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Reconstruction of a 3700 Ma transgressive marine environment from Isua (Greenland): Sedimentology, stratigraphy and geochemical signatures

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Abstract

The rare preservation of a stratigraphy in the northwest of the Eoarchean Isua supracrustal belt (Greenland) demonstrates the world's earliest-recognised marine transgression. Stratigraphically lowest is the ~3710 Ma Solvang Volcanic Formation of picrites, basalts and basaltic-andesites with arc-like geochemical signatures. Close to its erosional top, this formation's volcanic rocks show increase in K₂O with depletion of Na₂O, depletion in Sr with no alteration in Eu abundance and $\delta^{18}\text{O}_{\text{VSMOW}}$ increase to +16‰, interpreted as subaerial weathering at ~3700 Ma. The sedimentary Snowpatch Formation was deposited unconformably on the Solvang Volcanic Formation. Locally, the unconformity is marked by the laterally discontinuous Conglomerate Member dominated by rounded quartz clasts, but also with clasts of basalt and andesite up to >10 cm across, layered chert and ultramafic rocks. The Conglomerate Member carries sparse detrital zircons, the youngest of which are ~3710 Ma. The conglomerates are succeeded by the Sandstone and Dolostone Member of layered quartz and dolomite clastic sandstones that locally preserve relict shallow marine cross-bedding with scoured layers, tempestite breccia beds and very rare stromatolite horizons. The Sandstone and Dolostone Member is succeeded by the ~3695 Ma BIF Member. The Snowpatch Formation quartz-dolomite sandstones and interlayered stromatolites have seawater-like REE + Y trace element patterns variably modified by a negligible to significant influx of a terrigenous component. Trace element signatures such as Ti/V ratios and normalising REE + Y data to a 3710 Ma weathered volcanic rock (rather than Post Archean Average Shale) suggest this component was derived from a juvenile arc source, resembling the basement Solvang Volcanic Formation. The detailed field and geochemical evidence such as positive correlation between Fe/Mg and Pr/Yb* in the Snowpatch Formation dolostones and BIF (banded iron formation) indicates that the dolomitic lithologies developed in a shallow water setting with clastic sedimentation, during a marine transgression over a weathered ~3710 Ma volcanic arc basement, followed by BIF deposition in deeper water. Thus by 3700 Ma, shallow-water, exposed, settings had already been established, which were the site of stromatolite development.

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**Reconstruction of a 3700 Ma transgressive marine environment from
Isua (Greenland): Sedimentology, stratigraphy and geochemical
signatures**

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Keywords: Eoarchean; marine transgression; Isua; dolostone; Snowpatch Formation

1. Introduction

Eoarchean (3600-4000 Ma) rocks that survive up to today represent about a millionth of the crust and from this, only <5% are the sedimentary rocks needed to establish palaeoenvironments and to seek the evidence for early life forms. Most of these rocks are strongly deformed and some were metamorphosed up to the stage of incipient melting (e.g., Nutman et al., 1996). These processes destroy all but the most rudimentary evidence of sedimentary protoliths. However, some relict sedimentary and volcanic structures are preserved in the Eoarchean Isua supracrustal (volcanic and sedimentary) belt, allowing more insight into volcanic and sedimentary environments in deep time (Allaart, 1976; Nutman et al., 1984, 2014, 2016, 2017a,b; Appel et al., 1998; Komiya et al., 1999; Fedo, 2000; Fedo et al., 2001; Jenner et al., 2009).

This paper focusses on the northeastern domain in the Isua supracrustal belt's ~3700 Ma portion (Fig. 1; between the two Eoarchean mylonites marked 'A' and 'B'), because it contains the world's greatest inventory of preserved Eoarchean sedimentary and volcanic structures. Detailed mapping in this domain, with the recognition of facing directions from volcanic and sedimentary structures, zircon U-Pb geochronology and application of structural criteria to distinguish between tectonic boundaries and tectonised stratigraphic boundaries, permit the confident recognition of a stratigraphic succession, to which for the first time for the Eoarchean, we erect a formal Formation and Member nomenclature (Figs. 2 and 3). This account follows the initial recognition in the central domain of an unconformity between eroded mafic volcanic rocks and an overlying transgressive sedimentary sequence by Nutman and Friend (2009), which De

Wit and Furnes (2013) later reported as a new discovery. Following the erection of a formal stratigraphy based on field observations and some additional U-Pb zircon geochronology, this paper presents new whole rock geochemical data on the sedimentary rocks, from which interpretation of the Ti/V ratios and nuances in REE+Y patterns demonstrate a marine transgressive environment and basin deepening from ~3700 to ~3695 Ma, in an arc-like setting. The initially shallow marine setting is dominated by dolomitic rocks and is where the stromatolites of Nutman et al. (2016, 2019), contested by Allwood et al. (2018), are found. However, it is important to note that the shallow marine transgressive environment recognised here does not apply to all the volcanic and sedimentary sequences in Isua, which is an Eoarchean tectonic collage of rocks of different ages derived from environments ranging from deep basin to shallow marine and emergent (Nutman et al., 1984, 1997, 2017a; Fedo et al., 2001; Nutman and Friend, 2009).

2. The Isua supracrustal belt

The 35 km long Isua supracrustal belt is the largest supracrustal rock unit within the ~3000 km² Eoarchean Itsaq Gneiss Complex in southern West Greenland (e.g., Allaart, 1976; Nutman et al., 1996; Nutman and Friend, 2009). Similarities between the Isua supracrustal belt rocks and ophiolitic assemblages have been documented (e.g., Keto and Kurki, 1967; Polat and Hoffman, 2003; Dilek and Polat, 2008; Nutman et al., 2009; Friend and Nutman, 2010). All Isua supracrustal belt rocks have undergone polymetamorphism with the maximum grade ranging from low amphibolite (500-550°C) to middle amphibolite facies (up to 650°C) in different panels separated

by Eoarchean mylonites (Boak and Dymek, 1982; Rollinson, 2003; Nutman et al., 2013). The belt is bounded by intrusive complexes, with most contacts tectonically modified (Bridgwater and McGregor, 1974; Allaart, 1976; Nutman and Friend, 2009). The intrusive complex to the south is dominated by ~3800 Ma tonalite protoliths and that to the north by ~3700 Ma tonalite protoliths cut by 3650-3640 Ma granite sheets (Nutman et al., 1996, 1997; Crowley et al., 2002; Crowley, 2003; Nutman and Friend, 2009). To the west, the belt is in tectonic contact with Mesoarchean rocks (Nutman and Friend, 2009), whilst eastwards it is obscured by the Inland Ice.

U-Pb zircon dating with 95% confidence uncertainties of $\leq \pm 10$ Ma demonstrates that the Isua supracrustal belt contains two tectonically juxtaposed slices of unrelated supracrustal rocks ~100 million years different in age (Fig. 1; Nutman et al., 1996, 1997, 2002, 2009; Crowley et al., 2002; Crowley, 2003). The belt's southern portion, named here as the *Outer Arc Group* is not discussed further in this paper, consists of ~3800 Ma rocks. The belt's northern section comprises tectonic slices of ~3700 Ma rocks (Fig. 1; Nutman et al., 1996, 1997; Nutman and Friend, 2009, and references therein). The ~3700 Ma portion of the belt is named here the *Inner Arc Group* and consists of several Formations, of which the Solvang Volcanic Formation and the Snowpatch Formation are the focus of this paper. The parts of the belt differing in age by approximately 100 million years are separated from each other by a folded, metamorphosed and deformed Eoarchean mylonite, which probably formed by ~3660 Ma (Nutman and Friend, 2009; Nutman et al., 2009).

The dominant lithologies within the ~3700 Ma assemblage are amphibolites and

schists derived from basaltic, picritic, boninitic and andesitic volcanic rocks, felsic volcanic rocks, felsic volcano-sedimentary, and chemical sedimentary rocks, particularly chert and BIF, plus dolomitic rocks also of sedimentary origin (e.g., Allaart, 1976; Dymek and Klien, 1988; Nutman et al., 1984, 2007, 2009, 2010, 2013, 2016; Komiya et al., 1999; Polat et al., 2002; Polat and Hofmann 2003, Bolhar et al., 2004, 2005; Furnes et al., 2007; Friend et al., 2008). Gabbros and ultramafic rocks are volumetrically minor compared to sedimentary and volcanic rocks (e.g., Dymek et al., 1988; Friend and Nutman, 2011).

Primary volcanic and sedimentary structures have survived in only a few places, and the compositional layering in the volcanic and sedimentary rocks is mostly of transposed tectonic origin. The most common relict structures are pillows within mafic volcanic rocks, and more rarely, relict bedding which is found in cherts, banded iron-formation and dolomite-rich rocks together with graded bedding in felsic volcano-sedimentary rocks (e.g., Allaart, 1976; Nutman et al., 1984; 1997, 2007, 2016, 2017a; Appel et al., 1998; Komiya et al., 1999; Rosing, 1999; Solvang, 1999; Furnes et al., 2007).

3. Discrimination of stratigraphic versus tectonic boundaries in the Isua supracrustal belt

Within the Isua supracrustal belt's ~3700 Ma rocks, there is clear evidence of tectonic boundaries between some lithologies, particularly between ~3720 Ma amphibolites derived from metabasic rocks whose composition resembles modern boninites (Polat et al., 2002). This is demonstrated by all boundaries of the boninitic

rocks with other lithologies being mylonitic chloritic schists, with no relic pillow lava structures found at the contacts (Fig. 4A). Also, the chlorite schist margin to the boninitic unit is commonly discordant and/or truncates other lithological units (see 1:20,000 scale maps of Nutman and Friend, 2009). This is demonstrated particularly well from the northwestern end of the Isua supracrustal belt, where ~3690 Ma banded iron formation with metasedimentary rocks of broadly andesitic composition form an oblique sliver separated by mylonites from boninitic amphibolite units containing a ~3720 Ma gabbro and cut by a 3712 Ma tonalite dyke (Fig. 4B).

In contrast, the boundaries between some other lithologies are modified stratigraphic contacts. This is demonstrated via the cartoon of folded units in Figure 4A. The cores of some folds are low strain areas where there is rare preservation of volcanic or sedimentary structures in adjacent lithologically and rheologically contrasting units, with no strain gradient at the boundary. On the limbs of folds, the primary volcanic and sedimentary structures are destroyed by deformation, and the evidence that the boundary was stratigraphic rather than primarily tectonic is obliterated (Fig. 4A). Thus it is only in very rare small areas that stratigraphic relationships are preserved. Most fecund in this respect is the *northeastern domain* (Fig. 1, between the mylonites marked 'A' and 'B'). It is for this reason that the northeastern domain is the focus of this paper, although the ~3700 Ma stratigraphy described here will be applicable to *some* of the more strongly deformed rocks farther west in the belt.

4. A ~3700 Ma stratigraphy in the Isua supracrustal belt's northeastern domain

Low strain zones in ~3700 Ma sedimentary and adjacent volcanic rocks are concentrated in the area shown in Figure 1. Lesser amounts of low strain zones extend farther northeast to the edge of the Inland Ice, in the extensive, tectonically thickened, BIF at Isukasia (colloquially known as the *Iron Mountain*; Fig. 1 inset). The belt's eastern part with most abundant low strain domains is bounded to the northwest by an Eoarchean mylonite (B, Fig. 1), on the western side of which are staurolite + kyanite or garnet mica schists with peak metamorphic temperatures of 650-600°C (Boak and Dymek, 1982; Rollinson, 2003). The northeastern domain's southern boundary is also an Eoarchean mylonite, separating it from the belt's ~3800 Ma part and a unit of mylonitised ~3750 Ma metasedimentary rocks known as the *dividing sedimentary unit* (A, Fig. 1; Nutman and Friend, 2009; Nutman et al., 2009).

