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# Weathering of quartz as an Archean climatic indicator

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## Abstract

Chert and other hard monomineralic quartz grains weather mostly by mechanical processes in modern environments. Their clasts are overrepresented in conglomerates and sands relative to their sources regions. Conversely, macroscopic dissolution features, including quartzite karst, are rare but not nonexistent. The similar rarity of quartz dissolution in Archean deposits provides a paleothermometer for climate on the early Earth. For example, chert is overrepresented in conglomerates and sands of the ~3.2 Ga Moodies Group (South Africa) relative to the source region. Features related to the far-from-equilibrium dissolution rate are particularly diagnostic as it increases an order of magnitude over 25 °C, much more than solubility. Extrapolating from observed dissolution rates in modern environments that weather at ~25 °C, we expect obvious dissolution features in ancient climates above ~50 °C. Polycrystalline quartz and chert would readily disaggregate by solution along grain boundaries, yielding silt and clay. Quartz grains within slowly weathering granite would become friable, yielding silt and clay, rather than sand. At still higher temperatures, $Al_2O_3$-rich clays from weathered granite would stand above solution-weathered chert on low-relief surfaces. The observed lack of these features is evidence that the Archean climate was not especially hot.
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## 1. Introduction

Climate during the Archean Era (~3.8 to 2.5 Ga) is relevant to the history of life on Earth. However, only limited geological analysis bears on the topic. Oxygen-isotope studies of cherts provide oceanic temperature estimates for 3.5–3.2 Ga of 55–85 °C [1]. Evidence of thorough weathering in the Archean, despite the absence of vascular plants, has prompted temperature estimates as high as 85 °C [2,3]. In addition, the limited rock record shows that glaciation was uncommon in the Archean.

See the work of Young et al. [4] for a possible exception at 2.9 Ga.

Theoretical studies of Archean temperature model a greenhouse atmosphere composed of carbon dioxide and methane. The commonly cited upper limit, 85 °C, is model dependent [5–8]. Conversely, reasonable amounts of these gases do not necessarily imply temperatures much higher than those of the modern tropics or the Cretaceous Earth [8]. Limited direct estimates of atmospheric $CO_2$ come from observations that siderite is present in 3.2-Ga pebble weathering rinds [9] but is absent from a 2.75-Ga paleosol [10] (Fig. 1).

In this paper, we suggest that the weathering behavior of quartz in monomineralic quartzite and chert and

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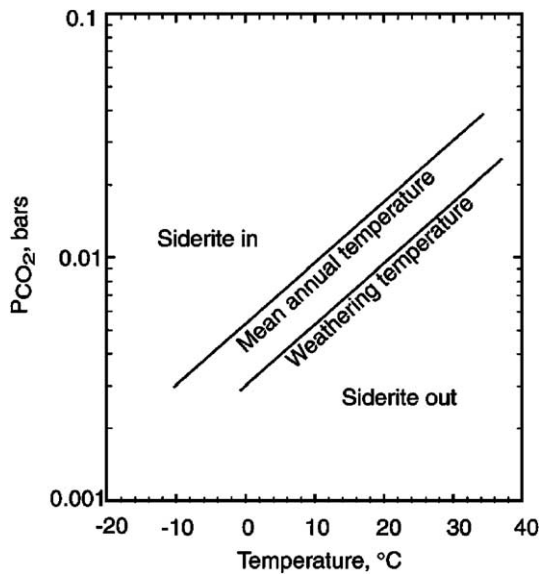    E-mail address: norm@pangea.stanford.edu (N.H. Sleep).

Fig. 1. Stability diagram of siderite in terms of weathering temperature and the partial pressure of $CO_2$ from Rye et al. [10]. The typical weathering temperature is ~10 K hotter than the global mean annual temperature [24]. Our 3.2-Ga pebbles [9] weathered under conditions on the upper left of the diagram while the paleosol of Rye et al. [10] weathered at 2.75 Ga under conditions on the lower left. Both situations are consistent with clement Archean climate. The present (pre-industrial) $CO_2$ pressure is ~$300 \times 10^{-6}$ bar.

as grains in granitic rocks is a viable Archean paleothermometer. The tendency on the modern Earth for quartz to weather mechanically, unlike the dissolution weathering of carbonates, is notorious. "As unrelenting flint to drops of rain." (Shakespeare, *Titus Andronicus*, Act II, Scene III). "He plies her hard; and much rain wears the marble." (Shakespeare, *The Third Part of King Henry the Sixth*, Act III, Scene II). There is an urge to regard evidence of this difference on the ancient Earth as unremarkable. Rather, quartz does dissolve some in modern environments [11]. Its solubility and dissolution rate of quartz are strong functions of temperature. Quartz will dissolve and chemically disaggregate readily in a sufficiently hot climate, as has been suggested for the Archean. Instead, field observations indicate that quartz in the Archean mostly resisted chemical weathering, like it does under modern clement conditions. Here, we quantify the effect using solubility and kinetic data to extrapolate from the chemical behavior of quartz observed in modern climates.

