ORIGINS OF CHERT: LAKE MAGADI BASIN, KENYA

BY

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Abstract

Petrographic, XRD, EDS, SEM and SIMS microanalysis demonstrate that Pleistocene Magadi cherts formed primarily from the precipitation of an amorphous siliceous gel and occasionally from hydrous sodium silicates, such as magadiite or kenyaite. Brine simulations and oxygen isotope analysis support the formation of these cherts from highly evaporated brines at modern lake temperatures near surface.

Fossils within chert, including, microorganisms, diatoms, gastropods, ostracods, and plant and insect fragments provide valuable paleoenvironmental information, including the presence of alkaliphilic fungal communities found in chert. Identifiable crystal habits in evaporite pseudomorphs of trona and gaylussite suggest saline conditions were present throughout much of the basin history.

Labyrinth patterns discovered in Magadi cherts indicate the precipitation of silica gels in the saline-alkaline Lake Magadi system near the surface in conjunction with chert formation. Hele-Shaw cell experiments conducted to replicate Magadi labyrinth patterns, however some of these patterns in nature occurred along non-horizontal planes. The orientations of the Magadi patterns imply invasion of air from above if confined to open cracks or infiltration from all sides if the gels dried and cracked in the vadose zone. Cherts developed from siliceous gel precursors have elevated δ¹⁸O values, from +41‰ to +47‰ indicating the formation in the presence of brines. Such brines, with total dissolved solids of ~ 220,000 to 300,000 mg/L, exist in the modern Magadi basin during
dry periods. Cherts with magadiite and other hydrous sodium silicates precursors form brines with lower salinities than cherts formed from gels. Cementing chalcedony and megaquartz crystals in chert have lower $\delta^{18}O$ values that require formation from waters at elevated temperatures, which suggests a hydrothermal origin. Finally, siliceous mudstone cherts show relatively wide ranges of $\delta^{18}O$, from +37‰ to +46‰, which suggests formation from subsurface brines.

Based on this new information, we have further classified the origins of chert in Lake Magadi, Kenya and extended the presence of a high salinity paleoenvironment to ~500 ka before present.
This work is dedicated to my grandmother, Wilma, who taught me to observe and appreciate our natural world.
Acknowledgements

I would like to thank Emma McNulty for inspiring me to join the Hominin Sites and Paleolakes Drilling Project in East Africa and the entire Hominin Sites and Paleolakes Drilling Project team. They have been an incredible group to be a part of; welcoming, inclusive and collaborative. I would also like to thank my advisor, Tim Lowenstein and my committee members for their insight, support and collaboration throughout this process.

I would also like to thank my friends and family for their support and encouragement along the way, it’s hard to put into words all the help you have each given me, I am forever grateful. To my children, Billie and Travis, who grew up along this journey, you have made me smile and laugh each and every day and I can’t thank you enough for that gift. To Ethan, you are the constant by my side, your steadfast love and support was invaluable, even when I was barely tolerable.

And finally, to Charlie, my golden retriever, you are the best office companion, I am so grateful you were able to accompany me to campus.
Preface

Lake Magadi, Kenya has been used as a modern analog system for understanding the origins of non-biogenic chert, however, the mechanisms by which these so-called “Magadi cherts” form remains poorly understood. Cores drilled to bedrock at Lake Magadi during the Hominin Sites and Paleolakes Drilling Project (HSPDP) in 2014 allowed for a unique opportunity to study chert in stratigraphic sequence and improve the understanding of chert formation at Lake Magadi. Petrographic and scanning electron microscopy of these cherts and associated sediments improved the paleoenvironmental interpretations of Lake Magadi, Kenya over the last one million years.

The first chapter covers the discovery of two dimensional branching “labyrinth patterns” in chert from petrographic thin section analysis and field emission scanning electron microscopy. Labyrinth patterns are a type of fractal “squeeze” pattern formed at air-liquid interfaces. Labyrinth patterns preserved in chert from Lake Magadi cores indicate invasion of air along planes in dewatering gels. These patterns support the precipitation of siliceous gels in the saline-alkaline Lake Magadi system, and syndepositional drying of gels in contact with air as part of chert formation. Recognizing cherts as syndepositional has been critical for our use of them for U/Th dating. Chapter 1 contains work that has been published in Geology in its entirety. This work is included as it was part of the programmatic line of research that comprised the dissertation. The inclusion of this work provides a coherent and sequenced investigation. As lead author, I served as the corresponding author on this work and have permission to republish it here.
The second chapter reports high precision oxygen isotope analysis of chert by secondary ion mass spectrometry (SIMS). Detailed petrographic observations and SIMS oxygen isotope analyses of these cherts constrain paleoenvironmental conditions, such as water temperature and salinity, at the time of chert formation. Nearly all cherts from the Lake Magadi cores exhibit high $\delta^{18}O$ values, ranging from $+41$ to $+46\%o$, indicating hypersaline environments for much of the basin history, from 750 ka to today. Petrographic analysis of these cherts show uncompacted, randomly oriented crystal pseudomorphs, plant fragments and other detritus indicative of syndepositional formation from a siliceous gel. Fewer samples show petrographic evidence for traditional “Magadi-type” chert formed after hydrous sodium silicates, such as magadiite. Isotopic analyses of chert formed from magadiite yielded slightly lower $\delta^{18}O$, from $+38\%o$ to $+40\%o$. At the base of the section, cherts with abundant gastropods and ostracods have relatively low $\delta^{18}O$ values, ranging from $+26\%o$ to $+35\%o$, which indicates lower salinity waters from ~1Ma to ~750 ka. Microanalysis of megaquartz within voids and fractures in chert showed the lowest $\delta^{18}O$, $+23\%o$ to $+30\%o$, indicating megaquartz formed from warm, likely hydrothermal waters. This chapter is in review for future publication.

The third chapter provides an overview of the observational evidence for syndepositional chert formation and classifies chert types on the basis of petrographic
characteristics and oxygen isotope composition. Previous work suggested formation of chert from magadiite or amorphous siliceous gel whereas others have suggested formation due to biological activity. Multi-method analysis of the cherts from the Lake Magadi cores shows a complex precursor history, with amorphous siliceous gels dominating the sequence but precursors and mechanisms were also observed. This chapter will be further developed for publication.
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<th>Abbreviation</th>
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</thead>
<tbody>
<tr>
<td>BSE</td>
<td>back scattered electrons</td>
</tr>
<tr>
<td>CT</td>
<td>cristobalite</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive x-ray spectrometry</td>
</tr>
<tr>
<td>HSPDP</td>
<td>Hominin Sites and Paleolakes Drilling Project</td>
</tr>
<tr>
<td>ITCZ</td>
<td>Intertropical Convergence Zone</td>
</tr>
<tr>
<td>KNMI</td>
<td>Royal Netherlands Meteorological Institute</td>
</tr>
<tr>
<td>KRV-WL</td>
<td>Kenya Rift Valley meteoric water line</td>
</tr>
<tr>
<td>LACCORE</td>
<td>National Lacustrine Core Facility</td>
</tr>
<tr>
<td>MAG</td>
<td>Magadi</td>
</tr>
<tr>
<td>MSA</td>
<td>Middle Stone Age</td>
</tr>
<tr>
<td>QGIS</td>
<td>Quantum Geographic Information System</td>
</tr>
<tr>
<td>SE</td>
<td>secondary electrons</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
</tr>
<tr>
<td>TDS</td>
<td>total dissolved solids</td>
</tr>
<tr>
<td>V-SMOW</td>
<td>Vienna Standard Mean Ocean Water</td>
</tr>
<tr>
<td>XPL</td>
<td>cross-polarized light</td>
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<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
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Chapter 1: Labyrinth patterns in Magadi (Kenya) cherts: Evidence for early formation from siliceous gels

Sedimentary cherts, with well-preserved microfossils, are known from the Archean to the present, yet their origins remain poorly understood. Lake Magadi, Kenya, has been used as a modern analog system for understanding the origins of non-biogenic chert. Here, we present evidence for synsedimentary formation of Magadi cherts directly from siliceous gels. Petrographic thin section analysis and field emission scanning electron microscopy of cherts from cores drilled in Lake Magadi during the Hominin Sites and Paleolakes Drilling Project (HSPDP) in 2014, led to the discovery of two-dimensional branching “labyrinth patterns” in chert, which are a type of fractal “squeeze” pattern formed at air-liquid interfaces. Labyrinth patterns preserved in chert from Lake Magadi cores indicate invasion of air along planes in dewatering gels. These patterns support the precipitation of silica gels in the saline-alkaline Lake Magadi system, and syndepositional drying of gels in contact with air as part of chert formation. Recognizing cherts as syndepositional has been critical for our use of them for U/Th dating. Identification of labyrinth patterns in ancient cherts can provide a better understanding of paleoenvironmental and geochemical conditions in the past.

1.1 Introduction

Although cherts occur in sedimentary rocks as old as the Archean, and have been widely studied for their well-preserved microfossils, their origins remain poorly understood. Sedimentary chert consists of beds or nodules of microcrystalline quartz (Renaut and
Owen, 1988; Knauth, 2003). Most Phanerozoic cherts formed diagenetically from biogenic opaline silica, such as diatoms, radiolarians, and sponge spicules (Knauth, 1993; DeMaster, 2003). However, other cherts, interpreted to be non-biogenic, have been described from saline alkaline lakes. Eugster’s (1967, 1969, 1970) studies of chert at Lake Magadi provided a model system for interpreting the origins of non-biogenic chert. The well-known “Magadi-type” cherts were interpreted by Eugster (1967, 1969) and Hay (1968) to have formed from magadiite ($\text{NaSi}_7\text{O}_{13}(\text{OH})_3\cdot\text{H}_2\text{O}$) and kenyaitie ($\text{NaSi}_{11}\text{O}_{20.5}(\text{OH})_4\cdot3\text{H}_2\text{O}$). But not all cherts from Lake Magadi have a magadiite precursor. Eugster and Jones (1968), for example, noted that some Pleistocene cherts in the Magadi basin, particularly those with soft-sediment deformation features, may have formed from a siliceous gel precursor. They hypothesized that during diagenesis, those gels might also convert to zeolites such as analcime, through leaching of sodium, or to sodic montmorillonite clay. Modern siliceous gels discovered in the Lake Magadi basin are associated with discharge of hot spring waters into Nasikie Engida, a perennial saline alkaline lake adjacent to Lake Magadi (Eugster and Jones, 1968; De Cort et al., 2019; Renaut et al., 2021).