Detailed geological mapping combined with extensive U-Pb zircon geochronology demonstrate that the belt's eastern part comprises a coherent sequence of different lithologies, that were first folded into isoclinal folds, upon which were superimposed a second generation of plunging parasitic folds, verging north-eastwards to a major synformal closure under the Inland Ice (Fig. 1; Nutman et al., 1984; 2002, 2014; Nutman and Friend, 2009). Both generations of folds are Eoarchean, because they are cut by the ~3510 Ma Ameralik (meta)dolerite dykes (Figs. 1 and 2; Nutman et al., 2004). The resulting geometry of units is now a series of nested synforms and antiforms of strongly non-cylindrical to sheath-like geometry (Fig. 1). These pre-3510 Ma tectonic events imparted a widespread strong lineation,

parallel to the axes of the second generation of folds. Post Ameralik dyke intrusion, there was overprinting by epidote amphibolite facies metamorphism, with localised additional shearing, as demonstrated by the development of amphibole tectonic fabrics locally in the Ameralik dykes (Nutman, 1986). In the area displayed in Figure 2, peak metamorphic temperatures throughout its protracted tectonometamorphic history are 500-550°C. This comes from geothermometry on the Ameralik dykes (Rollinson, 2003) and that there are domains where quartz + dolomite are in equilibrium (Nutman et al., 2016), which is only possible at moderate crustal pressures if temperature is <550°C and a fluid phase with high XCO₂ is maintained at peak metamorphic textures (cf. Winkler, 1974).

Volcanic rocks of picritic, basaltic to basaltic-andesitic affinity (Polat and Hofmann, 2003) are structurally the lowest, and are assigned here to the *Solvang Volcanic Formation*, from which a U-Pb zircon age of 3709 ± 10 Ma has been obtained (Figs. 1 and 2; Nutman et al., 2010). Structurally and stratigraphically above is the *Snowpatch Formation*, which is a diverse package of sedimentary rocks. The Snowpatch Formation is divided stratigraphically upwards into the (i) *Conglomerate*, (ii) *Sandstone and Dolostone* and (iii) *the BIF Members* (Figs. 1-3). Structurally above the Snowpatch Formation is a thick package of mafic rocks known previously as the ‘garbenschiefer’ unit (e.g., Allaart, 1976; Nutman et al., 1984). This unit is dominated by strongly deformed chloritic schists, with volcanic pillow structures surviving in local areas of low strain (Komiya et al., 1999; Friend and Nutman, 2010) and is separated by a folded thrust from the underlying footwall sedimentary, basaltic

and andesitic rocks revealed in antiforms (Fig. 1). The ‘garbenschiefer’ igneous protoliths have compositional similarities to Phanerozoic boninites (Polat et al., 2002). Farther west in the Isua supracrustal belt, the ‘garbenschiefer’ unit contains a differentiated gabbro body with a U-Pb zircon age of 3717 ± 11 Ma (Nutman and Friend, 2009) and is intruded by a tonalite dyke with a U-Pb zircon age of 3712 ± 6 Ma (Friend and Nutman, 2010), giving the *minimum* age of the unit. This demonstrates that in the belt’s northwest, covered by Figure 1, older rocks have come to rest tectonically above younger ones (Fig. 3).

The superimposed complex pattern of generally intense ductile deformation has left only small domains in which protolith structures in the volcanic and sedimentary rocks survive. These are mostly located in pre-Ameralik dyke fold cores, and are indicated on Figure 1. Using these rare low-strain domains, the palaeogeographic-environmental setting of the Solvang Volcanic and Snowpatch Formations can be reconstructed.

5. Geochemical data and analytical techniques

5.1. Whole rock geochemistry

This paper assembles data from several previous publications, integrated with new data presented here (Table 1). For the new whole rock geochemical data, major elements and a limited range of trace elements were analysed at the School of Earth, Atmospheric and Life Sciences, University of Wollongong. Whole-rock major- and trace-element X-ray fluorescence (XRF) analysis was carried out using a Spectro-Analytical Instrument (XEPOS) energy-dispersive spectrometer fitted with a

Si-diode detector, following the methods of Norrish and Chappell (1977). Major elements were measured on samples fused with Li borate, whereas trace elements were analysed from pressed pellets bonded with polyvinyl acetate (PVA). Calibration was made against a wide range of international reference materials and laboratory standards previously calibrated against synthetic standards. Loss-on-ignition was determined by heating a separate aliquot of rock powder at 1000°C. For a broader range of trace elements and the rare earth elements (REE), several methods were used. For bulk samples of rocks with overall high trace element abundances, samples were analyzed commercially at the Australian Laboratory Services (ALS) at Brisbane, Australia, using inductively coupled plasma mass spectrometry (ICP-MS; geochemical procedure ME-MS81). A prepared sample is added to lithium metaborate/lithium tetraborate flux, mixed well and fused in a furnace. The resulting melt is then cooled and dissolved in an acid mixture containing nitric, hydrochloric and hydrofluoric acids. This solution is then analysed by ICP-MS. Standards, OREAS 120 and STSD-1, were duplicated for the run as well as 3 blanks, with a <10% tolerance of error.

For a transect over a stromatolite structure and adjacent sedimentary layers sedimentary rocks in the Snowpatch Formation Sandstone and Dolostone Member, analysis was undertaken by LA-ICP-MS at the Australian National University using a Lambda Physik 193 nm UV excimer laser-ablation system, equipped with a dual-volume ANU HelEx chamber, coupled to a Varian 820 quadrupole ICP-MS. After laser pre-cleaning, data were acquired for 39 masses by ablation along a

continuous transect across the sample perpendicular to bedding using an 800 μm by 20 μm slit moving at 10 μm per second. Laser operating conditions were 5 Hz, 24.9 MJ and 17.0 kV. NIST 612 glass was used for calibration and an in-house dolomite standard was analysed as a quality control standard. The transect was 2.66 cm long and 850 μm wide, and was broken into 200 μm segments. This produced a large data cloud (133 analyses in supplementary data Table 1). The data were calibrated assuming $\text{Ca} = 200,000$ p.p.m., a value suitable for ferruginous dolomite. However, as this transect passes over a mosaic of dolomite + quartz $\pm$ magnesian biotite grains, this normalisation will only give accurate abundances when solely analyzing dolomite. Such transect parts are extracted as separate analyses and along with ‘spot’ analyses targeted on solely dolomite grains, are presented in Table 1. Because dolomite is the only calcareous mineral in the transect sample, the remaining transect parts with mineral species apart from dolomite will give abundances too-high via this calibration method. Therefore, appraisal below of transect data relies solely on elemental ratios, that will be immune to this normalisation issue.

5.2. *U-Pb zircon geochronology*

Zircons were concentrated using heavy liquid and isodynamic separation techniques at the mineral separation laboratory, Research School of Earth Sciences, the Australian National University (ANU). Using a binocular microscope, concentrates were hand-picked and selected grains, along with reference Temora zircons (Black et al., 2003), were cast into an epoxy resin disc. Once cured, the disc was ground to a mid-section level through the grains and then polished with 1 μm

diamond paste. Reflected, transmitted light and cathodoluminescence (CL) imaging was used to document the grains.

New zircon U-Th-Pb analyses presented here for samples G04/64 and G17/10 were undertaken on the SHRIMP RG instrument at the ANU (Table 2) following analytical protocols of Williams (1998). The raw data were reduced offline using the new ANU software ‘POXI-SC’ – a unified and more data-rich version of the old ANU software packages ‘PRAWN’ and ‘Llead’. Measurements of $^{206}\text{Pb}/^{238}\text{U}$ in unknown zircons were calibrated using the Temora standard (U-Pb ages concordant at 417 Ma; Black et al., 2003). The reference zircon SL13 (U=238 ppm) located in a set-up mount was used to calibrate U and Th in unknown zircons. The ISOPLOT program (Ludwig, 2003) was used to assess and plot the reduced and calibrated data. $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for close to concordant analyses were used to calculate ages.

5.3. Silicate whole-rock oxygen isotopes

Oxygen for isotopic analysis, at the University of Wollongong, was liberated from 9-12 mg of dried and thoroughly outgassed whole-rock powders by reaction with ClF_3 at 600°C. Isotopic analyses were performed on a dual-inlet PRISM III mass spectrometer. Linearity and proportionality of the $\delta^{18}\text{O}$ scale were maintained by analysing aliquots of three Oztech CO_2 gases with nominal $\delta^{18}\text{O}_{\text{VSMOW}}$ values of +10.59, +25.04 and +31.22‰, as unknowns, in every analytical session. The data are normalised to NBS-28 quartz ($\delta^{18}\text{O}_{\text{VSMOW}} = +9.64\text{‰}$; Coplen et al., 1983, Brand et al., 2014). On this scale, by direct analysis against NBS-28, the laboratory quartz working standard (UOW-Q) has a $\delta^{18}\text{O}_{\text{VSMOW}}$ value of +10.7‰, and is prepared and analysed

in each day's batch of ten ClF_3 reactions. All samples were analysed in at least duplicate and the data reproducibility (Table 3) is 0.1 to 0.3‰.

6. Stratigraphy and geochemical signatures

6.1. ~3710 Ma Solvang Volcanic Formation

The *Solvang Volcanic Formation* is the structurally and stratigraphically lowest unit considered here (Figs. 1-3). It is named as such because of relict pillow structures reported by Solvang (1999). The base of this formation is not observed and because of this and the ubiquitous heterogeneous deformation, its thickness can only be ascertained as >200 m. Especially in the fold closure containing the surviving stromatolites, the Solvang Volcanic Formation contains several occurrences of relict pillow structures. Where not obliterated by strain, asymmetry in pillow shape (Fig. 5A) indicates the younging direction in the pillowed rocks is always towards the adjacent Snowpatch Formation sedimentary rocks. In the antiformal fold closure shown in Figure 2, the Solvang Volcanic Formation is transitional upwards from massive, vesicular, (meta)volcanic rocks into the pillowed varieties. In which case, locally this unit might represent a single, thick (>50 m) subaqueous flow.

Other primary structures preserved in the Solvang Volcanic Formation are vesicles, largely infilled by carbonate, but also quartz (e.g., Touret 2003; Fedo et al. 2001; Fig. 5B) and, where not obliterated by deformation, preserved are interpillow interstices infilled with carbonate + quartz and carbonate-filled fractures within the pillows (Fig. 5A). Pre-tectonic quartz followed by carbonate veining is common in the formation (Fig. 5C).

The Solvang Volcanic Formation's top is an unconformable contact (Nutman et al., 2009) with the Snowpatch Formation. In a few places this contact is not sheared, and there is no indication of a strain gradient towards it. For example at the classic 'round pebble conglomerate' locality ('RPC' on Fig. 1), the aspect ratio of the Conglomerate Member's quartz clasts does not change towards the sharp contact with adjacent Solvang Volcanic Formation metavolcanic rocks. In which case, the Solvang Volcanic Formation top contact is interpreted as a modified stratigraphic unconformity, rather than being a tectonic break. Also, within the area covered in Figure 2 at the spot marked 'U', the unconformity between the Solvang and Snowpatch Formations is exposed, again with no change in the aspect ratio of pillow structures, demonstrating minimal strain gradient and no shearing at the contact. However, in most places, particularly on fold limbs, this boundary is strongly sheared (Fig. 4A).

The Solvang Volcanic Formation is overall basic to basaltic-andesitic in composition with rare picritic units. Where trace elements are least affected by secondary alteration, they display HFSE (high field strength elements) and REE (rare earth elements) patterns similar to those found in arc-related rocks formed by fluid-fluxing of ultramafic sources (Polat and Hofmann, 2003; Nutman et al., 2015). This is exemplified by Nb/Yb – Th/Yb and primitive mantle normalised 'spider' diagrams (Figs. 6A, B). Key features are that all rocks fall in the arc volcanic array in the former plot, and that in the spider diagram they all reveal negative Ti anomalies relative to Eu and Gd, and negative Nb and Ta anomalies relative to Th and La.

Following Polat and Hoffmann (2003), rocks now consigned to the Solvang

Volcanic Formation are interpreted as a variegated suite of arc-like, pillowed to massive picrites, basalts and basaltic-andesites, erupted at 3720-3710 Ma. The pillowed structure indicates that most, if not all, eruption was subaqueous. Despite the largely undisturbed HFSE and REE signatures, these rocks do show evidence of alteration from their igneous compositions. This is already apparent in the field, because towards the unconformity, these overall mafic rocks show abundant disseminated fine-grained biotite. In terms of whole rock chemistry, this is reflected by the high K₂O content, coupled with strong loss of Na₂O (Figs. 6C, D; Nutman et al., 2017a). This signature is strongest closest to the contact with the overlying sedimentary rocks. Gain in K₂O and loss in Na₂O is coupled with depletion in Sr without change in Eu (Fig. 6B; ruling out igneous plagioclase fractionation) a strong increase in $\delta^{18}\text{O}_{\text{VSMOW}}$ in these rocks to $> +16\text{‰}$ (Table 3). This signature is typical of that found in less metamorphosed early Precambrian weathering profiles, both pre- and post- the Great Oxygenation Event (e.g., McFarlane et al., 1994; Polat et al., 2012). Solvang Volcanic Formation mafic rocks distant from such contacts and correlative elsewhere in the belt show more typical igneous $\delta^{18}\text{O}_{\text{VSMOW}}$ values down to +6 to +8‰ (Table 3, Fig. 6E and in Furnes et al., 2007). As a result, there is a positive correlation between K₂O/Na₂O and $\delta^{18}\text{O}_{\text{VSMOW}}$ (Fig. 6F). The association of the most pronounced low temperature alteration with the unconformity strongly suggests that the alteration process was subaerial weathering.