Because the Barberton sequence (like most Mesoarchean sequences) is predominately syntectonic, we restrict our attention to sediments derived during periods of relatively slow exhumation, such that chemical weathering could proceed. We eschew stratigraphic levels dominated by highly immature sediments, like

the mechanically derived conglomerates or poorly fractionated volcaniclastic deposits underlying the Moodies Group.

## 2. Archean geological observations

Hessler studied well-preserved 3.2-Ga clastic sediments from Barberton Mountain Land for her thesis [12]. We concentrate on Moodies Group rocks north of the Inyoka Fault, which have been the subject of extensive geological work [13–17]. A striking feature of these rocks is that the degree of weathering prior to fluvial deposition is within the range of that observed at the warm, humid end of the climate spectrum on the modern Earth. This observation is elaborated below for each sedimentary size fraction within the Moodies Group. We cite other analogous localities from the Mesoarchean and Neoarchean.

### 2.1. Conglomerate

The conglomerate data are straightforward (Fig. 2). At the bottom of the section, interpreted to be alluvial fan and braided river deposits [13,16], conglomerate clasts are poorly sorted, spherical, mostly well rounded, and have an average diameter of ~3 cm [9,12]. Chert clasts of various colors dominate the pebble fraction of the rock. The rounded clasts upon visual inspection do not have embayments as expected from dissolution. Although the conglomerates are locally variable, chert clasts dominate across the study area (42–58%), despite chert covering <2% of the source region. Other rocks types that are expected to resist chemical weathering are also overrepresented compared to the source region. These include quartz-rich sandstone and sericite schist. Quartz-poor sandstone, ultramafic and mafic volcanic rocks, and shale are underrepresented. All the under-
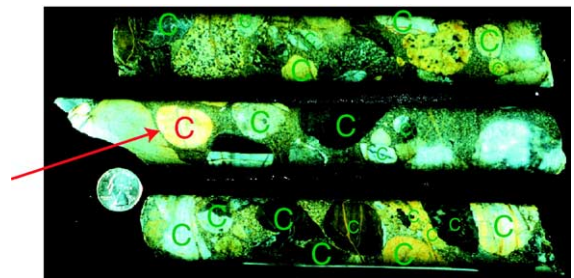


Fig. 2. Drill core from the Sheba Gold mine in the Barberton area shows the abundance of chert pebbles (marked C) in a 3.2-Ga Moodies Group conglomerate. The red arrow points to a well-rounded mechanically weathered clast. Fractures postdate deposition. U. S. quarter (25 mm) gives scale.

represented rock types, but shale (which is mechanically weak), are expected to weather chemically.

The predominance of chert where it occurs in the source region and the mechanical weathering of its cobbles seem to be a general characteristic of mid-Archean sequences (Roger Buick personal communication, 2003). An example is 3.5-Ga deposits in Australia [18].

## 2.2. Sandstone and shale

Abundant quartz sandstone in the basal 700–800 m of the Moodies Group indicates a braided alluvial plain [13,16]. Framework grains include abundant monocrystalline quartz (38–39%), potassium feldspar (9–15%), chert (9–15%), and quartz–sericite lithic grains (6–18%), depending on the location within the Barberton Greenstone Belt. Less common framework grains include plagioclase, polycrystalline quartz, felsic and mafic–ultramafic volcanics, lithic grains, and sedimentary lithic grains. The modal composition plots in the recycled orogen field of Dickinson and Suczek [19] (Fig. 3). It is important to note that chert is overrepresented in our sands relative to the source region, but to a lesser degree than in the conglomerates.

Overall the degree of weathering is greater than that observed in sands from modern rivers draining the
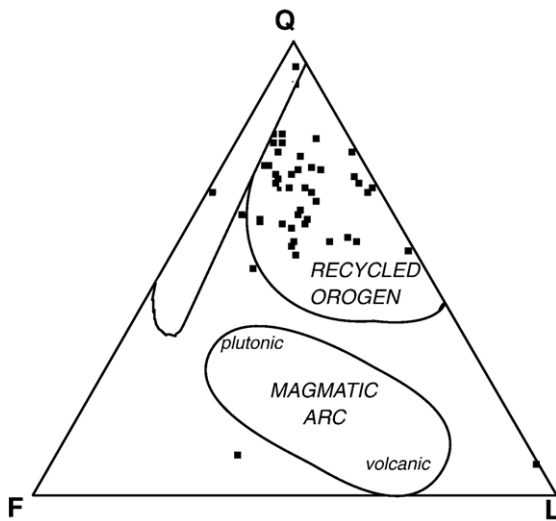


Fig. 3. Quartz–feldspar–lithic (QFL) ternary plot for Moodies Group sandstone, north of the Inyoka Fault and from within the lower alluvial and fluvial depositional facies. Data collected and compiled by Chandler [11]. Quartz in this diagram includes chert. Most of the points lie within the recycled origin tectonic province of Dickinson and Suczek [19]. The low abundance of lithic fragments and feldspar, despite their abundance in the source terrane [11], indicates significant chemical weathering.

nearby Kaap Valley pluton (Fig. 3). Moodies sands are less weathered than those generated in modern, extremely humid environments: qualitatively between the fluvial arkoses of the warm–temperate to subhumid Mallacoota Basin [20] and the quartz–arenite sands produced in the seasonally tropical Orinoco Basin, Venezuela [21].

