INTRODUCTION

The East African Rift System (EARS) is an area of active extensional tectonics formed in response to the rising of one or more mantle plumes (Hansen et al., 2012). Rifting began in the Miocene and over the last 25–30 Myr created a series of basins within the 3,000 km rift zone (Frostick, 1997; Ebinger, 2005). The Western and Eastern rift branches are characterized by normal faulting and volcanism ranging from basalt lavas to explosive pyroclastic eruptions. The EARS is currently the only locality on Earth producing carbonatites which are igneous rocks composed of at least 50% carbonate minerals (Bell et al., 1998). Rift-related basins were infilled by volcanoclastic sediments that archive rich fossil records of flora and vertebrate
faunal evolution, including humans (Bobe et al., 2007). The internally drained (i.e. endorheic) basins contain sediments deposited in a myriad of palaeoenvironments, providing records of continental climate comparable with marine climate records from the surrounding ocean basins. Thus, the EARS attracts a variety of scientists and researchers with broad interests.

The Olduvai Basin (3°S in northern Tanzania), in particular, has been extensively studied because an important hominin fossil, ‘Zinjanthropus’, was discovered there (Leakey, 1959; Figure 1). Olduvai quickly became world famous and has been called the ‘Cradle of Mankind’. It contains a 2 Myr record of palaeontology (including megafauna, birds, fish, micromammals and four hominin species) and archaeology (thousands of stone tools; Leakey, 1971; Bunn and Kroll, 1986; Yravedra et al., 2017). Over 100 m of Pleistocene ignimbrites, lavas and tuffs record Olduvai Basin’s volcanic and tectonic history (McHenry, 2004; Mollel, 2007; Stollhofen et al., 2008).

Clastic sedimentary rocks between the igneous tuffs and lavas contain the records of changing palaeoenvironments in this arid equatorial setting (Hay, 1976; Ashley and Hay, 2002; Ashley, 2007; Barboni et al., 2010). Carbonate rocks have, however, received comparatively little attention except for specialized studies of calcretes (Hay and Reeder, 1978), and carbonate palaeosols (Cerling and Hay, 1986; Sikes and Ashley, 2007; Bennett et al., 2012). Research on individual hominin-bearing archaeological sites describes freshwater limestones, each within its own local context (Liutkus and Ashley, 2003; Ashley et al., 2010a; 2010b) but, to date, there has not been a comprehensive study on the origin of freshwater limestones intercalated with the clastics and volcanics.

Recent mapping in the Olduvai Basin revealed an extensive carbonate unit at 1.8 Ma in age that varies spatially in thickness, field expression, petrography, geochemistry and freshwater fossil remains. The carbonate unit appears to be isochronous-stratigraphic because, where present, it occurs under the same air fall tuff, Tuff IF (Figure 2). This new find is an opportunity to understand the origin of freshwater continental limestones in the EARS. The objectives of this paper are to determine: (a) the environment(s) of deposition; (b) the processes involved in carbonate concentration, precipitation and diagenesis; and (c) the potential contribution of carbonatite volcanism.

Although ions for limestone formation are generally a common constituent in groundwater (Deocampo and Renaut, 2016), freshwater carbonates are relatively uncommon across global landscapes and are, volumetrically, of minor importance in the geological record (Tucker and Wright, 1990). Particular circumstances must, therefore, be responsible for the formation of appreciable continental limestone deposition (Ashley et al., 2014c). In Olduvai Gorge, siliciclastic sediments dominate the Pleistocene record but within a few centimetres of Tuff IF, a major stratigraphic marker bed, carbonate accumulated as laterally extensive limestones and dolomites to a degree not found elsewhere in the gorge (Figure 2).

1.1 | Geology

The Olduvai Basin is a shallow depression between crystalline metamorphic basement rocks that lie beneath the Serengeti Plain (west) and the Ngorongoro Volcanic Highland (east; Figure 1). Structurally the Olduvai Basin is a ‘rift-platform basin’ located on the margin of the Gregory Rift, the eastern branch of the EARS and at a point of bifurcation in the rift system termed the ‘Northern Tanzanian Divergence’ (Dawson, 2008; Le Gall et al., 2008). The igneous rocks are described by Hay (1976), McHenry (2004) and Mollel (2007).

Olduvai Basin sediments are cut by numerous rift parallel (north-south) normal faults (Hay, 1976; Ashley and Hay, 2002), two of which form a small graben within the basin (Figure 3). Olduvai began infilling with lavas, tuffs and reworked volcanoclastic material about 2 Ma (Figure 2). A saline-alkaline, silt and smectite-rich, playa lake, termed palaeo-Lake Olduvai by Hay (1976), occupied the centre of the basin (Hay and Kyser, 2001; Hover and Ashley, 2003; Deocampo, 2004). Spring tufa deposits and wetland sediments (siliceous clays) interfinger with lake clays on the playa lake margin (Deocampo et al., 2002; Liutkus and Ashley, 2003). Alluvial fan deposits, consisting in part of volcanoclastic material from the Ngorongoro Massif, built into the basin from the east and south (Ashley and Hay, 2002; Garrett, 2015). Quartzo-feldspathic sediments, derived from metamorphic basement rocks supplied from rivers draining the Serengeti Plain, encroached on the western margin (Sikes and Ashley, 2007). Rift-related tectonism during the Late Pleistocene caused tilting of the basin towards the east (Hay, 1976) and the Olduvai River incised through the basin creating Olduvai Gorge, exposing a +100 m thick sedimentary record.

FIGURE 1 Regional location map. Northern Tanzania Divergence and location of the Olduvai and Laetoli basins. Volcanoes and dates of known carbonatite eruptions (Satiman 3.6 Ma and Ol Doinyo Lengai and Kerimasi, modern) and the proposed carbonatite eruption of Olmoti (1.8 Ma) are depicted.
This study focuses on a time-equivalent carbonate horizon that appears to have covered a large area of the basin (Hay, 1976), however, outcrops of this unit are spatially limited to the position of the modern gorge (Figure 3). Study samples are from a nearly continuous series of outcrops along a north-south transect (Figure 4) and an outcrop in the middle of the dried out palaeo-Lake Olduvai playa (black dot on Figure 3).

Olduvai Basin’s stratigraphy is well dated using the magnetic polarity time scale and Single Crystal Laser 40Ar/39Ar dating of tuffs (Hay, 1976; Deino, 2012), providing excellent age control for the intervening sedimentary deposits (Figure 2). Hay’s (1976) comprehensive study ‘The Geology of Olduvai Gorge’ divides the sedimentary package into seven units. This study focuses on the time slice in the upper portion of Bed I (Figure 2B).

1.2 | Climate and Hydrology

Precipitation varies seasonally (two rainy seasons a year) and in the long term precipitation is astronomically controlled by Milankovitch, specifically precession, climate cycles (Ashley, 2007; Magill et al., 2013a; Deocampo et al., 2017). Estimates of palaeoprecipitation in Olduvai Gorge vary from 250 mm/year during precession dry periods to 700 mm/year during wet periods (Magill et al., 2013b). The modern mean annual temperature averages 25°C and the potential evapotranspiration is estimated at 2,000–2,500 mm/year (Dagg et al., 1970) i.e. four times the precipitation, resulting in a hydrological budget that is moisture limited. The modern Ngorongoro Volcanic Highland (to the east of the gorge) is over 3,000 m high. It traps moisture-laden easterly trade winds from the Arabian Sea and creates a rain shadow for Olduvai Basin that lies to the west. The modern rainfall on Ngorongoro is ca 900 mm/year (Norton, 2019) and could have been twice that during Milankovitch wet periods. Some rainfall runs off in ephemeral surface streams, but most infiltrates into the relatively porous volcanoclastic deposits of the Highland and moves westward in the subsurface into the Olduvai Basin (Figure 3). Today groundwater exits at the base of the slope contributing to a lake/swamp called Obalbal. Obalbal is a sump collecting groundwater flowing from the Highland to the east and seasonal run-off from the modern Olduvai River flowing from the west. The hydrogeological setting was likely similar in the past. High-resolution studies of palaeoclimatic and palaeoenvironmental reconstruction have revealed a number of springs and wetlands associated with archaeological sites in the Olduvai Basin indicating that groundwater discharged into the basin during both wet and dry portions of the precession cycle (Deocampo et al., 2002; Ashley et al., 2009; Deocampo and Tactikos, 2010).