6.2. Snowpatch Formation (~3700 Ma)

The Snowpatch Formation is named as such, because for the past decades the key

outcrops with the most relict protolith sedimentary structures were covered for the summer field season by a snow patch, and thus evaded discovery by many geologists who repeatedly passed by it.

6.2.1. Conglomerate Member of the Snowpatch Formation

Recognised in the early 1970s (e.g., Allaart, 1976), a laterally discontinuous unit of conglomerates (Figs. 1-3) is named the *Conglomerate Member*. Its type locality (RPC on Figs. 1 and 7A) has diverse interpretations (e.g., Allaart, 1976; Dimroth, 1982; Nutman et al., 1984, 2017a; Appel et al., 1998; Fedo, 2000; Myers, 2001; De Wit and Furnes, 2013). The unit comprises layers of conglomerate set in a pelitic through semi-pelitic to sandstone matrix interspersed with sandstone layers largely devoid of clasts (e.g. Fedo, 2000; Fedo et al., 2001). Although Myers (2001) argued that this lithology is an entirely tectonic artefact, the sum of evidence from all localities indicates that it is a genuine sedimentary conglomerate, albeit deformed (Dimroth, 1982; Fedo, 2000; Nutman et al., 2017a). The most compelling evidence for a sedimentary protolith is the spectacular polymict nature displayed at lesser-known localities – with diverse clasts of volcanic rocks, ultramafic rocks, chert and pelite (Fig. 7B). The conglomerate varies considerably in thickness but with a maximum of <25 m.

On Figure 1 the locality where the Conglomerate Member has been studied in most detail is capitalised as ‘RPC’, whereas other known localities are shown as lower case ‘rpc’. At the RPC type locality, previous workers have documented the polymict nature, with biotite-amphibolite, coarse-grained polycrystalline quartz, and rare

layered chert clasts in a biotite-rich matrix (Dimroth, 1982; Nutman et al., 1984, 2017a; Fedo, 2000). The biotite-amphibolite clasts are interpreted as altered (weathered) mafic volcanic rocks (Nutman et al., 1984; Fedo, 2000). A likely origin of the mono-mineralic quartz clasts could be vein quartz (Nutman et al., 2017a). An additional source of the quartz clasts is recrystallised massive chert. This is because conglomerate lenses in less-metamorphosed and younger greenstone belts such as the base of the Strelley Pool Formation (≤ 3426 Ma, > 3350 Ma) of the eastern Pilbara Craton, contain quartz-rich clasts that are fine-grained chert or highly silicified volcanic rocks (Lowe, 1983; Van Kranendonk, 2006). Upon higher grade metamorphism combined with ductile deformation, these would be transformed into coarser-grained clear quartz as found in the Isua conglomerates.

At the RPC type locality, the original relationships with the adjacent lithologies are displayed. At the basal side, the conglomerate has a sharp contact with fine-grained massive biotite-rich garnetiferous amphibolites (Fig. 7C). Given their non-igneous K_2O/Na_2O ratios and elevated $\delta^{18}O_{VSMOW}$ value of +16.6‰, these rocks are interpreted to be altered Solvang Volcanic Formation metabasalt/andesite (sample G12/99, Tables 1, 3). On the other side, interpreted as the member's top, the conglomerate is in sharp contact with fine-grained layered dolomite and dolomite + quartz rocks with accessory magnesian biotite. At this locality, there is *no* shearing apparent on both contacts of the conglomerate and *no* change in the aspect ratio of the conglomerate's quartz clasts. This indicates that here, the conglomerate's boundaries are not tectonic breaks, and that at least locally there is not even a significant strain

gradient across them. Therefore, both the member's base and top are interpreted to be stratigraphic (albeit deformed), with an unconformity at its base with underlying Solvang Volcanic Formation and a sedimentary one with the overlying Snowpatch Formation Sandstone and Dolostone Member (Figs. 1-3).

At other Conglomerate Member localities (indicated as rpc on Fig. 1), the conglomerate and its contacts are mostly strongly deformed. However, at site rpc-1 (65°10.399'N 49°48.076'W; Fig. 1), within a tight antiform cored by the conglomerate, there is a single low-strain lens within the unit (Fig. 7B). This contains a diverse range of clasts, most notably ones of intermediate to mafic volcanic origin. These are poorly sorted, ranging from <5 cm to >30 cm across. Chemical analysis of one of these clasts (sample G17/35) is presented in Table 1 and on Figs. 6A, B, and indicates an arc-like basaltic-andesitic signature, as seen for the underlying Solvang Volcanic Formation.

The Conglomerate Member's most north-easterly occurrence (site rpc-2; Fig. 1) is in a steep slope, much of which is often obscured by a snow patch. It is in an antiform cored by Solvang Volcanic Formation pillowed vesicular metabasalts and picrites (e.g., samples G17/12 and 13, Table 1), and its upper contact is sheared, such that there are only lenses of the Sandstone and Dolostone Member between it and the overlying hanging wall allochthonous 'garbenschiefer' boninitic rocks. The clasts are diverse, and include ultramafic rocks and gabbro, together with the more common fine-grained volcanic and quartz nodule clasts. Within this unit is a distinct layer of quartz, garnet, amphibole and mica rocks with internal bedding (Fig. 7D). In the southern end of the

fold's core, this unit (sample G97/10) is garnetiferous, but on the fold limbs garnet is retrogressed to give amphibole + plagioclase symplectites.

Zircon U-Pb geochronology has been undertaken on the Conglomerate Member at its RPC type locality (Fig. 1). An early attempt by Nutman focused on the quartz nodules that are the commonest clast variety. This attempt failed to yield any zircons, demonstrating that the clasts are not detrital quartzite derived from silica-saturated granitic source rocks. Kamber et al. (2005) undertook a zircon study of a RPC conglomerate bulk sample, and recovered a single grain (Table 2). Two analyses of this yielded a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3740 ± 7 Ma. Additionally, two zircons have been recovered from another composite matrix and clast sample at the same locality (G04/64; Fig. 8A; Table 2). On grain #1, a small oscillatory-zoned prism, three analyses were undertaken. Site 1.1 is slightly discordant, with a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3691 Ma, and the other two concordant sites yielded a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3707 ± 20 Ma (95% confidence). A single analysis on grain #2, an oscillatory-zoned fragment yielded a concordant age, with a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3746 ± 46 Ma (2σ). The age of grain #1 agrees with the unconformably underlying Solvang Volcanic Formation rock ages (sample G05/22 with a zircon U-Pb age of 3709 ± 10 Ma), and the age on grain #2 agrees (within its large analytical error) with that obtained on a single grain from the conglomerate by Kamber et al. (2005).

Zircon U-Pb dating was attempted on samples from localities rpc-1 and rpc-2 (Fig. 1). The mineral separation of aluminous andesitic clast sample G17/35 from rpc-1 (whole rock Zr = 8 p.p.m.) yielded only two small zircons. Both have ages of only ~3

Ma and because they are laboratory contaminants, are not considered further here.

Sample G97/10 from locality rpc-2 is the metasedimentary unit of layered amphibole + garnet + quartz + mica rocks, probably derived from a siliceous marl. It gave a small yield of small zircons. Again, two have ages of ~3 Ma (zircons were separated from this sample in the same laboratory batch as G17/36) and as laboratory contaminants, are not considered further here. Four G17/10 grains yielded Eoarchean ages. All grains show variable amounts of recrystallisation superimposed over oscillatory zoning (Fig. 7E). Grains #2 and 8 are prisms up to ~100 μm long. Five analyses on these grains yielded ~3700 Ma $^{207}\text{Pb}/^{206}\text{Pb}$ ages, and range from concordant to slightly discordant (Table 2). The multiple analyses indicate a scatter well beyond analytical uncertainty (MSWD=3.7), with the scatter pointing to two episodes of loss of radiogenic Pb (Fig. 8B). Removing analyses 2.1 and 8.2 which are interpreted to have undergone significant Archean disturbance, results in a regression for analyses 2.2, 2.3 and 8.1 with an upper concordia intercept of 3719 ± 19 Ma (95% confidence, MSWD = 0.10; lower intercept 573 ± 690 Ma). This agrees well with the $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3717 ± 16 Ma for the most concordant analysis 2.2. Two other distinctly smaller grains (#1 and 3; $<50\mu\text{m}$ long), yielded somewhat older ages between 3800-3850 Ma. Two other small grains (#6 and 7) lacking oscillatory zoning in CL images and with very low Th/U of <0.01 yielded Neoproterozoic ages, and indicate rare zircon growth in Isua during Neoproterozoic metamorphism (see also sample 810318 in Nutman and Collerson, 1991). The assembled U-Pb zircon data on four samples from the conglomerate demonstrate that from the youngest zircons the *maximum*

depositional age is constrained at 3710-3700 Ma, and that there are also some smaller zircons that yield older ages (Fig. 8C). The poor yield of zircons from the conglomerate is in accord with the whole rock geochemistry, which indicates provenance largely from basaltic to andesitic silica-undersaturated sources (Kamber et al., 2005); lithologies that will contain only scarce magmatic zircons. Note that all detrital grains from this member are *older* than the rare, small volcanogenic zircons recovered from the overlying BIF Member, which have ages of just less than 3700 Ma (Fig. 8C; Nutman et al., 2009).

Several depositional environments have been suggested for the conglomerate. Dimroth (1982) proposed that it formed in a tidal channel, whereas Fedo (2000) suggested that it represents a mass flow deposit, proximal to exposed, weathered mafic volcanic sources. Nutman et al. (2017) suggested instead it could represent a 'lag' deposit, formed by reworking of regolith material into topographic lows on an erosional surface, with only minor transport of debris. Another possible interpretation offered here is that these conglomerates represent discontinuous berms (storm-generated beach ridges) on an erosional surface, succeeded by the finer-grained, lower energy Sandstone and Dolostone Member cross-bedded sandstone protoliths. However, all interpretations concur that the provenance of material is local, being largely derived from the marginally older underlying basement of basaltic-andesitic rocks, and thus likely formed in an arc-like setting (Polat and Hofmann, 2003; Nutman et al., 2014).

6.2.2. *Sandstone and Dolostone Member of the Snowpatch Formation*

The *Sandstone and Dolostone Member* of the Snowpatch Formation encompasses the stromatolite locality of Nutman et al. (2016), but is also recognised in other low strain zones. It has non-tectonic contacts with both the underlying Conglomerate and the overlying BIF Members. It is currently estimated to have a thickness of <100 m.

The Sandstone and Dolostone Member is dominated by a diverse suite of calc-silicate (mostly tremolite) $\pm$ quartz $\pm$ carbonate rocks. In Isua, the protoliths of such rocks are much debated. Because of the overall abundance of tremolitic amphibole ($\pm$ talc) in these rocks, some workers have interpreted such Isua lithologies as mafic igneous rocks penetrated by CO₂-rich fluids during metamorphism (e.g., Rosing et al., 1996; Myers, 2001). In this scenario, these rocks' chemistry would be unrelated to Eoarchean sedimentary environments.

However, detailed field investigations, particularly at the fold closure shown in Figure 2, provide very clear evidence that a verifiable origin of many Isua calc-silicate rocks is by metamorphic reaction in a protolith that contained quartz + dolomite (Nutman et al., 2016). In this scenario, if quartz and dolomite are present in a ratio of 3:4 and H₂O was dominant in the intergranular fluid phase, the resultant rock would be solid tremolitic amphibole (Winkler, 1974); at the confining pressure and temperature conditions established for this locality (e.g., Rollinson, 2002). Such massive, dark amphibole-rich rocks can in the field give the erroneous superficial appearance of altered mafic igneous rocks. If the quartz and dolomite ratios are different, then the resultant rocks will carry the assemblage tremolite + quartz *or* tremolite + carbonate.