Most of the shale fraction appears to have bypassed the exposed region of deposition. Enough shale exists, however, to demonstrate that extensive chemical weathering did occur. $Al_2O_3$ ranges between 18 and 25 wt.%, above that in any reasonable source rock. Conversely, detrital chert comprises less than 2% of the shale material.

Although analogous data from sequences contemporaneous with the Moodies Group is lacking, extensive chemical weathering is also a common feature of Mesoarchean and Neoarchean sediments in the Canadian Shield [2,3,22–24] and South Africa [25]. Sandstones in the ~2.6 Ga Beaulieu Formation [3] and the ~2.6 Keskarrah Formation [2] show intense chemical weathering in a humid climate, which the authors interpret as being as hot as 85 °C. These samples, however, are more quartz-rich than those in the Moodies Group, plotting in the recycled orogen field of Dickinson and Suczek [19] at 62–90% [3] and 68–95% [2] quartz. As is expected, plagioclase and potassium feldspar are underrepresented relative to the assumed source region. Notably much of the quartz is polycrystalline, 85% and 56% of the grains, respectively, in the composite average. Highly mature quartzites occur in the ~2.80-Ga Central Slave Cover Group [24]. However, many of these rocks have recrystallized and point counts of quartz grain types are not available.

## 2.3. Weathering rinds and paleosols

There are no studied paleosols in our field locality, although weathering rinds on pebbles do exist and serve a similar purpose [9]. Rinds and broken rinds on felsic sericitized and carbonated volcanic rocks indicate they lingered long enough in transport for chemical alteration to occur. This indicates that there was time for chert pebbles to partly dissolve provided the streams were undersaturated in quartz and the kinetics of dissolution were rapid. Chert pebbles in the Moodies Group do not exhibit dissolution features, such as dog-tooth edge weathering or micro-karst indentations.

Outside of the Barberton Greenstone Belt, we know of one relevant erosion-surface exposure in Australia [18]. A chert bed appears to have been resistant to erosion relative to adjacent granites and greenstones,

overlain by a possible paleosol. The chert surface does not show any evidence of dog-toothed or karst features that would accompany rapid dissolution in extremely hot conditions.

## 3. Modern geological analogs

The weathering of modern granitic rocks to quartz-rich sand and clay-rich shale is well known. So is the occurrence of some dissolution features in quartz [11]. Modern weathering occurs when reaction rates are fastest, during the wet part of the year in seasonally humid climates and during the warm part of the year in temperate climates [26]. Modern weathering thus occurs at ~25 °C except at very high latitudes.

Although lower soil levels will be tapped during intensive erosion events, it is mostly the tops of weathering profiles that supply grains to fluvial environments and become the ancient sediments that we can use to infer surface conditions. Our sand grains encountered pristine rainwater and far-from-equilibrium conditions just before mobilization. They preferentially carried records of kinetically limited near-surface processes away from the outcrop. This is true even if the deeper weathering profile was saturated with respect to quartz.

### 3.1. Chert and quartzite

Chert is a relatively uncommon rock in modern source areas. Quartzite is analogous and more abundant. Like chert it is nearly monomineralic, has little porosity, and forms extended outcrops. It differs from chert in having a larger grain size, which will play a role in its mechanical breakdown. Karstic features in carbonate-sedimented sandstone are not relevant here as quartz dissolution is not involved.

Because chert is such a minor component of most source terranes, its overrepresentation in conglomerate or river gravel is an indication of its resistance to weathering and decomposition to sand-sized fragments, under a range of climatic conditions. Overrepresentation of chert clasts occurs in relatively recent, humid environments that were warm but not extreme. Cretaceous conglomerates in Iowa provide a example: locally derived chert clasts from Paleozoic carbonates occur together with jasper, quartzite, and vein quartz derived from the Canadian Shield [27].

Quartz, however, does undergo some chemical weathering in modern environments. Modern karst occurs in quartzite and other hard rocks [28,29], but is not known to occur on chert (S. Doerr personal communication, 2003). The region in Venezuela near

Angel Falls is a spectacular example of quartzite karst. The waterfall exits from a quartzite cave along the cliff face [28]. Here, karst formed at high elevations at mean temperatures as low as 14 °C and at a very high rainfall rate of ~5 m/yr. It is important to note that development of quartzite karst in this region was helped significantly by restricted mechanical weathering along the plateau's subdued topography.