Detailed studies of Magadi-type cherts have documented quartz replacement of magadiite lepispheres and later void- and fracture-filling chalcedony cement (Schubel and Simonson, 1990; Behr and Röhricht, 2000). Elevated $\delta^{18}$O values from Magadi cherts indicated that saline porewaters, not dilute groundwaters, were involved in their formation (O’Neil and Hay, 1973). These observations suggested a multistage origin of Magadi-type chert more complex than that originally proposed by Eugster (1967, 1969) and Eugster and Jones (1968). Understanding the timing of chert formation and possible
precursors is critical when dating chert by uranium-thorium disequilibrium methods (Goetz and Hillaire-Marcel, 1992). If chert formation can be shown to be syndepositional, then U/Th dating of those cherts can serve as a new geochronology tool (Sturchio et al., 1993; Owen et al., 2018).

Lake Magadi was cored to trachyte bedrock in 2014 as part of the Hominin Sites and Paleolakes Drilling Project (HSPDP) which aims to furnish the paleoenvironmental context for hominin evolution in East Africa (Cohen et al., 2016; Campisano et al., 2017). Chert is a major lithological component of the Magadi cores, comprising ~30% of the recovered sediment.

Here we present new evidence for synsedimentary formation of Magadi cherts from siliceous gels. Most significant has been the discovery of two-dimensional “labyrinth patterns” in Magadi chert, identical to those formed experimentally when granular fluids dry slowly (Sandnes et al., 2007). Fractal patterns, such as labyrinths, are a type of viscous fingering pattern formed at air-liquid interfaces influenced by friction and surface tension (Sandnes et al., 2007). Labyrinth patterns thus imply subaerial exposure. Their recognition in ancient cherts may enhance understanding of paleoenvironmental conditions of chert formation.

1.2 Geologic Background

Lake Magadi, an ephemeral, alkaline hypersaline lake in the southern Kenya Rift valley, lies in a hydrologically-closed basin bounded by north-south normal faults (Fig. 1). The climate in the region is semi-arid. Ephemeral Lake Magadi and nearby perennial lake Nasikie Engida are fed predominantly by alkaline springs that give the resulting
evaporated brines their high pH and Na-CO$_3$-HCO$_3$-Cl chemical composition. Lake Magadi brines range from 193,000 to 313,000 mg/kg TDS (total dissolved solids) with pH between 9.5 and 11.1 (Eugster, 1970). The high alkalinity allows high silica concentrations, greater than 1000 mg/kg, to develop in the lake brines (Jones et al., 1967; Eugster, 1970).

Four cores from two sites, four km apart, were recovered during drilling (MAG 14-1A, B, C; composite length 137m) and MAG 14-2A (198 m) (Fig. 2) (Cohen et al., 2016; Campisano et al., 2017; Owen et al., 2018). The cores are composed of zeolitic mud, chert, trona (Na$_2$CO$_3$•NaHCO$_3$•2H$_2$O), nahcolite (NaHCO$_3$), calcite and siliciclastic sand and gravel. The cores contain a record of Pleistocene-Holocene closed-basin paleoenvironments and paleoclimates in a tectonically-active rift basin. Cherts from the Magadi cores, dated by U/Th disequilibrium techniques, along with radiocarbon ages, $^{40}$Ar/$^{39}$Ar dates of tephras and the basement Magadi Trachyte, and paleomagnetic dating, provide a one-million-year chronology (Fig. 2; Owen et al., 2018).

The sediments in the cores record a shift from an early, broad and shallow freshwater lake from ~1,050-750 ka (ostracode/gastropod grainstones, clast-supported gravels, and sand/sandstone), that became an anoxic, moderately saline lake (laminated muds with organic matter, pyrite, and lack of burrows) at ~750-550 ka. A period of desiccation and subaerial exposure occurred ~550-420 ka (alluvial fan gravels, sandflat sands, and mudcracked mudstones). Perennial saline lake muds occur above the desiccated interval, followed by a 6 m-thick zeolite-rich tephra sequence, with four dated horizons ranging in age from 354-316 ka (Owen et al., 2018). Above the tephra sequence, perennial lake muds alternate with mudflat muds and alluvial fan sands and gravels.
Evaporites (bedded trona and massive mud with trona and minor diagenetic nahcolite), deposited in hypersaline lakes and saline mudflats, occur in the upper parts of the cores, first appearing at ~118.6 ka. The assemblage of chemical sediments (zeolites, chert, magadiite, trona, nahcolite) shows that saline alkaline conditions dominated during the most recent history of the Magadi basin (Surdam and Eugster, 1976, Owen et al., 2018).

1.3 Timing of Chert Formation

Petrographic thin sections and field emission scanning electron microscopy were used to divide cherts from the HSPDP cores into two categories: 1) “syndepositional” cherts, formed by replacement and crystallization prior to burial and compaction; and 2) later diagenetic cherts, which formed after burial and compaction.

Syndepositional cherts contain partial and whole diatoms (*Anomoeneis sphaerophora* and *Rhopalodia gibberula*), which are “floating” in chert. These cherts also contain randomly oriented permineralized plant fragments with preserved cellular structure (Fig. 3a) and silicified cyanobacterial filaments, interpreted to indicate chert formation prior to burial. Fragile fragments of volcanic glass are also preserved in layers of chert (Fig. 3b). Layers of chemically precipitated magadiite lepispheres, ~20 µm in diameter, and originally composed of variably aligned aggregates of micron-scale crystalline plates (now magadiite pseudomorphs), demonstrate early, constant-volume chert replacement (Schubel and Simonson, 1990). Finally, evaporite pseudomorphs, as randomly oriented crystals (Fig. 3c) or as competitively-grown mineral crusts, are preserved in chert in an uncompacted state, indicating early, constant volume replacement.
In contrast, other mudstones in the Lake Magadi cores contain cherts that formed in the subsurface following burial. The cherts in these mudstones contain aligned, flattened, rotated, and compacted plant fragments and sediment grains, which are interpreted to indicate chert formation after compaction.

1.4 Labyrinth Patterns in Lake Magadi Cherts

Petrographic thin sections of Lake Magadi cherts from the cores display intricate branching labyrinth patterns (Fig. 3d-3h). Labyrinth patterns are microscopic, two-dimensional fractal arrays of dark granular particles that resemble trellis and rectangular drainage networks. The maze-like patterns of 1 to 10 micron silicate mineral grains are entirely embedded in chert. Labyrinth patterns display uniform geometries (Fig. 3e) (Sandnes et al., 2007; Knudsen et al., 2008). Two dimensional arrays of branching labyrinth patterns occur along planes which indicates that a rigid to semi-rigid chert precursor susceptible to fissuring existed before pattern formation (Fig. 3f, g).

Other examples of branched labyrinth patterns comprise 20–100 μm diameter spherical bubble shapes composed of chert outlined against fine-grained sediment and chert (Fig. 3h). Individual bubbles are connected and outlined by dense accumulations of sediment grains.

Varieties of labyrinth and bubble patterns were identified at nine depthsss between 35 and 120 m in Core 2A, and 27.5 to 80 m in composite Core 1A, B, C (Fig. 2). Most cherts with labyrinth and bubble patterns are associated with desiccation and subaerial exposure features including mudcracked mud/mudstone, insect burrows, and unconsolidated gravels, interpreted as alluvial fan deposits. Reticulate crusts and v-
shaped cracks in chert from the HSPDP cores, interpreted to form from dewatering
(Eugster, 1969; Schubel and Simonson, 1990, Buatois et al., 2020) also occur with
labyrinth and bubble patterns.

1.5 Experimental Reproduction of Labyrinth Patterns

Sandnes et al. (2007) produced labyrinth structures in an experimental apparatus
known as a Hele-Shaw cell, in which grains suspended in viscous fluid gels confined
between two plates are reorganized by invading fingers of air as fluid is withdrawn.
These experiments produced labyrinth patterns and other viscous fingering effects known
as ‘bubble stick’ patterns (Sandnes et al., 2007, 2011; Knudsen et al., 2008). Sandnes et
al. (2007) showed that the labyrinth patterns are produced by the surface tension between
two immiscible fluids – air and water – and friction in confined geometries. The invading
fingers of air push grains into delicate patterns known as labyrinths (Fig. 3e). Variable
fractions of particles produce a range of patterns, with fewer grains and more fluid
producing labyrinth patterns whereas closely packed grains and less fluid lead to
formation of bubble patterns (Inset Fig. 3d, g; Eriksen et al., 2015).

