**Paleoenvironmental and paleohydrochemical conditions of
dolomite formation within a saline wetland in arid northwest
Australia**

Caroline C. Mather^{1*}, Grzegorz Skrzypek¹, Shawan Dogramaci¹², Pauline F. Grierson¹

¹West Australian Biogeochemistry Centre and Ecosystems Research Group, School of
Biological Sciences (M090), The University of Western Australia, 35 Stirling
Highway, Crawley, WA 6009, Australia

²Rio Tinto Iron Ore, 152-158 St. George's Terrace, Perth, WA 6000, Australia

*Corresponding author:

Caroline C. Mather, The University of Western Australia,
M090, 35 Stirling Highway, Crawley WA 6009, Australia
caroline.mather@research.uwa.edu.au

22 **Abstract**

23 Groundwater dolocrete occurring within the Fortescue Marsh, a large inland wetland in
24 the Pilbara region of northwest Australia, has been investigated to provide
25 paleoenvironmental and paleohydrological records and further the understanding of low
26 temperature dolomite formation in terrestrial settings over the Quaternary Period. Two
27 major phases of groundwater dolocrete formation are apparent from the presence of two
28 distinct units of dolocrete, based on differences in depth, $\delta^{18}\text{O}$ values and mineral
29 composition. Group 1 (G1) occurs at depth 20 to 65 m b.g.l. (below ground level) and
30 contains stoichiometric dolomite with $\delta^{18}\text{O}$ values of -4.02 to 0.71‰. Group 2 (G2) is
31 shallower (0 to 23 m b.g.l.), occurring close to the current groundwater level, and contains
32 Ca-rich dolomite $\pm$ secondary calcite with a comparatively lower range of $\delta^{18}\text{O}$ values (-
33 7.74 and -6.03‰). Modelled $\delta^{18}\text{O}$ values of paleogroundwater from which older G1
34 dolomite precipitated indicated highly saline source water, which had similar stable
35 oxygen isotope compositions to relatively old brine groundwater within the Marsh,
36 developed under a different hydroclimatic regime. The higher $\delta^{18}\text{O}$ values suggest highly
37 evaporitic conditions occurred at the Marsh, which may have been a playa lake to saline
38 mud flat environment. In contrast, G2 dolomite precipitated from comparatively fresher
39 water, and modelled $\delta^{18}\text{O}$ values suggested formation from mixing between inflowing
40 fresher groundwater with saline-brine groundwater within the Marsh. The $\delta^{18}\text{O}$ values of
41 the calcite indicates formation from brackish to saline groundwater, which suggests this
42 process may be associated with coeval gypsum dissolution. In contrast to the modern
43 hydrology of the Marsh, which is surface water dependent and driven by a flood and
44 drought regime, past conditions conducive to dolomite precipitation suggest a

45 groundwater dependent system, where shallow groundwaters were influenced by
46 intensive evaporation.

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48 Keywords: dolocrete; Pleistocene; paleolimnology; northwest Australia; Pilbara;
49 inorganic geochemistry; sediment mineralogy; stable isotopes; paleohydrology

1. Introduction

Dolomite, $\text{CaMg}(\text{CO}_3)_2$, is a relatively common mineral in carbonate deposits worldwide, mostly within marine dolostone formed by replacement of limestone. However, in recent decades dolomite has been recognised more frequently in continental sediments, often occurring in saline evaporitic environments in proximity to saline lakes or playas, in arid climates (Müller et al., 1972; Last, 1990). Surficial dolomite precipitates from carbonate-rich ground or surface waters and encompasses a variety of forms including palustrine and lacustrine dolomite precipitated in wetlands and lakes (Alonso-Zarza, 2003) as well as groundwater and pedogenic dolomite that develop by replacement and cementation processes in the phreatic to vadose zone (Wright and Tucker, 1991). However, the processes controlling dolomite precipitation and dolomitization in terrestrial environments remain largely unknown. Precipitation of dolomite is strongly controlled by reaction kinetics and is inhibited at surface temperatures and pressures (Morrow, 1982a), although laboratory studies by Vasconcelos et al. (2005) and Wright and Wacey (2005) have demonstrated primary dolomite precipitation in the presence of sulfate-reducing bacteria. More recently, Zhang et al., (2012a; 2012b) observed abiotic nucleation and growth of disordered dolomite from high dissolved sulfide solution and later with dissolved polysaccharides; and Roberts et al., (2013) demonstrated carboxyl groups may promote the nucleation of dolomite as Mg-ions are dewatered and bound to the carboxyl sites, overcoming the kinetic barriers of precipitation. These observations raise the question as to what hydrological conditions and environments may promote dolomite formation.

The presence of dolomite indicates specific hydrochemical conditions that have favoured dolomite formation, including elevated Mg/Ca, high salinity and high alkalinity

74 and therefore, high CO_3^{2-} activity (Folk and Land, 1975; Morrow, 1982a; Hardie, 1987;
75 De Deckker and Last, 1988). Evaporative concentration combined with calcite
76 precipitation along a hydrological flow path results in increasingly saline groundwater
77 and higher Mg/Ca waters, which may ultimately precipitate dolomite (Arakel, 1986;
78 Jones and Deocampo, 2003). Degassing of CO_2 from emerging waters at groundwater
79 discharge zones also promotes carbonate precipitation as it decreases total carbonate
80 species, while carbonate alkalinity remains constant, resulting in increasing pH of
81 groundwater during evaporative concentration and subsequently higher CO_3^{2-} activity
82 (Eugster, 1980; Morrow, 1982a). Dolomite may therefore, occur in depressions towards
83 the centre of drainage basins and at groundwater discharge zones (Mann and Horwitz,
84 1979). Higher Mg/Ca ratios in groundwater may also occur in basins where there has
85 been weathering of high-Mg rocks, such as marine dolomite or Mg-rich volcanics (Last
86 and De Deckker, 1990; Alonso-Zarza and Martín-Pérez, 2008; Jones et al., 2009;
87 Dogramaci and Skrzypek, 2015). Groundwater calcrete and dolocrete (based on the
88 genetic classification of calcrete types by Carlisle (1983), but pertaining to deposits
89 composed dominantly of dolomite), have been previously identified as part of the
90 continuum of groundwater precipitates along drainage and paleodrainage systems of
91 inland Australia and are often tens of metres thick and laterally expansive (Mann and
92 Horwitz, 1979; Arakel and McConchie, 1982; Arakel, 1986). Groundwater dolocretes
93 have also been recognised within alluvial sediments in the Paris Basin (Thiry, 1989; Spötl
94 and Wright, 1992) and Provence Basin (Colson and Cojan, 1996) in inland France; in the
95 Sado and Lisbon Basin in Portugal (Pimentel et al., 1996); and in the coastal region of
96 Kuwait along the Arabian Gulf (Khalaf, 1990; El-Sayed et al., 1991). The models
97 presented for groundwater dolocrete formation highlight the importance of groundwater

hydrochemical evolution in the lower reaches of closed basins (Mann and Horwitz, 1979; Arakel, 1986; Armenteros et al., 1995) as well as mixing between relatively fresh groundwater with saline groundwater, commonly surrounding saline-playa lakes in evaporitic basins (Colson and Cojan 1996; Jutras et al., 2007) but also marine groundwaters in coastal environments (El-Sayed et al., 1991; Williams and Krause, 1998; Khalaf et al., 2017). The mixing of groundwaters increases the alkalinity, which both increases silica solubility and reduces dolomite solubility, favouring replacement of silicate host sediments by dolomite (Arakel and McConchie, 1982; Deelman, 2003). The previous studies of groundwater dolomite have suggested that local groundwater chemistry was most likely conducive to direct or early diagenetic dolomite formation resulting in dolomitization of host sediments, evidenced by primary dolomite euhedral crystals and lack of calcite precursors (Arakel, 1986; Khalaf, 1990; El-Sayed et al., 1991; Spötl and Wright, 1992). This is in contrast to dolomitic horizons occurring within groundwater calcrete profiles, formed by dolomitization of calcite, usually within the capillary zone where evaporation has the greatest effect on shallow groundwater (Arakel, 1986). Dolocretes remain largely undocumented in comparison to calcretes and have also been neglected in the investigation of terrestrial dolomite formation, which has mostly focussed on lacustrine dolomite occurring in proximity of the coastline and influenced by marine groundwaters (Clayton and Jones, 1968; Rosen et al., 1989; Rosen and Coshell, 1992). Groundwater dolomite within inland continental settings may therefore provide new insights into the mechanisms of dolomite formation in terrestrial environments.

The chemistry and stable isotopic composition of carbonate minerals are indicative of the hydrochemical conditions in which they precipitated (Craig, 1953; Emrich et al., 1970; Vasconcelos et al., 2005) and have been used successfully as a tool

for paleoenvironmental reconstruction (eg. Hays and Grossman, 1991; Hay and Keyser, 2001; Deutz et al., 2001; Bustillo et al., 2002; Alonso-Zarza, 2003; Cyr et al., 2005; Bowen et al., 2008). Groundwater dolocrete associated with evaporitic basins in inland settings provides an important continental archive of paleoenvironmental and paleohydrological conditions, which has thus far been largely overlooked. A unique drilling program, conducted in 2011 by Rio Tinto Iron Ore at the Fortescue Marsh, a large inland wetland in the Pilbara region of northwest Australia, revealed dolocrete deposits of up to 20 m thick occurring with the Marsh sediments. This provided a new opportunity to utilise dolomite geochemistry to improve our understanding of the physiochemical environments and hydrological processes involved in groundwater dolocrete formation and therefore, advance knowledge of the conditions of terrestrial dolomite formation and provide paleoenvironmental and paleohydrological records. In this study we investigate the geochemistry and stable isotope compositions of dolomite and groundwater from various depths within the Marsh to; 1) produce a first assessment of the mineralogy and geochemistry of dolocrete within the Marsh; 2) understand the hydrological processes and chemical conditions resulting in dolocrete formation; and 3) utilise this information to produce records of paleoenvironmental and paleohydrological conditions.