Chemical analyses of groundwater at Angel Falls put the karst-forming process into geochemical context. Effluent water from the local quartzite near Angel Falls contains $SiO_2$ at ~2% of saturation [30]. This indicates that the dissolution of quartzite is kinetically limited. Amorphous silica does occur from local evaporation, but plays no part in the overall mass balance as this $SiO_2$ had to dissolve from quartzite in the first place.

Chert also forms a regolith in the warm humid mountainous Ashio region of Japan [31]. Water infiltrates into the chert regolith and exits from springs. Although, dissolution features are not evident within the chert bed, some dissolution does occur. Springs where just chert is available are at ~29% of quartz saturation (Tsuyoshi Hattanji, personal communication, 2005).

Karst weathering of quartzite to a friable rock also occurs in the semiarid climate near Delhi, India [32]. Weathering involves strong acids from oxidation of pyrite, which is inapplicable to anoxic conditions in the Archean but may be partially analogous to higher $CO_2$ levels proposed for the mid-Archean (9). Desiccation akin to salt weathering may also be important (J. Donald Rimstidt, personal communication, 2005). Beyond showing that quartzite can become friable under semiarid acid weathering in modern climates, this situation provides little insight into weathering in humid Archean climates.

### 3.2. Sand from granitic rocks

Quartz dissolution during the weathering of granite must be considered separately, due to interference from the simultaneous dissolution of additional silicates. Quartz sand forms from granitic rock when feldspar and mafic minerals weather to clay. Early in weathering the dissolution of feldspar may supersaturate the water with respect to quartz, thus precluding further quartz dissolution. Careful studies show that quartz grains do dissolve to some extent in the later stages of modern weathering despite the involvement of feldspar. Schulz and White [33] provide a field study of the modern weathering of a quartz diorite and include a review of

the literature. Their locality in Puerto Rico receives 4 m of rain per year but only 0.6 m soaks in. It takes water 12 yrs to traverse the 9-m thick regolith profile. The saprolite regolith contains iron oxides, biotite, quartz, and kaolinite. Dissolved silica increases linearly with depth to saturation at the base of the profile. Mass balance indicates that comparable amounts of $SiO_2$ come from dissolution of biotite and quartz.

Etch pits on grain surfaces are common. Schulz and White [33] calculate that they should form when the $SiO_2$ concentration is below 10–45% of saturation. This is a common feature of tropical soils [34]. Pits form quickly, for example, in <8000 yrs on dune sand in northeastern Australia [35].

Dissolution is enhanced because the real surface area of the diorite-derived quartz grains is large: ~100 times the geometric (equivalent sphere) area and independent of grain size. Dissolution occurs along grain boundaries and microcracks, making the grains somewhat friable, although no macroscopic size reduction of the quartz grains is evident. Schulz and White [33] note that their average grain radius is expected to change only from 0.23 to 0.22 mm in the 100 ka that it remains in the soil using kinetic data from Lasaga [36].

## 4. Inferences about Archean climate

We wish to compare the above modern analogs with the Archean record, particularly with the mid-Archean sediments preserved in the Moodies Group. To a first order, the Archean sediments we have discussed are similar to modern ones. If anything, quartz dissolution features are less common in the ancient rocks [11]. A tempting inference is that the Archean climate was like the modern. Yet we need to identify observations that are particularly temperature sensitive, because there were many features of the Archean that uniquely affected weathering (i.e. elevated $CO_2$ and the absence of plants). Temperature-sensitive observations include the absence of karst solution features in monomineralic quartz pebbles and on chert erosion surfaces and the survival of abundant polycrystalline quartz and chert in the sand fraction. Conversely, detection of mild solution features like pits on modern grains in tropical climates would be less useful. (Higher temperatures would only increase their rate of formation.) Such features are likely to be obscured by low-grade metamorphism.

Given the lack of modern hot climates, we apply an analogy to quantify the kinetics of quartz dissolution. Carbonates are common on the modern Earth. Their dissolution rates are fast enough that solubility often limits their denudation rates. Before discussing this, we

expose our ignorance of what a hot Archean climate would be like.

### 4.1. Archean climate and landscape

We discuss ~50 and ~75 °C climates in comparison to the modern Earth where weathering occurs at ~25 °C. Latent heat would buffer temperature daily, annually, and geographically. At saturation, there would be 0.12 and 0.39 bars of water vapor in the air, respectively, at 50 and 75 °C. The global average rainfall is of the order of a meter per year, as it is limited by the heat from sunlight, like at present.