To better understand the origin of the labyrinth patterns observed in Magadi chert,
we designed Hele-Shaw cell experiments using modern siliceous gel, zeolitic muds, and
magadiite, mixed with pure water and/or Lake Magadi brines [Supplemental Information,
Fig. S1]. Drying of the granular fluids between two glass plates in the Hele-Shaw and
modified Hele-Shaw experiments, [Supplemental Information, Table S1], allowed air to
invade, pushing the grains into labyrinth and bubble stick patterns (Fig. 3j-l).
**1.6 Interpretations and Discussion**

Labyrinth structures in Magadi cherts likely formed from dewatering of siliceous gels. Hydrous silica(te) gels form in the Magadi basin today where alkaline waters interact with modern sediments and bedrock (Eugster, 1967, 1969; Eugster and Jones, 1968; Surdam and Eugster, 1976). These gels incorporate detrital plant fragments, microbial cells and exopolymeric substances, and terrigenous grains (Fig 3i). Gels often accumulate along the northern shoreline of Nasikie Engida, where they provide a substrate for growth of microbial mats and efflorescent crusts when lake level drops (Renaut et al., 2021). As gels dewater, they form shrinkage cracks. When filled with sediment and water, those cracks act like the planes of a Hele-Shaw cell forming delicate labyrinth patterns as the granular fluid dries. This suggests that the entire process, from gel development to desiccation to chert formation happened near the surface.

Well-preserved plant fragments, volcanic glass and other delicate uncompacted material in the cherts support early, near syndepositional, diagenetic origin of the chert. Labyrinth patterns in Magadi cherts indicate: (1) precipitation of silica gels in the saline-alkaline Lake Magadi system, and (2) invasion of air along planes during syndepositional drying of gels in conjunction with chert formation. The mechanisms by which the original siliceous gels formed require further study, as does the Hele-Shaw cell analog for Magadi labyrinth patterns. In particular, Hele-Shaw cell experiments involve air intrusion from all sides, horizontally, whereas some Magadi labyrinth patterns occur along non-horizontal planes. The orientations of the Magadi patterns imply invasion of air from above if confined to open cracks or infiltration from all sides if the gels dried and cracked in the vadose zone.
Archean cherts have long been studied because they contain signs of the earliest life on Earth but the timing and mechanisms of chert formation are still poorly known. Undeformed microfossils in Archean and Proterozoic cherts show that early, pre-compaction silicification was required to preserve delicate cellular structures (Schopf et al., 1993; Sugitani et al., 2007). Identification of labyrinth patterns in such syndepositional cherts would provide support for the formation of siliceous gels at or near the Earth’s surface and would offer new clues about the environments in which early life on earth evolved. These features are unlikely to be found in Archean cherts of subaqueous origin, but may occur in terrestrial cherts, such as the hot spring facies of the 3.48 Ga Dresser Formation, where possible fossilized gas bubbles, perhaps trapped in exopolymeric substances, were identified (Djokic et al., 2017).
1.7 Tables, Figures and Captions
Modified Hele-Shaw experiments were conducted using sediments from the Lake Magadi basin. The modified Hele-Shaw cell consisted of a standard microscope slide; sediments were added to the center of the slide along with one to two drops of fluid and a standard cover slip was placed on top. The slides were then exposed to normal laboratory room temperature and humidity for 48 hours, allowing desiccation to occur. Photographs were taken at regular intervals and looped into videos to show pattern formation. Slides were then analyzed using a petrographic microscope to compare to petrographic thin sections of labyrinth patterns discovered in chert.

<table>
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<td>Water</td>
<td>20°C</td>
<td>Modern dehydrated siliceous gel and Pleistocene magadiite</td>
<td>Labyrinth</td>
<td><img src="Image1.png" alt="Image" /></td>
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<td>Brine</td>
<td>20°C</td>
<td>Modern dehydrated siliceous gel</td>
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<td><img src="Image2.png" alt="Image" /></td>
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<td>3</td>
<td>Brine</td>
<td>20°C</td>
<td>Pleistocene magadiite</td>
<td>Bubble stick</td>
<td><img src="Image3.png" alt="Image" /></td>
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<td>4</td>
<td>Water</td>
<td>20°C</td>
<td>Pleistocene magadiite</td>
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<td>Water</td>
<td>40°C</td>
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<td>Labyrinth</td>
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<td>Water</td>
<td>40°C</td>
<td>Pleistocene magadiite</td>
<td>Labyrinth</td>
<td><img src="Image6.png" alt="Image" /></td>
</tr>
<tr>
<td>7</td>
<td>Water</td>
<td>20°C</td>
<td>Modern dehydrated siliceous gel</td>
<td>Labyrinth</td>
<td><img src="Image7.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Table S1. Modified Hele-Shaw Experiment Parameters**
Figure 1.1 Southern Kenya Rift Valley Geological Map
A. The southern Kenya Rift Valley; B. Geologic setting of Lake Magadi and Nasikie Engida with locations of MAG14 cores (red stars) and hot springs (black stars).
Figure 1.2. Stratigraphic columns of cores MAG14-2A and composite MAG14-1A and -1C; locations shown on Figure 1B. Radiometric ages, major lithologies, paleoenvironments, depths of labyrinth patterns in chert, and subaerial exposure features plotted.
Figure 1.3. Image panel of Lake Magadi, Kenya cherts and siliceous gels

A. Photomicrograph of uncompacted plant fragment in chert. MAG14-2A: 89 m. Scale: 100 μm. B. Photomicrograph of uncompacted siliceous material in chert. MAG14-1A: 49.3 m. Scale: 100 μm. C. Photomicrograph of evaporite crystal pseudomorph, composed of chalcedony, and surrounded by microcrystalline chert. Depth in core MAG14-1A: 49.2 m. Scale: 100 μm. D. Photomicrograph of labyrinth pattern in chert. Thin section cut parallel to bedding. MAG14-2A: 84 m. Scale bar: 100 μm. Inset is digitized reproduction of labyrinth pattern (Knudsen et al., 2008). Dark areas show invading air pathways and light areas show sediments. E. Enlargement of D, a: spacing between branches, b: thickness of branches. MAG14-2A: 84 m. Scale: 10 μm. F. Photomicrograph of thick section showing labyrinth pattern developed at the boundary between chert with relatively pure (top) and abundant incorporated sediment (bottom). MAG14-2A: 84 m. Scale: 100 μm. G. Photomicrograph of labyrinth pattern in thick section. MAG14-2A: 87.5 m. Scale: 50 μm. H. Photomicrograph of bubble stick pattern showing sediments
(brown) and chert (gray). MAG14-2A: 87.5 m. Scale bar: 200 μm. Inset is computer model of bubble-stick pattern (Sandnes et al., 2011). White represents air and black shows grains displaced by air. I. Photograph of modern siliceous gel in plastic bag from Nasikie Engida. Scale: 1 cm. J. Photograph of labyrinth pattern produced in the laboratory using modern siliceous gel from Nasikie Engida. Dark lines show sediment accumulated when air invaded the confined layer. Scale: 200 μm. K. Photograph of Hele-Shaw cell type experiment using magadiite and hot brine. Scale: 0.4 cm. L. Hele-Shaw cell type experiment using desiccated Nasikie Engida siliceous gel sediments and cool water. Scale: 0.2 cm.
Figure S1.1. The Hele-Shaw cell experimental set up  Traditional Hele-Shaw cell experiments were conducted using Lake Magadi basin sediments. The experimental set up is comprised of two clear, rigid plastic plates, separated by a small gap. The plates measure 20 cm x 25 cm with a thickness of 2 mm. United States one cent coins are used in each corner as spacers between plates to create a gap. The viscous liquid used is a 50% glycerol 50% water by volume solution. Added to the glycerol solution were fine sand-sized grains collected from the Lake Magadi drill cores, sieved to 63–100 micron diameters. The solution was then injected into the gap between two parallel, horizontal acrylic plates and slowly withdrawn, 0.05 ml/sec, through a 3 mm hole in the upper plate via syringe and plastic tubing to simulate drying. Fluid was withdrawn at regular intervals over several hours to produce labyrinth pattern formation and then the fluid dried at ambient indoor air conditions for one day. Image above is at time zero prior to fluid withdrawal and pattern formation. Photographs were taken at five-minute intervals over periods of several hours. Invasion of air along the gap between plastic sheets slowly pushed grains into delicate labyrinth patterns. Sketch illustrates side view of experimental set up.
Chapter 2: Conditions of Formation of Magadi-type Cherts from SIMS Oxygen Isotope Microanalysis

Pleistocene cherts from Lake Magadi, Kenya, collected from cores drilled for the Hominin Sites and Paleolakes Drilling Project, were analyzed by secondary ion mass spectrometry (SIMS) to determine their oxygen isotope composition. Detailed petrographic observations and SIMS oxygen isotope analyses of these cherts constrain paleoenvironmental conditions, such as water temperature and salinity, at the time of chert formation. Nearly all of the cherts from the Lake Magadi cores exhibit high δ¹⁸O values, ranging from +41 to +46‰, indicating hypersaline environments for much of the basin history, from 750 ka to today. Petrographic analysis of these cherts show uncompacted, randomly oriented crystal pseudomorphs, plant fragments and other detritus indicative of syndepositional formation from a siliceous gel. Fewer samples show petrographic evidence for traditional “Magadi-type” chert formed after hydrous sodium silicates, such as magadiite. Isotopic analyses of these samples yielded slightly lower δ¹⁸O, from +38‰ to +40‰. At the base of the section, cherts with abundant gastropods and ostracods have relatively low δ¹⁸O values, ranging from +26‰ to +35‰, which indicates lower salinity waters from ~ 1Ma to ~750 ka. Microanalysis of megaquartz within voids and fractures in chert showed the lowest δ¹⁸O, +23‰ to +30‰, indicating megaquartz formed from warm, likely hydrothermal waters.
2.1 Introduction

Chert is an important biogenic/chemogenic sedimentary rock found in sedimentary sequences of all geologic ages. Phanerozoic bedded cherts include the Miocene Monterey Formation of California which displays gradations from unconsolidated layers of diatoms through porcelain-like beds to beds of microcrystalline chert (Isaacs, 1983). These deposits clearly show the stepwise replacement of biogenic opal-A of diatoms with opal-CT, and ultimately microcrystalline α-quartz. A similar biogenic origin of most Paleozoic and Mesozoic bedded cherts such as the Devonian white “novaculite” (chert) of Arkansas and Texas (Folk and McBride, 1976), and Mesozoic bedded cherts of the Alps (Grunau, 1965) is now widely accepted.