2. Site Description

2.1 Geological Setting

The Fortescue Marsh is an ephemeral wetland located in the semi-arid Hamersley Basin in the Pilbara region of northwest Western Australia (Fig. 1). The basement under the Marsh is composed of crystalline blue-grey dolomite of the Wittenoom Formation (Barnett and Commander, 1985; Skrzypek et al., 2013).

Figure 1: The location of the study area, the Fortescue Marsh of the Hamersley Ranges, Western Australia, and locations of boreholes drilled during this project. Colour indicates locations of dolocrete units (G1 and or G2 dolocrete), occurring within drill cores.

The incision of the Hamersley Basin sedimentary rocks in the Late Cretaceous to Paleogene, under a more humid climate, resulted in the formation of the Fortescue Valley paleodrainage (Barnett 1981; MacPhail and Stone, 2004). The Marsh occupies the lowest part (~400 m a.s.l), extending over ~1,100 km² between the Chichester and Hamersley Ranges in the Eastern Fortescue Valley and is the terminal basin of the Upper Fortescue River (Skrzypek et al., 2016). The Marsh is separated from the Lower Fortescue River by the Goodiadarrie Hills, located on the western edge of the Marsh (Fig. 1). The Fortescue Valley lowlands have filled with Cretaceous to Holocene alluvium and colluvium (Barnett 1981). Barnett (1981) described the sediments of the Western Fortescue Valley in the adjacent Lower Fortescue River catchment and found a sequence of colluvial,

alluvial and lacustrine sediments of up to 120 m thick. The sediments grade from Cretaceous to Paleogene iron-rich pisolitic and conglomerate fluvial and channel fill sediments overlying the Wittenoom Formation basement, through dolomite of the Millstream Formation, lacustrine clay and alluvial sediments (Barnett, 1981). Unconsolidated Quaternary alluvial and colluvial clay and silt sediments of up to ~30 m cover much of the valley (Barnett, 1981). However, due to the remote nature of the Marsh in the Eastern Fortescue Valley, lack of mineral resources in the Marsh itself and protection due to environmental and heritage significance, there is very limited information on the specific nature of the Fortescue Marsh sediments. The drilling program conducted by Rio Tinto Iron Ore in 2011, provided the first overview of the distribution of sediments within the Marsh, revealing ~15 to 80 m of alluvium, colluvium and chemical sediments overlying the Wittenoom Formation basement. Multi-metre carbonate dominated layers were found in several drill cores within the Marsh sediments. The recorded lithologies of drill cores for two transects across the Marsh are presented in Figure 2. However, as the cores were drilled by sonic rigs for hydrogeological research purposes the information is limited and no detailed lithological descriptions are provided.

176

177 *Figure 2: Cross sections across the Fortescue Marsh, showing the distribution of sediments, location of*
 178 *carbonate and recent groundwater level. Cross-section lines are shown in map Figure 1. The values*
 179 *provided on the cross-sections are δ¹⁸O_{VPDB} analysed in carbonates.*

Groundwater calcrete extends along drainage and paleodrainage channels throughout much of the Hamersley Basin and form large platforms of calcretised drainage plains in valley floors (Mann and Horwitz, 1979; Barnett and Commander, 1985; Payne, 2004). However, dolomite within the Millstream Formation is the only reported occurrence of terrestrial dolomite in this region and is considered to be of Miocene to Pleistocene age, most likely early-mid Pleistocene (Barnett, 1981; Macphail and Stone, 2004). The Millstream Formation is described as being up to 46 m thick and consists of interbedded dolomite, silcrete, calcareous clay and conglomerate with layers of illite-nonttronite clay occurring in the lower 10-15 m of the sequence (Barnett, 1981). The dolomite is often calcareous above the water table and has well developed secondary porosity which is commonly lined by chalcedonic silica (Barnett, 1981). Barnett (1981) proposed that the Millstream Formation was deposited as a lacustrine sequence of carbonate and clay sediments, indicated by the presence of gastropods and bivalves in some locations, punctuated by minor intervals of alluvial deposition. The origin of dolomite and silcrete is interpreted to have formed later by diagenetic alteration of the Millstream Formation sediments by circulating groundwaters. Lacustrine-fluvial carbonate deposits of presumed equivalent age are also reported within the Oakover Formation which overlies ironstone deposits proximal to the Marsh (Ramanaidou et al., 2003; Kneeshaw and Morris, 2014). Despite the widespread occurrence and potentially high value as records of paleoenvironment and paleohydrological conditions, terrestrial carbonates in the Hamersley Basin have not been studied. The archive is of particular interest as the Pilbara region has few proxies available for paleoenvironmental reconstruction (Reeves et al., 2013; O'Donnell et al., 2015; Rouillard et al., 2016).

2.2 Climate and hydrology

The Hamersley Basin experiences a semi-arid climate, with a low annual average rainfall of ~350 mm/y (www.bom.gov.au/climate/data/). Rainfall distribution is highly variable and characterised by extended periods of drought with occasional high intensity rainfall events, associated with tropical low pressure systems and cyclone activity (Rouillard et al., 2015). Rainfall is therefore seasonal, occurring mostly in summer between December and March. Mean maximum temperatures across the Hamersley Basin range from 35-40°C in summer (Dec-Mar) and 24-27°C in winter (Jun-Aug) (Newman and Wittenoom weather stations; www.bom.gov.au/climate/data/). The rate of evaporation is high and potential pan evaporation usually exceeds 2,600 mm annually (www.bom.gov.au/jsp/ncc/climate_averages/evaporation/index.jsp) an order of magnitude greater than rainfall.

The Marsh is a surface water dependent ephemeral wetland and acts as a hydrologically terminal basin for ~31,000 km² of the Upper Fortescue River catchment (Skrzypek et al., 2016). Surface flows and flooding across the Marsh are episodic, occurring in response to intense rainfall events (Rouillard et al., 2015). Floodplains located along the Fortescue River channel, referred to as the central Marsh, experience episodic inundation and contains some small permanent and semi-permanent pools (Rouillard et al., 2015). Flood waters are delivered from the east by the Upper Fortescue River and from numerous ephemeral creeks on the southern and northern flanks of the Marsh (Fig. 1; Skrzypek et al., 2013). The main aquifers under the Marsh are the colluvial and alluvial aquifers, which have highly variable permeability due to the complex range of unconsolidated to consolidated sediments (Skrzypek et al., 2016). These aquifers are locally confined by relatively impermeable horizons of massive clays and of cemented silcrete and calcrete (Dogramaci et al., 2012). The Wittenoom Formation comprises an

extensive regional fractured aquifer system, characterised by relatively fresh, bicarbonate rich groundwater (Dogramaci et al., 2012). However, underlying the Marsh, the Wittenoom Formation is not fractured and therefore connectivity between the overlying alluvial and colluvial aquifers is limited. The Wittenoom basement under the Marsh is variable but generally arises at the Marsh outlet restricting alluvial/colluvial groundwater outflow to a relatively narrow “alluvial window” $<0.35 \text{ km}^2$ (Skrzypek et al., 2016). Subsurface flow in the Marsh is approximately east to west, across the flood plain (Skrzypek et al., 2013). However, hydraulic gradients across the Marsh are close to zero and groundwater discharge to the Lower Fortescue River is extremely low i.e., $<2 \text{ GL/y}$ (Skrzypek et al., 2016). The groundwater level across the Marsh is between 0 and 5 m b.g.l. (below ground level) at the centre and up to $\sim 60 \text{ m b.g.l.}$ at the flanks on alluvial fans (Fig. 1; Skrzypek et al., 2016). Water table depth across the Marsh varies seasonally in response to the flood-drought regime.

The interaction between groundwater and surface water is a major controlling factor on the hydrochemical evolution of water within wetlands, such as the Marsh (Skrzypek et al., 2013), as well as the composition and distribution of precipitates (Bowler, 1986). Fresh floodwater becomes progressively brackish and evaporates completely (except in some small pools) with the onset of dry season (Rouillard et al., 2015). However, salt efflorescences are rarely present on the dried surface as they are washed away by vertical infiltration during subsequent flood events, delivering additional salt to the groundwater below the Marsh (Skrzypek et al., 2013). Despite continuous addition of salts to groundwater, the shallow waters (0-20 m b.g.l.) are mostly fresh to brackish whereas deep groundwater ($>50 \text{ m b.g.l.}$) is highly saline (Skrzypek et al., 2013). This setting is in contrast to the majority of inland wetlands and lakes in arid zones that

are groundwater dependent and most commonly have shallow groundwaters of higher salinity due to direct evaporation of inflowing groundwater (Johnson, 1980; De Deckker, 1988; Dutkiewicz et al., 2000).

3. Sampling and analytical methods

Eight out of the twenty bores drilled across the Marsh had carbonate units (calcrete/dolocrete) of at least 2 m thick, identified within the drill cores (Fig. 1). From these cores, 25 representative samples were obtained from carbonate-rich lithologies from varying depths (up to 63 m b.g.l.). Seven representative samples were also extracted from the basement rock of the Wittenoom Formation dolomite for comparison. The nature of the sonic drill core, which produces rock chips, and lack of outcrops at the Marsh meant that detailed lithological descriptions of the carbonate profiles was not possible and is in part, the reason for the study focus on geochemical and stable isotope analysis of powdered samples.

