2000; Chen et al., 2001; Hiatt et al., 2003; Kyser and Hiatt, 2003). At first appearance, the paleohydrology of Proterozoic sedimentary basins should be easy to understand relative to Phanerozoic analogs because the former were sand and gravel dominated, without terrestrial macrophytes to bind, stabilize and trap fine-grained sediment, thereby making mud-rich sediment deposition and preservation rare (e.g., Schumm, 1968; Dalrymple et al., 1985). Without the vast amounts of impermeable mud that mark post-Silurian continental sedimentary environments, understanding the paleohydrology of Proterozoic basins should be much simpler relative to their post-Silurian counterparts. Based on previous studies of three Proterozoic continental sedimentary basins (Kyser et al., 2000; Hiatt et al., 2003), this appears not to be the case. Diagenesis, including mechanical and chemical compaction, addition of authigenic minerals (especially quartz cement), and dissolution of framework grains, has drastically altered the hydraulic properties of these thick successions of sandstone and conglomerate (e.g. Kyser et al., 2000; Hiatt et al., 2003).

Quartz cementation is a major diagenetic process that controls porosity and permeability in sandstone (e.g. McBride, 1989; Bjørlykke and Egeberg, 1993; Bjørlykke, 1994; Worden and Morad, 2000), and because extensive cementation can transform lithologies that were near-surface aquifers initially into diagenetic aquitards (Hiatt et al., 2003; cf. Dutton and Land, 1988), quartz cement plays a fundamental role in basin hydrology during burial (e.g. Leder and Park, 1986; Dutton and Land, 1988; Bjørlykke and Egeberg, 1993; Hendry and Trewin, 1995; Aase et al., 1996; Worden and Morad, 2000; Hiatt et al., 2003). It is the timing and potential sedimentologic and stratigraphic controls over such cement that is important for understanding the paleohydrology of sedimentary basins because well cemented stratigraphic units are not mineralized and units that have little or no quartz cement were pathways for mineralizing fluids (Kyser et al., 2000). Most quartz cement forms at burial depths greater than 2 km (e.g., McBride, 1989; Bjørlykke and Egeberg, 1993). As a result, hydraulic properties of most quartz-rich sandstones evolve in a simple manner decreasing rapidly with mechanical compaction within the first kilometer, and then decreasing more slowly with chemical compaction and formation of cement overgrowths. Other major sources of dissolved silica from which quartz cements can precipitate include stylolites and dissolution of detrital quartz grains in contact with clay-rich interbeds (e.g. McBride, 1989; Aplin and Warren, 1994; Lander and Walderhaug, 1999; Worden and Morad, 2000). Clay diagenesis may be an unrealistic source of silica in Proterozoic continental successions, since mud rocks are a minor part of the stratigraphic record in these rocks. In these settings other sources of dissolved silica are needed. Some cases of what appear to be early-formed quartz cement that precipitated at the earth’s surface and the shallow burial setting (less than 2.5 km) have been reported (Milliken, 1979; Dutton and Land, 1988; McBride, 1989; Girard and Deynoux, 1991; Aplin and Warren, 1994; Hendry and Trewin, 1995; Hervig et al., 1995; Aase et al., 1996; Thiry and Marèchal, 2001), suggesting near surface cementation at temperatures less than 60 °C. Mobilization of silica and precipitation of authigenic quartz before the onset of pressure solution, however, requires a source of aqueous silica. In near-surface environments, for example, groundwater can readily alter reactive phases such as volcanic glass, reactive aluminosilicate minerals, or biogenic opal, resulting in silica-saturated porewater and quartz overgrowth precipitation in near-surface settings (e.g. McBride, 1989). As a result of early cementation quartz-rich sandstones can become effective hydrologic aquitards early in the evolution of a basin (e.g. Hiatt et al., 2003). The bulk of quartz cements, however, form at temperatures greater than 60 °C and at burial depths greater than 2 km (e.g. McBride, 1989; Bjørlykke and Egeberg, 1993; Aplin and Warren, 1994).
Typically these cements precipitate as well-crystalline syntaxial quartz overgrowths on detrital quartz (e.g., Leder and Park, 1986; McBride, 1989; Hiatt and Kyser, 2000), which reduce permeability and porosity in a systematic manner.

Geochemical analyses of quartz cement largely rely on oxygen isotope analysis of quartz overgrowths coupled with fluid inclusion analysis. Fluid inclusions in overgrowths, however, can be rare, especially when the cement precipitated slowly at low temperatures. Standard isotopic analysis techniques, which involve crushing, handpicking, and acid leaching to isolate cement requires relatively large samples (>5 mg) that often greatly exceed the scale of textural variation when multiple cement overgrowths are present. As a result, variation in quartz cement $\delta^{18}O$ values using standard techniques potentially reflects averaging of multiple cement phases and possible contamination from detrital grains. Potential intra-crystal variation and possible evidence for early, low temperature initial authigenic phases are likely obscured when bulk isotopic measurements are made using standard techniques (Hervig et al., 1995; Lyon et al., 2000). Micrometer-scale $\delta^{18}O$ analysis of quartz cements has been performed using secondary ion mass spectrometry (SIMS; e.g., Hervig et al., 1995; Graham et al., 1996; Williams et al., 1997a,b; Chen et al., 2001), but has not been used to identify effects of quartz cementation on hydrostratigraphic properties during basin evolution.