However, bedded cherts and silicified strata are common in Archaean greenstone belts and abundant in the early Proterozoic where they comprise approximately half of the enigmatic iron-rich deposits commonly referred to as Banded Iron Formations that dominate the Paleoproterozoic sedimentary record. The origins of Archean and Paleoproterozoic cherts are much more problematic and these cherts are commonly considered to be chemogenic in origin. A strictly chemical origin has also been proposed for cherts in Pleistocene lake deposits of the Lake Magadi area of Kenya (Eugster, 1967, 1969). These so-called “Magadi-type” cherts are found in lake deposits that also contain sodium carbonate minerals (Eugster 1967, 1969, Surdam and Eugster 1976, Hay 1970) and are now commonly cited in discussions of chemogenic cherts. However, there is less known about the silica sources and diagenetic conditions of formation of the Magadi cherts.
Eugster (1967, 1969) suggested that hydrous sodium silicates such as magadiite (NaSi$_7$O$_{13}$(OH)$_3$·3H$_2$O) and kenyaite (NaSi$_{11}$O$_{20.5}$(OH)$_4$·3H$_2$O) dewatered into cherts through leaching of sodium in contact with groundwater. Pleistocene cherts from Lake Magadi contain shrinkage cracks, complicated folds and “reticulate” patterns – deformation features interpreted to record shrinkage of the hydrous sodium silicates as they lost sodium and dehydrated. This diagenetic reaction was proposed to take place on time scales of hundreds to thousands of years (Eugster, 1969). The chemical precipitates were replaced fractionally by chert prior to compaction (Schubel and Simonson, 1990; Leet et al., 2021), and in places preserve laminae and other petrographic features of the original magadiite.

Others have suggested chert formation via in situ early diagenetic alteration of siliceous gel material in saline, alkaline lakes (Sheppard and Gude 1986, Hay 1968, Rooney 1969, Sebag 2001; Leet et al., 2021). Hay (1968), for example, suggested the potential for more direct precipitation of silica. This idea was based on the work of Peterson and von der Borch (1965) in the Coorong district of South Australia where abiogenic opal-CT gels precipitated at or just below the surface of carbonate lagoon sediments. The source of the silica was thought to be in situ dissolution of quartz under seasonal high pH conditions. The silica then reprecipitated as opal-CT when groundwater with lower pH came into contact with surface brines. Hay (1968) favored this scenario due to the absence of evidence of intermediary phases from field and petrographic analyses. X-ray diffraction analyses showed no intermediate opal (cristobalite peaks) although such precursors have been noted in other sublacustrine hydrothermal, sinter, cherts (Renaut and Owen, 1988, Renaut et al., 2002). Finally, Behr (2002) and Behr and
Röhricht (2000) noted the potential for biogenic chert formation based on the identification of coccoid cyanobacteria (*Pleurocapsa*) in cherts of the Magadi region. Much of the work on Magadi cherts has been based on petrographic observations, which can be ambiguous. Features such as reticulated crusts and dewatering fractures, mentioned above, for example, are common in cherts of different origins (Heaney and Post, 1992; Hattori, 1996; Bustillo, 2001; Behr, 2002).

The possibility of a strictly chemical origin of chert holds out the possibility for the use of oxygen isotopes in their study without having to consider the “vital effects” organisms can have in fractionating isotopes. The oxygen isotope signature of abiogenic chert should record the temperature and the isotopic composition of the waters from which it precipitated in a straightforward manner. Indeed, a number of such studies on the oxygen isotope compositions of Archean Greenstone cherts and Banded Iron Formation cherts have been done (Cammack et al., 2017).

O’Neil and Hay (1973) determined the $\delta^{18}\text{O}$ of Pleistocene cherts from the Lake Magadi, Lake Natron, and Olduvai regions of East Africa. They concluded that the waters involved in the conversion of amorphous siliceous gels and magadiite/kenyaite precursors to chert (quartz) largely involved moderately saline to highly saline waters. Groundwater and rainwaters are depleted in $^{18}\text{O}$ relative to evaporated brines (Epstein and Mayeda, 1953). Based on this relationship, the oxygen isotopic signature of lacustrine cherts should vary based on the conditions of the water (principally salinity as a proxy for evaporative concentration) at the time of chert formation. The problem, is, of course complicated by the timing of when the isotopic signature is “locked into” the cherts and the temperatures at which this occurs. Primary syndepositional cherts,
therefore, can record key paleoenvironmental information during the time of their
deposition much in the same way that they can be used to provide reliable dates of
formation (Leet et al., 2021).

Here we present detailed petrographic analysis of Lake Magadi cherts paired
with high-precision, secondary ion mass spectroscopy (SIMS) oxygen isotope
analyses of those cherts. We provide petrographic criteria for the origin of the
sediments associated with chert formation and the timing of chert formation. If
chert formed in uncompacted sediments, then its early formation suggests surface
waters may be involved in chert formation thereby locking in the isotopic signature.
Here we test the hypothesis that the isotopic composition of syndepositional cherts
can be used to constrain the types of waters from which chert formed. These data,
combined with petrographic analyses give a more complete understanding of the
formation of abiogenic cherts in saline-alkaline systems.

2.2 Geological Setting

Lake Magadi is a closed-basin, ephemeral, alkaline, and hypersaline lake located
in the southern Kenya segment of the East African rift valley bounded by north-south
normal faults. (Fig. 1). The East African rift climate is semi-arid, with more than 3500
mm/yr of potential evaporation and 450-500 mm of precipitation. Precipitation largely
falls in two seasons, February to April and October to November with the migration of
the tropical rain belt. Monthly average temperatures range from 24 to 29°C with lowest
monthly average temperature of 18.8°C and highest monthly average temperature of
34.7°C (Climate data from KNMI Climate Explorer https://climexp.knmi.nl/start.cgi and
climate-data.org). Perennial lake Nasikie Engida (referred to in older literature as Little Magadi) occurs north of Lake Magadi, Fig. 1. Both lakes are fed predominantly by alkaline spring waters that give the resulting evaporated brines their high pH and Na-CO₃-HCO₃-Cl-rich chemical composition.

2.2.1 Regional Water Data

Previous studies of precipitation and surface waters in the Lake Magadi region were reviewed and compiled for this study (Fig. 1 and Table 1 from Lee et al., 2017, Darling 1996, Allen 1989, and O’Neil and Hay, 1973).

2.2.2 Precipitation

Rainwater from the Lake Magadi region has δ¹⁸O values ranging from -2.1‰ to +0.8‰ and δ²H values from -14‰ to -3‰ (Darling, 1996).

2.2.3 Springs

In this study, springs were classified by temperature, with hot springs > 60°C and warm springs ranging from 34 to 49°C. All springs have a similar range of total dissolved solids, from 20,000 to 43,000 mg/l (Kamondo, 1988, Tole, 1990; 2002). Hot springs on the northern ends of Nasikie Engida and Lake Magadi have pH values between 8.8 and 9.5 and temperatures between 60 and 85°C (Table 2). Stable isotope values of hot spring waters range from δ¹⁸O of -1.2‰ to -0.1‰ and δ²H from -7‰ to -2‰ (Lee et al., 2017; Allen et al., 1989; Darling, 1996).
Warm springs on the margins of Lake Magadi have similar pH values as hot springs, ranging from 8.8 and 10 and temperatures between 34° and 49°C. Stable isotope values of warm spring waters range from $\delta^{18}O$ -3.2‰ to -1‰ and $\delta^2$H from -23‰ to +2‰ (Lee et al., 2017; Allen et al., 1989; O’Neil and Hay, 1973).

The isotopic composition of warm and hot spring waters is similar to the isotopic composition of rain water, which suggests that spring waters are meteoric in origin (Allen et al., 1989).

2.2.4 Rivers

The pH of the Ewaso Ng’iro River ranges from 7.8 to 8.2 and temperatures between 22 and 26°C (Darling 1996). The Ewaso Ng’iro River has measured $\delta^{18}O$ values of -2.9‰ to -1.5‰ and $\delta^2$H from -12‰ to -6‰, similar in composition to meteoric precipitation. Total dissolved solids are low, at 153 mg/l.

2.2.5 Lakes

Lake Magadi surface brines have total dissolved solids (TDS) that range from 67,000 to 313,000 mg/l and pH between 9.5 and 11.1, with temperatures between 23 and 48°C (Eugster, 1970, Jones, 1977, Lee et al., 2017). Alkaline lake brines allow for high concentrations of SiO$_2$, greater than 1000 mg/l, and SiO$_2$ concentrations in springs near 100 mg/l (Eugster, 1970). Nasikie Engida surface lake water temperatures (away from hot springs) range from 23 to 48°C, (Jones 1977, Renaut 2021). The $\delta^{18}O$ values of Lake Magadi brines range from +7.9‰ to +10.4‰ and $\delta^2$H ranges from +17 to +19‰, much higher than spring waters (Darling, 1996; O’Neil and Hay, 1973).
2.2.6 Sedimentology

The sediments beneath Lake Magadi were cored to trachyte basement rock in 2014 as part of the Hominin Sites and Paleolakes Drilling Project (HSPDP) (Cohen et al., 2016; Campisano et al., 2017; Owen et al., 2018). The HSPDP project aims to resolve how climate and climatic variability may have influenced human evolution. Near Lake Magadi, the Olorgesailie Early-Late Pleistocene archaeological site has been used to document the transition from Acheulean to Middle Stone Age (MSA) early hominin tool technology (Potts et al., 2018; Brooks et al., 2018).