Whether reaction between quartz and dolomite takes place at the established temperature of metamorphism (500-550°C; Rollinson, 2002), is governed by the grain boundary fluid phase composition during tectonothermal events. If high X_{CO_2} is maintained, then quartz + dolomite will remain in equilibrium (Nutman et al., 2016; Fig. 9A). On the other hand, if there is water influx leading to reduction in grain boundary X_{CO_2} , the reaction between quartz and dolomite is triggered, to produce calc-silicate minerals. This is illustrated on the outcrop scale, approximately 5 m from the site 'A' stromatolite locality of Nutman et al. (2016). On this outcrop, there is a kernel of dolomite + quartz rock layered on a scale of ~5 mm, which by the ingress of an H_2O -rich fluid has been converted into an amphibole-rich rock (Fig. 9B). Note, in this example, the alteration front is sharp, and discordant to the dolomite + quartz layering, that has been overprinted and destroyed. Such examples illustrate in an unambiguous fashion that the calc-silicate rocks widespread in the Sandstone and Dolostone Member result from alteration of a quartz + carbonate sedimentary protolith, and that they are *not* metasomatised mafic rocks. Thus, when Sandstone and Dolostone Member rocks are thoroughly hydrated, they can range in appearance from almost solid amphibole rocks, through to quartz-rich rocks with layers of amphibole. If strain remains low, the hydrated rocks will still display their original lithological layering from their sedimentary protolith. This is illustrated in Figure 9C, where a protolith with layers of originally different quartz:dolomite proportions has been converted into a rock with alternating quartz + tremolite layers (originally quartz + minor dolomite sandstone; *see* on Figure 9C) with layers with prominent amphibole

porphyroblasts + carbonate (originally of mixed quartz + more dolomite).

The first detailed studies on the Sandstone and Dolostone Member took place on quartz-rich rocks, on the northwestern limb of the fold shown in Figure 2 (Friend et al., 2008; Nutman et al., 2009). When these were investigated by us in the early 2000s, the nearby rocks with preserved depositional structures were always obscured by snow. These early 2000s samples (G04/54, 55A; Fig. 10A; Table 1) display seawater-like REE+Y PAAS-normalised (Post Archean Average Shale; Taylor and McLennan, 1985) patterns, with diagnostic positive Y anomalies relative to Ho and positive La and Ce anomalies relative to Pr and Nd. In terms of their Ca-Mg-Fe molecular proportions they fall between the field of dolomite-ankerite and ankerite/Fe-oxides (Fig. 10B). Other signatures are low abundance of Cr, Ni, Ti, Al and Zr, pointing to minimal input from mafic or felsic terrigenous sources (Table 1). Therefore the protolith quartz and dolomite/ankerite in these rocks was regarded to have equilibrated with low temperature surficial waters, indicating a sedimentary protolith.

The siliceous calc-silicate-bearing sample G04/54 displays a REE+Y marine-like trace element signature, albeit the abundances of total REE, Zr (13.5 ppm) and Al₂O₃ (1.72 wt%) are somewhat higher than typical for such rocks (Nutman et al., 2009). Therefore, it is interpreted as slightly contaminated with a volcanic or detrital component (Friend et al., 2008). G04/54 gave a small yield of zircons. In CL images, most grains are either non-luminescent or display complex recrystallisation domains. Therefore, only six grains with some relict oscillatory zoning were dated (Nutman et

al., 2009) Three grains were assessed to have ages of ~3707, 3731 (two analyses) and 3729 Ma, respectively (Table 2). The other three grains are much higher in U+Th, give younger discordant ages, and are interpreted to have lost radiogenic Pb in superimposed tectonothermal events. In strongly deformed likely correlatives of the Sandstone and Dolostone member in the western end of the Isua supracrustal belt, a similar age distribution of rare detrital zircons (3700-3710, ~3720 and ~3750 Ma) is found (Fig. 8C; Nutman et al., 2009)

In the early 2010s, the melting of the snow patch immediately west of the locality described above, revealed (meta)sedimentary rocks in a fold core low strain zones (Fig. 2; Nutman et al., 2016). The lowest strain area is dominated by quartz + dolomite rocks, in which alteration to calc-silicate minerals is minimal. The minor alteration is expressed by thin veins or more diffuse patches of calc-silicate minerals, formed when at peak metamorphism, water-rich fluids traversed along fissures across the equilibrium quartz + dolomite assemblages, triggering reaction. The main accessory phase in the Sandstone and Dolostone Member is magnesian biotite. A few distinct units also contain hyalophane (Ba-rich feldspar) ± pyrite.

In the low strain zone, there is preservation of cross-bedding in quartz-rich rocks (Fig. 9D). In quartz + dolomite rocks overlying the site 'B' stromatolite dolostone of Nutman et al. (2016), cross lamination with scour troughs is preserved (Fig. 9E; Nutman et al., 2017). The cross-lamination is hummocky, with clearly-developed erosional surfaces. This style of cross lamination is most widely developed in shallow water settings, particularly where there is repeated change of current direction, such as

controlled by tides (Van Kranendonk, 2006 and references therein). Such features indicate that the Sandstone and Dolostone Member quartz-rich protoliths are predominately clastic calc-arenites. However, with recrystallisation in more common levels of higher deformation, these clastic rocks have become coarser-grained and the cross-bedding is obliterated, giving rise to rocks that superficially resemble cherty chemical sediments (Fig. 9F; samples G04/54 and 55A). At the RPC locality (Fig. 1), where strain is also locally lower, the sedimentary clastic protolith of these interlayered quartz and quartz + dolomite rocks is also revealed by the preservation of fine scale layering within them.

An isolated outcrop of dolostone contains a lens of randomly-orientated shards of layered quartz-rich rock and dolostone, set in a more homogeneous quartz + dolomite matrix (Fig. 9G). Also present are lenses rich in quartz + hyalophane $\pm$ dolomite with disseminated pyrite. Also <2 m from the site 'A' stromatolite horizons and <1 m stratigraphically below them, there is a ~10 cm thick bed of similar rocks, in which the randomly-orientated clasts, some laminated, are well-displayed. The most likely origin of these rocks is as tempestites, when partly lithified layers of a shallow water sequence are ripped-up and jumbled by wave action, with the platy intracasts and slurry matrix locked into place once the wave-produced oscillating layer-parallel shear stresses have dropped below the deformation threshold (Seguret et al., 2001; Dibenedetto and Grotzinger, 2005). The Sandstone and Dolostone Member breccias are similar in geometry and scale to tempestites in the Pilbara (Australia) Paleoproterozoic shallow water sequences, such as in the Strelley Pool Chert Formation

(Fig. 9H)

The site 'A' stromatolites (Fig. 2; Nutman et al., 2016) are randomly distributed along three distinct layers (Fig. 11A). At the outcrop's base (stratigraphically higher) there is a poorly exposed additional layer, in which the stromatolites display distinct degradation of their form due to superimposed tectonothermal recrystallisation. At the outcrop's southwestern end, the stromatolites are also modified, with injection of carbonate veins sub-parallel to the bedding. The stratified interludes between the stromatolite horizons display varying proportions of quartz and dolomite, with some layers richer in magnesian biotite. There is a weak foliation in the outcrop, at a high angle to the stratification (Fig. 11A). In thin section this is revealed by some flakes of magnesian biotite orientated at a high angle to most biotite grains, which lie in the direction of stratification. The lower surface of the stromatolites is planar, with the stromatolite structures being distributed in an irregular fashion along the layers. In one instance, the outcrop displays a cluster of stromatolites, interfering with each other. The overlying layers are more quartz rich, and display onlapping lamination expressed by higher phlogopite content (Figs. 11A, B; Nutman et al., 2016).

Similar features are observed at the 'B' locality of Nutman et al. (2016). However in this case, the stromatolite mounds are expressed at the top of a single >15 cm thick dolostone (Fig. 11C). The overlying cross laminated clastic sedimentary rocks (see above) also display onlap laminae against the stromatolites (Fig. 11C). The case for the stromatolite's biogenic origin (Nutman et al., 2016) versus potential non biogenic origins is explored in fine detail in Nutman et al. (2019).

Given the repeated tectonothermal events with temperatures up to 550°C that these rocks have experienced, the upward-bowed stromatolite internal layering is weakly-preserved. However, layering degradation and carbonate replacement by silica are common in younger stromatolites, including those in the ~3,400 million-year-old Strelley Pool Chert Formation, universally-accepted as *bona fide* biogenic structures (Fig. 11D).

6.2.3. Banded Iron Formation Member of the Snowpatch Formation (~3695 Ma)

The *BIF Member* includes the ‘Iron Mountain’ BIF (Moorbath et al., 1973; Dymek and Klein, 1988; Nutman et al., 2009) by which Isua was discovered in the 1960s by the mineral exploration company Kryolitselskabet Øresund A/S (Kurki and Keto, 1966). Several banded iron formation samples have given low yields (a few grains per kilogram) of small (typically ~50 µm), stubby prismatic oscillatory-zoned zircons. These all yield an age of ~3695 Ma, have high Th/U ratios and REE trace element patterns indicating co-growth with plagioclase (a phase absent from the BIFs; Nutman et al., 2009). Consequently, these zircons are regarded as a minor volcanogenic (ashfall?) component, which give a ~3695 Ma proxy age of deposition of the BIFs (Fig. 1; Nutman et al., 2009). The BIF Member’s top is tectonic (Fig. 3) and thus its total thickness is unknown. However, judging from the extensive outcrops of it at the Iron Mountain, it must be >200 m thick.

Layering in the BIFs is mostly thin, with separation of quartz and magnetite ± amphibole into distinct anastomosing mesobands (Fig. 12A). This tectonic fabric was produced by the destruction and transposition of original sedimentary layering during

strong ductile deformation under amphibolite facies conditions, combined with metamorphic segregation of quartz and the recrystallization of Fe-bearing phases, mainly to magnetite. Associated with the BIF at Iron Mountain, particularly on its northwestern side, are thick units of quartz-rich rocks, with little or no magnetite, but carrying bands with calc-silicate minerals. Previously these have been assigned as metacherts, but based on appraisal of low-strain Sandstone and Dolostone Member quartz-rich rocks at the Figure 2 locality, these rocks could be strongly deformed and thoroughly recrystallised clastic calcarenites.

In low-strain domains in the BIF Member, preserved sedimentary layering, nodular diagenetic structures and mineralogical-textural relationships provide new insight into the deposition and diagenesis of these rocks (Nutman et al., 2017b). In low strain domains in the > 1 km thickness of intensely folded and possibly imbricated Iron Mountain BIF, pre-tectonic siliceous nodules reside in a fine-grained magnetite + quartz matrix (Fig. 12B; Nutman et al., 2017b). The pre-tectonic nodules consist of quartz + Fe-rich amphibole + accessory calcite $\pm$ accessory magnetite as a dusting of disseminated 5-10 μm grains (Nutman et al., 2017b). The nodule matrix is a fine-grained aggregate of magnetite + quartz, with the magnetite containing micron-scale inclusions of Fe-Mg silicate (amphibole?) and quartz (Nutman et al., 2017b). The nodules are interpreted as a metamorphosed analogue to the silica concretions formed during diagenesis of late Neoproterozoic – early Paleoproterozoic BIF, where patchy early silica cementation protected primary Fe-clay $\pm$ carbonate minerals from extensive oxidation and also the sedimentary structure from compaction

(Rasmussen et al., 2013, 2017). In other BIF Member low-strain lenses, sedimentary layering is preserved, albeit distorted by folding (e.g., Frei and Polat, 2007). In such cases layers are never entirely iron oxide, with always ≥ 20 wt% SiO₂ (Frei and Polat, 2007), which is compatible with the Fe-rich sedimentary layering reflecting post-depositional oxidation of Fe-clays giving rise to Fe-oxide + silica aggregates.