Petrographic analysis was completed on polished thin sections using transmitted light microscopy and using a Verios XHR scanning electron microscope (SEM) fitted with an Oxford instruments SDD-X-Max energy dispersive X-Ray (EDX) spectrometer at the Centre for Microscopy, Characterisation and Analysis, The University of Western Australia. Major element (Ca, Fe, Mg, Na, Rb, Si, Sr, Ti, Al) compositions were determined using X-ray fluorescence spectrometry (XRF) by Mineralogical Services, CSIRO, Adelaide. Approximately 5 g of each sample was powdered and fused with lithium metaborate/tetraborate flux (12:22 Norrish flux) at 1050°C to create a glass bead prior to analysis using a Philips PW1404 XRF spectrometer. Loss of ignition was determined at 1050°C. Samples were analysed as air-dried random powders by X-ray

diffraction (XRD) to determine bulk mineralogy. X-ray data was collected using a Philips PW1830 diffractometer, equipped with Cu K α radiation and operated at 50 kV and 20 mA. An angular range of 3 to 70° 2 θ was measured with a step size of 0.02° 2 θ and an integration time of one second. An internal halite (NaCl) standard was added to each sample and peak positions were adjusted by accurate location of reflections from the standard. The molar proportion of CaCO₃ in dolomite was estimated from the position of the d(104) reflection, using the linear equation derived by Lumsden (1980) to establish dolomite stoichiometry. Magnesium substitution in calcite was estimated based on curves developed by Goldsmith and Graf (1958) and Zhang et al. (2010). These data were combined with measured elemental compositions to calculate a semi-quantitative mineralogy.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonate samples were analysed using a GasBench II coupled with a Delta XL Mass Spectrometer (Thermo-Fisher Scientific) at the West Australian Biogeochemistry Centre at The University of Western Australia. Samples of carbonate powder were flushed with ultra-high purity helium (99.999%) and reacted with 0.05 mL of 100% phosphoric acid at 50°C (Paul and Skrzypek, 2006; Paul and Skrzypek, 2007). In order to obtain calcite and dolomite stable isotope compositions, each sample was analysed twice using different reaction times: 24 h for total carbonates (calcite and dolomite) and 15 minutes for calcite only. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonate samples were normalised to VPBD scale using three international reference materials (LSVEC = -46.6‰, NBS 18 = -5.01‰ and NBS 19 = 1.95‰ for $\delta^{13}\text{C}$ and; NBS 18 = -23.01 ‰ and NBS 19 = -2.2 ‰ for $\delta^{18}\text{O}$), following a three and two point normalisation and reported in per mil (Skrzypek, 2013; Brand et al., 2014). The external uncertainty of stable isotope analyses is <0.1‰ for $\delta^{13}\text{C}$ and <0.15‰ for $\delta^{18}\text{O}$ (1 standard deviation). The dolomite

stable isotope composition of mixed carbonate samples were calculated using a stable isotope mass balance model and the difference between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of total carbonates and calcite. The relative proportions of calcite and dolomite in samples were calculated based on sample weights and amount of produced CO_2 recorded as the area of all peaks for molecular masses 44-45-46. These values were in agreement with the proportion of dolomite determined by XRF and XRD. The $\delta^{18}\text{O}$ values of dolomite samples originally measured versus calcite standards were recalculated using acid isotope fractionation factors (Das Sharma et al., 2002).

Eleven samples from shallow (< 25 m b.g.l.) carbonate horizons were analysed for conventional radiocarbon age using accelerator mass spectrometry (AMS) at GNS Rafter Radiocarbon Laboratory, New Zealand, to test whether shallow carbonate was within the range of ^{14}C dating. Samples were surface etched by treating in 0.5 M HCl for 1 minute to remove potential contaminants. The treated samples were ground by mortar and pestle prior to combustion at 900°C for four hours in evacuated, sealed quartz tubes with cupric oxide and silver wire. Evolved CO_2 was cryogenically purified by passing through ethanol and dry ice traps to remove water then converted to graphite by reduction with hydrogen over an iron catalyst. The reported conventional ^{14}C ages of samples (Stuiver and Polach, 1977) were calibrated using OxCal 4.2 software (Bronk Ramsey, 2009) and SHCal13 (Hogg et al., 2013). All ^{14}C ages are reported as calibrated years before present (cal. yrs BP) with 95.4% probability (Bronk Ramsey, 2009).

Groundwater samples were collected from piezometers installed at 20 locations (Fig.1), screened in the various aquifers, after pumping out at least three casing volumes. Sampling was conducted five times over approximately two years (April 2013, August

2013, May 2014, October 2014 and May 2015), although not all bores were accessed for all sampling campaigns. Water samples for analyses of major ion concentrations, pH, electrical conductivity (EC), total dissolved solids (TDS) and alkalinity were collected in 0.5 L containers and analysed by SGS Laboratories Australia Pty Ltd in Perth, Western Australia. Samples were analysed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, method ref. APHA 3120B) for Ca, Fe, Mg, Na, K, Si and Sr cations, discrete Analyser in Water by Aquakem DA for SO_4^{2-} and Cl^- anions (method ref. APHA 4500), Br^- by ion chromatography (method ref. APHA 4110B) and HCO_3^- alkalinity by acid titration (method ref. APHA 2320). The aqueous geochemical modelling software, PHREEQC, was used to determine the activity of ions in solution and to calculate saturation indices (Parkhurst and Appelo, 1999).

The stable hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotope compositions of water samples were measured using an isotopic water analyser and a Picarro L1102-i (Picarro, Santa Clara, California, USA) at the West Australian Biogeochemistry Centre, The University of Western Australia. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were normalised to VSMOW-SLAP scale following a three point normalisation (Skrzypek, 2013) based on laboratory standards, each replicated twice and reported in per mil (‰) (Skrzypek and Ford, 2014). All laboratory standards were calibrated against international reference materials determining the VSMOW-SLAP scale (Coplen, 1996) provided by the International Atomic Energy Agency (IAEA) ($\delta^2\text{H}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ equals 0‰ and $\delta^2\text{H}_{\text{SLAP}} = -428.0\text{‰}$ and $\delta^{18}\text{O}_{\text{SLAP}} = -55.50\text{‰}$). The analytical uncertainty (one standard deviation) was determined as 1.0‰ for $\delta^2\text{H}$ and 0.1‰ for $\delta^{18}\text{O}$. Water samples were analysed for $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) using a GasBench II coupled with Delta XL Mass Spectrometer (Thermo-Fisher Scientific). Water samples were reacted at 25°C for

24 hrs. The $\delta^{13}\text{C}$ values were converted to VPBD after a three point normalisation based on international standards provided by the IAEA (L-SVEC, NBS19 and NBS18 with values as reported by (Coplen et al., 2006). The external error of $\delta^{13}\text{C}$ analyses is less than 0.1‰.

4. Results

4.1 Carbonate distribution, mineralogy and geochemistry

Two dolocrete units were identified within the Fortescue Marsh; Group 1, a lower unit, buried by 20 to 50 m of sediment; and Group 2, an upper unit, where if not occurring at the surface, was overlain by < 8 m of clay or gravelly clay. Both units did not occur at all locations, however, a number of drill cores in the Weeli Wolli alluvial fan did contain both dolocrete units (5D, 6D, 6E). The lower Group 1 (G1) was mostly 2 to 8 m thick but reached up to 20 m thick within the centre of the Marsh (Fig. 2 cross-section A-B; bores 3B, 6D, 7B and cross-section C-D; 5D and 6E). G1 was underlain by silcrete or siltstone and overlain by clay, which commonly contained gypsum, including centimetre scale lenticular gypsum crystals and clusters within 7B and 9B cores. Bore 6E also contained an additional 2 m of dolocrete (63 – 65 m b.g.l) directly overlying basement rock, separated from a G1 layer (38 - 45 m b.g.l) by 17 m of silcrete, as well as a shallow Group 2 layer occurring from 4 to 23 m b.g.l (Fig. 2). The upper Group 2 (G2) dolocrete ranged from 5 to 19 m thick and layers were relatively continuous throughout the mid to lower alluvial fan as well as at the Marsh inlet (Fig.2 cross-section A-B; bores 6D and 10A and cross-section C-D; bores 5D, 6E and 8G), but did not occur in the central Marsh. Carbonate-rich zones were observed at similar depths within silcrete units (8G and 7C), which were also abundant in the Marsh sediments. Two metres of carbonate was also

present at the surface at the outflow point of the Marsh at bore 2A, adjacent to Goodiadarrie Hills (Fig. 1). However, carbonate from 2A was not available initially and was not included in the geochemical and mineral analysis although was later accessed for radiocarbon dating. The G2 dolocrete is separated from the underlying G1 unit by clay dominated sediments, ranging from 4 m to 43 m thick. The G1 dolocrete is not laterally continuous across the Marsh, however, carbonate replacement and cementation was present within adjacent sediments but not as well developed. Other sediments within the Marsh were largely gravelly clay and siltstone alluvial deposits and to a lesser extent colluvial deposits of gravelly sands, which were more common towards the western edge of the Marsh, near Goodiadarrie Hills.