Details that would be useful to the field geologist are not evident without sophisticated meteorological calculations. These include the tendency of rain to fall orographically and in local torrential storms, maximum wind velocities, and the range of relative humidity. We note that halite occurs in the Archean [37], and that it indicates that the relative humidity was below ~0.75 either locally or temporally.

We also have poor constraints on Archean geomorphology. Land plants were absent. Conceivably, microbial mats stabilized the surface and enhanced weathering. No land fossils are known from the Archean [38], but this does not mean that the soils were sterile. The 2.76-Ga Mount Roe (Australia) paleosol shows evidence of weathering assisted by microbes [39]. For now, we can discount weathering aided by abundant humic acids at 3.2 Ga.

We note that a recently denuded and sterilized slope is not a perfect analog for the Archean. Given time, however, low-relief surfaces on grade with chemical weathering developed in the Archean, as evidenced by the presence of Archean shales and mature sands. We do not consider places where rapid mechanical denudation on high relief surfaces overwhelmed chemical weathering nor do we consider arid environments.

### 4.2. Carbonate analog

Carbonates form karst as well as microkarst features on weathering surfaces and pebbles. Carbonate karst has been found in the Archean [40], which implies that chert or quartzite karst might have been found if they were abundant. Typically, the kinetics of carbonate dissolution is geologically fast. It provides an analog where solubility, rather than dissolution kinetics, is rate limiting.

We discuss quartz solubility to put carbonate solubility in context. Here we are interested in rainwater, groundwater, and river water in a humid climate. As

abundant humic acids are unlikely in the Archean and as there is likely to be significant $CO_2$ in the air, we restrict $3 \leq pH \leq 7$ and the ionic strength to <1 mmol. In these conditions, the solubility of quartz is a moderate function of temperature and a weak function of pH and dissolved $CO_2$. Quartz solubility is 11, 21, 37, and 67 ppm at 25, 50, 75 and 105 °C, respectively, [41]. A meter per year of saturated infiltration would remove 4, 8, 14, 25 m of rock in 1 m.y., respectively.

The solubility of calcite ($CaCO_3$) in rainwater in the presence of modern air is 50 ppm and its (organic soil) solubility at 0.01 bar $CO_2$ is 160 ppm [42]. The solubility is higher if humic acids are abundant, but this situation is unnecessary to form karst, as in the Archean [40]. The solubility of dolomite (which also forms karst) in rainwater is between that of calcite and quartz at ~25 °C, but is poorly determined [42]. Initial porosity is not needed for carbonate karst. It forms in hard limestone and marble [e.g., Mueller [43]].

### 4.3. Quartz dissolution kinetics

Overall, the solubility of quartz is only modestly below that of carbonates. We need to look to the slow dissolution rate of quartz at ~25 °C to explain the rarity of quartzite karst on the modern Earth, especially since effluent water from the Venezuelan quartzite karst has only ~2% of quartz saturation [27]. For the Archean, we need to look at the dependence of dissolution rate on temperature, and we use the far-from-equilibrium rate in moles per square meter of exposed surface per time. This dissolution rate of quartz at 50 and 75 °C is a factor of ~10 and ~100 respectively above the solution rate at 25 °C and a weak function of pH and $CO_2$ concentration for the ranges of interest [44].

Rainwater falls essentially devoid of $SiO_2$ so that the bulk of the dissolution occurs at the far-from-equilibrium rate. Rainwater percolates through the soil dissolving quartz, leaving the effluent either undersaturated as in the Venezuelan karst locality [27] or essentially saturated as in Puerto Rico [33]. The bulk of the dissolution occurs at water–quartz contacts where replenishment maintains far-from-equilibrium conditions. The rest of the real grain surfaces are not efficiently replenished, and here slow dissolution will occur at or near equilibrium conditions. It should be emphasized that field observations are necessary for calibration as the field rate is less than the laboratory rate and the real surface area of grains is much greater than equivalent spheres [33].

Grain size and framework structure of the rock control development of dissolution features related to chemical weathering. In a quartzite or chert, the quartz grain boundaries dissolve first and the rock disaggregates as chert or quartz sand grains, which are thus washed away [28,29]. Chert has more grain boundaries than quartzite, and the smaller grains formed during grain-boundary dissolution are more easily carried away. Therefore, quartzite and chert karst may develop at somewhat lower macroscopic dissolution rates than carbonates, where most of the material leaves the sedimentary system in solution.

### 4.4. Quartz dissolution as a paleothermometer

To show that quartz dissolution is a paleothermometer, we consider a 105 °C humid climate. This is higher than we have seen proposed for the Archean, but we want to start with a case that is observably different from the modern Earth. We consider a low-relief surface with granitic and chert outcrops. By assumption, the low-gradient streams in this terrain readily carry material in solution from the watershed, but are ineffective at removing solids including clays.

At this temperature, sand size grains equilibrate with water on a laboratory scale of weeks [45]. The effluent water from the chert and quartzite is saturated with quartz. The denudation rate at 1 m per year of rain is 25 m per m.y.