7. Discussion

7.1. High field strength element chemistry and provenance of the silica and carbonate rich sedimentary rocks

HFSE (High Field Strength elements) are widely applied to identify the source of igneous rocks, and the sediments derived from them (e.g., Taylor and McLennan, 1985; Kamber, 2009). This is because these signals are least modified in superimposed weathering alteration and metasomatism during superimposed tectonothermal events. The efficacy of the HFSE in identifying sources for Isua supracrustal belt basic igneous rocks is documented in detail by Polat and Hofmann (2003). Two representative plots are presented; Nb/Yb versus Th/Yb (Pearce, 2008) and a histogram of Ti/V (Figs. 13A, B). In the former plot, all data from the Sandstone and Dolostone Member (including the Laser Ablation transect over a stromatolite structure and bounding sedimentary rocks) form a cloud in the arc volcanic field, centred on typical compositions of the marginally older Solvang Volcanic Formation arc-like basalts and basaltic andesites and the allochthonous boninitic rocks (Polat et al., 2002; Fig. 13A). None of the data points falls within the mantle array containing N-MORB and E-MORB compositions.

In the Ti/Vi histogram, most compositions have Ti/V between 10 and 20, with most of the remainder have Ti/V <10 (Fig. 13B). Only a few analyses have slightly higher Ti/V, of up to 23. From appraisal of large amounts of Ti/V data, Shervais (1982) demonstrated that Ti/V values between 10 and 20 are typical of arc basalts, values <10 are found in low-Ti arc basalts and boninites, whereas MORB and Back arc basin basalts display Ti/V from 20 to 50. Therefore, the Ti/V data on the Sandstone and Dolostone and the BIF Members indicate their deposition in the proximity of an active convergent plate boundary, whose volcanic edifices were contributing small, variable amounts of material to the ~3700 Ma sedimentary rocks. Other strands of information support this conclusion. Firstly, the BIF Member contains rare small prismatic oscillatory-zoned zircons with typical chondrite-normalised REE spectrum of enrichment in HREE versus LREE and negative Eu anomalies, typical for igneous zircons (Nutman et al., 2009). Also, Frei and Polat (2007) demonstrated that some BIF Member Nd was derived from a juvenile source.

7.2. Geochemical traverses over a stromatolite and bounding sedimentary rocks

A laser ablation ICPMS traverse was undertaken along a ~2.66 cm transect over a stromatolite structure and the sedimentary layer above (Fig. 14A). Some analyses from this traverse were presented by Nutman et al. (2016), but here we explore the full data set, integrated into 200 µm segments, giving a total of 133 ‘analyses’ (Supplementary data Table 1). As explained in the analytical section, uniform calibration to Ca=200,000 p.p.m. along this traverse of variable mineralogy (pure dolomite to quartz-rich) means that this data set can only be viewed in terms of

element ratios, not in terms of absolute elemental abundances.

Several ratios are plotted on Figure 14B. These have been multiplied by factors of 0.001 to 1000, solely for the reason of making the diagram clearer to read. $\text{Pr}_{(\text{N})}/\text{Yb}_{(\text{N})}$ is used as a monitor of a seawater-like signature and is generally within the range observed for seawater (below unity). Values spiking to near unity indicate a significant terrigenous component present in that part. Likewise, $\text{Y}_{(\text{N})}/\text{Ho}_{(\text{N})}$ is above 1 for the entire traverse, pointing to a persistent seawater-like signature. Mg/Si is used as a proxy for dolomite versus quartz content, because in the traverse Mg is mostly within dolomite and Si is in quartz ($\pm$ phlogopite $\pm$ hyalophane). This signal shows more or less irregular scatter, indicative of traversing over a polygranular sample with at any one position variable amounts of quartz and dolomite present under the laser beam. Al/Si is presented as a proxy of quartz versus the other accessory silicate minerals magnesian biotite and hyalophane. In this instance, the abundance of magnesian biotite $\pm$ hyalophane is marginally less in the stromatolite layer compared with the bounding sedimentary rocks. This trend is mimicked very closely by Rb/Sr , which shows Rb being carried in the magnesian biotite.

7.3. *Where does all the sedimentary quartz come from?*

The Snowpatch Formation Sandstone and Dolostone Member has abundant quartz-rich rocks, and where these are least deformed, sedimentary structures such as cross-bedding indicate that much quartz was deposited as detrital grains (Figs. 9D, E). This might extend to the site 'A' (Nutman et al., 2016) stromatolites, whose mounds might have formed with quartz as well as dolomite. Silica-saturated granitic rocks are

absent as clasts in the Conglomerate Member or as significant volcanic or plutonic components in the underlying Solvang Volcanic Formation. Combining this with the rarity of detrital zircons in the Conglomerate and the Sandstone and Dolostone Members, it is unlikely that granitic rocks were the source of the quartz (this paper and Kamber et al., 2005; Nutman et al., 2009).

Therefore, an alternative quartz source needs to be identified. One possibility is that it originated from veins, vesicle infills and pillow interstices from the underlying Solvang Volcanic Formation rocks. For example, in modern deserts, low-angle land surfaces can be littered by quartz clasts derived from the substrate. The accumulation of such clasts on an erosional surface could at least explain the quartz nodules that abound in the Conglomerate Member. However, it is uncertain if this could be the source of many orders of magnitude more quartz in the overlying Sandstone and Dolostone Member.

An alternative explanation is that much of this quartz could have been precipitated as granules from the silica-saturated Archean ocean, and then was reworked as detrital material in a shallow water environment to form clastic sandstones. In recent years such a model has been used to reinterpret some Archean ‘chert’ silica-rich sedimentary rocks as detrital, rather than previously as direct *in situ* chemical precipitates (Stefurak et al., 2014). In a detailed petrographic examination of well-preserved Paleoarchean ‘cherts’ from southern Africa and Western Australia, Stefurak et al. (2014) documented that the protoliths contained detrital granules of quartz, in a quartz cement.

Archean seawater was likely close to saturation for silica (Siever, 1992). Silica solubility is less at lower temperatures and is favoured by mildly acidic water (Siever, 1962; Iler, 1979). Given that the early atmosphere was probably more CO₂ rich (Kasting, 1987; Nutman et al., 2017b) commensurate acidic water would therefore have favoured precipitation of silica from seawater. Previously, it has generally been assumed that silica was precipitated as continuous layers, but the observations of Stefurak et al. (2014) indicate that precipitation as granules is most likely. Once formed, granule transportation and reworking could give rise to cross-laminated clastic sedimentary rocks in the Sandstone and Dolostone Member. With deformation and metamorphism, such subtle textures would be obliterated, as demonstrated by the transition ~50 m laterally into coarsely-recrystallised quartz rich rocks with tremolite and carbonate seams as layers (G04/54, -54A site, Fig. 2). Consequently, when observing strongly deformed quartz rich ± tremolite ± carbonate rocks, it is no longer possible to establish whether they were deposited directly from the water column as cherts, or if they are recrystallised clastic rocks, with the protolith depositional textures entirely obliterated.

7.4. Origin of dolomite

Dolomite is the dominant carbonate in the Sandstone and Dolostone Member, and its origin is explored here. Dolomite (encompassing here magnesian ankerite) is a common low temperature sedimentary and diagenetic mineral in carbonate sediments from sabkha to deep ocean environments (e.g., Wright and Wacey, 2005). More than two centuries of intense research, numerous low-temperature physico-chemical

experiments, including one running for >30 years at 1000 times oversaturation, have failed to precipitate dolomite without biomediation (e.g., Land, 1998; Wright and Wacey, 2004). Precipitation of dolomite from a fluid or by replacement of CaCO_3 has only been produced experimentally at higher temperature hydrothermal conditions (e.g., Lumsden et al., 1995; Land 1998). Despite this, vast amounts of sedimentary (low-temperature) dolomite are present in the geological record, especially in the Precambrian.

Anaerobic microbial mediation is documented to precipitate dolomite in modern groundwater-basalt systems and sediments (e.g., Roberts et al., 2004; Wright and Wacey, 2005), and this process has been replicated in the laboratory under controlled conditions (e.g., Vasconcelos et al., 1995; Roberts et al., 2004; Wright and Wacey, 2004, 2005). This makes a compelling case that microbial mediation is essential for low-temperature precipitation of dolomite in saline solutions.

Linked with the presence of REE+Y seawater-like trace element signatures in the Sandstone and Dolostone Member, the above reasoning and observations make a robust case that this formation's low temperature dolomite is of biogenic origin (Nutman et al., 2016). However, as noted above, low strain zones in this formation indicate the preponderance of clastic sedimentary rocks. Thus, it is likely that much dolomite was not formed *in situ*, but was reworked in the high energy shallow marine environment. This will also extend to the stromatolites, which from study of better-preserved younger varieties, will consist of an accumulation of detrital granules of quartz and carbonate, with additional biogenic carbonate cement. Such reworking

of carbonates is commonplace in the Phanerozoic sedimentary record. For example, the limestones of a highly productive Cenozoic carbonate shelf along the coasts of eastern South Australia and western Victoria were repeatedly reworked in the Ice Age, to form overlying calcarenite sequences (Murray-Wallace, 2018).

7.5. ~3700 Ma ocean chemistry

Oxygenated modern marine settings display marked negative Ce* (PAAS normalised) anomalies, whereas deeper anoxic waters lack these negative anomalies (e.g., German and Elderfield, 1990). The ~3700 Ma Isua samples are all devoid of negative Ce* anomalies, pointing to an anoxic environment (Bolhar et al., 2005; Friend et al., 2009; data in this paper) as is in accordance with sulfur mass-independent-fractionation (S-MIF) anomalies in BIF that we ascribe to the Snowpatch Formation BIF Member (data in Whitehouse et al., 2005; Papineau and Mojzsis, 2006). MIF signatures also occur in pyrite of the Sandstone and Dolostone Member (Avila, Bennett and Nutman unpublished data). As with all Archean sedimentary rocks displaying seawater-like REE+Y patterns, the Sandstone and Dolomite and the BIF Member rocks display Pr/Yb* (PAAS normalised) in the range 0.2 to 0.4, compared with post-Great Oxygenation Event (GOE) event examples, where Pr/Yb* ranges to >1.0 (e.g., Planavsky et al., 2010). This is because in post-GOE redox-stratified basins, REE fractionation increases markedly across a redoxocline (e.g., Sholkovitz and Elderfield, 1988). This strong effect is not seen in the Isua ~3700 Ma rocks, due to the entire ocean column being anoxic. Instead, in the Archean with increasing water depth, there is a more subtle Pr/Yb* fractionation and

increase in Y/Ho, which is likely due to aquatic REE processing along a gradient related to water depth (Kamber and Webb, 2001; Planavsky et al., 2010). In an Archean water-depth model correlating with REE+Y chemistry, these features are related to an iron concentration chemocline, rather than a redoxocline at younger times (Planavsky et al., 2010). Incorporating facies relationships of shallow water (Mg-Ca) carbonates and silica-rich rocks and deeper-water banded iron formation (e.g., Bekker et al., 2010), Pr/Yb* fractionation and increase in Y/Ho should also correlate positively with Fe/Mg (Planavsky et al., 2010).

To identify clean seawater-like signatures in ‘chemical’ sedimentary rocks, it is first necessary to apply stringent filters to remove samples with significant terrigenous and/or volcanic input (Kamber et al., 2014). This is because the input of LREE from such sources will distort the Pr/Yb* fractionation and eventually obliterate the seawater signature. This is clearly shown by the non-seawater-like REE+Y pattern of Fortescue Group stromatolites deposited in a non-marine, probably lacustrine setting (Bolhar and Van Kranendonk, 2007). This is also demonstrated for the Snowpatch Sandstone and Dolomite Formation (analysis A-2 in Nutman et al., 2016, and reproduced here on Fig. 10A), with A-2, a more marly layer, having a distinctly higher Pr/Yb* and reduced Y/Ho. However, at modest contamination levels, the HREE and Y/Ho will be less disturbed. Elements for filtering the data are high Al, Th, Ti, Rb and Zr (e.g., Nutman et al., 1989; Kamber et al., 2010). Most Sandstone and Dolostone and the BIF Member samples contain detectable non-seawater components, as demonstrated by low yields of volcanogenic zircons (Nutman et al., 2009), and

variable amounts of disseminated magnesian biotite, which reflects a minor mud component in the protolith sediment (Nutman et al., 2016). Thus for assessing Pr/Yb* variation, any samples with >10 ppm Ti, >1 ppm Zr, >1 ppm Rb and >0.5 ppm Th have been rejected here. This results in data at the two extremes of Fe/Mg; the ‘clean’ IFG (international BIF standard from the Iron Mountain) analyses (Govindaraju, 1995; Bolhar et al., 2005) and targeted carbonate within the ‘site A’ stromatolites of Nutman et al. (2016). These data comply with the observations of facies variation in Archean seawater-like signatures of Planavsky et al. (2010); with a positive correlation between Fe/Mg and Pr/Yb*, Y/Ho (Fig. 15A, B). Additionally data from Frei and Polat (2007) from a single sawn block of BIF can be used. However, in that paper, the only major elements reported are SiO₂ and Fe₂O₃. On the assumption that shortfall in the totals of these analyses is due entirely to missing MgO and not MgO + CaO (and other elements), maximum Fe/Mg ratios can be calculated. This dataset also has to be filtered, because some REE+Y spectra deviate from ‘clean’ seawater signatures, which in some analyses (e.g. 491243-A) is linked with high Rb, Sr and Zr. The remaining analyses provide additional high Fe/Mg points, which like the IFG analyses, display higher Pr/Yb* and Y/Ho than the dolomites. These geochemical traits are incorporated into the basin reconstruction shown in Figure 16.