Distinctions in the mineralogy, geochemistry and stable oxygen isotope compositions were apparent between the two dolocrete units (Table S1, S2, and S3). The mineralogy of G1 dolocrete consisted of dolomite, with lesser proportions of quartz, palygorskite-sepiolite clay and Fe-oxides. G1 dolomite was stoichiometric (49-52 mol% CaCO_3), contained no traces of calcite and had $\delta^{18}\text{O}$ values of -4.02 to 0.71‰ (mean = -2.40‰; Fig. 3; Table S1). The G2 mineral assemblage was more varied and consisted of dolomite, palygorskite-sepiolite clay $\pm$ calcite $\pm$ Fe-oxides $\pm$ kaolinite. G2 dolomite was Ca-rich (54-58 mol% CaCO_3) with a comparatively lower and narrow range of $\delta^{18}\text{O}$ values of -7.18 to -6.42‰. Calcite in G2 mostly occurred close to groundwater level and was the dominant carbonate mineral in six samples analysed. The calcite was low-Mg (<5 mol% MgCO_3) and $\delta^{18}\text{O}$ values ranged from -7.74 to -6.03‰. The stable carbon isotopic compositions of dolomite were similar for both units. The $\delta^{13}\text{C}$ values of the G1 dolomite ranged from -6.92 to -4.72‰. G2 samples fall within a slightly narrower range with values of -6.4 to -4.91‰ for dolomite and -5.99 to -4.92‰ for calcite. There is a general decrease

in $\delta^{13}\text{C}$ values with depth ($R^2 = 0.44$, $p = 0.013$) for G1 carbonates (Fig. 3). The $\delta^{13}\text{C}$ values of basement Wittenoom dolomite samples are isotopically distinct from the dolocrete samples and fall within a narrow range of -0.41 to 0.23 ‰, indicative of their marine origin (Table S1).

Figure 3: The stable carbon and oxygen isotope composition and Mg/Ca with depth of G1 and G2 carbonate samples.

The micromorphology of dolocrete samples displays the replacive nature of the deposits, where the host sediment fabrics are preserved but have been mostly replaced by dolomite (Figure 4). G1 host sediment predominantly has clay and silt size matrix and some samples have peloidal fabrics (Fig. 4A) with peloids of ~ 100 μm to 2mm , which have been replaced by dolomite. Partially to fully replaced allochems of detrital quartz and compound clasts of mixed sediments were observed in some samples, but were relatively rare other than for #23 at 3B, which contained coarser heterogeneous host

sediment including Fe-oxide dominated nodules (Fig. 4B), silicate grains and compound clasts, the latter two almost entirely replaced by dolomite and palygorskite. G1 dolomite textures are predominantly unimodal with crystals mostly ranging between ~1 and 20 μm and often finely intermingled with clays, most commonly authigenic palygorskite (Fig. 4E). The crystal boundaries were most commonly planar-subhedral but varied between samples and within samples and included planar euhedral and non-planar boundaries, likely due to differences in host sediment texture. Intracrystalline dissolution of zones or cores of dolomite crystals (Fig. 4E and 4G) was evident to some degree in all G1 samples and resulted in nano to micron scale porosity. Porosity also occurs as subspherical vughs (~20-200 μm) and subspherical to angular voids, which appear to be from loss of minerals or grains. Isopachous dolosparite cement was often present along void edges and around grains (Fig. 4E). No evidence of calcite precursor was found from petrographic observations and EDX analysis of G1 samples. Dolomite accounts for >80% of the mineral assemblage with the exception of samples from 6E, which contain significant authigenic silica. Replacive and pore-filling silica is present as mosaics of microcrystalline to macrocrystalline quartz (Fig. 4H). Crystal size generally increases towards the centre of voids, with crystals of up to ~500 μm . Sutured contacts of microquartz and fibrous chalcedonic silica is also observed.

Figure 4: Photomicrographs of dolomite thin sections; (A) Dolomicrite and clay matrix with peloidal fabric in G1 #12 -6E at ~44 m b.g.l.; (B) Muddy sand host sediments containing Fe-oxide cemented pisoliths and clayey –dolomite matrix in G1 #23 – 3B ~27 m b.g.l.; (C) Calcitized dolocrete with matrix of partially calcitized dolomite, often with oriented calcite rims and calcite microspar and spar cements fill in G2 #14 – 6D ~ 7 m b.g.l.; (D) Clusters of partially calcitized dolomicrite surrounded by oriented calcite rims, brecciated and cemented by silica in G2 #29–10A ~7 m b.g.l.; (E) Backscattered electron (BSE) micrograph of unimodal dolomite matrix with crystal diameters of ~1 to 10 μm , intermingled with palygorskite and surrounding a dolospar infilled void, the morphology suggests dissolution of earlier mineral or grain. MnO precipitate around void edge (#12, 6E at ~44 m b.g.l.); (F) BSE image of etched quartz grain surrounded by calcite cement within a matrix of partially calcitized dolomite. (#14, 6D ~7 m b.g.l.); (G) BSE micrograph of dolomite rhombs (~10 to 50 μm) with partially dissolved zones, interspersed with palygorskite in G1 #23 – 3B ~27 m b.g.l and; (H) cross-polarised micrograph showing layering of pore-filling micro to macrocrystalline quartz (#8, 6E ~63 m b.g.l). Dol = dolomite, Pal = palygorskite, MnO = manganese oxide.

The host sediment of G2 dolocrete includes mudstone and sandy mudstones. Coarser sediments, such as muddy and gravelly sands occurring at 8G and 7C, are less replaced by carbonate and are associated with silcrete units. Sand size grains in G2 are mostly detrital quartz, some of which are partially dissolved and etched, and compound clasts of clay and Fe-oxide minerals (Fig. 4F). The clayey matrices have been largely replaced by dolomite, interspersed with authigenic and remaining detrital clay. XRD and EDX analysis indicates palygorskite is common, as well as smectite and sometimes kaolinite. G2 dolomite displays massive fabrics, unimodal crystal distribution with crystals mostly <10 µm and planar-subhedral boundaries. However, the majority of G2 dolocrete has been altered by dedolomitization and silicification. Calcite in G2, appears to be secondary and occurs as replacement of dolomite cores or zones, oriented fibrous calcite and as intercrystalline or void infill phreatic cements (Fig. 4F). Radial fibrous calcite is common around Mg-rich centres, where calcite has replaced dolomite cores. Some fine-scale porosity occurs where dissolved cores remain empty. This was observed in the majority of G2 samples, including in some samples where the calcite was not sufficient to have been detected by XRD. The calcitization is highly variable within profiles and occurs at a range of depths of up to 20 m (6E – calcite observed only in thin section). Dolocrete occurring at the inlet to the Marsh (10A) has been brecciated and occurs as clusters of partially calcitized dolomicrite, surrounded by oriented calcite rims, cemented by silica (Fig. 4D). The silicification is pervasive and has impregnated matrix materials and largely replaced remaining host sediments.

4.2 Radiocarbon dating of carbonates

Radiocarbon dating of G2 carbonates (4-23 m b.g.l.) revealed calibrated ^{14}C ages ranging from 37 to >45 ka BP (Table 1), with a number of samples older than 45 ka.

Table 1: Radiocarbon ages of carbonates from calcrete samples obtained using ^{14}C AMS method from the cores collected across the Fortescue Marsh. T, M and B represent approximate top, middle or bottom of the carbonate horizon. Sample numbers are also added where they correspond to carbonate samples analysed for other properties. Sample BR1 is a surface sample from the centre of the Marsh (gypsum dominated).

Radiocarbon laboratory code ^a	Core ID	Sample Group	Sample elevation		Conventional age	Calibrated median age	Calibrated range of ages (probability 95.4%)
			(m a.s.l.)	(m b.g.l.)			
R 40731/1	BR1	not defined	407	0 (surface)	1,126±26	0.98	0.93-1.1
R 40731/2	2A-M	not defined	407	1.1	16,544±63	19.9	19.7-20.1
R 40776/2	2A-B	not defined	406.1	2	34,249±558	38.7	37.1-40.1
R 40731/3	5D-T	2	403.1	9.5	44,306±1,744	>>45	-
R 40776/3	5D-B-20	2	396	16.6	44,999±1,856	>>45	-
R 40776/4	6D-T	2	407.5	2	45,067±1,871	>>45	-
R 40731/4	6D-B-14	2	402.5	7	37,025±705	41.5	40.2-42.6
R 40776/5	6E-T	2	416.1	4	39,580±957	43.4	42.1-45.2
R 40776/6	6E-B	2	397.1	23	>>45 ka	>>45	-
R 40731/6	10A-M-29	2	393.1	7	34,052±487	38.5	37.0-39.7
R 40776/8	10A-B-30	2	386.1	14	>>45 ka	>>45	-

^a Samples analysed by Rafter Radiocarbon, GNS Science, New Zealand and calibrated using OxCal 4.2 (Bronk Ramsey, 2009) and the SHCal13 calibration curve for Southern Hemisphere (Hogg et al., 2013)

The radiocarbon ages represent total carbonates and therefore may include some secondary calcite. Calibrated median ^{14}C ages from near the top and base of G2 carbonate layers in the Weeli Wolli alluvial fan are as follows; samples from 5D at depths of 9.5 and 16.6 m b.g.l were both >45 ka; carbonate from 6E had a median age of 43.4 ka BP at

4 m depth and of >45 ka at 23 m b.g.l; carbonate from 6D had a calibrated age of >45 ka at 2 m depth, whereas a deeper sample from 7 m b.g.l had a median age of 41.5 ka BP and; samples from 10A had a median age of 38.5 ka BP at 7 m b.g.l and of >45 ka at 14 m b.g.l. Other carbonate analysed for radiocarbon included samples from a carbonate horizon at bore 2A which had calibrated median ^{14}C ages of 19.9 ka BP at 1.1 m depth and 38.7 ka BP at 2 m.