Within a granitic rock in this hypothetical terrane, the high temperature speeds up the break-down of feldspars and the dissolution of quartz. The weathered soil is $Al_2O_3$-rich clay according to Wolery [46]. (That is, the presence of clays alone is not a good paleothermometer.) The clay soil, however, needs to be removed mechanically for open-system weathering to proceed. As already noted, rainfall and runoff were comparable to present, as were mechanical denudation processes that depended on available water, such as those generating the Moodies Group braided stream deposits. The clay surface on granite becomes the high ground if its denudation rate is less than that of the chert. This would occur if relief were adequately low, so that seasonal drying might turn the clay into a resistant adobe-like surface.

We now look more closely at the chert and at the quartz grains housed in the granitic rock. Dissolution along grain boundaries readily disaggregates the chert and other polycrystalline quartz into a fine-grained material. It also acts along the microcracks in quartz grains making them friable. At low denudation rates, the quartz and chert that do not dissolve end up as clay and silt-sized fragments.

We clearly do not see these features in the Archean. Chert is highly resistant, underlying high ground and decomposing only partially into pebbles and sand, and

only modest amounts of clay-sized grains. Polycrystalline quartz is abundant in sands and has not entirely broken down along fine-scale grain boundaries into silt- or clay-sized fragments.

Can we use these observations, together with constraints provided by modern quartz dissolution, to quantify Archean surface temperature? A transition to the expected 105 °C weathering products must occur somewhere between that temperature and 25 °C. We expect that it occurs closer to 25 than 105 °C primarily because the dissolution rate is an order-of-magnitude function of temperature over the range of interest, while solubility is a factor-of-a-few function. In other words, the temperature does not have to be much higher than at present for kinetically controlled dissolution effects to become evident.

We do not have any known climates with weathering temperatures significantly above 25 °C, and so we must extrapolate from measured modern systems. We do note that the dissolution features of quartz we have discussed do occur modestly on the modern Earth. In particular, faster dissolution at temperatures somewhat above 25 °C enhances disaggregation along cracks and grain boundaries that leads to karstic features. Such dissolution involves only a minor volume in the grains so it is more sensitive to kinetics than solubility. Its last stages (in ancient sediments that we can actually observe) occurred near the erosion surface by interaction with far-from-equilibrium rainwater.

Using the Puerto Rican exposure [33], quartz grains in granitic rock became "somewhat friable" in ~100 ka of exposure time in an area of significant mechanical denudation although the bulk diameter of the grains remains. That is, the grains are to the point that they would fracture and largely disintegrate during transport. They would break in situ given more weathering or modestly faster dissolution kinetics. Extrapolating linearly from the Puerto Rican quartz grains (as dissolution rate increases a factor of 10 with every 25 °C temperature increase), the observed amount of friability should occur after 10 and 1 ka at 50 and 75 °C, respectively.

Quartzite karst formed in a favored environment in Venezuela even though the effluent water is ~2% of quartz saturation. Again extrapolating linearly, the effluent would be ~20% saturated at 50 °C and nearly saturated at 75 °C, thus inferring much more rapid karst formation and quartzite disaggregation.

## 5. Conclusions

We have applied rather banal observations on Archean sediments and modern environments to obtain a paleothermometer for surface conditions on the early Earth. We concentrated on quartz because it is a simple common mineral for which chemical data exist. Its weathering is not strongly affected by atmospheric $CO_2$. The observations are quite low-tech involving point counts of sediments, visual observation of pebbles, and microscopic observations of grains in sediments and weathered rock. In the Archean as at present, quartz is a major component of most clastic sediments. Hard monomineralic quartz, as in chert and quartzite, resisted solution weathering. In the Moodies Group, in particular, chert is overrepresented in conglomerate relative to the source region. Sandstones with abundant quartz grains are common. Polycrystalline quartz escaped disaggregation. We have no evidence of karstic features on Archean quartz pebbles or erosion surfaces.

It is easier to say that that the Archean data are consistent with modern weathering temperature than that they preclude elevated weathering temperatures. Importantly, features related to friability involve positive evidence rather than absence of evidence. In particular, monocrystalline quartz, polycrystalline, quartz, and chert are common in the Archean sand fraction. Our chert pebbles behaved as hard, not friable, rocks. As noted in Section 4, friability and disaggregation involve small volumes of quartz and hence are measures of dissolution rates more than solubility. We expect that friability strongly affects the sand fraction even at 50 °C.

Finally, our conclusions are not in direct conflict with ocean temperatures inferred from oxygen isotopes in chert [1]. Our data come from a later time when these marine cherts were exposed to erosion. As noted in Section 4.1, we have no good theoretical constraints on the long-term and geographic variability of Archean climate. A geologist who discovers pronounced quartz solution features in ancient sedimentary rocks can easily turn our argument around. Further examination of the rock record is warranted.

in Barberton, South Africa. This work was performed as part of a collaboration with the NASA Astrobiology Institute Virtual Planetary Laboratory Lead Team.