Herein, we present oxygen isotopic data obtained by in situ ion microprobe analysis of quartz cement overgrowth zones in sandstone lithologies in the economically important Paleoproterozoic Athabasca, Thelon and McArthur basins. These are all examples of continental basins which, due to the presence of sediment-hosted mineralization, have been studied extensively in terms of their mineralization, paragenesis, stratigraphy, and burial histories. Samples were collected from recently drilled cores that, because of the paucity of outcrop exposures typical of Proterozoic basins, allow an improved understanding of stratigraphic relationships of these successions and, critical to this study, diagenetic relationships can be put in spatial context.

The purpose of this study was to quantitatively constrain the timing of regionally extensive, petrographically distinct, paragenetically early, quartz cement phases with respect to burial evolution and consider their effect on paleohydraulic properties. We do not attempt to document isotopic variability regionally or stratigraphically of individual phases, but instead show that previously unrecognized quartz cement phases largely formed under near-surface paleohydraulic conditions. In situ SIMS analysis provides an independent means to characterize quartz cement when fluid inclusions are either too small or nonexistent. All three Proterozoic basins included in this study are known to have experienced intense, prolonged water–rock interaction with migration of metal-bearing pore water to sites of mineralization, and as a result, are host to major unconformity-type uranium deposits, and in the case of the McArthur Basin, host to major sediment-hosted Pb–Zn mineralization (Kyser et al., 2000). Diagenesis, stratigraphic architecture, and original detrital composition are interrelated in each basin; their combined effects exerted control over the movement of diagenetic fluids (Kyser et al., 2000; Hiatt et al., 2003; Hiatt and Kyser, 2006). Understanding changes in the hydraulic properties of basin-filling successions is important for mineral exploration in these, and similar sedimentary basins, because fluid movement drove mineralization during basin evolution (Kyser et al., 2000).

2. Geological considerations

The Athabasca, Thelon and McArthur basins (Fig. 1) are all Paleoproterozoic basins filled with thick (greater than 1 km) elastic sedimentary rock successions consisting of basal conglomerate and mature coarse-grain sandstones (Fig. 2), and rare, thin (generally less than 4 cm thick) mudstone beds. The sediments were deposited in alluvial fan, high-energy proximal to low energy distal braided stream systems, and to a lesser extent, upper shoreface to colian systems. These sediments unconformably override Archean and Paleoproterozoic basement metasediments, plutonic and volcanic rocks. The Athabasca and Thelon basins formed during approximately the same time interval, between 1750 Ma and 1780 Ma, whereas the McArthur Basin began to evolve somewhat earlier (Kyser et al., 2000). All three sedimentary basins included in this study are known to have had protracted and complex diagenetic histories, with quartz cement as the first preserved stage of diagenesis in each (Fig. 3; Kyser et al., 2000). Multiple, basin-wide fluid events are characterized by petrographically and isotopically distinct diagenetic mineral assemblages and fluid inclusions that indicate the bulk of the quartz cements formed from evolved seawater and low-latitude meteoric waters at 100–200 °C, whereas peak diagenetic clay minerals formed at higher temperatures from these same fluids (Kotzer and Kyser, 1995; Kyser et al., 2000; Renac et al., 2002). Similar in many respects, these basins nonetheless exhibit important differences, including original detrital grain composition, differences in
Fig. 1. A.) Location map that shows the location of the Proterozoic Athabasca and Thelon basins in Canada. B.) Location map showing the study area in the McArthur Basin of Australia.
Fig. 2. General stratigraphic relationships in the basal Athabasca Basin (A) stratigraphic nomenclature based on Ramaekers (1981), the Thelon Basin (B) stratigraphic nomenclature based on Gall et al. (1992) and Rainbird and Hadlari (2000), and the basal, northwestern part of the McArthur Basin (C) stratigraphic nomenclature based on Sweet et al. (1999).
Fig. 3. Diagrams showing mineral paragenesis in the (A) Athabasca, (B) Thelon, and (C) McArthur basins. Note initial similarities and subsequent divergence among diagenetic events between the basins (modified from Kyser et al., 2000). Earliest age of uranium mineralization in the McArthur Basin (1648 Ma) is from Polito et al. (2004).
depositional settings, and diagenetic histories, as outlined below.

2.1. The Athabasca Basin

The Athabasca Basin, located in Northern Saskatchewan, hosts the two largest high-grade uranium deposits in the world; both are believed to have formed by large-scale migration of basinal brines (Fig. 1; e.g. Kyser in the world; both are believed to have formed by large-scale migration of basinal brines (Fig. 1; e.g. Kyser et al., 2000). The Manitou Falls Formation is a 1–2 kilometer-thick succession of sandstone and conglomerate that makes up much of the basin-fill (Fig. 2A). These sediments were deposited in alluvial fan to braided fluvial environments (Ramaekers, 1981, 1990; Ramaekers and Catuneanu, 2004), and have an estimated minimum depositional age of approximately 1700 Ma (Kyser et al., 2000). A well-developed paleosol extends several meters into the crystalline basement rocks just beneath the basal unconformity that underlies the Athabasca Group (Ramaekers, 1981, 1990).

The framework grains in the Manitou Falls Formation are composed of almost 100% quartz with very minor muscovite, although some beds near the base of the Manitou Falls can contain up to 15% lithic clasts (quartzite, gneiss, schist, and sandstone), and rare heavy minerals, such as zircon and apatite. The absence of preserved feldspar and rarity of other minerals further suggests relatively long transport, intense weathering in the source area, and later diagenetic alteration of remaining feldspar during burial diagenesis.