2 | METHODS

2.1 | Field

Carbonate outcrops that occur within the map area shown in Figure 4 and one outcrop in the centre of the playa were sampled (Figure 3). The carbonate horizon was physically traced in the field. Six stratigraphic sections (0.50–1.4 m high) were excavated, logged using scaled drawings and photographed. Sample locations were documented using a global-positioning system. Forty-two samples were collected for this study. An
additional 27 samples of tufa (data published in Ashley et al., 2014b) are included in this study’s dataset for completeness.

2.2 | Laboratory

2.2.1 | Petrography

Forty-two, 30 µm thick, standard-size thin sections were stained with potassium ferricyanide and alizarin red-S (Dickson, 1966) and photomicrographs were taken using a Leica S6D microscope with a Leica ICC50 HD camera.

2.2.2 | X-ray diffraction

Microsamples from each carbonate lithology (micrite ± sparry calcite, dolomite) for a total of 27 samples were obtained using a Dremel microdrill at low rpm. Each sample was drilled under a magnifying glass to avoid visibly different constituents. Samples were run at Franklin and Marshall College on a PANalytical X’pert Pro PW3040 X-ray diffraction (XRD) spectrometer using Cu K Alpha radiation, an automated diffraction slit and a X’Celerator detector, according to standard procedures (scans from 6 to 70° 2θ with a NIST traceable Si metal used to check goniometer accuracy). Results are in Table 1.

2.2.3 | Trace element analyses

Thirty five samples, referenced to the appropriate thin sections, of carbonate (0.05 g micrite ± sparry calcite, 0.25 g dolomite) were microdrilled under a microscope to avoid visible impurities. Samples were subsequently dissolved in 10% HNO₃ and analysed at Franklin and Marshall College using a SPECTROBLUE inductively coupled plasma optical emission spectrometer (ICP-OES), with 750 mm focal length, a Paschen-Runge optical system and 15 linear CCD array detectors. Calibrations were made to seven standards, diluted to appropriate concentrations, from Specpure commercial stock solutions referenced to known standards. The ICP-OES was calibrated before each run with a tuning solution to account for instrumental drift. Standard curves with 5+ points were compiled for each element with correlation coefficients >0.998. Standards

FIGURE 3  Inset map shows the location of Olduvai on the margin of the EARS (East African Rift System). Map is a palaeogeographic reconstruction of the Olduvai Basin at the time of the study ca 1.8 Ma. Outline of expanded and contracted playa lake, direction of groundwater flow from fringing volcanoes of the Ngorongoro Volcanic Highland, faults and the two study site locations are shown: (a) area within the rectangle labelled Figure 4 and (b) black dot in middle of playa.
Jls-1 and JDo-1 were run at the beginning and end of the run and were within <5% relative standard deviation (RSD) error of established values. Duplicate samples were within <1% RSD. Results are reported in parts per million (ppm; Table 1).

2.2.4 Rare earth analyses

Dried concentration splits were re-dissolved and diluted in 2% ultrapure HNO₃ and subsequently analysed by inductively coupled plasma mass spectrometry on a Thermo iCapQ™ mass spectrometer at Rutgers University. Concentrations were determined using a synthetic standard mixture with 100 ppb of each element. Barium, Rb, Sr, Y and rare earth elements (REE) were measured using three channels per isotope (spacing 0.1 amu), with 10 passes and 10 repeats for each sample. Dwell times for each isotope measured were 10 ms. Standard calibration regressions yielded $r^2$ values of >0.99 for all elements.

2.2.5 Stable isotope analyses

Approximately 100 µg of powdered sample was loaded into a reaction vial for the automated stable isotope analysis using a Multiprep device attached to a Micromass Optima mass spectrometer. Samples were reacted for 800 s in phosphoric acid at 90°C and the evolved CO₂ was collected in a liquid nitrogen cold finger. Stable isotope values are reported relative to Vienna Pee Dee Belemnite (V-PDB) through analysis of in-house laboratory reference material (RGF1). The 1-sigma standard deviation of RGF1 made during these analyses (typically 8 RGF1 analyses for every 24 samples) is 0.05 and 0.09‰ for $\delta^{13}$C and $\delta^{18}$O, respectively. The RGF1 is routinely calibrated to NBS-19 to insure consistency, using values of 1.95 and $-2.20$‰ for $\delta^{13}$C and $\delta^{18}$O, respectively (Coplen, 1994). The internal laboratory reference material differs from NBS-19 by +0.10 and +0.04‰ for $\delta^{13}$C and $\delta^{18}$O, respectively. The laboratory analyses NBS-18 to monitor changes in source linearity for $\delta^{18}$O values. The average $\delta^{18}$O value of NBS-18 identified during the analytical period in question is $-23.07$‰, similar to Coplen’s value of $-23.01$‰ (Coplen, 1994). Therefore, no correction for linearity was made. Data are summarized in Table 1.

3 LITHOLOGIC CHARACTERISTICS AND INTERPRETATION

Five distinct lithologies are recognized based on field relationships, petrography, trace element geochemistry, stable isotope (C and O) values and ostracod preservation. Four of these lithologies record primary characteristics of the carbonate-rich depositional environments that occurred in a catena-like pattern over a heterogeneous landscape (Figure 4). The deposits occur as discreet units, 25–140 cm in thickness, and are not directly associated with previously documented carbonate palaeosols (Hay and Reeder, 1978; Cerling and Hay, 1986; Sikes and Ashley, 2007; Bennett et al., 2012). Since each deposit has its own subtle characteristics, including field, petrographic, isotopic and geochemical signatures, they reflect depositional conditions particular to each location and are thus described as separate lithologies. These carbonate lithologies are (a) light-coloured, porous, chalky tufa; (b) buff-coloured silty marl with ostracod shell fragments; (c) light grey micritic mudstone with articulated ostracods; and (d) white silty dolomicrite (Figure 5A through D). All show some degree of post-depositional modification which produced a slight pedogenic overprint. In one locality a very pronounced nodular fabric reflects pedogenic processes that have obscured any primary limestone features. This lithology (e), a nodular carbonate, is described and interpreted under Diagenetic Features below.