Of additional note is that the depletion of LREE and high Y/Ho in the BIF Member is not consistent with precipitation of Fe-oxides in a transition zone between oxic and anoxic water. This pattern rules out oxides being the original Fe-bearing phases in the ~3700 Ma Isua BIF sediment protolith. Oxides not being the first Fe-bearing phases in

Isua BIF, is also supported by detailed petrographic studies of rare low strain zones in Isua BIFs (Nutman et al., 2017) and as summarised above. This comes from two observations. First, in magnetite-rich BIF, diagenetic silica nodules encapsulate disseminated early Fe-bearing silicate minerals absent outside of the nodules. Secondly, where diagenetic silica concretion has not occurred, Fe rich layers consist of micro-mosaics of quartz and magnetite instead of solid magnetite. These mosaics are interpreted as post-depositional partial oxidation of primary iron-silicate clay minerals such as greenalite (Nutman et al., 2017). Such petrographic and mineralogical observations match those made on younger banded iron formations (e.g., La Berge, 1964; Rasmussen et al., 2013, 2017).

7.6. REE+Y normalisation using PAAS – appropriate for Archean rocks?

For sedimentary rocks, it is convention to normalise REE+Y abundances to a reference like PAAS (Post Archean Average Shale of Taylor and McLennan, 1985) or MuQ (alluvial sediment composite of Kamber et al., 2005). Using PAAS normalisation, modern seawater displays enrichment from Pr to Lu, but with enrichment of La relative to Pr (expressed as $La_n/[Pr_n \times (Pr_n/Nd_n)^2]$), a distinct positive anomaly of Y relative to Ho (i.e. suprachondritic Y/Ho ratio) and a subtle positive Gd anomaly relative to Tb (expressed as $Gd_n/(Tb_n^2 \times Sm_n)^{1/3}$; Fig. 15C; from Zhang and Nozaki, 1998). This pattern is derived from the modern geochemical ‘profile’ of dissolved material in the oceans, formed when (continental) fluvial REE + Y flux meets seawater in estuarine or coastal regions (see Lawrence and Kamber, 2006 for review). However, does the uniform application of PAAS for normalisation,

regardless of the sedimentary rock's age and provenance, end up distorting data? As pointed out by Kamber (2010), in an Archean world dominated by a flux of dissolved material from exposed mafic-tonalite rather than average granodioritic crust, normalisation using PAAS (or MuQ) will lead to distortion, particularly rotation, of the classic seawater REE + Y signature.

Any normalisation scheme (e.g., PAAS or N-MORB) will demonstrate the following features of a seawater-like REE+Y signature (La enriched over Nd and with suprachondritic Y/Ho, and even the subtle positive Gd anomaly; Table 1). This is illustrated in Figure 15C, where the REE+Y abundances for the internal part of a Sandstone and Dolostone Member locality 'A' stromatolite (data from Nutman et al., 2016) have been normalised using different compositions; N-MORB, PAAS, sample G05/22 (weathered andesite from the Solvang Volcanic Formation's top) and sample G04/86 (fresh andesite from the Solvang Volcanic Formation).

Normalising using PAAS gives a Pr_n/Yb_n slope on the low side of that seen for modern sea-water (Fig. 15C). N-MORB and fresh, unaltered Solvang Volcanic Formation metabasalts such as G04/86 give too-high Pr_n/Yb_n , values (>0.5), again demonstrating that these are unlikely representative of the dissolved load. Normalising using weathered basaltic-andesitic rock G05/22, gives rise to Pr_n/Yb_n of ~ 0.25 , a value similar to modern shallow seawater (as reviewed by Kamber et al., 2014). This suggests that a weathered mafic to intermediate volcanic source was the REE input into seawater, and best represents the REE+Y contribution to the Sandstone and Dolomite Member sedimentary rocks.

7.7. 3700 Ma depositional environment

Figure 16 illustrates a paleoenvironmental reconstruction for the Solvang Volcanic and Snowpatch Formations. A basement of basaltic to basaltic andesitic and more rarely picritic rocks of island arc-like chemical affinity is the stratigraphically-lowest unit. These were variably weathered, as demonstrated by $\delta^{18}\text{O}_{\text{VSMOW}}$ to $>+16\%$, with gain of K and loss of Na due to clay minerals replacing plagioclase (Fig. 6). Locally the unconformity is marked by the Snowpatch Formation Conglomerate Member, which contains clasts of variably-weathered mafic to intermediate arc rocks, quartz derived from veins, inter-pillow infills and chert. Thus provenance is proximal and from the underlying mafic volcanic sequence (e.g., Fedo, 2000; Nutman et al., 2017a).

The Sandstone and Dolostone and the BIF Member sedimentary rocks all show seawater-like REE+Y signatures, quite distinct from signatures seen in other environments where quartz and carbonate may be formed, such as hydrothermal discharges and lacustrine environments (Kamber et al., 2014). This contrast is demonstrated by the REE+Y PAAS-normalised trace element pattern of a metasomatic magnesite vein (sample G17/38; Table 1) cutting the Sandstone and Dolostone Member, ~20 m from 'site A'. This shows strong REE fractionation, without positive La and Y anomalies (Fig. 10A), very high Ni (>500 ppm) and low Sr (<5 ppm). In the low strain lens where sedimentary structures are preserved best, structures such as the tempestite breccias and cross-lamination support shallow water deposition. This is in keeping with these rocks having been deposited unconformably on an eroded, weathered surface of volcanic rocks. The sporadic elevated barium

contents are suggestive of, but do not prove, restricted basin evaporative conditions. Therefore these rocks are interpreted as a ~3700 Ma transgressive sequence over a mafic volcanic basement, with first shallow water dolomitic rocks, and then with deepening water, the deposition of BIF.

Despite the metamorphism of Isua rocks to amphibolite facies, low strain domains in them show that this stratigraphy has close lithological similarities to transgressive sequences preserved in Paleoarchean (~3400 Ma) North Pole Dome area volcanic and sedimentary rocks of the Pilbara Craton, Western Australia (e.g., Van Kranendonk et al., 2019 and references therein).

7.8. 3700 Ma Paleogeographic setting and geodynamic framework

In a broader paleogeographic context, we regard the Solvang Volcanic Formation and the Snowpatch Formation as both life stages of a maturing arc, rather than the Snowpatch Formation representing a passive margin developed on an arc whose activity terminated at ~3710 Ma with the Solvang Volcanic Formation. The reason for this is that the BIF Member of the Solvang Formation contains sparse tiny prismatic, euhedral, oscillatory-zoned (igneous) zircons, whose REE chemistry indicates that they equilibrated with plagioclase (a phase absent in the BIFs; Nutman et al., 2009). These zircons are interpreted as originated from distal ash-fall from renewed volcanism. Although volcanic rocks as young as 3695-3690 Ma have not been located in the Isua supracrustal belt, the gneiss 'dome' to the north (Fig. 1) is dominated by tonalites of that age and contains sparse enclaves of 3710 Ma diorites – matching the 3710 Ma andesites of the Solvang Volcanic Formation (Nutman et al., 2015, 2017a

and references therein). We contend that the unconformable Snowpatch Formation (with its three Members of sedimentary rocks) represents a brief hiatus in arc volcanism, with (distal) volcanism resuming for ~3695-3690 Ma.

This study adds to the growing body of evidence from the rock record for formation of ~3700 Ma arc-related assemblages. This originates from geochemistry via recognition of boninites (Polat et al., 2002) and basalts whose REE, Nb-Ta and Ti signatures indicate shallow mantle fluid-fluxing of peridotites rather than anhydrous decompression melting (e.g., Polat and Hofmann, 2003). The chronology of the ~3700 Ma Inner Arc Group also matches that of a maturing arc (*sensu* Shervais, 2001), with early ~3720 Ma basalts and boninites, followed by ~3710 Ma andesites, and then the northern ‘dome’ extensive 3695-3690 Ma tonalites as the proxy for dacitic volcanic rocks of that age (Nutman et al., 2015, 2017a). Additionally, tectonic evidence such as Eoarchean thrust sheets of ~3720 Ma boninites as the hanging wall over the ~3695 Ma BIF Member of the Snowpatch Formation and also intercalations in the Inner Arc Group of ≥ 3720 Ma upper mantle peridotites exhumed from depths equivalent to >2 GPa with sub-arc geochemical signatures and olivine fabrics (Friend and Nutman, 2010; Kaczmarek et al., 2016) indicate crustal shortening and juxtaposition of unrelated crustal and mantle rocks). On the modern Earth, such successions, chronological sequences and tectonic features reflect convergent boundary plate tectonic processes and thus provide another line of argument for plate tectonics on the early Earth. Alternatively, models calling for formation of early crust of the type preserved in the Isua supracrustal belt by stagnant lid processes need to be able to

provide an explanation for creation of arc-like sequences, chronologies and tectonic architecture in the absence of some form of subduction of once near surface material.

7.9. 3700 Ma environments and the diversity of early life

Rosing (1999) supported by Ohtomo et al. (2014) and Hassenkam et al. (2017) conclude that micro-flakes of low $\delta^{13}\text{C}_{\text{VPDB}}$ graphite in ~3700 Ma deep-water volcano-sedimentary greywackes in the northwestern Isua supracrustal belt represent organic carbon derived from deceased planktonic microbes, that fell to the seafloor. Combined with the evidence of stromatolites presented by Nutman et al. (2016), this demonstrates that at 3700 Ma life was already ecologically diverse, with planktonic habitation of open seawater (evidenced by Rosing's graphite as a proxy) and sessile organisms inhabiting a shallow water setting (the stromatolites of Nutman et al., 2016).

On the modern Earth, microbial life forming biomediated dolomite has been detected at depths of >1 km in fissured volcanic rocks (Roberts et al., 2004). In the low strain zones in the Solvang Volcanic Formation there are carbonate-bearing interpillow voids and also evidence of early (pre-tectonic) fissuring and emplacement of carbonate and quartz veins. Such sites represent an as-yet unexplored niche to seek evidence of life at ~3700 Ma.

8. Conclusions

(1) In the Isua supracrustal belt's northeastern domain (Fig. 1), there is a recognisable stratigraphy; the ~3710 Ma Solvang Volcanic Formation is unconformably overlain by

the Snowpatch Formation comprising the laterally-discontinuous Conglomerate Member succeeded by the more extensive Sandstone and Dolostone Member and then the ~3695 Ma BIF Member. The exposed top of the BIF Member is an Eoarchean thrust, with a hanging wall of older (>3712 Ma) boninitic volcanic rocks.

(2) Sedimentary rocks in the Sandstone and Dolostone Member display diverse shallow water sedimentary structures with locally interbedded stromatolites.

(3) The Snowpatch Formation is a transgressive sequence over a weathered, slightly older sequence of volcanic rocks (Solvang Volcanic Formation) erupted in an arc-like setting. The Sandstone and Dolostone Member was deposited in shallow water above the storm wave base, whereas the succeeding BIF Member was deposited in deeper water below the iron chemocline.

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Figure Captions

Figure 1. Geological map of the northeastern domain, Isua supracrustal belt.

Figure 2. Detailed geological map where the Snowpatch Formation depositional structures are best preserved.

Figure 3. Schematic cross section, indicating the relationships and geochronological age constraints on the units described in this paper. Note that this comprises information gathered from more than one locality, and therefore should not be regarded as an accurate stratigraphic log.