Two cores, MAG 14-1A and 1C (composite) and MAG 14-2A, 137 m and 198 m long, respectively, were recovered (Fig. 2). The cores are composed of trona (Na$_2$CO$_3$•NaHCO$_3$•2H$_2$O), nahcolite (NaHCO$_3$), zeolitic mud, chert, sand/gravel, and calcite. The cores preserve a record of Pleistocene/Holocene closed-basin paleoenvironments and paleoclimates in a tectonically active rift basin. A one million year chronology for the HSPDP cores was obtained through U-Th dating of chert, radiocarbon dating of organic material, including shells, Ar-Ar dating of tephra and trachyte, and determination of the stratigraphic position of the Brunhes-Matuyama paleomagnetic reversal (Fig. 2; Owen et al., 2018). Cherts, both nodular and bedded, were recovered from all lithofacies in the core (Fig. 2).

The HSPDP sediment cores and nearby exposures document an early (~1,050 - 750 ka), broad and shallow freshwater lake, with ostracod and gastropod grainstones, clast supported gravels, silt/siltstone, and sand/sandstone (Owen et al., 2018). Between ~750-550 ka, the lake evolved into a narrower, at times anoxic, stratified saline lake, characterized by laminated muds, organic matter, pyrite, and lack of burrowing (Owen et
Narrowing of the hydrologic low point of the Magadi basin was produced by faulting (Owen et al., 2019). A period of desiccation and subaerial exposure is interpreted from the alluvial fan gravels, sandflat sands, and mudcracked muds deposited between ~550-420 ka. Perennial saline lake muds occur above the desiccated interval, followed by a 6 m thick zeolite-rich tephra sequence, with 4 dated horizons ranging in age from 354-316 ka (Owen et al., 2018). Above the tephra sequence, perennial lake muds alternate with mudflat muds and alluvial fan sands and gravels. Evaporites of bedded trona and massive mud with trona and nahcolite deposited in hypersaline lakes and saline mudflats occur in the upper sections of the cores, first appearing ~118.6 ka. The assemblage of chemical sediments, particularly chert, but also including, zeolites, indicate alkaline conditions existed over much of the one million year history of the Magadi basin. Diatom occurrences, however, argue for periods of fresher water lakes over much of the lake history (Owen et al., 2018).

2.3 Methods

More than 100 chert samples and associated minerals such as magadiite were selected from the MAG 14 cores for thin section petrography, x-ray diffraction, scanning electron microscopy (SEM), and energy dispersive x-ray spectrometry (EDS) analysis. Nine samples, representative of the various types of chert in the Lake Magadi drill cores, were selected for detailed δ^{18}O measurement by SIMS (Table 1, Figure 2, core depths indicated by yellow stars). Photomicrographs in plain and cross-polarized light (XPL) were made of each analysis area. SEM images were taken in secondary electron and backscattered electron modes. Cathodoluminescence of samples showed no zonation or
variation as is typical of diagenetic quartz, so it was abandoned. SEM analysis was conducted at the Binghamton University Analytical and Diagnostics Lab using a Zeiss Field Emission SEM, Supra 55 VP. EDS analysis using the SEM was used to identify unknown minerals. Before and after SEM imagery for SIMS spot analyses was georeferenced using Quantum Geographic Information System (QGIS).

SIMS analyses were conducted at the University of Wisconsin SIMS lab using a CAMECA-1280 ion microprobe. Procedures were described in previous publications (Kelly et al., 2007, Kita et al., 2009, Valley and Kita, 2009). Samples were mounted and polished to a low relief surface along with two or more grains of UWQ-1 quartz standard ($\delta^{18}$O = +12.33‰) (Kelly et al., 2007). Measurements of 191 standards and 765 samples were completed on 7 mounts. The average precision was ~0.3‰ (Supplemental Fig. 1). SIMS $\delta^{18}$O data are reported in Supplemental Table 1. Samples with relative yields greater than 1.1 and less than 0.8 were rejected. After analysis, analysis pits were re-imaged on the SEM to verify petrographic textures and minerals. Care was given to omit analysis pits that intersected organic material, epoxy, fractures, or minerals other than quartz.

2.4 Origin of Cherts: Timing and Formation

Magadi cherts exhibit a variety of petrographic textures and fabrics and an assortment of incorporated material. For this study, we focused on four main varieties: Type 1 cherts with incorporated materials that show no compaction; Type 2 “Magadi-type” cherts with evidence for relict lepispheres; Type 3 chalcedony and megaquartz within cherts, and, Type 4 cherts with incorporated materials that show significant
compaction, such as grain flattening and rotation. The relative abundance of chert types 1 to 4 is based petrographic analysis of more than 60 thin sections from the Lake Magadi cores. Loss of material during the coring process and the difficulty of preparing thin sections from small nodules indicate sample bias toward thicker chert beds and underrepresentation of nodules and thin lamina of chert.

2.4.1 Type 1 Cherts

Type 1 cherts comprise ~80% of the cherts in the Magadi cores and commonly occur as centimeter to decimeter thick layers, (Fig. 3A). They are characterized by little to no compaction or deformation of incorporated material within the cryptocrystalline chert matrix. Cryptocrystalline here refers to chert in which individual quartz crystals are indistinguishable in thin sections at a magnification of 1000X. Incorporated material consists of plant fragments, crystal pseudomorphs, diatoms, detrital grains, and zeolites. Chert from a depth of 49.27 m contains abundant crystal pseudomorphs. Pseudomorphs with chalcedony rinds are randomly oriented and isolated in cryptocrystalline chert matrix (Fig. 3B and C). The original mineral(s) are unknown but the saline mineral gaylussite is a possible candidate on the basis of the pseudomorph crystal habit and the occurrence of gaylussite in modern alkaline hypersaline environments, including Nasikie Engida (Olson and Lowenstein, 2021; Renaut et al., 2021). A decimeter thick chert bed at 70.63 m contains abundant plant fragments and organic matter (Fig. 3D). These plant fragments are uncompacted, undeformed, and randomly oriented (Fig. 3E and F). Type 1 cherts also commonly possess dewatering features such as v-cracks (Fig. 3G), some now filled with chalcedony, (Fig. 3H), and labyrinth patterns (Fig. 3I). Labyrinth patterns
display evidence for a near surface conversion of siliceous gel to chert (Leet et al., 2021). Labyrinth patterns form when a granular fluid, for example siliceous gel, contracts when dried. As air invades the gel, grains are pushed into delicate maze-like labyrinth patterns. Preservation of labyrinth patterns suggests that drying of gel and conversion to chert occurred at or near the surface (Leet et al., 2021).

Chert beds from a depth of 88.97 m contain v-cracks and diatoms, (Fig. 3J). Diatoms (*Anomoeoneis sphaerophora* and *Rhodalodia gibberula*) are randomly oriented, uncompacted, and float in a matrix of cryptocrystalline chert (Fig. 3K and 3L). Another chert bed from 76.00 m has incorporated and well-preserved microbial material, and possibly the coccoid cyanobacteria *Pleurocapsa*, as interpreted earlier by Behr (2002) (Table 2). Limestone with deformed layering and abundant chert at 179.09 m (Fig. 3M), contains shells of ostracods surrounded by cryptocrystalline chert (Fig. 3N) and gastropod shells filled with cryptocrystalline quartz and chalcedony (Fig. 3O).

Type 1 cherts contain uncompacted incorporated materials within a cryptocrystalline chert matrix, shrinkage features, and labyrinth structures which suggests *in situ* early diagenetic alteration to chert from a siliceous gel (Hay, 1968; Leet et al., 2021). Siliceous gels form today in nearshore lake waters of Nasikie Engida in close proximity to hydrothermal spring inflow (Renaut et al., 2021).

2.4.2 **Type 2 Cherts**

Type 2 cherts comprise ~10% of the cherts in the Magadi cores and contain relict lepispheres and cross-hatch patterns (Schubel and Simonson, 1990) and occur as fine laminations or nodules (Fig. 4A). These cherts are microcrystalline quartz with little to no
incorporated material. Microcrystalline defined here refers to chert in which individual quartz crystals are visible in thin sections at a magnification of 1000X. Type 2 cherts contain dewatering and shrinkage features such as reticulated crusts and v-cracks (Fig. 4B). In thin section, the microcrystalline quartz of type 2 cherts exhibits platy, groundmass textures (Fig. 4C), described by Schubel and Simonson (1990) as relict magadiite lepispheres. Following Schubel and Simonson (1990), type 2 cherts are interpreted to have formed from a chemically precipitated hydrous sodium silicate, such as magadiite or kenyaite, later replaced by chert.

2.4.3 Type 3 Cherts

Type 3 cherts comprise less than 5% of the cherts in the Magadi cores. Type 3 cherts commonly occur as isolated patches of chalcedony or megaquartz within the cryptocrystalline and microcrystalline quartz of type 1 and type 2 cherts. Chalcedony consists of fine intergrowths of quartz and moganite, as spherulites or as fibrous rinds. Fibrous rinds are common along the exteriors of crystal pseudomorphs (Fig. 3B and 3C), and within some dewatering fractures (Fig. 3H). Megaquartz (euhedral quartz crystals larger than 20 µm) partially to completely fills the void spaces within ostracod shells (Fig. 4D, 4E) and fractures (Fig. 4E, 4F). Cross-cutting relationships and cementation textures indicate that chalcedony and megaquartz formation are the last of multiple stages of silica diagenesis in type 1 and type 2 cherts (Fig. 4E).
2.4.4 Type 4 Cherts

Type 4 cherts comprise 5-10% of the chert in the Magadi cores. Type 4 cherts are laminated (Fig. 4G) with abundant aligned plant fragments, flattened and rotated into sub-horizontal orientation (Fig. 4H). Individual laminae with variable amounts of detrital grains and zeolites alternate with purer chert layers (Fig. 4I). The compressed materials incorporated in Type 4 cherts indicate later, post compaction, diagenetic conversion of siliceous material to chert. Some laminae consist of cryptocrystalline quartz with little to no incorporated material, whereas other, detrital-rich layers, have pumice fragments, silt and sand sized grains, and zeolites, now replaced or cemented by chert.