3.1 Tufa

3.1.1 Description

These carbonates occur within Upper Bed I, directly under Tuff IF (Figure 5A) and are described and interpreted in
| Sample number | $\delta^{13}$C (‰) | $\delta^{18}$O (‰) | Fe (ppm) | Mg (ppm) | Mn (ppm) | Sr (ppm) | Lith | XRD mineralogy |
|---------------|---------------------|---------------------|----------|----------|----------|----------|------|----------------|
| GA-1-08       | −2.3                | −4.3                | 1,128    | 9,227    | 634      | 499      | Soil  | B cal          |
| GA-3-08       | 0.0                 | −2.9                | 557      | 10,307   | 199      | 733      | B     | nm            |
| GA-6-08       | −1.1                | −3.2                | 969      | 8,433    | 326      | 511      | B     | nm            |
| GA-24-13      | 0.2                 | −3.3                | 915      | 10,684   | 2,153    | 1,602    | B     | nm            |
| GA-42-16      | −1.5                | −1.9                | 383      | 71,403   | 153      | 4,950    | B     | cal, ank, Mg-cal, dol |
| GA-43-16      | −0.3                | −2.2                | 155      | 74,412   | 212      | 4,763    | B     | cal, Fe/Mg-cal, dol |
| GA-44-16      | −0.1                | −1.9                | 402      | 74,425   | 167      | 4,855    | B     | dol, silicate |
| GA-30-09      | −3.0                | −4.6                | 1,253    | 11,036   | 177      | 683      | Wetland | C nm        |
| GA-13-10      | −4.9                | −4.9                | 3,126    | 17,551   | 134      | 352      | C     | nm            |
| GA-14-10      | −4.8                | −5.1                | 1,686    | 11,010   | 121      | 293      | C     | nm            |
| GA-83-11      | −4.8                | −5.6                | 5,305    | 25,330   | 141      | 403      | C     | nm            |
| GA-84-11      | −4.4                | −5.0                | 530      | 7,664    | 164      | 677      | C     | nm            |
| GA-85-11      | −4.6                | −5.1                | 1,150    | 12,510   | 137      | 413      | C     | nm            |
| GA-91-11      | −5.8                | −4.7                | 1,854    | 15,077   | 144      | 299      | C     | nm            |
| GA-93-11      | −5.6                | −6.0                | 1,202    | 10,588   | 124      | 256      | C     | nm            |
| GA-94-11      | −4.8                | −5.7                | 623      | 2,554    | 117      | 186      | C     | nm            |
| GA-45-16      | −3.2                | −4.7                | 702      | 14,732   | 111      | 807      | C     | cal, Mg-cal, silicate |
| GA-46-16      | −3.6                | −5.4                | 1,538    | 16,724   | 213      | 437      | C     | cal, qtz      |
| GA-47-16      | −4.6                | −5.5                | 1,159    | 15,377   | 122      | 455      | C     | cal, qtz      |
| GA-48-16      | −5.0                | −5.4                | 3,275    | 25,597   | 190      | 800      | C     | cal, dol, qtz |
| GA-49-16      | −4.6                | −5.5                | 1,857    | 20,771   | 94       | 658      | C     | cal, Mg-cal, silicate |
| GA-50-16      | −5.0                | −5.4                | 1,504    | 18,274   | 74       | 528      | C     | cal, qtz, Mg-cal |
| GA-8-08       | −3.5                | −4.8                | 2,728    | 17,119   | 40       | 1,113    | Lake/pond | D nm |
| GA-98-11      | −4.9                | −5.9                | 2,181    | 20,167   | 58       | 2,241    | D     | nm            |
| GA-12-15      | −6.0                | −5.7                | 4,021    | 22,906   | 17       | 250      | D     | nm            |
| GA-18-15      | −4.7                | −4.9                | 529      | 6,838    | 52       | 370      | D     | nm            |
| GA-21-15      | −4.9                | −5.3                | 706      | 7,473    | 40       | 240      | D     | nm            |
| GA-23-15      | −4.1                | −5.0                | 180      | 4,233    | 67       | 632      | D     | nm            |
| GA-2-16       | −5.4                | −5.5                | 686      | 12,736   | 78       | 202      | D     | cal, Mg-cal, silicate |
| GA-34-16      | −6.4                | −5.9                | 1,820    | 17,557   | 158      | 469      | D     | cal, qtz      |
| GA-37-16      | −6.2                | −5.9                |         |         |         |         | D     | cal, qtz      |
| GA-38-16      | −6.0                | −5.8                | 2,637    | 22,101   | 83       | 389      | D     | cal, Mg-cal, qtz |
| GA-39-16      | −3.8                | −4.9                | 2,498    | 23,110   | 113      | 1,135    | D     | cal, Mg-cal, silicate |
| GA-51-16      | −4.1                | −5.7                | 69       | 4,183    | 11       | 580      | D     | cal, Mg-cal |
| GA-54-16      | −7.0                | −6.4                | 770      | 4,546    | 13       | 294      | D     | cal, qtz      |
| GA-55-16      | −6.4                | −6.5                | 374      | 5,656    | 7        | 239      | D     | cal, Mg-cal, qtz |
| GA-47A-18     | −3.1                | −2.1                | 7,226    | 81,962   | 1,143    | 5,126    | Dolomicrite | A dol ± ank, anl, Mg-cal, qtz |
| GA-47B-18     | −3.1                | −1.9                | 8,054    | 77,884   | 1,514    | 4,758    | A     | dol, anl, qtz |
| GA-47C-18     | −3.0                | −2.2                | 7,260    | 81,022   | 1,532    | 4,966    | A     | nm            |
| GA-47D-18     | −3.0                | −2.2                | 7,368    | 78,326   | 1,761    | 4,730    | A     | nm            |
| GA-47E-18     | −3.0                | −2.2                | 8,524    | 86,162   | 1,653    | 5,260    | A     | dol, Mg-cal/ank, anl, qtz |
| GA-47F-18     | −2.8                | −2.3                | 6,587    | 78,374   | 1,500    | 4,600    | A     | nm            |

Abbreviations: ank, ankerite; anl, analcite; cal, calcite; dol, dolomite; nm, not measured; qtz, quartz.
Depositional characteristics
The lithology occurs as a long, narrow deposit that varies in thickness from 0.30 to 1.4 m following the north-south Zinj Fault (Driese and Ashley, 2016; Figure 4). There are very few east-west oriented outcrops, but where exposed the width is <20 m. The carbonate is light-coloured (white to tan) calcite and may have a chalky texture (Figure 5). Micrite is structureless to vaguely laminated with inter-laminations of yellowish brown smectitic clay. Root casts, brown to yellow clay patches, with spongy, nodular and platy fabrics are common.

Petrographic characteristics
The carbonate consists of porous, friable to moderately indurated micrite with non-ferroan calcite spar and very rare secondary dolomite. Ostracod shells, peloids and detrital grains are abundant and root moulds and rhizoconcretions are also present (Ashley et al., 2014c; Figure 6A).

Stable isotopes
Data show the isotope values have a strong covariance with a very narrow range of δ18O values from −5.78‰ to −3.78‰ and a wide range of δ13C values from −5.57‰ to −1.83‰ (Figure 7; Baluyot, 2011). The mean oxygen isotope value is −5.19‰ while the mean carbon isotope value is −4.7‰ (Table 2).

3.1.2 Interpretation
Based on field, petrographic and δ18O isotopic evidence that carbonate precipitation likely happened quickly from degassing of CO2 (Ashley et al., 2010a), carbonate deposits are interpreted as tufa precipitating from springs sourced from...
groundwater debouching along the Zinj Fault (Ashley et al., 2010a; Figure 4). Fault-derived water collected in a series of springs and shallow ponds along the fault trend. This environment is similar to cool, fresh water carbonates previously described (Pedley, 1990; Ford and Pedley, 1996; Capezzuoli et al., 2013; Lee et al., 2013).

3.2 Silty Marl with ostracod fragments

3.2.1 Description

Depositional characteristics
The carbonate unit is ca 50 cm thick and occurs under Tuff IF, separated from it by a 5 cm thick greyish brown clay (2.5Y 5/2 Munzel colour; Figure 5B). The limestone is a buff-coloured, powdery, structureless, massive bedded carbonate with internal blebs, streaks and laminations of brown clay. The samples cluster in an area indicated in green on Figure 4.

Petrographic characteristics
Silt to fine sand-sized, angular to subangular, detrital grains occur within bioturbated, clayey micrite, with ostracod shell fragments (Figure 6B). Micrite is characterized by clotted, mottled and/or peloidal textures and micrite intraclasts are common. Smectite clay micronodules and Mn-oxide dendrites are associated with burrows or root traces. Circumgranular cracks, usually filled with sparry, non-ferroan calcite, are abundant.