Figure 4. (A) Cartoon demonstrating the differing strain states along the boundary of the boninitic amphibolites with other lithologies, and the contact between the Solvang Volcanic Formation and the Snowpatch Formation. (B) Geological map of part of the northwest Isua supracrustal belt. See text for explanation.

Figure 5. Solvang Volcanic Formation volcanic structures. (A) volcanic pillow structure (P; 65°10.765'N 49°48.208'W), where the asymmetry in shape indicates younging direction (arrow) and showing triangular interstice between pillows infilled by carbonate and quartz (int). Blue pen (right) for scale. (B) Vesicles within vesicular basalt. The infill is mostly quartz. (C) Pre-tectonic quartz followed by carbonate veining of vesicular basalt. B and C are at the same locality (65°10.768N 49°48.141'W). (D) Pillow structure in picrites, Solvang Volcanic Formation at the rpc-1 locality of Figure 1 (65°10.840N 49°47.305'W). A5 notebook for scale.

Figure 6. Solvang Volcanic Formation and felsic clast geochemistry. (A) Nb/Yb – Th/Yb plot. (B) Primitive mantle normalised trace element plot. (C) Na₂O – K₂O (wt%) plot. (D) M (mafic) – F (felsic) - W (weathering) indices plot. (E) Histogram of oxygen isotope data for Solvang Volcanic Formation igneous rocks ($\delta^{18}\text{O}_{\text{VSMOW}}$). (F) $\delta^{18}\text{O}_{\text{VSMOW}}$ – K₂O/Na₂O plot. Symbols the same on (A), (C), (D) and (F).

Figure 7. Conglomerate Member field relations and zircon images. (A) Conglomerate at the type locality. Quartz nodule (q) and mafic schist (m) clasts are indicated. (B) Low strain area in rpc-1 occurrence of the conglomerate, showing abundant large polymict mafic to intermediate fine-grained volcanic clasts. (C) Non-tectonised contact of the RPC with underlying altered Solvang Volcanic Formation basaltic-andesitic volcanic rocks, indicated by red arrow. Pen in foreground (ringed) for scale. (D) Garnetiferous marly/sandstone unit associated with the conglomerate at the rpc-2 locality (65°10.840N 49°47.305'W; Fig. 1). (E) Cathodoluminescence images of rare zircons from the Conglomerate Member, sample G17/10 from the rpc-2 locality. (F) Conglomerate lens at the top of the Mt. Ada Basalt unconformably below dolostones with stromatolites of the Strelley Pool Formation, Pilbara Craton (21°11.740'S 119°18.392'E). Note the large amount of chert clasts derived from chert lenses and layers in the Mt. Ada Basalt.

Figure 8. (A) $^{238}\text{U}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ concordia plot of sample G04/64 zircons. (B) $^{238}\text{U}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ concordia plot of sample G17/10 Eoarchean zircons. (C) $^{207}\text{Pb}/^{206}\text{Pb}$ age histogram and cumulate frequency distribution of rare zircons extracted from the Conglomerate Member. In A, B and C errors depicted at the 2 σ level.

Figure 9. Sandstone and Dolostone Formation geological relations. (A) Back-scattered electron image of equilibrium quartz (qtz) + dolomite (dol) $\pm$ magnesian biotite (phlog) assemblage within sedimentary rock at the stromatolite ‘A’ locality on Figure 2. Note also pyrite (py) partly oxidised to magnetite (mag). (B) Alteration of a finely layered quartz + dolomite rock into a coarse-grained tremolite-rich assemblage by influx of a water-rich fluid, <10 m from the stromatolite ‘A’ locality on Figure 2. The red arrow indicates the hydration front, behind which the tremolite has formed. (C) Metasedimentary rock with alternating sandstone (now tremolitic quartzite; sample G17/08A in Table 1) and quartz + dolomite layers (now tremolite porphyroblasts + carbonate; sample G17/08B in Table 1). (D) Cross bedding in sandstones, <50 m from the stromatolite localities on Figure 2. (E) Scouring troughs in laminated quartz + dolomite sandstone capping dolostone of the site ‘B’ stromatolite locality (Nutman et al., 2016). (F) Deformed quartz-rich calc-silicate-layered rocks at the samples G04/54, -55 locality, approximately 50 m from the cross bedded sandstones shown in frame (D). The increased deformation with recrystallisation has obliterated any sedimentary structures. (G) Tempestite breccia associated with dolostone close to the stromatolite ‘B’ outcrop. (i) Tempestite in the Paleoproterozoic Pilbara Craton Strelley Pool Chert Formation (21°11.797’S 119°18.421’E).

Figure 10. Geochemistry of the Snowpatch Formation Sandstone and Dolostone and the BIF Members. (A) PAAS normalised REE+Y plot. (B) Molecular Ca, Mg, Fe plot.

Figure 11. (A) Best-preserved stromatolite layer in the site ‘A’ outcrop of Nutman et al. (2016). (B) All four sides of a rectangular cut block from a site ‘A’ stromatolite demonstrating the onlap of sedimentary layers overlying the stromatolite structures. (C) Transmitted light

photomicrograph of site 'B' stromatolite, demonstrating the onlap by overlying sedimentary layers. (D) Pilbara Craton Paleoarchean Strelley Pool Chert Formation stromatolites, showing extensive recrystallisation (rex) that obliterates their original layering (lay).

Figure 12. (A) Strongly deformed banded iron formation of the BIF Member. The original sedimentary layering has been destroyed, and replaced by a tectonothermal fabric of alternating discontinuous quartz-rich and magnetite-rich bands. (B) Pre-tectonic quartz nodules in banded iron formation at the Iron Mountain ($65^{\circ}12.339'N$ $49^{\circ}45.868'W$).

Figure 13. Snowpatch Formation Sandstone and Dolostone Member geochemistry. (A) Nb/Yb – Th/Yb plot. (B) Histogram of Ti/V ratios (MORB is mid-ocean ridge basalt, BABB is back-arc basin basalt).

Figure 14. (A) 133, 200 μ m-long segments of the LA-ICP-MS traverse of a site 'A' stromatolite and bounding sedimentary layers normalised to PAAS. (B) Various elemental ratios in the traverse.

Figure 15. (A) Pr/Yb* and (B) Y/Ho versus Fe/Mg plots for the Snowpatch Formation Sandstone and Dolostone and the BIF Members. (C) REE+Y normalisation modelling. A dolomitic portion of the locality 'A' stromatolite (Nutman et al., 2016) is normalised using different compositions (see text). Seawater values (pmol/kg) normalised to PAAS (p.p.m.) are at station F in the northwest Pacific (Zhang and Nozaki, 1998).

Figure 16. Reconstruction of the basin in which the Snowpatch Formation was deposited as a consequence of a transgression over the eroded and variably subaerially weathered ~3710 Ma Solvang Volcanic Formation volcanic rocks.

1392

1393 Table 1. Whole rock geochemistry

1394 Table 2. Summary of zircon U-Th-Pb data

1395 Table 3. Summary of O-isotope data

1396

1397 Supplementary Table 1. LA-ICP-MS geochemical traverse

Fig 3a. Generalised stratigraphy

For panels A, C, D & F

- Solvang Volcanic Formation picrites, basalts and basaltic andesites
- Round pebble conglomerate
- examples of unaltered ~3700 Ma diorite and tonalite

site 'A' stromatolite - sawn block

B

C

site 'B' stromatolite - thin section

~3695 Ma volcanic zircon from dust gives proxy for deposition time of the Snowpatch Formation BIF Member

Banded iron formation dominated by deposition of Fe-clay flakes and silica granules with silica cement, plus some turbiditic components. On the seabed, if early silica cement is limited, the Fe-clays are converted first to oxyhydroxides + more silica. In later diagenesis and/or metamorphism, these are converted into magnetite + quartz.

Proterozoic water column

Silica granules precipitating out of the Si-saturated ocean. Iron first precipitated as Fe-clays, dolomite forms in shallow water above the iron chemocline

Snowpatch Formation, BIF Member (~3695 Ma)

Magnetite banded iron formation With early diagenetic chert nodules

Snowpatch Formation, Sandstone and Dolostone Member

Dolostone, marl and siliceous rocks, with relict stromatolites, cross-bedding and tempestite breccias

Snowpatch Formation, Conglomerate Member

Lenses of locally-sourced conglomerate on unconformity

Unconformity (tectonised)

Solvang Volcanic Formation (~3710 Ma)

Picrites, basalts and basaltic-andesites (pillowed and massive). Variably weathered with high K/Na and high $\delta^{18}\text{O}_{\text{VSMOW}}$ values towards unconformity.

Table 1. Geochemical analyses

sample	G17/12	G04/86	G04/87	G17/13	G04/58	G12/99	G05/21	G04/61	G05/22
stratigraphy	S.Fm.	S.Fm.	S.Fm.	S.Fm.	S.Fm.	S.Fm.	S.Fm.	S.Fm.	S.Fm.
lithology	picrite	basalt	basalt	basalt	bas-and	bas-and	bas-and	bas-and	bas-and
age (Ma)	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	3709
lat. (N)	65°10.84'	65°10.28'	65°10.28'	65°10.84'	65°10.77'	65°10.14'	65°10.77'	65°10.90'	65°10.77'
long. (W)	49°47.31'	49°48.97'	49°48.97'	49°47.31'	49°48.20'	49°49.48'	49°48.21'	49°47.88'	49°48.21'
SiO ₂	41.09	46.40	50.45	52.16	59.76	60.54	60.75	60.81	63.04
TiO ₂	0.41	1.03	0.84	0.76	0.77	0.40	0.79	0.77	0.84
Al ₂ O ₃	4.80	13.40	11.01	8.51	12.38	11.50	12.54	12.29	13.36
Fe ₂ O ₃	11.63	19.45	17.17	12.10	11.99	10.79	10.53	8.59	7.67
MnO	0.24	0.30	0.25	0.21	0.36	0.23	0.27	0.26	0.25
MgO	21.24	7.08	7.56	12.05	3.38	2.24	3.00	2.82	2.85
CaO	7.63	10.29	11.11	10.31	3.51	3.99	2.00	6.15	3.17
Na ₂ O	0.15	2.46	2.10	1.86	0.51	0.13	0.67	1.58	0.65
K ₂ O	1.06	0.26	0.25	0.46	5.46	4.40	5.29	3.15	5.25
P ₂ O ₅	0.05	0.09	0.05	0.08	0.10	0.01	0.11	0.08	0.13
LOI	11.27			2.46	1.53	5.54	3.88	0.08	2.54
SO ₃	0.07			0.03		0.01			
total	99.64	100.75	100.78	101.00	99.75	99.77	99.81	96.58	99.77
trace elements p.p.m.									
Cr	578	162	358	1266	480	515	485	465	529
Ni	1590	100	132	452	87.8	125	107	69.1	89.9
V	80.1			137		143			
Rb	32.2	1.71	2.62	11.9	148	122	135	72.5	118
Sr	96.6	113	97.1	181	25.7	14.0	22.2	75.2	30.4
Ba	200	6.80	6.30	110	583	724	645	652	425
Y	6.9	21.0	18.1	13.8	17.6	8.0	15.4	16.3	20.6
Nb	2.10	2.79	2.23	3.60	4.08	2.00	4.32	4.23	4.65
Zr	49.3	76.5	59.0	78.7	116	42.0	117	115	126
Hf	1.50	2.26	1.75	2.30	3.26	1.00	3.35	3.22	3.58
Ta	0.13	0.18	0.13	0.23	0.32	bld	0.33	0.32	0.35
Th	0.89	0.66	0.50	1.43	4.10	bld	4.22	3.92	4.41
U	0.20	0.15	0.12	0.30	0.62	bld	0.61	0.74	0.73
La	6.90	5.52	4.55	11.8	15.9	19.0	13.1	17.4	15.5
Ce	15.9	14.3	11.6	26.9	35.0	3.8	30.1	37.3	34.2
Pr	2.10	2.17	1.77	3.61	4.34		3.71	4.55	4.25
Nd	9.70	11.0	8.99	15.9	17.6		15.1	18.5	17.7
Sm	1.95	3.46	2.79	3.36	3.87		3.26	4.02	4.03
Eu	0.43	1.19	0.96	0.86	1.12		1.05	1.18	1.13
Gd	1.71	4.08	3.39	3.08	3.73		3.14	3.90	4.05
Tb	0.24	0.71	0.62	0.45	0.61		0.52	0.64	0.70
Dy	1.34	4.09	3.59	2.73	3.38		2.92	3.44	3.96
Ho	0.26	0.82	0.73	0.52	0.67		0.58	0.66	0.77
Er	0.70	2.30	2.04	1.42	1.90		1.68	1.86	2.15
Tm	0.10			0.2					
Yb	0.60	2.06	1.76	1.15	1.74		1.59	1.67	1.84
Lu	0.08	0.30	0.25	0.18	0.26		0.24	0.25	0.27
methods	XRF-UOW	XRF-GA	XRF-GA	XRF-UOW	XRF-GA	XRF-UOW	XRF-GA	XRF-GA	XRF-GA