A complex fluid history related to diagenesis, mineralization, and late-stage alteration is recorded in the Athabasca Basin (Kotzer et al., 1992; Kotzer and Kyser, 1995; Fayek and Kyser, 1997). Burial quartz cement (Q1) is found throughout the basin and, based on fluid inclusion microthermometry, formed at 150–170 °C (Kotzer and Kyser, 1995). Variable proportions of illite and dickite produced by the alteration of detrital aluminosilicates characterize peak diagenesis in the basin (Fig. 3A). An assemblage consisting of hydrothermal illite and kaolinite intergrown with authigenic quartz, dravite, Al–Mg chloride, and hematite occurs near faults, fractures, and ore deposits in association with hydrothermal alteration that occurred during the late stages of peak diagenesis and uranium mineralization (Kyser et al., 2000).

2.2. The Thelon Basin

The Thelon Basin is located in the western part of Nunavut, Canada, between the Slave and Churchill geologic provinces (Fig. 1). This basin hosts two minor uranium deposits (Gandhi, 1989). The Thelon Formation is a conglomerate–sandstone succession that is part of the Upper Dubawnt Group and unconformably overlies a basement complex that includes Archean gneiss, Paleoproterozoic metamorphic rocks of the Amer Group, and the overlying Paleoproterozoic sedimentary and volcanic rocks of the Wharton Group (Fig. 2B; Gall et al., 1992). A paleoregolith is preserved on the sub-Thelon Formation unconformity (Gall, 1994), which is marked by a thin, but regionally developed silcrete (Ross and Chiarenzelli, 1985; Gall, 1994). The regolith and basal units of the Thelon Formation contain diagenetic fluorapatite minerals with U–Pb ages of 1720 to 1760 Ma that provide an approximate age for the onset of Thelon Formation sedimentation (Miller et al., 1989). The maximum age of the basin is constrained by the age of emplacement of fluorite-bearing granites into the underlying Amer Group at ca. 1753 Ma (Miller, 1995).

Quartz to sub-arkosic arenite dominate the Thelon Formation, which exhibit a complex diagenetic history that involves early phosphate cementation, quartz cementation (Q1) as overgrowths on detrital quartz, formation of diagenetic illite and much later infiltration of fluids that resulted in K-feldspar and chlorite replacement of illite at approximately 200 °C (Fig. 3B; Renac et al., 2002). The upper unit in the Thelon Basin is a succession of interlayered thinly bedded sandstone, siltstone, and mudstone capped by dolostone and siliceous dolostone (Fig. 2B; Gall et al., 1992). These lithologic trends indicate a transition from fluvial to marine depositional environments (Gall et al., 1992).

2.3. The McArthur Basin

The McArthur Basin in the Northern Territory of Australia is a large Proterozoic sedimentary basin (Fig. 1) that hosts numerous world-class sedimentary-hosted Pb–Zn–Ag deposits and, in the northwestern portion of the basin, is associated with unconformity-type uranium deposits of the Alligator Rivers Uranium Field. The study area is located approximately 200 km southeast of Darwin on the Arnhemland Plateau and is centered on a sub-basin of the larger McArthur Basin, the Kombolgie sub-basin.

McArthur Basin samples included in this study come from the Kombolgie Subgroup, which is the basal succession of the flat-lying Proterozoic Katherine River Group that fills the Kombolgie sub-basin (Needham, 1988; Sweet et al., 1999). This succession unconformably overlies Archean gneiss and metasedimentary, metavolcanic, and intrusive Early Proterozoic rocks. The Kombolgie is comprised, in ascending stratigraphic order, of alluvial fan to braided fluvial facies of the
Mamadawerre Formation, the mafic Nungbalgarri Volcanics, the proximal to distal braided fluvial facies, to upper shoreface and eolian facies of the Gumarrimbang Formation, the basaltic Gilruth Volcanics, and the distal braided fluvial to upper shoreface Marlgowa Formation (Fig. 3C; Kyser et al., 2000). Interfingering with the Marlgowa are glauconitic and phosphatic marine upper shoreface facies of the McKay Formation (Hiatt and Kyser, 2002). Detrital phases in the Kombolgie are quartz (90–100%) and lithic fragments (0–10%). Post-orogenic felsic intrusions of Jimbu Microgranite (Rawlings and Page, 1999) and mafic intrusions of Oenpelli Dolerite (1720 Ma) intruded the Kombolgie Group (Fig. 2C; Kyser et al., 2000).

Sandstones in the Kombolgie sub-basin record a complex fluid history related to diagenesis, the intrusion of the Oenpelli Dolerite, and later tectonic events (Fig. 3C; Kyser et al., 2000). Early stages of diagenesis are characterized by the formation of burial quartz overgrowths (Q1) at 80–130 °C (Kyser et al., 2000). Porosity was greatly reduced during compaction and this stage of diagenesis, especially in well-sorted lithologies. Peak diagenesis is marked by filling of remaining pore space with illite and, near the unconformity or volcanic units, precipitation of chlorite at about 200 °C from basinal brines evolved from the meteoric-marine fluid responsible for the earlier-formed quartz cements (Fig. 3C; Kyser et al., 2000).