2.5 SIMS Microanalysis of Chert

Nine chert samples from the four cherts types (Table 2) were selected for SIMS microanalysis to determine whether oxygen isotopic values correlated with chert type or varied with some other factor, such as the paleoenvironment at the time of formation.

Type 1 cherts analyzed by SIMS were from uncompacted areas of chert layers or nodules. The type 1 chert with evaporite pseudomorphs (49.27 m) had a mean $\delta^{18}$O of +42.7‰ V-SMOW (Fig. 5). The Type 1 chert at 70.63 m, with incorporated plant fragments had a mean $\delta^{18}$O of +45.3‰ V-SMOW, (Fig. 5). Type 1 cherts at 76.00, 83.64 and 88.97 m had mean $\delta^{18}$O of +43.7‰, +42.6‰ and +44.5‰ V-SMOW, respectively (Fig. 5). One Type 1 chert from near the base of the core at 179.09 m had a low $\delta^{18}$O mean value of +32.1‰ V-SMOW.
The Type 2 chert at 143.99 m, with evidence for a magadiite precursor had a relatively low mean $\delta^{18}O$, $+39.3\%\text{oo}$ V-SMOW, compared to other Type 1 cherts, which all had mean $\delta^{18}O$ values greater than $+40\%\text{oo}$.

Type 3 cherts are later diagenetic quartz phases, chalcedony and megaquartz. Chalcedony and megaquartz are commonly found within cryptocrystalline and microcrystalline cherts, typically as a replacement of evaporite crystals or in fractures and pores. SIMS microanalysis allowed for precision study of chalcedony and megaquartz. Chalcedony analyzed in the sample at 70.63 m had a mean $\delta^{18}O$ value of $+41.8\%\text{oo}$ V-SMOW. The sample at 76 m with chalcedony had a mean $\delta^{18}O$ of $+42.0\%\text{oo}$ V-SMOW. Megaquartz partially filling the interior of an ostracod shell, at 179.09 m, (Fig. 4N) shows $\delta^{18}O$ values of $+26.99\%\text{oo}$ and $+28.40\%\text{oo}$ V-SMOW. All megaquartz analyses in the sample at 179.09 m had a mean of $+25.88\%\text{oo}$ V-SMOW.

Type 4 siliceous mudstone cherts samples at 49.38 and 61.36 m had a mean $\delta^{18}O$ of $+40.9$ and $+41.1\%\text{oo}$ V-SMOW, respectively, (Fig. 5.).

2.6 Isotopic Interpretations

$\delta^{18}O$ values from modern spring waters, river waters, and rainwaters, all fall between $\delta^{18}O$ of $-5\%\text{oo}$ to $+1\%\text{oo}$ and $\delta^2H$ of $-20\%$ to $0\%$, close to the Kenya rift valley meteoric water line, (KRV-WL) (Fig. 6; Darling, 1996). The similarity between warm and hot spring $\delta^{18}O$ values and the $\delta^{18}O$ of precipitation suggests recirculation of meteoric water in the near surface environment in the Lake Magadi basin (Darling, 1996). Oxygen isotope values increase significantly as waters evaporate to lake brines, which have $\delta^{18}O$ values of $+7\%\text{oo}$ to $+11\%\text{oo}$ and $\delta^2H$ of $+18\%\text{oo}$ to $+20\%\text{oo}$ (Fig. 6). Recent isotopic study of
East African rift system waters noted a similar ~10‰ positive shift in δ¹⁸O between precipitation, groundwaters and springs versus evaporated lakes (Markowska et al., 2022).

The δ¹⁸O of quartz is dependent on the temperature of formation, which is represented by an equation expressing the variation of the fractionation factor, α, with temperature. Several have been published and here we use the equation from Vho et al. (2019).

\[
1000 \ln \alpha_{\text{qz-H}_2\text{O}} = \left( 4.11 \pm 0.11 \times \frac{10^6}{T^2} - 3.33 \pm 0.61 \times \frac{10^3}{T} + 0.00 \pm 0.15 \right). \quad (Eq. 1)
\]

It is important to note that although application of this fractionation equation is recommended for T ≥ 200°C, others have noted consistent results at lower temperatures (French et al., 2021). We used the Vho et al. (2019) fractionation equation, (Eq. 1), to calculate δ¹⁸O curves for quartz-water fractionation as a function of temperature and formation water isotopic composition (Fig. 7). The temperature and δ¹⁸O of modern surface waters in the Magadi basin are also plotted on Figure 7, which can then be used to assess the temperature and δ¹⁸O values of the waters from which the four types of Magadi cherts formed.

2.6.1 Isotopic Interpretations – Type 1

Most Type 1 cherts have high δ¹⁸O values between +41‰ and +47‰ (Fig. 5). These cherts are interpreted as original siliceous gels formed in saline alkaline lakes, such as Nasikie Engida, that converted to chert at near surface conditions (Leet et al., 2021; Renaut et al., 2021). The δ¹⁸O of Lake Magadi brines, +7.9‰ and +10.4‰, and modern
lake water temperatures in the Magadi Basin, 23° to 47°C, are the type of saline water capable of forming Type 1 chert (light purple shaded area of Figure 7). Siliceous gels, for example, reported from several location of Nasikie Engida, were associated with brines ranging in concentration from 30,000-35,000 mg/l near spring inflow at the north shore to ~300,000 mg/l at the south shore, where trona was precipitating (Renaut et al., 2021). Petrographic evidence for a near surface syndepositional conversion of gel to chert constrains the environment of formation of isotopically heavy (+41‰ to +47‰) Type 1 cherts to hypersaline lake brines at typical modern water temperatures (Fig. 7).

Near the base of the core, where there is evidence for freshwater lacustrine environments, including gastropod and ostracod fossils, Type 1 cherts occur with anomalously low $\delta^{18}O$ values, between +26‰ and +35‰. The blue shaded box on Fig. 7 shows that the range of $\delta^{18}O$ values from which the isotopically light cherts formed overlaps with the $\delta^{18}O$ values and temperatures of modern warm springs in the Magadi Basin. This suggests the waters involved in formation of these cherts were less evaporated compared to all other Type 1 cherts that formed from hypersaline brines.

2.6.2 Isotopic Interpretations – Type 2

Type 2 cherts formed from magadiite have $\delta^{18}O$ values between +38‰ and +40‰, somewhat lower than the $\delta^{18}O$ values obtained from Type 1 cherts associated with hypersaline brines. The lamination style of magadiite in the Magadi cores and in outcrops suggests formation in alkaline lakes (Owen et al., 2018; Renaut et al., 2020). If so, the $\delta^{18}O$ of lake waters involved in the formation of Type 2 cherts was lower, between +2‰ and +9 ‰ at modern lake water temperatures of 23° to 47°C (purple shaded area of
Figure 7), than the $\delta^{18}$O of modern hypersaline lake brines from Lake Magadi (+7.9‰ and +10.4‰) (Fig. 7). This implies that marginally lower salinity, less evaporated waters were involved in the formation of Type 2 cherts. Magadiite is predicted to precipitate during evaporation of Nasikie Engida brines before any other evaporite minerals form, such as trona or gaylussite, at total dissolved solids between ~30,000 and 220,000 ppm (Renaut et al., 2020). Similarly, O’Neil and Hay (1973) hypothesized that true Magadi-type cherts (type 2), formed from magadiite, and with lower $\delta^{18}$O values, +34.7 to +40.9‰, than other cherts, also formed from “moderately” saline waters.

2.6.3 Isotopic Interpretations – Type 3

The lowest $\delta^{18}$O values, +24 to +30‰, were obtained from megaquartz. Petrographically, megaquartz is the last-formed phase of the Magadi cherts. There are no surface waters in the Magadi Basin, at temperatures between 23°C and 47°C, with $\delta^{18}$O values low enough (below ~ +27‰) to form megaquartz (Fig. 7). Modern warm spring waters with a $\delta^{18}$O range of -5‰ to 0‰, and temperatures between 34°C and 49°C, cannot form quartz with $\delta^{18}$O values below +27‰ (Fig. 7). If the waters from which Type 3 megaquartz formed are similar to those in the Magadi Basin today, then it must have formed at elevated temperatures (red shaded area, Fig. 7). Modern Magadi basin hot spring waters all fall within the temperature and formation water $\delta^{18}$O range suitable for megaquartz precipitation. We therefore conclude that waters with elevated temperatures, hydrothermal waters, are required to form Type 3 cherts.
2.6.4 Isotopic Interpretations – Type 4

Finally, siliceous mudstone Type 4 cherts, from depths of 49.38 m and 61.36 m, display abundant evidence for compaction and alignment of plant fragments and detrital grains. These compaction features indicate chert formation after burial. Type 4 cherts have a particularly wide range of $\delta^{18}$O, from 37‰ to 46‰. Borehole temperatures from the Lake Magadi drill sites range from 33°C near the surface to 38°C near 180 m (Supplemental Figure 1). At 61 m, borehole temperatures are 36°C. Type 4 cherts with $\delta^{18}$O values ranging from 37‰ to 46‰ and formed during burial at temperatures between 33°C and 36°C, require parent waters with $\delta^{18}$O ranging from +4‰ to +13‰. Such waters occur as hypersaline pore fluids in the Magadi basin today.