Trace elements
Iron concentrations (average 1,784 ppm) are between the values obtained from the carbonate nodule facies (lower) and those from the dolomite facies (higher). They are most similar to the lacustrine facies samples although there are some with higher concentrations (Table 1; Figure 8). Magnesium concentrations in palustrine samples average 14,986 ppm, Mn values have an average of 137 ppm and Sr averages

**FIGURE 6** Stained photomicrographs of four carbonate lithologies. (A) Root mottled lime mudstone (spring) sample GA-30-09. (B) Lime mudstone with ostracod fragments (wetland) sample GA-91-11. (C) Micrite with articulated ostracods (lacustrine) sample GA-34-10. (D) Dolomicrite is the brownish matrix, with dolomite crystals in cavities (centre), siliciclastic silt grains, and unidentified shell fragments sample GA-47B-18. (A) through (C) are limestones with original calcite mineralogy, (D) had a precursor Mg-calcite mineralogy that was replaced with dolomite during diagenesis.

**FIGURE 7** Stable isotope plot of the five groups of carbonates by interpreted palaeoenvironment. The wetland and lake/pond lithologies overlap likely due to playa lake-level changes, the other lithologies plot in their own isotope space. The δ18O value of −6.0‰ (vertical straight line) is for CaCO3 in equilibrium with rainfall at 25°C.
483 ppm. The Mg and Sr average values are similar to those from the lacustrine samples (see below).

**Stable isotopes**

The $\delta^{18}O$ values range from $-3.03\permil$ to $-4.95\permil$ and average $-4.58\permil$. These are correlated with the $\delta^{13}C$ values that range from $-4.59\permil$ to $-5.96\permil$ and average $-5.24\permil$ (Figure 7; Tables 1 and 2).

### 3.2.2 | Interpretation

The interpreted depositional setting is a wetland which typically has elements of both submerged and subaerial environments (Alonso-Zarza, 2003). Wetlands are characterized by features indicative of standing water, such as ostracods, overprinted by features indicative of exposure and paedogenesis (Alonso-Zarza et al., 2006). The limestones described here contain ostracod shell fragments in bioturbated lime mud, suggesting that standing water was present and conditions were suitable for sediment infauna and aqueous fauna. The plethora of broken ostracod shells suggests that the water was shallow enough for episodic turbulence (likely seasonal storms and/or large animal wallowing) that broke up the shells (Ashley and Liutkus, 2002). Post-depositional paedogenesis may also have contributed to shell fragmentation. Siliciclastic grains in the limestone indicate that fluvial and/or aeolian processes brought fine-grained silt and sand into the wetland area. Relatively low trace element concentrations suggest that the wetland waters were oxidizing, therefore, iron and manganese would not be in their reduced valency ($2^+$) and thus be unlikely to replace $\text{Ca}^{2+}$ in calcite. The abundance of circumgranular cracks, mottles, glaebules and possible root traces indicates episodic shallowing and subaerial exposure (Balin, 2000). Similar deposits are described from Polish Upper Triassic freshwater limestones (Szulc et al., 2006). This carbonate lithology is, therefore, interpreted as having formed in a shallow wetland environment that experienced episodic subaerial exposure (Figure 9). Uribelarrea et al. (2014) make the same palaeoenvironmental interpretation for mixed siliciclastic-carbonate deposits in this same location in the gorge, but in a much older (by 40,000 years) stratigraphic horizon, suggesting that it was a topographic low area for a long time.

### 3.3 | Micritic Mudstone with articulated ostracods

#### 3.3.1 | Description

**Depositional characteristics**

In this unit, 40 cm of dense, pale grey carbonate becomes progressively more laminated up section. Overlying, a 60 cm thick, greenish grey waxy claystone is separated from the overlying Tuff 1F by 2 cm of clay (Figure 5C).

**Petrographic characteristics**

Bioturbated lime muds contain articulated ostracod shells (Figure 6C). Abundant burrow structures are filled with non-ferroan calcite spar and typically have diffuse halos around them. The halos are characterized by denser micrite, clay aggregates and/or Mn-oxide dendrites surrounding the burrow. Siliciclastic grain content is variable with some samples consisting of nearly pure micrite compared to others that are packed with angular feldspar grains, lithic fragments and carbonate intraclasts. Terrigenous clay is present as thin (millimetre-scale) lenses. Shelly material is less abundant in the siliciclastic-rich intervals. Intraclasts are concentrated in sandy–silty horizons.

**Trace elements**

The trace element concentrations in the lacustrine carbonates are generally low; average Fe is 1,476 ppm, average Mg is 12,971 ppm, average Mn is 56 ppm and average Sr is 627 ppm (Table 1; Figure 8). These micrites contain the lowest average Mg values compared to the other lithologies and are similar in composition to the wetland carbonates.

**Stable isotopes**

The $\delta^{18}O$ values range from $-4.79\permil$ to $-6.54\permil$ with an average value of $-5.59\permil$. These values are strongly correlated with the $\delta^{13}C$ values that range from $3.46\permil$ to 7.05\permil and average $-5.23\permil$ (Figure 7; Tables 1 and 2).

#### 3.3.2 | Interpretation

An abundance of articulated ostracods indicates generally quiet water conditions usually associated with the

### Table 2

Average trace elements and stable isotopes by lithology

|          | Fe (ppm) | Mg (ppm) | Mn (ppm) | Sr (ppm) | $\delta^{13}C$ (%) | $\delta^{18}O$ (%) |
|----------|----------|----------|----------|----------|--------------------|--------------------|
| Spring   | 1,919    | 17,369   | 222      | 697      | $-4.1$            | $-5.2$            |
| Solid    | 644      | 36,984   | 549      | 2,559    | $-0.7$            | $-2.8$            |
| Wetland  | 1,784    | 14,986   | 137      | 483      | $-4.6$            | $-5.2$            |
| Lake/pond| 1,476    | 12,971   | 56       | 627      | $-5.2$            | $-5.6$            |
| Dolomicroite | 7,503  | 80,621   | 1,517    | 4,906    | $-3.0$            | $-2.1$            |
sublittoral zone (Dean and Fouch, 1983). An active infauna, evidenced by burrows and bioturbation in the Olduvai micritic mudstone indicates that bottom sediments were oxygenated, and ostracods indicate oxygenated water, thus it was likely that this Upper Bed 1 carbonate represents deposition in a shallow, non-stratified small lake, or pond (Figure 9). The presence of laminated upper layers suggests that as water-levels fell and/or the water chemistry shifted, algal/cyanobacterial mats colonized the sediment surface, forming laminations similar to those seen today in the Florida Everglades (McCormick et al., 1998) and atoll lakes in Polynesia (Defarge et al., 1994). Alternatively, the laminar fabric may have formed at the junction between the phreatic and vadose zones within a meteoric water table, per Hay and Reeder’s (1978) interpretation of other laminar carbonates above and below Bed I in the Olduvai stratigraphy.

The Olduvai small lake formed south of the previously described wetland in a topographic low adjacent to the Zinj Fault. Water ponded here due to down dropping of the fault’s hangingwall (Figures 3 and 4). The claystone below this limestone is interpreted as a palaeosol horizon (Ashley et al., 2014a) which functioned as an aquitard, collecting water and concentrating ions for limestone formation.

**FIGURE 8** Plots of four trace elements (Mg, Mn, Sr vs. Fe) in the carbonate lithologies: soil, wetland, lake/pond, dolomicrite

**FIGURE 9** Schematic diagram highlights the importance of groundwater and a fluctuating water table on processes of carbonate deposition in lake margin environments: springs, wetland, lake and playa, as well as pedogenesis in soil formation (after Alonso-Zarza, 2003)
The relatively low concentrations of trace elements within the micrite (Figure 8) suggest fresh water without significant evaporative cation enrichment. Correlated negative stable isotopes suggest relatively rapid precipitation (Figure 7). Alkaline water conditions, favourable to carbonate precipitation, were necessary to produce the micrite matrix. Clays carried in suspension into the lake settled out during quiescent periods, producing the thin mud lenses. Samples rich in siliciclastic grains and locally-derived intraclasts suggest that episodic high energy events washed lithic material into the lake and were capable of ripping up nearby littoral zone semi-lithified sediment to form intraclasts. Grainification, the breakup of lacustrine micritic muds by desiccation and/or roots (Bustillo and Alonso-Zarza, 2007), may also have produced some of the intraclasts.