2.4. Comparison of basin characteristics

Sediments that filled the Thelon and McArthur basins contained detrital feldspar so that the most common diagenetic mineral after quartz is illite (Renac et al., 2002; Polito et al., 2004); feldspar replacement by illite is pervasive. In addition, compositionally mature (essentially 100% quartz) lithologies, such as quartz arenite that represent regionally extensive upper shoreface and eolian facies are marked by pervasive pore-occluding quartz cement. The presence of multiple unconformity-bound stratigraphic sequences within the Thelon and McArthur basins, indicate a dynamic and proximal source region (Kyser et al., 2000).

The Manitou Falls Formation represents a less dynamic tectonic and sedimentological history. After initial basin formation, stratigraphic units in the upper half of the Manitou Falls Formation accumulated as the Athabasca basin underwent relatively simple subsidence (Kyser et al., 2000). The sandstone is relatively devoid of detrital feldspar, but abundant kaolin minerals suggest that weathering may have been much more intense in the source region (Kotzer and Kyser, 1995). In marked contrast to the lower units in the Thelon and McArthur basins, the presence of well-cemented marine and eolian lithologies are rare in the Manitou Falls Formation. Differences in the basin-fill composition between the three basins profoundly affected their diagenetic histories (Kyser et al., 2000).

3. Methods

Six drill cores from the eastern Athabasca Basin were described, sampled and logged in detail and 80 samples from major stratigraphic units were analyzed petrographically. Ten drill cores and four outcrop exposures were described, sampled and logged, and approximately 100 thin sections were examined to constrain diagenetic relationships in the eastern Thelon Basin. Fourteen drill cores and twelve outcrops were described, sampled and logged in detail in the northwestern portion of the McArthur Basin, and approximately 180 thin sections were analyzed petrographically.

Approximately 360 samples were examined using standard petrographic techniques to constrain the relative timing of diagenetic relationships, and identify cement phases that appear to have precipitated before significant mechanical and chemical compaction. Oxygen isotopic compositions of detrital quartz and quartz overgrowths from 12 samples from the three basins were measured with a modified CAMECA ims 4f SIMS at Oak Ridge National Laboratory using a Cs+ primary beam and monitoring O-secondary ions with extreme energy filtering of 300 eV as described by Riciputi et al., 1998. The ∼2 nA primary ion beam was focused to a 10×20 μm spot using a 100 μm aperture in the primary column. The accuracy was verified by analyzing quartz of a known isotopic composition and the precision was assessed by multiple analyses of samples and standards. The overall precision was ±0.7‰ (1σ), with all values reported in units of ‰ relative to Vienna-Standard Mean Ocean Water (V-SMOW). Several isotopic fractionation equations have been proposed (e.g. Clayton et al., 1972), and some may be more applicable for low temperature precipitation of quartz cement (e.g. Kawabe, 1978; Kita et al., 1985), our goal was to assess the isotopic signatures of each cement phase analyzed, and not to evaluate the validity of these equations. Paleotemperature calculations were therefore made using the quartz-water fractionation equation of Clayton et al. (1972).

4. Results

Quartz cement phases in sandstones that fill the three basins included in this study have distinctive morphologies...
that range from small grain-fringing crystals, to blocky syntactical crystal overgrowths. Cements are referred to here as microcrystalline when they form non-syntactical crystallite coatings on underlying detrital grains that have a-axial diameters less than 20 μm (cf. Milliken, 1979; Aase et al., 1996). Figs. 4, 5, and 6 contain photomicrographs representative of stratigraphic units within all three of the sedimentary basins included in this study. The spots analyzed by SIMS with resulting δ18O values, are precisely plotted on the photomicrographs (Figs. 4E–H, 5C–E, 6B–F) and plotted with calculated temperatures in Fig. 7.

In the Manitou Falls Formation of the Athabasca Basin the earliest quartz cement phase forms meniscal bridges between grains that, based on the lack of pressure solution, precipitated before significant mechanical or chemical compaction (Qa; Fig. 4A, B). We use the label Qa for this cement phase because it clearly predates widespread burial quartz cement Q1 documented by Kotzer and Kyser (1995). Pore-filling syntactical overgrowths with hematite inclusions are found below paleo-weathering surfaces horizons marked by dissolution vugs, mechanically infiltrated clays, and intense hematite stain; these cements provided rigid frameworks that largely preserve grain-to-grain spatial relationships (Qa; Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D). The Qa cement phase is overlain by clear euhedral syntaxial overgrowths devoid of hematite (Fig. 4C, D).