2.7 Paleosalinity and relationship to $\delta^{18}$O

Our results indicate that water salinity and evaporative concentration of surface waters exert the strongest control over the $\delta^{18}$O of the chert, as originally hypothesized by O’Neil and Hay (1973). SIMS microanalysis of Lake Magadi cherts reveals that most formed from siliceous gels and hydrous sodium silicates in the presence of saline brines. Most Magadi cherts are early synsedimentary in origin and formed at normal surface temperatures from brines with $\delta^{18}$O values similar to modern spring waters and lake brines. Megaquartz cements require formation at elevated temperatures.

It is interesting to note that fossils within chert can be potentially misleading with regard to paleoenvironmental interpretations. The mean $\delta^{18}$O value of the Type 1 chert with diatoms is +44.5‰ (depth 88.97 m, Fig. 5). The diatoms are widely dispersed in the
crypto-crystalline quartz matrix with no indication for replacement of a layered diatomite, with shells in point contact. Instead, this sample contains uncompacted plant fragments along with diatoms, and internal fractures, suggestive of a gel parentage. The high $\delta^{18}O$ values indicate formation from hypersaline brines, not typical environments for diatoms. This paradoxical association between diatoms and hypersaline brines can be resolved if the diatoms were transported into the hypersaline lake from marginal fresh water springs and ponds during flooding events.

2.8 Conclusions

The Pleistocene cherts of Lake Magadi, Kenya, are often used as an analog for ancient cherts, but their precursors and mechanisms of formation are debated. SIMS microanalysis of the oxygen isotope composition of Lake Magadi cherts shows a wide range of isotopic values from +24 to +45‰ V-SMOW. These cherts faithfully record isotopes of the lake waters during formation and can provide key paleoenvironmental information on temperature and salinity.

Cherts developed from siliceous gel precursors (Type 1) have elevated $\delta^{18}O$ values, from +41‰ to +47‰ that are diagnostic of formation in the presence of brines. Such brines, with total dissolved solids of ~ 220,000 to 300,000 mg/L, exist in the Magadi basin during dry periods, such as today. Cherts with magadiite and other hydrous sodium silicates precursors (Type 2) formed from brines, but with lower salinity than cherts formed from gels. Megaquartz crystals that fill fractures and void space in chert (Type 3), have $\delta^{18}O$ values that require formation from waters at elevated temperatures,
which suggests a hydrothermal origin. Cherts formed in siliceous mudstone (Type 4) showed relatively wide ranges and high values of \( \delta^{18}O \), from +37‰ to +46‰, which suggests formation from brines. Type 4 cherts, however, formed after burial and compaction, which suggest hypersaline pore waters were involved in their formation.

This data presented here support and expand the work of O’Neil and Hay (1973) who thought that the \( \delta^{18}O \) values of Magadi chert showed formation from saline waters. Most of the cherts from the Lake Magadi cores have elevated oxygen isotopes values, which further supports the hypothesis that saline environments existed in the Magadi over the last 750,000 years. Lower oxygen isotopic values from chert in fossiliferous limestone from the base of the section supports previous interpretations for freshwater lake environments during the earliest history of rifting, ~750,000 to 1 million years ago.
<table>
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<tr>
<th>Sample Location</th>
<th>Sample Number</th>
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<th>δ18O‰</th>
<th>δ2H‰</th>
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<td>150 m. S of Bird Rock</td>
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<td>O’Neil &amp; Hay 1973</td>
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<td>45</td>
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<td>125 m. S of Bird Rock</td>
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<td>&quot;</td>
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<td>&quot;</td>
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<td>Average Salinity</td>
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<td>--------------</td>
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<td>E Magadi</td>
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**RAINWATER**

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<th>Average Salinity</th>
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**LAKE BRINES – AVG TDS 273,000 mg/l**

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<td>O’Neil &amp; Hay 1973</td>
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**RIVERS & STREAMS – AVG TDS 153 mg/l**

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<td>Ewaso Ng’iro River 2</td>
<td>K32</td>
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<td>7.85</td>
<td>-2.9</td>
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*formerly called Little Magadi

**Table 2.1. Summary stable isotopic composition of waters from the Lake Magadi Basin, Kenya.** Results in per mil V-SMOW, from previous studies (O’Neil and Hay, 1973, Allen et al., 1989, Darling, 1996, Lee et al., 2017). Sample numbers plotted on Fig. 1 show locations.
<table>
<thead>
<tr>
<th>SAMPLE DEPTH IN CORE</th>
<th>SAMPLE DRIVE</th>
<th>DESCRIPTION</th>
<th>INTERPRETATION</th>
<th>RESULTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.27 m 1A-34Y-1 3-6 cm</td>
<td>4 cm thick bedded chert with abundant crystal shapes and pseudomorphs with fibrous chalcedony. Uncompacted. Compacted silicified mudstone above and below chert. Thick trona deposit immediately above.</td>
<td>Type 1: Early diagenetic (precompaction) silicified gel with incorporated evaporite (gaylussite?) crystals. Later burial silicification of mud.</td>
<td>42.7‰</td>
<td></td>
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<tr>
<td>49.38 m 1A-34Y-1 14-16 cm</td>
<td>2 cm thick chert layer with uncompacted plant fragments, and contorted layers with well-compacted silicified mudstone above and below primary siliceous layer.</td>
<td>Type 4 at upper and lower boundaries of chert bed, later burial silicification of mud.</td>
<td>40.9‰</td>
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<tr>
<td>76.00 m 1A-49Y-1 68-70 cm</td>
<td>Cm thick bedded chert with contorted layering. Reticulate crust and v-cracks, Pleurocapsa?</td>
<td>Type 1 with some Type 3 growth in v-cracks and reticulate crusts: Early diagenetic (precompaction) silicified gel with incorporated coccoid cyanobacteria</td>
<td>43.7‰</td>
<td></td>
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<tr>
<td>61.36 m 2A-29Y-1 1-3 cm</td>
<td>laminated siliceous mudstone, layering defined by detrital or zeolitic material alternating with primary siliceous layer.</td>
<td>Type 4: Silicified mud after compaction</td>
<td>41.1‰</td>
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<td>70.63 m 2A-32Y-1 13-19 cm</td>
<td>cryptocrystalline quartz in 8 cm thick, poorly bedded chert, uncompacted well preserved, plant fragments (twisted), internal fracturing (v-cracks), some with inward growth of chalcedony, upper boundary shows reticulate crust and fracturing patterns, labyrinth gel patterns.</td>
<td>Type 1 with some Type 3: Early silicification from gel; possible subaerial exposure</td>
<td>45.3‰</td>
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<td>83.64 m 2A-39Y-1 85-92 cm</td>
<td>4 cm thick chert nodule/discontinuous bed; labyrinth structure in cryptocrystalline quartz. Conglomerate and mudcracked mud immediately above.</td>
<td>Type 1: Early (pre-compaction) silicification from gel following subaerial exposure</td>
<td>42.6‰</td>
<td></td>
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<tr>
<td>88.97 m 2A-42Y-1 19-22 cm</td>
<td>Thin bedded chert (cryptocrystalline quartz) with incorporated diatom fossils and reticulated surface. Voids and pyrite concentrated along chert boundaries, polygonal organization, uncompacted plant fragments.</td>
<td>Type 1: Early diagenetic (precompaction) silicified gel</td>
<td>44.5‰</td>
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<td>143.99 m 2A-65Y-1 39-41 cm</td>
<td>white chert nodule with reticulated surface in disturbed core “breccia”, gridwork orientation of microcrystalline quartz crystals (Schubel and Simonson, 1990), internal fracturing with no chalcedony.</td>
<td>Type 2: Chert formed from replacement of hydrous sodium silicate (magadiite)</td>
<td>39.3‰</td>
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<td>179.09 m 2A-88Q-2 0-10 cm</td>
<td>massive chert with gastropods and ostracods, uncompacted material in cryptocrystalline chert with plant fragments, diatoms and calcite crystals.</td>
<td>Type 1 with diagenetic Type 3 in void space: Chert replacement of siliceous gel.</td>
<td>32.1‰</td>
<td></td>
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Table 2.2. Descriptions and interpretations of chert samples selected for SIMS microanalysis.
Figure 2.1. Geological map of the Lake Magadi and Nasikie Engida region. Core drill sites labeled with yellow stars. Water sample sites color coded by classification and labeled S, from Lee et al. (2017), K from Darling (1996), A from Allen et al., (1989), and O or IS from O’Neil & Hay, (1973), see Table 2.
Figure 2.2. Stratigraphic column of core MAG14-2A and composite cores MAG14-1A and 1C; locations shown on Figure 1B. Cherts are indicated by red wavy lines for continuous chert beds and red ovals for nodules. Radiometric ages, major lithologies, paleoenvironments, chert with labyrinth patterns, and subaerial exposure features are plotted. Chert samples selected for SIMS microanalysis are shown by yellow stars. M: mud/mudstone, S: sand/sandstone, G: gravel/conglomerate, E: evaporite.
Figure 2.3. Photo panel of Type 1 cherts from the Lake Magadi cores.