3.4 | Silty Dolomicrite

3.4.1 | Description

Depositional characteristics
A 10 cm thick white dolomite bed occurs in the centre of the basin about 6 km west from the other carbonate deposits, but in the identical stratigraphic position as the previously described limestones, just under Tuff IF (Figures 2, 3 and 5D). It is separated from the tuff by ca 2 cm of green smectitic clay. The site is Hay’s LOC 80 (Hay, 1976; Hay and Kyser, 2001). The silty dolomicrite overlies a thick sequence of clayey siltstones with calcite crystals and calcite nodules (3-8 mm) randomly dispersed within it.

Petrographic characteristics
The silty dolomicrite lithology is characterized by dense dolomicrite, with abundant clays giving it a brown colour in thin section, and dolomite rhombic cement crystals (Figure 6D). Subangular silts, poorly preserved shell fragments and burrows are present, Mn-rich dendrites are associated with burrows.

Trace elements
The dolomite-rich samples have the highest concentrations of all four trace elements analysed; average 7,503 ppm Fe, 80,621 ppm Mg, 1,517 ppm Mn and 4,906 ppm Sr (Tables 1 and 2; Figure 8). The XRD results show stoichiometric dolomite, analcime, ±Mg-Fe-carbonate and Mg-calcite as the minerals present. Trace amounts of quartz are also present in most of the samples.

Stable isotopes
The $\delta^{18}O$ values range from $-1.90\%$ to $2.39\%$ and average $-2.15\%$ while the $\delta^{13}C$ values range from $2.95\%$ to $3.07\%$ and average $-2.98\%$ (Figure 7; Tables 1 and 2).

3.4.2 | Interpretation
Continental fine-grained dolomite, or dolomicrite, may be the product of evaporation and the subsequent increase in the Mg/Ca ratio (Bustillo and Alonso-Zarza, 2007). This may occur within a shallow groundwater setting, forming a dolocrete (Wright and Tucker, 1991), or during drying of a playa or marginal lake area (Bustillo and Alonso-Zarza, 2007). In either setting, dolomitization of carbonate mud may occur when Ca or Mg bicarbonate-bearing waters mix with Ca or Mg sulphate-rich waters. Thus dolomitization is preferentially favoured where drainage converges and/or flow gradients decrease (Wright and Tucker, 1991). In the case of Upper Bed 1, the dolomite horizon is located within a former playa lake which was a low area in the regional drainage system, and is a location where fresher groundwater likely encountered more saline groundwater, associated with the former playa, thereby replacing primary micrite with dolomite. Hay and Kyser (2001) interpret the dolomitization as a ‘replacement event’, whereby Mg-calcite was converted to dolomite as mixed fresh-saline fluids percolated through the bed. The high concentrations identified for all carbonate minor elements in this study support this interpretation, suggesting that the former playa lake’s saline waters, rich in cations, were concentrated in the dolomitizing fluid and incorporated into precipitated dolomite. The presence of analcime (XRD analysis) indicates that sodium was available in the groundwater, further indicating that saline playa water percolated into underlying groundwater. If the dolomite formed from groundwater as a replacement mineral, it is likely that a Mg-calcite precursor phase was present, and was converted to dolomite through the mixing of fresh and saline fluids (Humphrey, 2000). The matrix mix of Mg-calcite and amorphous carbonate, shown by XRD results, suggests that dolomitization was incomplete, resulting in only partial replacement of the primary mineralogy. The dolomite that is present is generally stoichiometric, based on XRD results. The dolomicrite lithology has been included as part of the suite of primary carbonates under Tuff 1F based on the interpretation that it had a carbonate precursor mineralogy, although the final product is the result of early diagenetic reactions.

The array of carbonate minerals and lithologies documented here indicates that the pre-Tuff 1F time period was characterized by an unusual amount of carbonate formation simultaneously across a wide swath of the gorge in numerous depositional settings (Figure 9).

4 | Diagenetic Features and Interpretation
As described above, each lithology has a suite of primary depositional characteristics, but all of them also contain features
indicative of subsequent subaerial exposure and minor paedo-
genic modification. The silty dolomicrite lithology seems to be the exception, in that case Mg-calcite micrite was partially replaced by dolomite in the shallow subsurface, rather than through paedogenesis. In one locality, however, paedogenesis produced a distinctive suite of carbonate nodules that are part of the pre-Tuff 1F story because they also indicate a significant accumulation of carbonate coeval with the limestones previously described. The nodular lithology is included under diagenesis because it reflects paedogenic processes, and all paedogenesis is interpreted here as diagenetic (per a long-standing debate, see Wright and Tucker, 1991), importantly, the nodules reflect significant CaCO3 precipitation at the same time as the other limestones formed prior to Tuff 1F.

4.1 | Nodular Soil Lithology

4.1.1 | Description

Depositional characteristics
The carbonate occurs under Tuff IF separated by a thin clay layer and varies in thickness from 15 to 50 cm (Figure 10A). The samples in this group occur in a cluster on what was a topographically high and well-drained terrain, a short distance from the spring localities (Figure 4). The deposit is characterized by carbonate nodules ranging in diameter from 0.5 to 3.0 cm and associated with small blebs of clay within a fine-grain micrite matrix. The carbonate occurs within a sequence of stacked clay-rich palaeosols containing paedogenic slickensides, as well as columnar and angular blocky peds. These palaeosol (vertisols) are described in Beverly et al. (2014).

Petrographic characteristics
Nodules exhibit two types of internal microfabrics: (a) calcite rosettes (Figure 10B) or (b) irregularly shaped, indurated micritic micronodules with halos. All nodules are embedded in a clayey micrite matrix rich in angular to subangular silt and sand-sized siliciclastic grains, predominantly feldspar and quartz, but also volcanoclastic rock fragments. Irregular, poorly preserved burrow or root traces are generally present. The rosettes consist of acicular calcite in zoned irregularly shaped lumpy spheres. The sphere centre may be brown micrite or spar, brown micrite inclusions define rings and fan rays, and the rosettes are in situ as noted by their intergrown and sutured margins (Figure 10B). In some cases, parts of the rosettes are calcite while other parts are composed of gypsum. Relict inclusions of calcite and/or anhydrite and gypsum may be present in these rosettes (see XRD results, Table 1) and their complex interrelationships indicate multiple stages of replacement. Yellow smectite and other clay minerals form small lenses or nodules outside of the rosette clusters, with associated circumgranular shrinkage cracks. Detrital siliciclastic grains are rare inside the rosettes but are abundant within the host micrite.

The irregularly shaped nodules composed of dense micrite and microspar, with halos of dark micrite and microspar, possibly including organic matter, are also in situ, with crystal growth extending beyond the halo rim into the adjacent micrite. Detrital siliciclastic grains are abundant within and around the halos. Finer-grained micrite is diffusely distributed away from each nodule, grading into brown micrite. The ICP data (Table 1) and XRD results indicate that the dark halos are enriched in Mn-oxide which stains the micrite a dark reddish-brown.

All of the nodular carbonates are characterized by shrinkage cracks around grains, burrow or root traces and micronodules. Vertical desiccation cracks are common. Sparry, non-ferroan calcite fills most of the cracks although unfilled vugs and cracks are present. Sparry calcite cement crystals commonly rim siliciclastic grains. Manganese oxides are abundant as dendrites associated with cracks, burrows and/or root traces. Glaebules and smectite clay clusters also occur within the nodular micrite strata.