Hematite inclusion-rich quartz cement (Qa) has δ18O values that range from 13.2‰ to 22.8‰, with a mean of 17.9‰ (n = 8; Table 1; Fig. 4E–H). The two samples analyzed, however, have distinctly different isotopic signatures, with a mean value of 22.4‰ (n = 4) for sample A-224-493.2, and 13.5‰ (n = 4) for sample A-224-493.7 (Table 1; Fig. 4E, F, G and H). The polished thin section A-224-493.7 had a very pitted appearance; its lighter isotopic values may reflect hydrothermal alteration that occurred along a nearby fracture not cut by the drill core. The overlying euhedral quartz cement (Q1) has δ18O values that range from 16.1‰ to 21.1‰ with a mean of 19.2‰ (n = 4; Table 1; Fig. 6E). The more abundant, syn- to post-compaction quartz overgrowths (Q1; Fig. 3C) have lower δ18O values ranging from 13.8‰ to 16.5‰ with a mean of 15.2‰ (n = 4; Table 1; Figs. 3C and 6F). Underlying detrital quartz grains have δ18O values ranging from 5.9‰ to 25.1‰ (Table 1; Figs. 5C and 6B–D), a range typical for quartz grains with diverse sources (Williams et al., 1997b; Aleon et al., 2002). Palmer et al. (2004) showed that detrital grains in the Thelon Formation do indeed come from diverse sources, including igneous, metamorphic, and sedimentary material with ages ranging from 1.8 to >3.5 Ga. The IQC phase is not widespread and is restricted to the Pitz Formation and eolian facies of the Thelon Formation (Fig. 2B). The last stage of cement precipitation is marked by pore-filling quartz (Q1), which filled open pores and has δ18O values that range from 16.3‰ to 28.2‰, with a mean of 22.6‰ (n = 4; Figs. 5C–E and 6B–D). Lithofacies that were not cemented early have abundant intergranular clay matrix, which appears to have both inhibited quartz cementation (cf. Lander and Walderhaug, 1999 and references therein) and, where cement is present, is associated with replacement of quartz cement and detrital grains.

The McArthur Basin samples contain overgrowths in units composed of well sorted, quartz arenite upper shoreface to eolian facies. This quartz cement forms syntactical overgrowths on detrital quartz that based on their uncompacted grain-to-grain textures, appear to have formed before the onset of significant compaction; this phase (Qa) has δ18O values that range from 16.1‰ to 21.1‰ with a mean of 19.2‰ (n = 4; Table 1; Fig. 6E). The more abundant, syn- to post-compaction quartz overgrowths (Q1; Fig. 3C) have lower δ18O values ranging from 13.8‰ to 16.5‰ with a mean of 15.2‰ (n = 4; Table 1; Figs. 3C and 6F). Underlying detrital grains in the McArthur Basin samples range from 9.7‰ to 14.2‰, with a mean of 12.6‰ (n = 6; Table 1; Fig. 6E and F).

5. Discussion

The degree to which compaction-driven grain-to-grain pressure solution has occurred in sandstones gives an indication of relative timing for quartz cementation with respect to burial depth (e.g. Rittenhouse, 1971; Leder and Park, 1986; McBride, 1989; Bjørlykke and Leder and Park, 1986; McBride, 1989; Bjørlykke and Leder and Park, 1986; McBride, 1989; Bjørlykke and Leder and Park, 1986; McBride, 1989; Bjørlykke and Leder and Park, 1986; McBride, 1989; Bjørlykke and Leder and Park, 1986; McBride, 1989; Bjørlykke and
Fig. 4. A) Photomicrograph in plane-polarized light (PPL) showing quartz pebble conglomerate with angular to well rounded sand and gravel detrital grains (DQ) with a poorly sorted, clast-supported texture characteristic of the proximal braided fluvial lithofacies (Fig. 2). Quartz cement (Qa) appears to pre-date significant grain-to-grain compaction and, although it effectively blocks pore throats, the moderate amount of mud matrix (MC) present inhibited further cementation. B) Same field of view as in A), but in cross-polarized light (XPL) with the mica plate (1/4 wavelength) inserted to highlight subtle differences in birefringence. Sample MAC-224–387. Scale bars in A and B are 1000 μm long. C) Photomicrograph in PPL that shows a well sorted, well rounded medium-grained quartz arenite from the MFa lithofacies in which detrital quartz grains (DQ) are completely surrounded by syntaxial overgrowths of quartz cement (Qa). The cement predates significant compaction as indicated by the minor degree to which grains have experienced pressure solution, and often contains abundant hematite inclusions. D) Same field of view as in C), but in cross-polarized light with the mica plate inserted. Sample MAC-224–493.2. Scale bars in C) and D) are 500 μm long. E) Photomicrograph in reflected light showing the early inclusion-rich pore-occluding quartz cement (Qa) and later inclusion-free euhedral quartz overgrowth (Q1). White circles represent spots analyzed for δ¹⁸O by SIMS in per mill relative to V-SMOW. Data are in Table 1. Scale bar is 100 μm long; sample MAC-224-493.2 Athabasca Basin. F) Photomicrograph of the same area as in E) but in plane-polarized light. G) Photomicrograph in plane-polarized light showing detrital quartz and hematite inclusion-rich syntaxial overgrowths (Qa). White circles represent spots analyzed for δ¹⁸O (in per mill relative to V-SMOW) by SIMS. Black box outlines area in H). Scale bar is 250 μm long; sample MAC-224-493.7 Athabasca Basin. H) Detrital quartz grains overlain by inclusion-rich overgrowths (Qa) and very minor overgrowths of later Q1. White circles represent spots analyzed for δ¹⁸O (in per mill relative to V-SMOW) by SIMS. Black box outlines area in H). Scale bar is 250 μm long.
Egeberg, 1993). Pressure solution typically starts at burial depths greater than 2 km (Bjørlykke and Egeberg, 1993). In stratigraphic units that experienced quartz cementation at relatively shallow depths (<2 km), grain-to-grain relationships, such as an open spacing of grains with few pressure-solved, sutured, or long to convex–concave contacts, suggest little compaction occurred before addition of the cement (Figs. 4A–D, 6A and B). Quartz cement with these petrographic characteristics is found in all three basins included in this study (Fig. 8). These are found only in facies that lack detrital clay and/or feldspar, such as eolian and upper shoreface facies and makes up 10–30 vol.% of these units (Fig. 8). In all three basins these cements appear to be related to paleoweathering, and in the case of the Thelon and McArthur basins, alteration of volcanics (Figs. 2 and 8). Typical syntaxial overgrowths formed during burial are rare, make up less than 5% of intergranular pore volume, and occur sporadically throughout the successions.