4.3 Groundwater chemistry

Groundwater within the Marsh was neutral to mildly alkaline (pH: 6.7-8.4) and the salinity (TDS) ranged from fresh (0.2 g/L) to brine (170 g/L) (Table S5). The salinity generally increased with depth and towards the centre of the Marsh, with the exception of two bores of >100 g/L TDS (7B and 9B), located in the centre of the Marsh, which had higher salinity in shallow water compared to deep. Salinity and $\delta^{18}\text{O}$ values were strongly correlated ($R^2 = 0.93$; $n = 118$; $p = <0.001$; Fig. 5A) and the Marsh groundwater can be broadly divided into; fresh-brackish water (TDS: <35 g/L, median = 7 g/L), ranging from -6.7 to -9.5‰ $\delta^{18}\text{O}$; and saline-brine water (>35 g/L, median = 91 g/L) ranging from -6 to +2.3‰ $\delta^{18}\text{O}$. An exception is 5E-D, located in the SW of the Weeli Wolli alluvial fan, which was saline (47-57 g/L) but had a $\delta^{18}\text{O}$ signature similar to brackish waters (mean = -6.9‰). The median $\delta^{18}\text{O}$ value of fresh-brackish water was -8.02‰ which is representative of alluvial groundwater in the Upper Fortescue catchment (Dogramaci et al., 2012). The $\delta^{13}\text{C}$ values of DIC in groundwater (Fig. 5B), measured from 19 bores at multiple depths, was quite variable ranging from -11.63 to -4.96‰ (median -9.28‰). The $\delta^{13}\text{C}$ values of groundwater from bores containing dolocrete ranged from -11.63 to -7.92‰ (median -10.13‰) with the most positive value corresponding to the 7B bore.

Saline bores had generally higher $\delta^{13}\text{C}$ values compared to brackish bores and $\delta^{13}\text{C}$ values are weakly correlated with $\delta^{18}\text{O}$ ($R^2=0.28$, $p<0.001$).

Figure 5: The stable isotope and chemical composition of groundwater collected from the Marsh area during 2013 and 2014. Groundwater symbols are split into fresh-brackish (TDS = <35 g/L) and saline-brine (TDS = >35 g/L). D) The water samples below pH 7 are from the 7B shallow bore, located in the centre of the Marsh. (F) The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of groundwater and the Local Meteoric Water Lines (LMWL) for the Hamersley Basin for rainfall events >20 mm and <20 mm and the local evaporation line (LEL) as calculated by (Dogramaci et al., 2012).

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of fresh-brackish groundwater fall to the right of the local meteoric water line (Dogramaci et al., 2012; Fig. 5F) and are distributed close to the local evaporation line (LEL), indicating up to 20% evaporation of modern recharge (Skrzypek et al. 2013). However, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of saline-brine groundwater diverges far to the right of the LEL (Fig. 5F). Skrzypek et al. (2013) previously noted that the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of saline-brine groundwater at the Marsh is consistent with mixing between modern recharge and relatively old, highly saline groundwater, formed under a different hydrological regime. To understand the range of possible groundwater

compositions for carbonate precipitation and the relative influence of the two groundwater end members, we produced a simple mixing model for Cl content and stable oxygen isotope values of groundwater. Modern groundwaters are characterised by a range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signatures and can be represented by fresh water inflowing to the Marsh as a result of flooding ($\delta^{18}\text{O} = -9.3\text{‰}$, $\text{Cl} = 1.4 \text{ g/L}$ measured at bore 5E) to more saline, evaporated water ($\delta^{18}\text{O} = -6.9\text{‰}$, $\text{Cl} = 3.6 \text{ g/L}$, measured at bore 10A). The second end-member is represented by deep brine groundwater ($\delta^{18}\text{O} = +2.3\text{‰}$, $\text{Cl} = 87 \text{ g/L}$, measured at bore 9B). The ratios between the two end-members calculated independently from mixing mass balance models using Cl concentration and $\delta^{18}\text{O}$ signatures agrees within $\pm 10\%$ (2A, 2B, 3A, 3C, 4C, 6D, 7B, 7C and 9B). Two bores from the central Marsh, 3B and 4B, are exceptions and may experience significant additional salt load from seasonal wetting and drying processes (Skrzypek et al., 2013). Brackish groundwater with the isotope composition diverging below the slope of the LEL (Fig. 5F; 1C, 1B, 5E, 6D-S, 6E, 5D, 8G-D) represents minor mixing with the brine water.

Na and Cl ions dominated the cations and anions in groundwater, with lesser amounts of Ca, Mg and SO_4 . The percentages of Na and Cl ions increased from $\sim 45\%$ in the relatively fresh groundwater ($\text{TDS} \sim 10 \text{ g/L}$) to 90% at the higher end of salinity spectrum. Mg/Ca ratios ranged from 0.7 and 10.7 with all but three samples < 6 (Fig. 5C). The Mg/Ca ratios generally increased at higher salinities with a median of 1.6 for fresh-brackish groundwater and of 2.8 for saline-brine groundwater. We assessed the potential for precipitation or dissolution of minerals from groundwater in the Marsh using the thermodynamic saturation index based on measured groundwater chemistry (Plummer et al., 1988). The majority of water samples were saturated in respect to calcite and dolomite and the saturation indices generally decrease with increasing salinity. Calcite is more

soluble than dolomite in saline waters and reaches below saturation for the highly saline waters ($> \sim 50$ g/L Cl; 7B-S, 9B, 6D-D, 4C-S and 3A-D), suggesting potential for calcite dissolution from the aquifer matrix. Dolomite saturation is sustained into more saline waters, despite the decreasing trend and was only undersaturated in the shallow, brine waters of 7B due to low alkalinity. Gypsum saturation increases with salinity and beyond the 36 g/L threshold, as gypsum saturation is reached and remains nearly constant with increase Cl concentrations and was oversaturated in most saline-brine bores (7B-S and I, 9B, 4C, 4B-D, 3B, 3C-D, 7C-D, 3A, and 2B). All measured groundwater in the Marsh is undersaturated in respect to amorphous silica indicating there is no current silica precipitation and SI values are similar (median = -0.85) regardless of salinity. The $p\text{CO}_2$ of all measured groundwater, determined from PHREEQC speciation modelling (Parkhurst and Appelo, 1999), is higher than that of atmospheric $p\text{CO}_2$ ($\sim 10^{-3.5}$), with the majority of samples being an order of magnitude higher (median = $10^{-2.58}$).

5. Discussion

5.1 Mode of dolomite formation

The Fortescue Marsh dolomites are interpreted to be groundwater dolomite, developed by replacement and cementation of host sediments within the Fortescue Valley paleodrainage. The groundwater origin of dolomites is supported by replacement textures, evident from the preservation of host sediment fabric and inclusion of partially replaced detrital grains and etched quartz grains, phreatic cements and the lack of biogenic structures (Wright and Tucker, 1991; El-Sayed et al., 1991; Spötl and Wright, 1992). Predominantly massive dolomite textures with unimodal crystal distribution, which are common in the Fortescue samples, are often observed in groundwater calcrete and

dolocrete deposits attributed to the relatively uniform conditions, compared to the vadose zone (El-Sayed et al., 1991; Spötl and Wright, 1992; Colson and Cojan, 1996). These characteristics, in addition to the multi-metre thickness of dolocrete units and heterogeneous distribution within the Fortescue Marsh is consistent with “valley dolocrete” as defined by Carlisle et al. (1983) and Nash and Smith (2003). The morphology of the Fortescue dolocretes, dominated by dolomicrite to dolomicrospar, often containing grains of Fe-oxide pisoliths and quartz, is similar to the descriptions by Barnett (1981) of the Millstream Formation. The Fortescue host sediments, characterised largely by clay and siltstones, may represent a similar sequence of lacustrine and alluvial sediments, as that of the Western Fortescue Valley. Establishing whether dolomite formed by primary precipitation or dolomitization of a carbonate precursor, can be difficult (Last, 1990). Barnett (1981) suggested dolomite in the Millstream Formation formed by dolomitization of calcrete and lacustrine carbonate from Mg-rich groundwaters, sourced from the Wittenoom Formation, indicated by the fact dolomite above the water table was calcareous and presumably not dolomitized. However, petrographic observations of G2 dolocrete suggested calcite occurring above the water table was secondary and no calcite pre-cursors were observed in G1 and G2. The peloidal fabrics observed in a number of samples could be indicative of a lime mud host sediment, which has been later replaced by dolomite, but it is also possible that dolomicrite developed peloids replacing rounded clay bodies formed within channel sediments. Previous studies suggest groundwater dolocretes mostly develop within non-carbonate host sediments (Arakel, 1986; Khalaf, 1990; El-Sayed et al., 1991; Spötl and Wright, 1992). Relict silicate sediments are observed in G1 and G2 dolocrete, in addition to abundant authigenic clay and silica, where dissolution of silicate host sediments during

dolomite formation has increased Si concentrations in groundwater and ultimately precipitated new minerals. The authigenic palygorskite-sepiolite Mg-clays suggests high Mg concentrations in groundwater and, in addition to silica, is typical of dolomite deposits formed in evaporitic environments (Wright and Tucker, 1991; Aqrabi, 1995; Bustillo et al., 2002). Gypsum within overlying and adjacent sediments is also indicative of saline and evaporitic conditions (Armenteros et al., 1995). Overall, while there may have been carbonate-rich mud present in the Marsh, it is likely that dolomite developed by fairly massive replacement of fine-grained sediments of varied composition. The fabric selective replacement of mostly clay-silt matrix and peloids, with coarser and recalcitrant grains of Fe-oxide pisolites and quartz remaining, may partly account for the heterogeneous distribution of dolomite across the Marsh. Factors such as porosity, permeability and variation in topography and depth to basement may also result in localised differences in groundwater flow and physio-chemical environments affecting the distribution of carbonate precipitation (Skrzypek et al., 2016).