## References

[1] L.P. Knauth, D.R. Lowe, High Archean climatic temperature inferred from oxygen isotope geochemistry of cherts in the 3.5 Ga Swaziland group, South Africa, Geol. Soc. Amer. Bull. 115 (2003) 566–580.

[2] P.L. Corcoran, W.U. Mueller, E.H. Chown, Climatic and tectonic influences on fan deltas and wave- to tide-controlled shoreface deposits: evidence from the Archaean Kesharrah Formation, Slave Province, Canada, Sediment. Geol. 120 (1998) 125–152.

[3] P.L. Corcoran, W.U. Mueller, W.A. Padgham, Influence of tectonism and climate on lithofacies distribution and sandstone and conglomerate composition in the Archean Beaulieu Rapids Formation, Northwest Territories, Canada, Precambrian Res. 94 (1999) 175–204.

[4] G.M. Young, V. von Brunn, D.J.C. Gold, W.E.L. Minter, Earth's oldest reported glaciation: physical and chemical evidence from the Archean Mozaan Group (similar to 2.9 Ga) of South Africa, J. Geol. 106 (1998) 523–538.

[5] J.K. Kasting, Earth's early atmosphere, Science 234 (1993) 1383–1385.

[6] J.F. Kasting, J.L. Siefert, Life and the evolution of earth's atmosphere, Science 296 (2002) 1066–1068.

[7] A.A. Pavlov, J.F. Kasting, L.L. Brown, K.A. Rages, R. Freedman, Greenhouse warming by $CH_4$ in the atmosphere of early earth, J. Geophys. Res. 105 (2000) 11981–11990.

[8] N.H. Sleep, K. Zahnle, Carbon dioxide cycling and implications for climate on the ancient earth, J. Geophys. Res. 106 (2001) 1373–1399.

[9] A.M. Hessler, D.R. Lowe, R.L. Jones, D.K. Bird, A lower limit for atmospheric carbon dioxide 3.2. billion years ago, Nature 428 (2004) 736–738.

[10] R. Rye, P.H. Kuo, H.D. Holland, Atmospheric carbon-dioxide concentrations before 2.2-billion years ago, Nature 378 (1995) 603–605.

[11] F.W. Chandler, Quartz arenites: review and interpretation, Sediment. Geol. 58 (1988) 105–126.

[12] A. M. Hessler, Evidence for climate and weathering in siliclastic sedimentary rocks of the 3.2 Ga Moodies Group, Barberton Greenstone Belt, South Africa, Ph.D. Stanford University, 2001, p. 258.

[13] K.A. Eriksson, Alluvial and destructive beach facies from the Archean Moodies Group, Barberton Mountain Land, South Africa and Swaziland, Fluvial Sedimentology, Canadian Society of Petroleum Geologists Memoir, vol. 5, 1978, pp. 287–311.

[14] K.A. Eriksson, Marginal marine depositional processes from the Archean Moddies and Fig Tree Groups, Barberton Mountain Land, South Africa: evidence and significance, Precambrian Res. 8 (1979) 153–182.

[15] K.A. Eriksson, Marginal marine depositional processes from the Archean Moddies and Fig Tree Groups, Barberton Mountain Land, South Africa: evidence favoring an Archean continental margin, Precambrian Res. 12 (1980) 141–160.

[16] Heubeck, C.E. Geology of the Archean Moodies Group, central Barberton Greenstone Belt, South Africa. Ph.D. thesis, Stanford University, 1993, 390 pp.

[17] C.E. Heubeck, D.R. Lowe, Depositional and tectonic setting of the Archean Moodies Group, Barberton Greenstone Belt, South Africa, Precambrian Res. 68 (1994) 257–290.

[18] R. Buick, J.R. Thornett, N.J. McNaughton, J.B. Smith, M.E. Barley, M. Savage, Record of emergent continental crust ~3.5 billion years ago in the Pilbara craton of Australia, Nature 375 (1995) 574–577.

[19] W.R. Dickinson, C.A. Suczek, Plate tectonics and sandstone composition, Am. Assoc. Pet. Geol. Bull. 63 (1979) 2164–2182.

[20] H. Nesbitt, G. Young, S. McLennan, R. Keays, Effects of chemical weathering and sorting on the petrogenesis of siliclastic sediments, with implications for provenance studies, J. Geol. 104 (1996) 525–542.

[21] M. Johnsson, R. Stallard, R. Meade, First-cycle quartz arenites in the Orinoco River basin, Venezuela and Colombia, J. Geol. 96 (1988) 263–277.

[22] J.A. Donaldson, E.A. de Kemp, Archaean quartz arenites in the Canadian shield: examples from the Superior and Churchill Provinces, Sediment. Geol. 120 (1998) 153–176.