5.1. Isopachous Quartz Cement (IQC)

The IQC phase is the most distinctive cement morphology of this study and is found below paleoweathering surfaces in upper shoreface and eolian facies.
of the Thelon Basin. Occurrences in sandstones of the Pitz Formation (Fig. 5A–E) are related to weathering on the sub-Thelon unconformity surface and probably formed in association with widespread silcrete development (Ross and Chiarenzelli, 1985; Gall, 1994). This is the only stratigraphic unit in which vadose pendant morphologies are observed; the IQC phase is present 35 m below the top of the Pitz Formation, suggesting transport of silica from the overlying weathering surface down to at least this depth. The IQC phase may represent opal that recrystallized as the rocks were buried (cf. Thiry and Milnes, 1991; Aplin et al., 1993; Thiry and Maréchal, 2001; Lima and De Ros, 2003). Weathering of the sub-Thelon Formation regolith altered the abundant rhyolitic detrital clasts contained within; the source of rhyolitic material (clasts and possible ash) was interbedded rhyolitic extrusive units of the Wharton Group (Fig. 2B). Cement morphologies suggest that precipitation of silica released from the volcanic material probably occurred in the paleo-vadose and phreatic zones. Precipitation of the grain-fringing IQC cement phase would have bridged pore throats and

Fig. 6. A) and B) Photomicrographs in plane-polarized and cross-polarized light, respectively, of a sandstone from the eolian facies of the Thelon Formation, Thelon Basin (Fig. 2B), with early microcrystalline isopachous quartz cements (IQC) and later pore-filling quartz cement (Q1). The abundance of “floating” grains and the absence of grain-to-grain pressure-solution indicate that cementation began before compaction. White circles on B) represent spots analyzed for $\delta^{18}O$ (in per mill relative to V-SMOW) by SIMS. Scale bar is 250 μm; white box on B) shows the approximate area enlarged in C) and D). C) and D) Photomicrographs in plane-polarized and cross-polarized light, respectively, of the sample shown in A) and B) above at higher magnification. The microcrystalline isopachous quartz cement phase (IQC) directly overlies the detrital quartz grains (DQ), and is overlain by a blocky, burial quartz cement phase (Q1). Note the intergrowth of IQC crystals in pore throats. Points represent $\delta^{18}O$ values in per mill relative to V-SMOW analyzed by SIMS. Data are in Table 1. Scale bar is 125 μm; Sample 42c. E) Photomicrograph in cross-polarized light of detrital quartz grains (DQ) and quartz cement (Qa) that preserves pre-compaction grain-to-grain spatial relationships in a quartz arenite of the eolian facies, Mamadewerre Formation, McArthur Basin, sample 98KR-2. White circles represent spots analyzed by SIMS and the resulting $\delta^{18}O$ values (in per mill relative to V-SMOW). Scale bar is 125 μm. F) Photomicrograph in cross-polarized light of a coarse-grained quartz arenite from the braided fluvial facies of the Mamadewerre Formation, northern McArthur Basin. Detrital grains have sutured boundaries in these units; the cement (Q1) formed syn- to post compaction. Scale bar is 250 μm long. White circles represent spots analyzed for $\delta^{18}O$ (in per mill relative to V-SMOW) by SIMS. Sample DAD001-86.
reduced hydraulic conductivity and would have provided a rigid framework preventing pressure solution initially (cf. Lima and De Ros, 2003). Compaction-driven pressure solution could have produced the paragenetically later blocky, syntaxial Q1 phase that occludes much of the remaining pore space (Fig. 4C, D, and E).

5.2. Syntaxial cement overgrowths (Qa & Q1)

The earliest quartz cement phases in the Athabasca and McArthur basins are thick (up to 250 μm) euhedral syntaxial, and in the case of the Athabasca are quartz overgrowths rich in hematite inclusions that, based on petrographic evidence, appear to have precipitated prior to significant mechanical and chemical compaction (Qa; Figs. 4A–H and 6E–F). In the Athabasca Basin the earliest quartz overgrowth phase (Qa; Fig. 4A–H) is marked by abundant hematite inclusions and forms patchy meniscal bridges between clasts in coarse-grained facies (Fig. 4A and B) to pore-filling overgrowths that appear, based on the minor degree of grain-to-grain pressure solution (Fig. 4C and D), to have precipitated early in the burial history.

The last stage of cementation in all of the basins involved quartz precipitation associated with deep burial through compaction-driven, grain-to-grain pressure solution (Q1; Figs. 4E, F, 5D, E, 6A–F). Quartz cement with this morphology is common in sandstones in general (e.g., McBride, 1989; Bjørlykke and Egeberg, 1993). This burial cement phase precipitated in open pores adjacent to grain–grain pressure solution points and can overgrow earlier phases, such as the isopachous cement phase in Thelon Basin samples (Figs. 5C–E, 6A–D), and the open framework-preserving inclusion-rich syntaxial cement phase in the Athabasca Basin (Qa; Fig. 4E–F). The Q1 overgrowths on the earlier-formed IQC phase of the Pitz Formation have significantly higher isotopic values than the other examples analyzed here probably because it resulted from precipitation of silica derived from pressure solution of the isotopically heavy...
IQC phase. In all three basins, stratigraphic units that did not experience significant pre-to syn-compaction quartz cementation are marked by detrital grains with abundant concave–convex to sutured contacts.