G1 dolomite is texturally mature, comprised of almost entirely authigenic minerals. The stoichiometric dolomite in G1 may be due to stabilisation over time and loss of excess Ca from the crystals (Morrow 1982a). The partial to complete dissolution of zones within G1 dolomite may reflect this process where less stable Ca-rich zones have been lost. High Mg/Ca ratios in groundwater may have also favoured formation of stoichiometric dolomite (Tucker and Wright, 1990). Non-stoichiometric Ca-rich dolomite, such as G2, is more common, particularly in younger sediments due to less time for diagenetic stabilisation (Armenteros, 2010; Morrow, 1982a). The higher proportion of Ca in G2 dolomite may also be due to alteration during calcitization of the dolomite, although G2 samples with no evidence of calcite also contain non-stoichiometric

dolomite. Textures observed in the calcitized dolomite were similar to some observed in other dolocretes including radial fibrous calcite rims, occurring around some grains and carbonate clusters (Khalaf and Abdal, 1993; Arenas et al., 1999; Rossi and Cañaveras, 1999). Empty cores within some G2 dolomite crystals suggests there was intracrystalline dissolution, followed by precipitation of calcite cement into many cavities (Khalaf and Abdal, 1993; Colson and Cojan, 1996). This may indicate dissolution occurred at some earlier stage, creating fine intergranular and intracrystalline porosity, as also observed in G1 dolomite, post-dated by calcite cement. However, Colson and Cojan (1996) described this texture as fabric-preserving and most likely linked to a rise in lake and groundwater levels and influence of dilute waters in contact with dolomite, resulting in concomitant leaching of dolomite cores and precipitation of calcite. The calcitization of G2 dolomite may therefore, be associated with the influence of fresher meteoric water with low Mg/Ca ratios (Calvo et al., 1995; Colson and Cojan, 1996; Arenas et al., 1999; Rossi and Cañaveras, 1999; Sanz-Rubio, 2001). In particular, flood events occurring at the Marsh, result in flushing of shallow sediments with fresher alluvial groundwater as well as infiltration of fresh surface water (Skrzypek et al., 2013; 2016). Phreatic cements and the radial fibrous calcite also suggests precipitation from groundwater, possibly around a fluctuating water table (Rossi and Cañaveras, 1999). The variability of the degree of calcitization in G2 dolomite may be due to heterogeneous porosity and permeability as well as groundwater level fluctuation (Colson and Cojan, 1996; Sanz-Rubio et al., 2001).

5.2 $\delta^{18}O$ signatures and hydrochemical conditions of carbonate precipitation

Previous models for groundwater dolomite formation (Mann and Horwitz, 1979; Arakel, 1986; Jacobson et al., 1988; Armenteros et al., 1995) highlight the importance of chemical modification of groundwater by evaporative concentration and mineral

precipitation along the hydrological flow path towards the centre of the drainage basin, promoting conditions conducive to dolomite formation, whether by primary precipitation or dolomitization. Evaporative concentration and calcite precipitation upstream, evidenced by extensive calcrete along drainage and paleodrainage channels leading to the Marsh (Mann and Horwitz, 1979; Barnett and Commander, 1985; Dogramaci et al., 2012), would have resulted in higher salinity and Mg/Ca of groundwaters reaching the terminal Marsh. These processes are also apparent for modern groundwater chemistry where Ca-HCO₃-Cl type fresh water delivered by rainfall has evolved to a Ca-Cl-HCO₃ type fresh-brackish water entering the Marsh, with median Mg/Ca ratios of ~1.6 (Dogramaci et al., 2012).

The $\delta^{18}\text{O}$ signatures of carbonates reflects the hydrochemical conditions in which the carbonates precipitated, in particular the salinity, which is strongly correlated with $\delta^{18}\text{O}$. The Fortescue Marsh dolomite, in particular G1, have $\delta^{18}\text{O}$ signatures that overlap those reported for dolomite in a number of dolocrete, lake margin and mud flat deposits (Spötl and Wright, 1992; Aqrabi 1995; Calvo et al., 1995; Arenas et al., 1999; Bustillo et al., 2002; Casado et al., 2014; Alonso-Zarza et al., 2016; Khalaf et al., 2017) and are relatively lower compared to the majority of reported primary lacustrine dolomites which have high, often positive, $\delta^{18}\text{O}$ values due to formation from intensively evaporated saline waters (Dutkiewicz et al., 2000; Wacey et al., 2007). Relatively low $\delta^{18}\text{O}$ values are consistent with a phreatic origin for the Marsh dolomites (Mann and Horwitz, 1979; Spötl and Wright, 1992; Calvo et al., 1995; Bojar et al., 2005; Last et al., 2012) as groundwater is usually less evaporated than surface water. The $\delta^{18}\text{O}$ values of G2 dolomite are notably lower, indicating a stronger influence of ^{18}O -depleted fresher flood waters and alluvial groundwater entering the Marsh (Skrzypek et al. 2013). The $\delta^{18}\text{O}$ values of G1 and G2

dolomites are significantly different ($p < 0.001$) and indicate the hydrochemistry of the precipitating groundwater changed between the two episodes of dolocrete formation.

The phreatic origin of the Marsh dolomites, with massive and unimodal dolomite textures, suggests formation in relatively uniform conditions with stable groundwater temperatures (Sibley and Gregg, 1987; Colson and Cojan, 1996). Therefore, assuming the precipitation of carbonates has occurred in isotopic equilibrium with the precipitation solution we can calculate the $\delta^{18}\text{O}$ values of the source water based on a probable range of groundwater temperatures using mineral-water oxygen isotope fractionation equations. Modelled $\delta^{18}\text{O}$ values can be compared to measured groundwater compositions to estimate the degree of mixing between the two groundwater end members (Fig. 5F). For this calculation, carbonate $\delta^{18}\text{O}_{\text{VPDB}}$ has first been converted to the $\delta^{18}\text{O}_{\text{VSMOW2-SLAP2}}$ scale (Brand et al., 2014; Kim et al., 2015). Considering modern groundwater temperatures of 28-32°C in the Marsh, the relationship between the $\delta^{18}\text{O}$ values of the carbonate minerals and source water was modelled for a larger range of temperatures between 20 and 40°C following; equation 1 for low temperature dolomite precipitation (Vasconcelos et al., 2005; Fig. 6A); and equation 2 for calcite (Coplen, 2007; Fig. 6B). The $1000\ln\alpha$ equations calculate the fractionation between the mineral phase and water which is then deducted from measured carbonate $\delta^{18}\text{O}$ values to provide the $\delta^{18}\text{O}$ values of the paleogroundwater (Table S4).

$$1000\ln\alpha_{\text{(dolomite-water)}} = 2.73 \times 10^6 T^{-2} + 0.26 \quad (\text{Equation 1, Vasconcelos et al., 2005})$$

$$1000\ln\alpha_{\text{(calcite - water)}} = 17.44 \times 10^3 T^{-1} - 28.6 \quad (\text{Equation 2, Coplen, 2007})$$

For G1 dolomite, the modelled water isotopic compositions using Eq. 1 falls within the range of saline-brine groundwater for temperatures of 18-35°C ($\delta^{18}\text{O}_{\text{VSMOW}}$ -3.4 to +1.5‰, median = -2.0‰ at 30°C; Fig. 6A). Formation at higher temperatures of >35°C would be less likely as this would suggest higher $\delta^{18}\text{O}$ values than that have been measured within the Marsh. Based on a probable range of groundwater temperature of 26-34°C ($\pm 2^\circ\text{C}$ from modern temperatures), the modelled $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{VSMOW}}$ -4.2 to +1.9‰) fall in the mid to upper range of saline-brine groundwater (TDS: 79-150 g/L calculated from the linear regression equation for TDS- $\delta^{18}\text{O}$ relationship; $\text{TDS} = (\delta^{18}\text{O}_{\text{VSMOW}} + 8.762) / 0.0678$ for $\delta^{18}\text{O}$ values at 30°C) and correspond to groundwater compositions dominantly influenced by the brine end member. Modelling $\delta^{18}\text{O}$ values for G2 dolomite samples is more complex due to heterogeneous calcitization of the dolocrete. However, the $\delta^{18}\text{O}$ values for G2 carbonates fall within a narrow range and therefore, it seems both earlier dolomite and calcitized samples have a similar signature. In contrast to G1, modelled $\delta^{18}\text{O}$ values for G2 dolomite samples using Eq. 1 indicates precipitation from relatively fresher water ($\delta^{18}\text{O}_{\text{VSMOW}}$ -6.6 to -5.7‰, median = -5.9‰ at 30°C; TDS: 33-46 g/L) and the range of modelled $\delta^{18}\text{O}$ values for temperatures between 26-34°C is consistent with mixing between inflowing fresh-brackish groundwater with saline-brine groundwater (Fig. 6A). The formation of G2 dolomite from only the fresh-brackish end-member would suggest temperatures of <26°C. However, this would be improbable as fresh-brackish waters with mostly Mg/Ca ratios of <2 would be unlikely to overcome the kinetic barriers of dolomite precipitation (Morrow, 1982a; Machel and Mountjoy, 1986).

Figure 6: A) Graph of temperature versus $\delta^{18}\text{O}$ of groundwater showing the range of $\delta^{18}\text{O}$ values of the precipitating fluid (paleogroundwater) modelled from G1 and G2 dolomite using equation 1 (Vasconcelos et al., 2005) and; B) G2 calcite using equation 2 (Coplen, 2007) between 20 and 40 °C. The average groundwater temperature is 30 °C, but ranges from 28 to 32 °C which is indicated by the vertical shaded area. The dashed lines indicate the range of measured groundwater compositions for saline-brine and fresh-brackish groundwater. C) Graph of average measured $\delta^{18}\text{O}$ values of groundwater versus $\delta^{18}\text{O}$ values of the precipitating fluid, at the corresponding bore, modelled from dolomite (equation 1) at 30 °C and; D) calcite (equation 2) at 20 °C and 30 °C. Grey shaded area represent 1:1 line $\pm$ 0.4 ‰ to represent the range of groundwater temperatures measured in the Marsh (28 to 32 °C) as the difference in modelled values is 0.4 ‰ per 2 °C, between 28 to 32 °C.