Trace elements
The carbonate nodules are typically enriched in Mn, Sr and Mg relative to the wetland and lacustrine samples (Table 1; Figure 8). Iron values are variable, ranging from a low of 155 ppm to a high of 1,128 ppm, but have an average value of 644 ppm, lower than the other lithologies in this study.

FIGURE 10 Soil-related carbonate. (A) Photograph of section outcrop depicted in Figure 2D showing Tuff 1F and a 10 cm thick clay layer overlying nodular limestone. (B) Stained thin section photomicrograph of nodular calcite expressed as calcite crystal fans, forming soil rosettes
4.1.2 | Interpretation

The samples in this group occur in a cluster on what was topographically high and well-drained terrain (Figure 4). The clayey carbonate host sediment with root traces and/or burrows, siliciclastic grains, abundant circumgranular and vertical cracks, mottles and clay concentrations, has characteristics typical of soils from semi-arid climates (Hay and Reeder, 1978; Tanner and Lucas, 2006). Carbonate soils form when carbonate ions are plentiful in groundwater or surface water and accumulate due to plant photosynthesis driving CO₂ intake, as well as evaporative concentration (Wright and Tucker, 1991). Delta²⁸O values from the nodules indicate evaporation associated with their formation (Figure 7). Features such as circumgranular cracks and vertical mud-cracks are typically ascribed to desiccation leading to shrinkage around grains or other features and sediment cracking (Armenteros and Huerta, 2006). The presence of these features, in conjunction with the isotopic evidence, indicates that nodule precipitation was associated with evaporative concentration during paedogenesis.

The nodules also indicate episodes of ion concentration under specific conditions, for example, coalescent glaebules or other nucleation sites are interpreted as forming where diffusing carbonate ions begin to collect (Wright and Tucker, 1991). As circumgranular cracks form around the zone of carbonate concentration, larger voids, which dry out more quickly than the surrounding micrite, will expand, lowering the partial pressure of CO₂ around them, promoting further carbonate precipitation and enhancing nodule growth (Chadwick et al., 1987; Wright and Tucker, 1991). Micritic nodules are common in many paedogenic calcrites and may form part of a continuum from thin calcareous grain coatings to indurated layered deposits (Wright and Tucker, 1991). Micrite nodules may reflect concentric growth due to progressive replacement of primary micrite with microspar due to localized dissolution and recrystallization, potentially in conjunction with intercrystal cracking and infilling under near-surface conditions (Tandon and Friend, 1989).

The results of this investigation indicate that similar processes were responsible for the range of nodule fabrics seen here; rosettes, micrite micronodules and crystal fans. Calcite, gypsum and anhydrite crystal fans and spindles indicate significant evaporation and the growth of crystals subaerially or in the uppermost sediment layer, as interpreted by Bennett et al. (2012) for nodular calcites elsewhere in the basin. Previous work documented that elsewhere in the Olduvai stratigraphy carbonate nodules, with rosettes similar to those documented here, were enriched in Ba and formed as barite or gypsum rosettes to be subsequently replaced by calcite (Bennett et al., 2012; Ashley et al., 2014c). The formation of rose-like nodular fabrics seen in this study is interpreted as having formed paedogenically, in this case as gypsum, subsequently partially replaced by anhydrite and calcite. Similar complex replacement evaprorite/calcite patterns are reported from Cretaceous gypsum deposits (Warren et al., 1990) and Miocene strata from the Ebro Basin, Spain (Salvany and Ortí, 1994).

Mount and Cohen (1984) document significant Mn-oxide precipitation in rhizolith-rich Plio-Pleistocene strata from East Lake Turkana, Kenya and interpret it as indicative of plant decay, coupled with Mn-enriched groundwater sourced from volcanic deposits mixing with alkaline water along the lake margin. Upper Bed 1 Mn-oxide dendrites and clusters are similarly interpreted as indicating that Mn-enriched groundwater also travelled through volcanoclastic deposits and encountered evaporating alkaline playa waters subsequent to precipitating as oxides during paedogenesis. The relatively high trace element concentrations of Mg, Mn and Sr in these samples suggest that soil forming processes concentrated these elements into the calcite nodules. Iron, which is less mobile in oxidizing surficial settings, remains low. Collectively, evidence from the Upper Bed 1 nodular calcite horizon is interpreted as having formed as a soil carbonate associated with sediment drying and remobilization of carbonates and sulphates in the vadose or shallow phreatic zone (Figure 9).

All of the other carbonate lithologies in this study exhibit some or all of the features described from the Soil Nodule lithology. Circumgranular cracks, generally filled with equant, low Mg-calcite spar, Mn dendrites and burrow halos, and smectite clay clusters are the most abundant dia-genetic products prevalent in all four depositional facies. Such features commonly form within a subaerial setting, often modifying an existing carbonate (Platt, 1989; Alonso-Zarza, 2003; Bustillo and Alonso-Zarza, 2007; De La Horra et al., 2008) and are interpreted here as indicative of incipient soil development. In some localities, a millimetre to centimetre thick greenish waxy clay overlies the carbonate unit. This is interpreted as a palaeosol horizon (Ashley et al., 2014b), confirming that subaerial exposure and paedogenesis affected the limestones prior to the deposition of the regional Tuff 1F blanket that ended this phase of limestone deposition and carbonate soil development (Figure 9).

4.2 | Rare Earths by Environment

Analysis of the REE provides a means of comparing particular carbonate lithologies (Figure 11A,B) with potential volcanic source rocks (Figure 11C). The REE patterns fall...
into natural groups by sedimentary environment. They are described and interpreted below.

4.2.1 | Description

Lake/pond

The REE patterns (La-Lu+Y) for lacustrine carbonates are 10-100xCI chondrites, concave up (Figure 11A,B); with light rare earth element (LREE) enrichment and small negative Eu anomalies. Abundances of REE in lacustrine and wetland carbonate are distinct with only minor overlap (Figure 11B).

Wetland

The REE concentrations in the wetland carbonates are lower than in the lake facies but are higher than in the soil carbonates (Figure 11B). The REE patterns (La-Lu + Y) are concave up with elemental abundances at about 2-3xCI chondrites rising from heavy REE (Figure 11A); to LREE enrichment (20-50xCI) and small negative Eu anomalies.

Soil

The soil REE patterns are low and fairly flat at 0.5-1xCI but La and Ce rise to 5-7xCI with positive Ce anomalies. Overall patterns are slightly concave up with negative Eu anomalies (Figure 11A).

4.2.2 | Interpretation

The lake/pond carbonate, the wetland and soil facies show counterclockwise rotation of the REE pattern and dilution with increasing inferred paedogenesis (Figure 11B,C). The REE abundances of the lake/pond carbonates most resemble carbonatitic/volcanogenic sources. The LREE abundances are significantly higher in carbonatite (Figure 11C) than in the lake tufa and the Satiman volcanics are closer to the lake tufa value. The REE dilution in groundwater, together with the observed counterclockwise rotation of the REE patterns with increasing paedogenesis, may account for the differing patterns more readily for a carbonatitic starting composition than for a volcanogenic starting composition.