5.3. Oxygen isotopic analysis and depth of quartz cementation

The sandstones that fill all three basins included in this study experienced peak diagenetic temperatures of approximately 200 °C, and at maximum burial, are estimated to have reached depths of at least 5 km (Kyser et al., 2000). Based on published fluid inclusion analysis of the burial cement phases (Q1; Fig. 3), however, the Q1 cements precipitated well below 200 °C in all three basins (Kotzer and Kyser, 1995; Kyser et al., 2000; Renac et al., 2002). Fluid inclusions in early-formed quartz overgrowths (Qa and IQC) are very small (less than 2 μm in diameter) and exceedingly rare making analysis by microthermometrics impossible. Cement oxygen isotopic values were used here to estimate temperatures at which the cements precipitated; pore water (δ18Owater) from which the Q1 cements precipitated has been estimated to have been in the range of −4 to +4‰ (e.g. Kotzer and Kyser, 1995; Kyser et al., 2000).

The sandstones of the Manitou Falls Formation in the Athabasca Basin have quartz overgrowths (Q1; Figs. 3A, 4C–E) with fluid inclusions that have homogenization temperatures of 150–170 °C, between 10 and 25 wt.% NaCl, δD values of −50‰, and calculated pore water δ18Owater values from −4 to 0‰ (Kotzer and Kyser, 1995; Kyser et al., 2000). This range is characteristic of low-latitude, near coastal meteoric waters, but the high salinities suggest 18O enrichment during water–rock interaction with evaporites and/or siliciclastics. Analyses of rare fluid inclusions in burial quartz cements (Q1) from the Thelon Basin indicate formation at 100–160 °C from NaCl brines having about 17 wt.% equivalent NaCl and δ18Owater values of approximately 0‰ (Renac et al., 2002) suggesting formation in mixed seawater and meteoric water. The δD values of the fluids from inclusions in burial cements and those calculated for illite associated with peak diagenesis were relatively constant at −50±15‰. In conjunction with the high salinities of these fluids, the isotopic values are similar to those produced by mixing of evaporated seawater and low-latitude meteoric waters. Renac et al. (2002) found that δ18O values of peak diagenetic fluids responsible for precipitation of illite and uranium mineralization (Fig. 3B) were higher relative to that associated with Q1 cement due to greater water–rock interaction associated with mineralizing fluids. Inclusions preserved in Q1 cements from the McArthur Basin indicate burial fluids reached temperatures between 80–130 °C, had low salinities (i.e. <10 wt.% NaCl), δD values near −30‰, and δ18Owater values that ranged from −4 to +4‰.

### Table 1
Data for in situ analyses of detrital quartz and quartz cements

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<th>Sample</th>
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Error given is the standard deviation (1σ).
Fig. 8. Stratigraphic sections for each Proterozoic continental basin included in this study showing the stratigraphic intervals that contain paragenetically early quartz cement phases. See Fig. 2 for more detailed stratigraphic nomenclature. These intervals are marked by well-sorted, quartz-rich lithofacies deposited in eolian, upper shoreface, and to a lesser extent, distal fluvial environments.

EXPLANATION:
- Volcanic/Intrusive Units
- Peritidal Dolostone
- Upper Shoreface
- Braided Fluvial
- Alluvial Fan

Sedimentary Structures:
- Major Paleosol/Regolith
- Cross Beds
- Pebbles
- Current Ripple Marks
- Mudcracks
- Unconformity
- Wave Ripple Marks
- Heavy Minerals
- Mud Rip-Up Clasts
- Eolian Facies

Stratigraphic Units Where Early Quartz Cement Phases are Present:
suggesting a seawater-meteoric water mixture (Kyser et al., 2000).