The precipitation of G1 dolomite from highly saline and brine groundwater suggests strongly evaporitic conditions occurred at the Marsh. This may have been a groundwater dependent playa lake to saline mud flat environment, where shallow groundwater undergoing intensive evaporation developed more positive $\delta^{18}\text{O}$ signatures

and promoted dolomite formation (Eugster, 1980; Arakel, 1986; Armenteros et al. 1995). This hypothesis is supported by the presence of gypsum, which developed in shallow sediments or as surface crusts, within adjacent and overlying sediments, characteristic of playa lakes (Mann and Deutscher, 1978; Eugster, 1980). Salt recycling (halite and gypsum) during wetting and drying processes is evident from the salt load in the Marsh (Skrzypek et al., 2013), resulting in Na-Cl brine groundwater and the fluctuating chemistry ensuing from wetting and drying cycles may have also contributed to dolomite formation (Arakel and McConchie, 1982; Deelman, 2003). Saline-formed G1 dolocrete sampled from fresh-brackish groundwater bores (Fig. 6C), also underlying G2 dolocrete in some locations (5D, 5E and 6E), demonstrates there has been a shift of the interface between fresher water and saline-brine groundwater, exposing G1 to fresher water compared to that from which it formed in the past. The larger range of $\delta^{18}\text{O}$ values for G1 dolocrete suggests slightly more variable hydrochemical conditions occurred during formation, compared to G2 dolocrete. However, there was no pattern between $\delta^{18}\text{O}$ values with lateral or vertical distribution within G1.

The lower $\delta^{18}\text{O}$ signature of paleogroundwater forming G2 dolomite suggests there was a change in hydrological regime between the formation of the two units and likely an increase in the delivery of fresher groundwater to the Marsh. The mechanism of dolomite precipitation from mixing of groundwaters, suggested for modelled $\delta^{18}\text{O}$ values of G2 source water, has been previously described for dolomite forming in evaporitic environments (Khalaf et al., 2017; El-Sayed et al., 1991; Aqrawi 1995; Colson and Cojan, 1996; Williams and Krause, 1998). Mixing of fresher inflowing groundwater, with higher HCO_3 concentrations, with saline-brine groundwater around the Marsh margin, would have raised alkalinity and promoted dolomite precipitation (Armenteros, 2010; Deelman,

2003). The higher $p\text{CO}_2$ of groundwater, relative to the atmosphere, may have also increased CO_3^{2-} activity as shallowing groundwaters entering the Marsh, due to topography, would have likely outgassed CO_2 (Eugster, 1980; Morrow, 1982a; Drever, 1988). Mixing of fresh and saline waters has been previously presented as a model for dolomitization, referred to as the “mixed water” or “mixing zone” dolomitization model (Morrow, 1989b) and is most commonly associated with mixing of marine and meteoric groundwaters (Hanshaw et al., 1971; Humphrey, 2000; Khalaf et al., 2017). This model has been controversial and often discounted for large scale dolomitization as the dilution of saline water would more likely decrease the Mg/Ca ratio and reduce the saturation state of dolomite (Machel, 2004). In these coastal settings, dolomitization may be driven by mixing as it promotes water circulation through the precursor sediments and dolomitization does not necessarily require mixing to provide the favourable hydrochemical conditions (Machel, 2004). In the terrestrial setting and hydrologically closed system of the Fortescue Marsh, inflow and the resulting mixing of groundwaters is imperative to provide a long-term source of ions to the Marsh for dolomite formation (G1 and G2), whether it be primary precipitation or dolomitization. G2 dolomite occurring at the Marsh margin within the mixing zone presents similarities with the “mixing zone” dolomitization model and whilst the setting may vary, factors linked to “mixing zone” dolomite, such as periodic mixing (Mazullo, 2006) from episodic or seasonal events, in addition to high microbial activity (Khalaf et al., 2017; Petrash et al., 2017) may also play a role in dolomite formation at the Marsh. G2 dolomite sampled from matrix of fresh-brackish aquifers have consistently higher modelled $\delta^{18}\text{O}$ values compared to measured groundwater in the corresponding bore for the range of modern groundwater temperatures of 28–32°C (+0.6 to 3.2‰ at 30°C; Fig. 6C), which may

suggest the interface of fresh to saline groundwaters has further shifted since the formation of G2.

Infiltrating meteoric waters and fresh flood waters within shallow alluvial sediments may be responsible for the replacement of dolomite with more stable low Mg-calcite (dedolomitization) in G2 dolocrete. Modelled water isotopic compositions for calcite (Fig. 6B) in G2 samples ($\delta^{18}\text{O}_{\text{VSMOW}}$ -6.0 to -4.3‰, median = -5.9‰ at 30°C; Fig. 11) using Eq. 2, indicates formation from moderately saline water ranging from ~40-66 g/L TDS based on a temperature of 30°C. Considering a lower temperature of 20°C, possible from inflow of flood waters or infiltrating meteoric waters, the range of modelled $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{VSMOW}}$ -8.0 to -6.3‰, median = -7.9‰ at 20°C) would correspond to lower salinities of ~11 to 37 g/L TDS and suggests formation from mostly brackish water with a similar $\delta^{18}\text{O}$ values to measured groundwater in the corresponding bores (Fig. 6D). Groundwater temperatures below 20°C would be unlikely as this is lower than average winter soil temperature for the region (Bureau of Meteorology; soil temperatures at 100 cm deep at Carnarvon 1970-2015) and the majority of large rainfall events and flooding are associated with tropical cyclones in summer months (Rouillard et al., 2015). The precipitation of calcite from brackish to saline groundwater, assuming groundwater temperature would mostly range from 20°C to the average temperature of 30°C, suggests that to some extent dedolomitization may be associated with coeval gypsum dissolution, locally increasing salinity and driving calcite precipitation (Arenas et al., 1999; Rossi and Cañaveras, 1999; Sanz-Rubio et al., 2001; Jin et al., 2010; Dogramaci et al., 2017). The saturation index (SI) values of gypsum in groundwater changes from a negative (strongly sub-saturated) towards equilibrium as the TDS concentration increases. Conversely, the SI values for calcite decrease with increasing TDS from > +1.0 (super saturation) to < 0.0

(under saturation). This suggests that there is a strong potential for gypsum dissolution and calcite precipitation from fresh-brackish groundwaters that are characterised by Cl ion concentrations of < 36 g/L (Mann and Deutscher, 1978). Therefore, a fluctuating shallow alluvial groundwater table and or infiltrating meteoric or flood waters would all have the potential to result in gypsum dissolution. When simultaneous equilibrium with respect to calcite and dolomite is combined with the dissolution of gypsum, the process of de-dolomitization may occur (Appelo and Postma, 2005). The increasing Ca concentration due to gypsum dissolution causes saturation with respect to calcite and increase in SO₄ concentration. The net result is that the dissolution of gypsum induces the transformation of dolomite to calcite in the sediments and produces water with progressively lower Ca/SO₄ ratios (Appelo and Postma, 2005; Jin et al., 2010).

5.3 $\delta^{13}\text{C}$ signatures of carbonates and groundwater

The $\delta^{13}\text{C}$ value of carbonates reflects that of the DIC of the precipitating solution and therefore the origin of the initial source of carbon (Emrich et al., 1970). The difference ($\Delta^{13}\text{C}$) between $\delta^{13}\text{C}$ values of HCO₃⁻ in modern DIC (-11.63 and -4.96‰), and the Marsh carbonates (-6.92 to -4.72‰) is higher than the expected fractionation between HCO₃⁻ and calcite (1.9-2.0‰) and dolomite (3.5-3.7‰) at temperatures between 20° and 30°C (Deines et al., 1974; Mook et al., 1974; Golyshev et al., 1981). At the majority of locations (3B-D, 5D-S, 6D-S, 6E-I, 7C) the $\Delta^{13}\text{C}_{\text{HCO}_3\text{-Carb}}$ difference ranged from 4.5 to 6.4‰. The relatively higher $\delta^{13}\text{C}$ values of carbonates and disequilibrium may be due to a change in source of C over time, shifting to currently more negative $\delta^{13}\text{C}$ values. However, the $\delta^{13}\text{C}$ values of DIC and any precipitating carbonates will also increase due to fractionation during CO₂ degassing (Deines et al., 1974; Talbot, 1990). Both modern DIC and the range of $\delta^{13}\text{C}$ values of carbonates indicate a source of biogenic

C, contributing to lower $\delta^{13}\text{C}$ signatures (Salomons et al., 1978; Cerling and Hay, 1986; Arenas et al., 1997). If the source of CO_2 in the precipitating solution was purely from atmospheric CO_2 (-7‰) or weathering of the Wittenoom Dolomite (-0.41 to 0.23‰), the $\delta^{13}\text{C}$ values of carbonates would have been in the range of ~ -0.4 and $\sim +5.2$ ‰ for dolomite and ~ -2.2 to $+3.2$ ‰ for calcite (assuming fractionation at temperatures of 20-30°C between dolomite and $\text{CO}_2(\text{g})$ of +10.9 to +12.2‰, and between calcite and $\text{CO}_2(\text{g})$ of +9.3 to +10.2; Deines et al., 1974; Golyshev et al., 1981). Potential sources of biogenic C to DIC includes; CO_2 originating from decomposition of plant organic matter and; very negative $\delta^{13}\text{C}$ values from bacterial activity in surface aquatic environments and groundwater in the Pilbara (Fellman et al., 2011; Fellman et al., 2014; Siebers et al., 2016). For modern DIC, soil CO_2 is not considered as a substantial C-source as Pilbara soils have very low concentration of organic carbon (<1%) (Rouillard et al., 2016), whereas high bacterial activity are a likely source of negative $\delta^{13}\text{C}$ in modern DIC at the Marsh (Dogramaci et al., 2017) and may have also contributed to the $\delta^{13}\text{C}$ signature of G1 and G2 carbonates in the past.