**FIGURE 11**  Rare earth abundance patterns (including Rb, Sr, Ba and Y) for carbonate from directly below Tuff IF in Olduvai Basin. (A) Raw patterns for carbonate. Symbols are grouped according to environment as seen in (B). (B) Three distinct facies: lake/pond, wetland and soils are shown as bands in CI-Chondrite normalized diagram. Bands are colour coded to match Figure 4 regions near Zinj Fault. Included are three patterns from Ol Doinyo Lengai carbonatite volcano for comparison. (C) REE patterns for nepheline from the nearby Satiman volcano (Zaitsev et al., 2012) and natrocarbonatite from Ol Doinyo Lengai.
5 | DISCUSSION

5.1 | Sedimentary environments and processes

The carbonate horizon immediately beneath Tuff 1F reflects a pastiche of depositional settings where CaCO₃ was concentrated enough to form limestone. Freshwater springs or seeps associated with faults and/or groundwater discharge sites at the margin of palaeo-Lake Olduvai plain are documented in Ashley et al. (2014c). Here, fault-controlled spring waters tapped relatively enriched groundwater, introducing Fe, Mg, Mn and Sr into precipitating calcite in a range of depositional environments. Based on field and petrographic observations and geochemistry, some of the limestones precipitated as primary deposits of the mineral calcite (XRD data, Table 1) forming tufa, silty marble and micritic mudstone lithologies. The petrography indicates that the dolomitic limestone had a precursor Mg-calcite mineralogy, which is a less stable polymorph of calcite, and may be prone to dolomitization during diagenesis (Hay and Kyser, 2001), therefore, the dolomitic limestone is considered evidence of primary Mg-calcite accumulation in a playa lake setting, time equivalent to the other primary limestones, but it was altered to dolomite during diagenesis.

The nodular carbonate described here is attributed to paedo-genesis, considered a diagenetic process in this study (although the primary or secondary origin of soil carbonate remains a controversial topic). Comparison between the nodules described here and nodules studied elsewhere in Olduvai Gorge (Bennett et al., 2012; Ashley et al., 2014c) suggest that these nodules likely also had a barite/gypsum/aragonite precursor mineralogy and underwent diagenetic stabilization to calcite.

Topography within the basin had a large influence on where the limestones formed. For example, the Zinj Fault controlled spring distribution, producing a linear band of spring-fed limestones (Figures 4, 9 and 12). Localized low relief associated with the downthrown side of the fault formed a wetland when it intersected the water table. This shallow depositional environment accumulated carbonate, forming a marly limestone deposit, what Pedley (1990) referred to as a paludal tufa. Sufficient standing water was present for ostracods to become established, but they are poorly preserved due to subsequent, and probably repeated, high energy events coupled with subaerial exposure and paedo-genesis.

Low relief also created a small lake that was isolated when the previous large lake (palaeo-Lake Olduvai) contracted. Articulated ostracods in the micrite indicate quiet water deposition, with some clay deposition as marl lenses. Carbonate-rich lake water, similar to the wetland water, was relatively low in trace elements when compared to the soil nodule facies where trace elements were concentrated into nodules by diffusion processes (Raiswell, 1987; Bennett et al., 2012).

In contrast, where carbonate accumulated at the site of a former playa lake, the location where the silty dolomite occurs, cations were in plentiful supply due to evaporative concentration of playa waters, which, being saline and dense, percolated downward, enriching the local groundwater. Precipitating carbonate incorporated magnesium to the point of dolomite as a replacement for primary Mg-calcite. The XRD results show that most of the dolomite is generally stoichiometric, but some of it consists of calcium dolomite. This suggests that diageneis is probably responsible for increasing mineral structural ordering, but that the process is incomplete, with some Mg being incorporated in proto-dolomite or Ca-rich dolomite. Hay (1976) and Hay and Kyser (2001) provide additional detail about this dolomite horizon.

Elsewhere, surface water seeped into clayey sediments, mixed with groundwater and became concentrated at nucleation sites to form nodular limestone, in some instances replacing primary gypsum. Variation in nodule type, from calcite rosettes to micrite with halos, suggests variability in groundwater-related formation processes. For example, calcite rosettes may be associated with a high and fluctuating groundwater table (Ashley et al., 2014c; 2016) while Mn/Fe halos indicate changing redox conditions (Retallack, 2001). Playa lake shoreline fluctuations are associated with Milankovitch-driven climate change (Ashley, 2007; Magill et al., 2013a) and precipitation changes would also be reflected in water table fluctuations resulting in variable groundwater saturation and redox conditions. The shallow groundwater responsible for the soil nodules was derived from seepage from the Zinj Fault, thus variable discharge rates may have further influenced nodule formation in the adjacent vadose zone sediments (Figure 9).

Desiccation cracks, circumgranular cracks, mottles, halos, Mn dendrites and/or root traces are interpreted...

FIGURE 12 | Block diagram showing the environmental context at the time the extensive carbonate deposit formed (just prior to 1.8 Ma). The playa lake had contracted into the central basin leaving small water bodies stranded in landscape irregularities on the playa lake margin. The depressions, some likely the result of small-scale faulting, temporarily supported groundwater-fed environments. Calcium carbonate-rich groundwater flowed from the Zinj Fault and possibly the Fifth Fault. The reconstruction is not to scale...
as pedogenic features that reflect syn-depositional to post-depositional sediment alteration. Almost every sample from the limestone horizon under Tuff 1F, irrespective of depositional facies, shows evidence for subaerial exposure. This makes sense because Upper Bed I was deposited during a period of regional drying (Magill et al., 2013b). Although each limestone lithology has petrographic evidence for pedogenesis, they exhibit relatively distinct isotopic and minor element geochemistry. The nodular soil and dolomicrite samples in particular form geochemical clusters that separate them from the wetland, spring and lacustrine samples. Maximum overlap occurs between the wetland and lacustrine samples, which is not surprising since they formed in environments that were geographically adjacent and depositionally similar. It is possible that they were deposited in different zones within the same setting, for example, the broken ostracod shells in the wetland limestone may reflect sublittoral conditions on a fluctuating shoreline where wave action and subaerial exposure alternated breaking up the shells. Whole shells in the lacustrine limestone may reflect sublittoral conditions, possibly in the same body of water. Whether the wetland and lacustrine limestones formed in one setting or two, their geochemical signatures are distinct from those lithologies reflecting more evaporative concentration, i.e. the soil nodules and dolomicrite. This indicates that although they experienced some level of pedogenesis based on petrographic evidence, it was insufficient to significantly reset their isotopic or geochemical values. Sarangi et al. (2019) show that pedogenesis may shift stable isotope values away from their depositional signatures, and the $\delta^{18}O$ and $\delta^{13}C$ values in this study may have shifted via pedogenesis, but in this case, the pattern of distinct isotopic fields suggests that the limestones reflect different depositional processes regardless of their absolute values.

The presence of non-ferroan calcite spar lining and/or filling some of the pedogenic cracks and vugs suggests that locally some carbonate was dissolved, remobilized and reprecipitated before the deposition of Tuff 1F essentially sealed the limestone system from significant further diagenetic alteration.

5.2  |  Source of Carbonates

5.2.1  |  Volcanism

The Ngorongoro Volcanic Highland is a >3,000 m high massif consisting of nine volcanic centres at a junction where the single valley of EARS (occupied by Lake Natron) splits into two rift valleys (Figure 1). Active volcanism of predominantly basalt/trachyte/andesite composition began ca 5 Ma and continued episodically to 0.6 Ma. Of particular interest is the history of carbonatite eruptions. The Satiman volcano (Figures 1 and 3) erupted carbonatite ash (3.6 Ma) in which hominin Laetoli fossil footprints are preserved (Hay and Leakey, 1982; Zaitsev et al., 2011; 2012) and the Kerimasi volcano produced carbonatites during the Holocene (Hay, 1983). Ol Doinyo Lengai is the only currently active carbonatite-producing volcano on Earth. Midway along the SW-NE track is Olmoti, which erupted Tuff IF (1.8 Ma), disgorging an enormous volume of magma that is characterized by a silica-undersaturated trachytic to phonolitic composition (Figure 1).

There is no direct record of carbonates being erupted either prior to or during Tuff 1F deposition. However, carbonatites are highly soluble and thus underrepresented in the geological record (Stoppa et al., 2009). However, because they are soluble it is reasonable to investigate groundwater proxies, such as limestones, from that time period to look for a carbonatite signature.