ICP-ALS ICP-ANU ICP-ANU ICP-ALS ICP-ANU

ICP-ANU ICP-ANU ICP-ANU

Stratigraphy: S.Fm. = Solvang Volcanic Formation; C.Mem. = Conglomerate Member; S-D.Mem. = Sandstone and dolomite
GPS positions according to the WGS84 datum. Samples without GPS positions were collected pre-1992

Major element (wt%) and limited trace element methods: XRF-GA = XRF at Geoscience Australia; XRF-Cph = XRF at the
Trace element and REE methods: ICP-ANU = ICPMS at the Australian National University; ICP-ALS = ICPMS at ALS Limited

G17/35	292285	G17/10	G17/08A	G17/08B	G17/09	G17/28	G18/02	G11/72	G11/63
C.Mem.	C.Mem.	C.Mem.	S.D.Mem.	S.D.Mem.	S.D.Mem.	S.D.Mem.	S.D.Mem.	S.D.Mem.	S.D.Mem.
clast	matrix	marl(?)	sst	dol-sst	sst	sst	sst	dol	dol
~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710	~ 3710
65°10.40'		65°10.84'	65°10.78'	"	65°10.90'	65°10.74'	65°10.74'	65°10.77'	65°10.77'
49°48.08'		49°47.31'	49°48.13'	"	49°47.87'	49°48.28'	49°48.28'	49°48.30'	49°48.29'
48.31	60.04	51.31	82.62	35.75	39.04	89.82			
0.30	0.59	0.49	0.01	0.02	0.06	0.12			
18.75	14.99	19.42	0.48	0.55	2.99	2.86			
8.86	13.97	19.19	3.18	15.12	9.13	3.21			
0.18	0.22	0.66	0.20	0.96	0.75	0.08			
1.30	2.11	1.92	1.67	9.26	7.54	0.33			
7.92	0.76	0.82	6.29	22.57	16.62	0.48			
0.45	0.23	0.40	< 0.04	0.26	0.51	0.28			
8.91	5.65	5.05	0.08	0.04	0.78	1.40			
0.02	0.04	0.00	0.00	0.07	0.04	< 0.01			
1.00		0.96	5.10	17.14	23.33	1.02			
0.41		0.43	0.01	0.01	0.01	1.16			
96.40	98.60	100.64	99.65	101.77	100.80	100.75			
602	779	576	416	88.4	149	374		140	210
233	115	163	18.8	45.4	21.2	29.1			
190		329	4.7	9.8	47.2	56.6	195		
95.7	163	118	2.10	3.50	18.1	22.6	36	17.0	22.4
98.7	6	16.1	7.3	23.7	62.6	7.2	20.1		
220	904	3701	42.5	8	937	5300	1560	9640	1295
6.1	13	16.7	0.8	2.6	3.0	0.8	6.9	8.0	6.6
0.8	2	1.2	0.8	0.7	0.7	0.7	4	0.6	0.5
8.4	51.0	22.6	1.2	2.7	3.8	12.1	51.6	14.0	9.0
0.4	1.43	0.7	2.0	3.3	4.0	0.4	1.5	0.5	0.3
0.05	0.09	0.07	0.05	0.05	0.05	0.05			
0.17	0.9	0.32	0.02	0.07	0.1	0.19	0.78	0.25	0.13
0.10	0.16	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.06
1.1	4.35	1.9	0.5	1.1	1	1.3	4.7	2.4	2.2
2.79	8.83	4.89	0.55	1.85	1.53	2.18	12.3	3.5	3.4
0.43	1.09	0.74	0.07	0.23	0.18	0.27	1.8	0.39	0.41
2.3	4.56	3.7	0.2	0.9	1	1.1	9.2	1.4	1.6
0.69	1.09	1.09	0.06	0.25	0.23	0.22	3.1	0.29	0.4
0.58	0.36	0.24	0.04	0.16	0.21	0.06	0.75	0.15	0.28
0.89	1.08	1.64	0.08	0.25	0.31	0.15	2.54	0.67	0.66
0.15	0.17	0.34	0.01	0.03	0.05	0.02	0.33	0.12	0.11
1	1	2.43	0.08	0.24	0.33	0.12	1.71	0.73	0.66
0.21	0.22	0.57	0.02	0.06	0.08	0.03	0.33	0.19	0.17
0.66	0.62	1.89	0.06	0.17	0.23	0.08	0.73	0.53	0.46
0.1		0.3	0.01	0.02	0.03	0.01	0.09	0.08	0.07
0.62	0.59	2.11	0.06	0.14	0.26	0.1	0.51	0.49	0.46
0.1	0.09	0.35	0.01	0.02	0.04	0.02	0.06	0.08	0.09
XRF-UOW	XRF-Cph	XRF-UOW	XRF-UOW	XRF-UOW	XRF-UOW	XRF-UOW		XRF-UOW	XRF-UOW

ICP-ALS NA-Risø ICP-ALS ICP-ALS ICP-ALS ICP-ALS ICP-ALS ICP-ALS ICP-ALS ICP-ALS

te Member; BIF.Mem. = BIF Member

› Geoscience Institute, Copenhagen; XRF-UOW = XRF at University of Wollongong
mitted, Brisbane; NA-Risø = Neutron activation at the Risø reactor facility, Denmark

G91/75	IFG	G04/81
BIF Mem.	BIF Mem.	BIF Mem.
chert'	BIF	pelite
3695	~3695	~3695
		65°12.34'
		49°45.87'
97.07	41.20	60.11
0.00	0.01	0.52
0.16	0.02	14.87
2.62	55.85	15.39
0.08	0.04	0.24
0.67	1.89	1.98
0.94	1.55	0.27
0.01	0.03	0.12
0.00	0.01	4.21
0.01	0.06	0.10
		1.40
0.01		0.48
101.58	100.67	99.70
12.6	4.00	101
8.07	22.5	57.8
0.391	0.040	106
1.61	3.00	7.13
1.0	1.50	1060
0.850	9.0	13.9
0.027	1.0	3.09
0.516	0.04	77.9
0.024	0.10	2.15
0.006	0.20	0.211
0.026	0.10	3.09
0.012	0.02	0.648
0.461	2.80	12.46
0.610	4.0	27.2
0.063	0.40	3.20
0.251	1.80	12.4
0.066	0.40	2.44
0.056	0.39	0.774
0.083	0.74	2.01
0.014		0.333
0.087	0.80	2.01
0.021	0.20	0.450
0.059	0.63	1.36
0.060	0.60	1.28
0.008	0.09	0.18
XRF-GA		XRF-GA

ICP-ANU

ICP-ANU

labels	site	U	Th	Th/U	comm	$^{238}\text{U}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	%conc
		ppm	ppm		206%	ratio	ratio	date (Ma)	
SM/GR/93/01 conglomerate (Conglomerate Member; Kamber et al., 2005)									
01a	m,osc,p	185	91	0.49	0.13	1.274 ± 0.034	0.3577 ± 0.0018	3740 ± 8	100
01b	e,osc,p	247	146	0.59	<0.01	1.132 ± 0.031	0.3573 ± 0.0035	3739 ± 15	109
G04/64 conglomerate clast and matrix at RPC locality (Conglomerate Member)									
1.1	e,osc,p,fr	223	109	0.489	0.73	1.368 ± 0.077	0.3463 ± 0.0029	3691 ± 13	96
1.2	e,osc,p,fr	203	98	0.481	0.21	1.309 ± 0.072	0.3501 ± 0.0032	3707 ± 14	99
1.3	e,osc,p,fr	246	117	0.474	0.09	1.303 ± 0.072	0.3499 ± 0.0033	3706 ± 14	99
2.1	osc,frag	201	93	0.463	0.16	1.283 ± 0.075	0.3592 ± 0.0054	3746 ± 23	99
G17/10 marl(?) at rpc-2 locality (Conglomerate Member)									
1.1	e,osc,eq	113	74	0.655	0.10	1.267 ± 0.017	0.3846 ± 0.0030	3850 ± 12	97
2.1	e,osc,p	391	186	0.476	0.13	1.357 ± 0.015	0.3433 ± 0.0016	3678 ± 7	97
2.2	e,osc,p	288	150	0.520	0.06	1.296 ± 0.015	0.3523 ± 0.0019	3717 ± 8	99
2.3	e,osc,p	201	106	0.526	0.38	1.440 ± 0.017	0.3481 ± 0.0025	3699 ± 11	92
3.1	e,osc,eq	126	29	0.232	<0.01	1.264 ± 0.017	0.3755 ± 0.0029	3814 ± 12	99
4.1*		257	132	0.512	44.09	3363 ± 432		3 ± 0.22	
5.1*		1516	588	0.388	<0.01	2346 ± 84		3 ± 0.10	
6.1	e,h,eq	1328	3	0.002	0.15	1.868 ± 0.019	0.1934 ± 0.0007	2771 ± 6	100
7.1	e,h,eq	39	0.1	0.002	0.55	2.003 ± 0.033	0.1884 ± 0.0050	2728 ± 43	96
8.1	e,osc,p	91	72	0.786	0.13	1.392 ± 0.019	0.3483 ± 0.0033	3700 ± 14	94
8.2	e,osc,p	52	38	0.736	0.80	1.338 ± 0.021	0.3435 ± 0.0050	3678 ± 22	98
G04/54 quartz, carbonate, tremolite rock (Friend et al., 2008; Sandstone and Dolostone Member)									
1.1	m,osc,eq	394	267	0.677	0.19	1.375 ± 0.063	0.3499 ± 0.0023	3707 ± 10	95
2.1	m,osc,p	960	549	0.572	0.21	1.401 ± 0.062	0.3399 ± 0.0114	3662 ± 52	95
3.1	m,osc,p	88	51	0.583	0.30	1.235 ± 0.073	0.3555 ± 0.0046	3731 ± 20	103
3.2	m,osc,p	114	67	0.585	0.16	1.341 ± 0.070	0.3555 ± 0.0046	3731 ± 20	96
4.1	e,osc,p	1496	970	0.648	0.23	1.471 ± 0.034	0.3110 ± 0.0011	3526 ± 5	95
5.1	m,osc,p,fr	260	162	0.621	0.07	1.235 ± 0.070	0.3552 ± 0.0107	3729 ± 47	103
6.1	e,osc,p	1817	1649	0.907	0.24	1.683 ± 0.044	0.2694 ± 0.0012	3303 ± 7	91

all uncertainties in the Table are given at 1 sigma
Site: x,y, x=grain number, y=analysis number. *=laboratory contaminant
Grain and site character: p=prism, eq=small aspect ratio prism, ov=oval, fr=grain fragment
m=middle of grain, e=edge of grain
Cathodoluminescence character: osc=oscillatory zoned, h=homogeneous
Common Pb correction: comm 206%= percentage of ^{206}Pb that is non-radiogenic, based on measured ^{204}Pb
and common Pb modelled as Cumming and Richards (1975) for likely age of rock

sample	type	$\delta^{18}\text{O}_{(\text{VSMOW})}$	$\pm 1\sigma$
G04/61	Solvang Volcanic Formation weathered andesite	14.7	0.1
G05/21	Solvang Volcanic Formation weathered andesite	15.7	0.1
G05/22	Solvang Volcanic Formation weathered andesite	16.8	0.1
G12/99	Solvang Volcanic Formation weathered andesite	16.6	0.1
G04/86	Solvang Volcanic Formation less-altered basalt	12.1	0.1
G04/87	Solvang Volcanic Formation less-altered basalt	12.6	0.1
G05/33	fresh basalt, Solvang Volcanic Formation correlative	6.9	0.1
G05/34	fresh basalt, Solvang Volcanic Formation correlative	8.3	0.1
G07/26	fresh basalt, Solvang Volcanic Formation correlative	8.2	0.1