5.4 Timescales of dolocrete formation

Calcretes and dolocretes are widespread in the sedimentary record and numerous studies have identified Neogene to Quaternary deposits worldwide, for example; in Australia (Mann and Horwitz, 1979; Arakel, 1986); Kuwait (Khalaf, 1990); India (Khadkikar et al., 1998); Spain (Alonso-Zarza et al., 1992; Nash and Smith, 2003) and; Turkey (Kadir et al., 2010). Many ancient deposits such as; Triassic dolocretes in the Paris Basin, France (Spotl and Wright, 1992); Paleogene deposits in the Provence Basin, France (Colson and Cojan, 1996) and Portugal (Pimentel et al., 1996) and Carboniferous

calcretes in Eastern Canada (Jutras et al., 2007), have also been recognised. However, the timescales of calcrete and dolocrete formation are difficult to establish and direct age determinations are extremely limited (Netterberg, 1969; Mann and Horwitz, 1979; Yijian et al., 1998). The primary issue is the lack of carbonate dating techniques capable of dating the appropriate age range for the deposits. Consequently, the majority of studies establish the possible maximum age of calcrete and dolocrete formation by knowledge of host sediment ages and stratigraphic position (Netterberg, 1969). At the Fortescue Marsh, aggradation of the valley following a climatic shift to more arid conditions since the mid to late Miocene (Bowler, 1976; Payne, 2004) provides an upper constraint as dolocretization occurred after host sediments had been deposited in the Marsh. The depth of G1 dolomite of >20 m b.g.l indicates there has been further infill of the Marsh following G1 formation as groundwater dolocrete forms from shallow groundwaters undergoing evaporative concentration, usually within ~5 m of the surface (Mann and Horwitz, 1979). Similarities and proximity to dolomite of the adjacent Millstream Formation suggests the Fortescue Marsh dolocrete may be of similar age, presumed to have formed in the early-mid Pleistocene (Barnett, 1981).

Direct dating of Late Quaternary carbonates has been possible for some deposits using U/Th (<500 ka) or radiocarbon dating (<45 ka). Whilst U/Th dating provides a larger dating range, the technique can be limited for impure carbonate samples, common for calcrete and dolocrete, which are often contaminated by Th from intercalculated clay minerals. U/Th dating was attempted on samples of G1 dolocrete from ~35 m b.g.l from the 7B core in the central Marsh but produced results with very high uncertainty so was not included in this study. Radiocarbon dating was attempted on several samples of the younger G2 dolocrete. ^{14}C ages represent total carbonates and therefore, samples

reporting ages within the range of dating (<45 ka) must contain a considerable proportion of carbonate of <45 ka. However, direct carbonate ^{14}C dating constitutes several challenges due to a large amount of “dead carbon” primarily originating from erosion of 2.5 Ga old basement Wittenoom Formation as well as other geological units in the catchment (Trendall et al., 2004) and multiple stages of precipitation and potential dissolution. Dating of G2 samples, therefore, also reflects later calcitization of the dolocrete. Only three G2 samples were in the range of ^{14}C dating, ranging from median ages of 38.5 to 43.4 ka BP, and in theory provide an estimation of the maximum age of carbonate precipitation. The ages reported for 6D indicates the deeper sample is in fact younger with the sample from 7 m b.g.l. reporting a median calibrated age of 41.5 ka BP compared to carbonate from 2 m b.g.l. reporting > 45 ka. This anomaly has been previously reported by Mann and Horwitz (1979) and is attributed to mounding of carbonate during dolocrete formation, whereby precipitation of carbonate at groundwater level over time displaces previously formed carbonate up and outward, resulting in older carbonate being lifted above the water table. The inverted age could also be due to samples from 7 m b.g.l containing greater proportion of secondary calcite, lowering the age of total carbonates. Indeed, geochemical analyses of carbonate from the same depth (samples 14 and 15) contain mostly calcite. The remaining five G2 samples, with depths ranging from 2 to 23 m b.g.l, reported ages outside of the technique, although some very close to the 45 ka boundary. This suggests that while some G2 carbonate formed within <45 ka a large proportion formed prior to 45 ka. ^{14}C dating of some shallow carbonate at 2A (1-2 m b.g.l) confirms some more recent carbonate precipitation within <20 ka (19.9 ka BP at 1.1 m depth) and indicates formation rates of ~20,889 y/m. The samples within <45 ka were from ≤ 7 m.b.l and likely contained significant proportions of secondary

calcite. Therefore, it may be more likely that the relatively recent precipitation indicated by ^{14}C dating is from the calcitization of G2 dolocrete. Approximate dates have been established for other calcrete deposits in inland Australia; ages of ~20-60 ka BP were reported by Yijian et al., (1998) for calcrete in the Amadeus Basin of central Australia, using multiple dating techniques (ESR, U/Th and radiocarbon) and; calcrete hardpans in tropical Northern Australia were constrained to the late Pleistocene using a combination of ESR and U/Th dating (Nanson et al., 1989). Mann and Horwitz (1979) ^{14}C dated three calcrete samples from Lake Way in central-south Western Australia, which ranged from ~20-37 ka BP. These estimates may also be limited by multiple stages of carbonate dissolution and precipitation, however, the similarities in ages between the studies and the Fortescue Marsh G2 dolocrete suggests there was extensive carbonate precipitation and preservation occurring within inland regions of Australia in the terminal Pleistocene. In contrast, the increasing influence of fresher waters (Rouillard et al., 2016), flushing of sediments with periodic flood events and the groundwater level of >5 m b.g.l. in most locations across the Marsh (Skrzypek et al. 2013), suggests the potential for modern groundwater dolocrete formation and preservation is lower than in the past, despite the oversaturation of calcite and dolomite in the majority of measured groundwaters.

6. Conclusions

Two geochemically distinct units of groundwater dolocrete were identified within the Fortescue Marsh; a deeper unit (G1), containing stoichiometric dolomite with higher $\delta^{18}\text{O}$ values, indicating formation from more evaporatively evolved groundwater; and a shallower unit (G2), close to current groundwater level, containing Ca-rich dolomite and calcite with a comparatively lower range of $\delta^{18}\text{O}$ values, consistent with formation from

910 relatively fresher groundwaters. Petrographic observations of both units suggested
911 formation within the phreatic zone and may have formed as primary dolomite, as there
912 was no evidence of a calcite precursor. A primary or early diagenetic origin of dolomite
913 has also been reported for many other groundwater dolocretes (Arakel, 1986; Khalaf,
914 1990; El-Sayed et al., 1991; Spötl and Wright, 1992) and investigation of these deposits
915 may contribute to the understanding of low temperature dolomite formation in terrestrial
916 settings, which has thus far largely focussed on lacustrine environments. The chemistry
917 and distribution of carbonates provides a proxy to reconstruct the environment and
918 hydrological conditions occurring at the time of precipitation. In particular, the stable
919 oxygen isotopic signatures of carbonates provides a footprint of changing groundwater
920 salinity and highlights changes in the groundwater processes operating at the Fortescue
921 Marsh between the formation of the two dolomite units, during the Quaternary. Modelled
922 $\delta^{18}\text{O}$ values of paleogroundwater from which G1 dolomite precipitated, indicated highly
923 saline source water, which had similar compositions to relatively old brine groundwater
924 within the Marsh, developed under a different hydroclimatic regime (Skrzypek et al.
925 2013). The higher $\delta^{18}\text{O}$ values suggested highly evaporitic conditions occurred at the
926 Marsh, which may have been a playa lake to saline mud flat environment, where shallow
927 groundwaters underwent intensive evaporation. In contrast, the $\delta^{18}\text{O}$ values of G2
928 dolomite suggested formation most likely from mixing between inflowing fresher
929 groundwaters with saline-brine groundwater within the Marsh. The position of G2
930 dolomite overlying the saline formed G1, suggests the fresh-saline interface has shifted
931 towards the centre of the Marsh and inflow of fresher groundwater may have increased
932 between the formation of the two units. Infiltrating meteoric waters and flushing of
933 sediments with flood waters may be responsible for the de-dolomitization and

precipitation of low-Mg calcite in G2 dolocrete occurring close to and above groundwater level. The $\delta^{18}\text{O}$ values of the secondary calcite indicates formation from brackish to saline groundwater, which suggests this process may be associated with coeval gypsum dissolution and calcite precipitation driven by the common ion effect (Jin et al., 2010). Whilst the data presented here does not provide high-resolution paleoenvironmental and paleohydrological records due to lack of chronological control, the information obtained on the precipitation conditions of carbonates has improved knowledge on the hydrological evolution of the Marsh and how hydroclimatic conditions have changed over time. The distribution of groundwater dolocrete and calcrete in many arid and semi-arid drainage basins worldwide, may therefore provide a hitherto underutilised archive for paleoenvironmental conditions in inland continental settings, where there are often few proxies available.

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Appendices

Electronic supplementary data, Tables S1, S2, S3, S4 and S5, to this article can be found online at...

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