[23] W.U. Mueller, P.L. Corcoran, Late-orogenic basins in the Archaean Superior Province, Canada: characteristics and inferences, Sediment. Geol. 120 (1998) 177–203.

[24] K.N. Sircombe, W. Bleeker, R.A. Stern, Detrital zircon geochronology and grain-size analysis of a ~2800 Ma Mesoarchean proto-cratonic cover succession, Slave Province. Canada, Earth Planet. Sci. Lett. 189 (2001) 207–220.

[25] B.G. Els, The auriferous Archaean sedimentation systems of South Africa: unique palaeo-environmental conditions? Sediment. Geol. 120 (1998) 205–224.

[26] D.D. Ekart, T.E. Cerling, I.P. Montañez, N.J. Tabor, A 400 million year carbon isotopic record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide, Am. J. Sci. 299 (1999) 805–827.

[27] R.L. Brenner, G.A. Ludvigson, B.L Witzke, P.L. Phillips, T.S. White, D.F Ufnar, L.A. González, R.M. Joeckel, A. Goettemoelerr, B.R. Shirk, Aggradation of gravels in tidally influenced fluvial systems: Upper Albian (Lower Cretaceous) on the cratonic margin of the North American Western Interior foreland basin, Cretac. Res. 24 (2003) 439–448.

[28] S.H. Doerr, Karst-like landforms and hydrology in quartzites of the Venezuelan shield: pseudokarst or "real" karst, Z. Geomorphol. 43 (1999) 1–17.

[29] R.A.L. Wray, A global review of solution weathering forms on quartz sandstones, Earth-Sci. Rev. 42 (1997) 137–160.

[30] M. Mecchia, L. Piccini, Hydrogeology of $SiO_2$ geochemistry of the Aonda Cave system (Auyan-Tepui, Bolivar, Venezuela), Boll. Soc. Venezolana Espel. 33 (1999) 1–11.

[31] T. Hattanji, Y. Onda, Coupling of runoff processes and sediment transport in mountainous watersheds underlain by different sedimentary rocks, Hydrol. Process. 18 (2004) 623–636.

[32] J.K. Tripathi, V. Rajamani, Weathering control over geomorphology of supermature Proterozoic Delhi quartzites of India, Earth Surf. Process. Landf. 28 (2003) 1379–1387.

[33] M.S. Schulz, A.F. White, Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico III: quartz dissolution rates, Geochim. Cosmochim. Acta 63 (1999) 337–350.

[34] H. Eswaran, G. Stoops, Surface textures of quartz in tropical soils, Soil Sci. Soc. Am. J. 43 (2) (1979) 420–424.

[35] K. Pye, J. Mazzulo, Effects of tropical weathering on quartz grain shape: an example from northeastern Australia, J. Sediment. Res., Sect. A Sediment. Pet. Proc. 64 (3) (1994) 500–507.

[36] A.C. Lasaga, Chemical kinetics of water–rock interactions, J. Geophys. Res. 89 (1984) 4009–4025.

[37] C.A. Boulter, J.E. Glover, Chert with relict hopper molds from Rocklea Dome, Pilbara Craton, western Australia — an Archean halite-bearing evaporite, Geology 14 (1986) 128–131.

[38] R. Buick, Life in the Archean, in: D.E.G. Briggs, P.R. Crowther (Eds.), Paleobiology II, Blackwell Science, Oxford, 2001, pp. 13–21.

[39] A. Neaman, J. Chorover, S.L. Brantley, Element mobility patterns record organic ligands in soils on early earth, Geology 33 (2005) 117–120.

[40] T.P. Kusky, P.J. Hudleston, Growth and demise of an Archean carbonate platform, Steep Rock Lake, Ontario, Canada, Can. J. Earth Sci. 36 (1999) 565–584.

[41] J.D. Rimstidt, Quartz solubility at low temperatures, Geochim. Cosmochim. Acta 61 (1997) 2553–2558.

[42] K.B. Krauskopf, D.K. Bird, Introduction to Geochemistry, McGraw-Hill, New York, 1995, 647 pp.

[43] M. Mueller, Karst hydrogeology of the Takaka Valley, Golden Bay, Northwest Nelson, N. Z. J. Geol. Geophys. 34 (1991) 11–16.

[44] P.M. Dove, The dissolution kinematics of quartz in sodium-chloride solutions at 25-degrees-C to 300-degrees-C, Am. J. Sci. 294 (1994) 665–712.

[45] H.U. Rimstidt, H.L Barnes, The kinetics of silica–water reactions, Geochim. Cosmochim. Acta 44 (1980) 1683–1700.

[46] Wolery, T. J. EQ3/6: a software package for geochemical modeling of aqueous systems. (The Regents of the University of California and Lawrence Livermore National Laboratory, 1997).