5.2.2  |  Sedimentary record

The REE (+Rb Sr Ba Y) patterns from three carbonates: (a) lake, (b) wetland and (c) nodular soil (Figure 11A,B) are recognized. The REE patterns (La-Lu) for the lacustrine carbonates are concave up at about 10-100xCI chondrites (Figure 11B); with LREE enrichment and small negative Eu anomalies. The wetland carbonates have lower abundances (1-70xCI) but retain the concave up pattern with LREE enrichment. The nodular soil REE patterns have markedly lower abundances (0.5-10xCI) with positive Ce anomalies.

For comparison, Ol Doinyo Lengai natrocarbonatite (Simonetti et al., 1997) and modern Ca-carbonatite samples collected in 2008 from the summit of Ol Doinyo Lengai by Sara Mana are presented in Figure 11C and B, respectively. Carbonatite patterns are also slightly concave up with negative Eu anomalies but with higher abundances than the studied facies. The REE patterns of the wetland and lacustrine carbonates also resemble the REE signature from the Satiman volcano (Zaitsev et al., 2012), Figure 11, but lack its Eu anomaly.

Carbonates from lacustrine to wetland to nodular soil deposits are depleted in LREE relative to Ol Doinyo Lengai carbonatite samples (and data from Simonetti et al., 1997). A progressive increase in the $\delta^{18}O$ values of the limestones parallels the REE depletion trend (c.f. Figure 7), suggesting that increased interaction between carbonatite and groundwater may be responsible for REE variation between the limestones. The Ba and Sr concentrations show dramatic variability from 20xCI to 700xCI between the limestones, but with a reversal of the enrichment factors seen for the REE. Wetland carbonate contains Sr and Ba at abundance levels comparable to the LREE while nodular soil samples are strongly enriched in

<...>
Ba and Sr, suggesting that these elements are influenced by pedogenic processes.

Wetland and lake limestone REE patterns mirror carbonatite values (Figure 11B), which may indicate that they had a carbonatite source, either derived from carbonatite dissolution, releasing REE elements into the groundwater, and/or weathering of silicate lavas associated with the carbonatite eruption. For example, nephelinites from the Satiman volcano (data from Zaitshev et al., 2012) have similar REE patterns to the wetland and lacustrine limestones, absent the Eu anomaly (Figure 11C).

At present it is impossible to distinguish between carbonatite and associated silicate lavas as sources for the limestone's REE values, but the similarity between their REE patterns is suggestive of a link between volcanism and limestone following a 10–100 dilution factor. The nodular soil shows the most extensive modification of the REE patterns relative to carbonatite, while the wetland and lacustrine carbonates retain overall REE patterns that mimic a carbonatite groundwater source. The counterclockwise rotation of the REE patterns from carbonatite through lacustrine to nodular soil is consistent with increasing dissolution of REE in groundwater (McLennan, 1989).

The δ18O values from the lacustrine limestone suggest that lake waters experienced relatively little evaporative loss and thus may be closest in composition to the original groundwater debouching from the volcanic highland. Hence the high REE abundances seen in that limestone means that the precipitation of carbonate sources from either carbonatite or related lavas is plausible. The wetland limestone also resembles diluted carbonatite in terms of its REE chemistry (ranging from 10-100xCI), whereas nodular soil samples have the most depleted REE abundances (between 0.5 and 3xCI). The relative enrichment of Sr in the soils may indicate a precursor aragonite polymorph as orthorhombic aragonite readily accommodates the large Sr cation (Reeder, 1983). The XRD results from this study do not indicate aragonite but rather gypsum and anhydrite that were partially replaced by carbonate, and may host Sr (and Ba) in appreciable quantities (ICP data, Table 1, Figure 8). In addition, positive Ce anomalies suggest an oxidizing regime as expected for pedogenic soils.

Hay and Reeder (1978) suggest that carbonatite ash was the major source of calcite in calcrites within Olduvai Gorge. This is consistent with the high Sr and Ba enrichment (relative to CI-chondrites) seen in the nodular soil facies. The lake facies is the most REE enriched and most closely resembles carbonatite patterns. This facies has δ18O values comparable with fresh groundwater that has suffered little evaporative loss and is hence the most similar to groundwater from the surrounding volcanic highland. The wetland and soil deposits are, in contrast, depleted in REE, suggesting more evolved source waters.

5.3 The depositional model

The carbonate is an isochronostratigraphic unit because it is everywhere capped with an airfall tuff (Tuff IF). It formed in at least five different depositional environments, most are believed to have been groundwater-fed. The groundwater-supplying the basin was likely sourced from rainfall on the 3,000 m high Ngorongoro Volcanic Highland that lies ca 25 km to the east. The REE evidence suggests that there may have been at least one carbonatite eruption just prior to Tuff IF. The hot spot that moved from the Satiman volcano (3.6 Ma) to its current position at Ol Doinyo Lengai would have been in the vicinity of Olmoti at ca 1.8 Ma (Figure 1). Any highly soluble carbonatite ash would likely dissolve entering the groundwater system yielding carbonate-rich water (Hay, 1983).

The rift valley is seismically active today (Le Gall et al., 2008) and would have likely been so in the past. The carbonate is believed to have formed from a recurring seismically-induced increase in aquifer porosity and permeability with carbonate-enriched groundwater episodically discharged onto the land surface, interacting locally with both fresh and alkaline ponded water (Sneed et al., 2003). Figure 12 is a block diagram that conceptualizes the environmental context at the time of carbonate deposition.

Upper Bed I deposition occurred during the drying portion of the precession climate cycle (Magill et al., 2013b). The playa lake had contracted into the central basin leaving small water bodies stranded in landscape irregularities. These depressions temporarily supported groundwater-fed environments (springs, small lakes, wetlands) and it is likely that calcium carbonate-rich groundwater flowed from the Zinj Fault, and possibly the Fifth Fault, across the topography.

6 CONCLUSIONS

1. A carbonate deposit formed simultaneously in a variety of depositional environments in a catena-like pattern across the Olduvai Gorge palaeolandscape.

2. A synthesis of outcrop and petrographic studies and trace element and stable isotope data reveals distinctive ‘fingerprints’ for five carbonate lithologies; those forming in primary settings; spring, wetland, and lacustrine environments; one that formed via diagenetic modification of a precursor Mg-calcite, the dolomicrite horizon; and carbonate nodules that formed through diageneric pedogenesis.

3. The plot of the carbonate δ18O versus δ13C values indicates that the water source was meteoric (rainfall was −0.6‰ V-PDB), modified as groundwater, and that some evaporative fractionation of δ18O is reflected in the soil
and in the dolomicrite in particular. Plots of δ¹⁸O versus δ¹³C values show covariance, indicative of a closed system (Li and Ku, 1997). Variation in δ¹³C values reflects different sources of carbon in the five environments.

4. Trace element plots revealed that three of the deposits; nodular soils, wetland and lacustrine, have strongly overlapping trace element abundances, but the dolomicrite and some soil samples are significantly enriched in Sr. In contrast, the REE abundances of the carbonate lithologies vary, but overlap the range of alkaline volcanics from EARS. The REE data suggest that the carbonates derived their trace elements from alkaline igneous rocks or carbonatites such as those found at Ol Doinyo Lengai and Olmoti.

5. It is hypothesized that the glut of carbonate in the Olduvai Basin prior to eruption of Olmoti and the deposition of Tuff IF was due to a carbonatite eruption. Although carbonatites do not usually leave a physical record of ash or tuff, the REE pattern recorded in the carbonates shows elevated concentrations of Sr and Ba (earmarks of carbonatites) and is therefore consistent with a carbonatite source.

6. The conceptual model for the origin of this widespread deposit suggests a link between rift volcanism (specifically carbonatite) and precipitation of freshwater carbonate. Highly soluble carbonatite ash would have quickly entered the groundwater system and seismicity associated with volcanism may have increased the porosity and permeability of aquifers discharging onto the land surface.

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DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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