Although the influence of meteoric water, which could have interacted with evaporites and siliciclastic grains, may have been substantial in the early phases of basin evolution, all three basins appear to have occupied low paleolatitude, near-coastal settings, making major deviations from near seawater values (0±4‰) unlikely (e.g., Kotzer et al., 1992; Idnurm and Giddings, 1995; Kyser et al., 2000). Using δ18O values for pore fluid of −4, 0‰, and +4‰ the depth at which quartz cement formed was estimated assuming a geothermal gradient of 30 °C/km (Fig. 7). The geothermal gradient could have varied slightly, however, these differences would not greatly affect the estimates. The equilibrium δ18O values of quartz were calculated as a function of temperature and plotted as curves in Fig. 7. The δ18O values derived from the microcrystalline phase (IQC) in the eolian facies of the Thelon Formation correspond to low temperatures and near-surface conditions (0.0–1.9 km; Fig. 7B). Pore-filling syntaxial overgrowths (Q1) in the same sample correspond to higher temperatures and greater depths (0.4–1.9 km; Fig. 7B). Microcrystalline quartz cement in the Pitz Formation (Fig. 2B) associated with paleoweathering on the sub-Thelon Formation regolith has values that are lighter (20.4–25.5, mean=22.3‰) than those of the eolian facies (30.2–33.2, mean=31.7‰) in the overlying Thelon Formation (Fig. 2B; Table 1). Using the assumed −4 to +4‰ range for δ18Owater of the pore fluid, however, temperatures of 126 to 67 °C are suggested, which corresponds to burial depths of 1.4 to 3.4 km (Fig. 7B). This cement phase has distinct morphologies that indicate a near-surface vadose to phreatic zone origin. It is possible that this phase formed in equilibrium with meteoric water that was isotopically lighter than those used in our fractionation calculations, since no one has assessed the source of porewater in the Pitz Formation. Alternatively, the IQC phase may represent recrystallization of a pre-existing phase, such as opalline or chalcedony cement in a burial setting (cf. Hendry and Trewin, 1995; Thiry and Maréchal, 2001; Goldstein and Rossi, 2002; Aplin et al., 1993). We examined this cement phase using cathodoluminescent petrography, however, and observed no intracrystal banding or other evidence that such recrystallization occurred (cf. Goldstein and Rossi, 2002). This microcrystalline phase, however, does contain distinctly heavier isotopic values than those of the overlying pore-filling, blocky syntaxial Q1 phase in the same sample (Fig. 5D–E) suggesting two distinct cementation events.

Samples of the hematite inclusion-rich Qa cement phase in the Athabasca Basin (Fig. 4C–H) were collected from below paleosoil horizons; in sample MAC-224-493.2, the earliest overgrowth has isotopic values that correspond to relatively shallow burial depths (1.3 to 3.2 km). These cements, like those associated with the sub-Thelon regolith, may have been precipitated from meteoric water more isotopically depleted than assumed by earlier workers (−4 to +4‰). Therefore, they may have formed in a more shallow setting than that predicted using a seawater-like δ18O water values (Fig. 7A). Quartz cement (Qa) in eolian and beach facies (Qa; Figs. 2, 6E) in the McArthur Basin formed during burial at depths less than 4.5 km (1.9–4.2 km; Fig. 7C). The Q1 phase, however, is the volumetrically most important quartz cement in each basin, and formed at depths of 4 to 5 km, which is consistent with results obtained using isotopic analyses of mechanically separated cements and fluid inclusion analysis (Kotzer and Kyser, 1995; Renac et al., 2002).

5.4. Implications for mineralizing fluid flow

Proterozoic continental basins are fundamentally different than most of their Phanerozoic counterparts due to the near absence of muddy facies and the fact that they are filled by sands and gravels deposited by braided rivers (e.g. Schumm, 1968). In these basins lithofacies representing deposition of compositionally and texturally mature sediments in eolian and regionally extensive upper shoreface palaeoenvironments, and horizons beneath major paleosoils were preferentially subjected to early quartz cementation (Fig. 8) with meniscus and pendant to isopachous and blocky morphologies (Figs. 4–6). These early cements reduced initial permeability; as a result, stratigraphic units that were aquifers initially (depositional aquifers), became aquitards. Regional stratigraphic units composed of compositionally and texturally less mature sediments, such as those deposited in braided fluvial systems, would have had moderate to low porosities and permeabilities initially, and as diagenesis proceeded, their hydraulic conductivity was reduced; however, through feldspar dissolution, clay diagenesis and lack of early pore throat-bridging quartz cement, their conductivities selectively allowed movement of burial brines. Consequently, these units remained potential conduits for subsequent fluid movement. Quartz-rich well sorted facies that experienced early cementation (Fig. 8; diagenetic aquitards) appear to have channeled fluids into these poorly-cemented, clay-bearing stratigraphic units (diagenetic aquifers; Hiatt et al., 2003). Thus, even without significant depositional aquitards (mud-rich or evaporite stratigraphic units) these three continental
Proterozoic basins underwent significant reorganization of their paleohydrologies wherein depositional aquifers became diagenetic aquitards through relatively early quartz cementation. Stratigraphic units with intermediate hydraulic conductivities initially remained stratigraphic conduits for fluid movement in the burial setting where chemically active basinal fluids transported and later deposited uranium and other metals. Later igneous intrusion, as in the case of the McArthur Basin, and possible joint and fault development in all the basins disrupted this hydrostratigraphy.

6. Conclusions

Quartz cement plays a major role in controlling the hydraulic properties of sandstones. Its importance is great in Proterozoic continental sedimentary basins. In such basins the only significant hydrologic barriers to burial fluid migration would have had a diagenetic origin because, without land plants to bind alluvial plain sediments, mud-rich depositional units are rare. Quartz cementation occurred in stratigraphic intervals during burial in the Athabasca, Thelon, and McArthur basins; early cement phases identified petrographically and isotopically only occur in certain sedimentary facies. These early phases are observed only in quartz arenites that were free of detrital clay and, in some cases, were associated with paleoweathering surfaces. Based on petrographic relationships, and in the case of the Thelon Basin, isotopic composition, the earliest cement phases precipitated before significant burial. Addition of quartz cement prior to significant burial would have reduced the hydraulic conductivity of these originally very permeable stratigraphic units. It is this facies-controlled selective cementation that ultimately controls the hydraulic properties of these Proterozoic basin-filling continental basin successions. Diagenetic processes that change paleohydraulic properties have important implications for understanding the relationship between stratigraphy, quartz cementation, basin evolution, and formation of sedimentary basin-hosted mineral deposits.

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