A. Photograph of chert bed from core drive MAG14 1A 34Y-1. Depth 49.27 m. Scale bar 1 cm. B. Photomicrograph of cryptocrystalline chert (cc) surrounding evaporite crystal pseudomorph replaced with chalcedony on the rim (arrow) and megaquartz partially filling the core. Grey oval is air bubble trapped in open void of the crystal. Depth 49.27 m. Scale bar 200 µm. C. Photomicrograph (cross-polarized light) showing cryptocrystalline chert (cc) surrounding crystal pseudomorph with fibrous chalcedony lining the outer wall of the crystal (white arrow) and radial chalcedony partially filling the interior (blue arrow). Grey oval to left of blue arrow is air bubble trapped in open
void of the crystal. Depth 49.27 m. Scale bar 200 µm. **D.** Photomicrograph of a portion of a decimeter thick chert bed with laminated mudstone below chert unit from core drive MAG 14 2A-32Y-1. Depth 70.63 m. Scale bar is 0.5 cm. **E.** Photomicrograph of twisted, uncompacted plant fragment, surrounded by cryptocrystalline chert. Depth 70.63 m. Scale bar 200 µm. **F.** Photomicrograph of well-preserved, uncompacted plant fragment, surrounded by cryptocrystalline chert. Depth 70.63 m. Scale bar 100 µm. **G.** Photomicrograph of chert with dewatering fractures from core drive MAG 14 2A-39Y-1. Grey ovals are air bubbles trapped in pore space during thin section preparation. Depth 83.64 m. Scale bar 0.5 cm. **H.** Photomicrograph (cross-polarized light) of cryptocrystalline chert with chalcedony growth in fractures. Grey ovals are air bubbles trapped during thin section preparation. Depth 83.64 m. Scale bar 100 µm. **I.** Photomicrograph of cryptocrystalline chert with preserved labyrinth pattern. Dark grey ovals are air bubbles trapped during thin section preparation. Depth 83.64 m. Scale bar 100 µm. **J.** Photomicrograph of centimeter thick chert beds with dewatering fractures from core drive MAG 14 2A-42Y-1. Depth 88.97 m. Scale bar 0.5 cm. **K.** Photomicrograph of cryptocrystalline chert with uncompacted, well-preserved diatoms (arrow). Dark grey ovals are air bubbles trapped during thin section preparation. Depth 88.97 m, Scale bar 100 µm. **L.** Photomicrograph of cryptocrystalline chert with uncompacted, well-preserved diatoms, possibly *Anomoeoneis sphaerophora* (left diatom). Depth 88.97 m. Scale bar 20 µm. **M.** Photograph of limestone thin section with deformed layering and abundant chert. Chert cement fills shell cavities of ostracods and gastropods, Lake Magadi core drive MAG14 2A-88Q 2. Depth 179.09 – 179.18 m. Scale bar is 0.5 cm. **N.** Photomicrograph of ostracod shell (arrow) surrounded by cryptocrystalline chert (cc). Depth 179.09 m. Scale bar 200 µm. **O.** Photomicrograph of gastropod shell (arrow) cemented by cryptocrystalline chert and chalcedony, and surrounded by cryptocrystalline chert. Depth 179.09 m. Scale bar is 500 µm.
Figure 2.4. Photo panel of cherts and SIMS results from cherts in the Lake Magadi cores.

Panels A-C are Type 2 cherts, formed after magadiite. A. Photograph of white finely laminated chert bed and fractured nodular white chert from core drive MAG14 2A 65Y-1. Depth 143.99 m. Scale bar 2 cm. B. Photomicrograph of chert with dewatering fractures (arrow) and microcrystalline chert. Note absence of plant fragments, grains, air bubbles, void space, and other incorporated material. Depth 143.99 m. Scale bar 200 µm. C. Photomicrograph (cross-polarized light), cryptocrystalline chert with platy groundmass. Scale bar 20 µm. Panels D-F show Type 3 cherts, with evidence for later
**diagenetic formation of chalcedony and megaquartz.** D. Photomicrograph (cross-polarized light) of ostracod shell surrounded by cryptocrystalline quartz (cc) with interior filled with megaquartz cement (MQ), from core drive MAG14 2A 88Q-2. Depth 179.09 m. Scale bar 100 µm. E. Photomicrograph (cross-polarized light) of cryptocrystalline chert (cc) with chalcedony in fracture (arrow) and megaquartz in void space of shell fragment (MQ). Depth 179.09 m. Scale bar 500 µm. F. Photomicrograph (cross-polarized light) of megaquartz (MQ) growth into void space surrounded by cryptocrystalline chert (cc). Depth 179.09 m. Scale bar 50 µm. **Panels G-I represent Type 4 cherts with evidence for late-stage diagenetic post-burial compaction.** G. Photomicrograph of finely laminated siliceous mudstone from core drive MAG14 2A-29Y-1. Depth 61.36 m. Scale bar 0.3 cm. H. Photomicrograph of siliceous mudstone, with rotated and aligned plant fragments. Depth 61.36 m. Scale bar 100 µm. I. Photomicrograph of primary siliceous layer (Si) of cryptocrystalline quartz with finely laminated layers of rotated, aligned and compacted plant fragments, all now chert. Depth 61.36 m. Scale bar 100 µm. **Panels J-O are SIMS analysis pits representative of chert types analyzed.** J. SEM image of SIMS microanalysis sample pit from Type 1 chert, δ¹⁸O +45.75‰. Depth 70.63 m. Scale bar 7 µm. K. SEM image of SIMS microanalysis sample pits from Type 1 chert, δ¹⁸O +42.49‰ and +42.39‰. Depth 49.27 m. Scale bar 20 µm. L. SEM image of SIMS microanalysis sample pits from Type 1 chert, δ¹⁸O +42.30‰. Depth 83.64 m. Scale bar 10 µm. M. SEM photograph of SIMS microanalysis sample pit from Type 2 chert, δ¹⁸O +38.56‰. Depth 143.99 m. Scale bar 12 µm. N. SEM photograph of SIMS microanalysis sample pit from Type 3 chert, megaquartz (MQ) analyzed at δ¹⁸O +26.99‰ and +28.40‰, cryptocrystalline chert (cc) analyzed at δ¹⁸O +31.44‰. Pits within shell did not produce reproducible results as they are not quartz and contain epoxy from sample preparation. Depth 179.09 m. Scale bar 100 µm. O. SEM photograph of SIMS microanalysis sample pit from Type 4 chert, δ¹⁸O +40.38‰. Depth 61.36 m. Scale bar 10 µm.
Figure 2.5. Histograms $\delta^{18}O$ V-SMOW (chert) from SIMS analysis, arranged by sample depth (mbs, meters below surface) and shaded by Type 1, 2, 3 and 4 cherts. Vertical red lines show mean values of samples. Black bars represent cryptocrystalline and microcrystalline quartz. Orange bars indicate chalcedony and megaquartz. Blue and purple shading show the range of oxygen isotope values reported in Lake Magadi cherts by O'Neil & Hay (1973) interpreted by them to form in low salinity and high salinity environments, respectively.
Figure 2.6. δ²H vs. δ¹⁸O of modern hot and warm springs, lake brines, Ewaso Ng’iro River, and rainwater in the Lake Magadi, Kenya region from previous studies (Table 2, from O’Neil and Hay, 1973; Allen, 1989; Darling, 1996; Lee, 2017), Global meteoric water line (MWL) from Craig (1961). KRV-WL is the Kenya rift valley water line from Darling (1996).
Figure 2.7. Curves of $\delta^{18}O$ values calculated for equilibrium precipitation of quartz as a function of water $\delta^{18}O$ value and water temperature, using fractionation factors from Vho et al. (2019). Curves bracket the range of measured $\delta^{18}O$ values from Lake Magadi cherts, from $+24\%_{\text{o}}$ to $+48\%_{\text{o}}$, at $4\%_{\text{o}}$ intervals (Fig. 5). Modern Magadi water $\delta^{18}O$ values and temperatures are shown as colored dots (Table 2). Red dots are modern hot springs, temperatures above 50°C. Yellow dots are modern warm springs, temperatures between 20 and 50°C and blue dots represent modern lake brines. The $\delta^{18}O$ values of type 1 chert with cryptocrystalline quartz and evaporite pseudomorphs formed from siliceous gels, ranges from $+41\%_{\text{o}}$ to $+47\%_{\text{o}}$. Light purple area shows range of modern lake brine $\delta^{18}O$ values, $\sim+5\%_{\text{o}}$ to $+15\%_{\text{o}}$, and temperatures, 23 to 47°C, from which cherts with relatively high $\delta^{18}O$ values ($+41$ to $+47\%_{\text{o}}$) are interpreted to have formed. The $\delta^{18}O$ in type 1 chert but with cryptocrystalline quartz surrounding gastropod and ostracod shells, ranges from $+26\%_{\text{o}}$ to $+35\%_{\text{o}}$. Blue area shows range of modern water $\delta^{18}O$ values from $-2\%_{\text{o}}$ to $0\%_{\text{o}}$ and temperatures, 34 to 49°C, consistent with values from modern warm springs. Cherts with relatively low $\delta^{18}O$ values (Fig. 5, 179.09 m: $+26\%_{\text{o}}$ to $+35\%_{\text{o}}$) are interpreted to have formed from these waters, consistent with modern warm springs. The $\delta^{18}O$ of type 2 chert with microcrystalline quartz and relict magadiite lepispheres ranges from $+38\%_{\text{o}}$ to $40\%_{\text{o}}$. Purple area shows $\delta^{18}O$ values, from $+2\%_{\text{o}}$ to $+7\%_{\text{o}}$, and temperature range, 23 to 47°C, of the lake waters from which type 2 cherts are interpreted to have formed. The waters are less evaporated than modern lake brines. The $\delta^{18}O$ of type 3 chert, megaquartz, ranges from $\sim+23\%_{\text{o}}$ to $+30\%_{\text{o}}$. The red area shows the
range of modern hot springs water $\delta^{18}$O values and modern hot spring temperatures, 60 to 85°C $\delta^{18}$O values which represents the type of water from which megaquartz cements (+23‰ to +30‰) are interpreted to have formed. The $\delta^{18}$O values of type 4 cherts, siliceous mudstones, range from (+37‰ to +46‰). The brown shaded area shows the range of water $\delta^{18}$O values and borehole brine temperatures, 33 to 38°C, from which burial cherts are interpreted to have formed.
Chapter 3 Bedded Cherts of the Lake Magadi Basin:
Observations and origins

3.1 Introduction

Cherts formed in saline-alkaline environments, such as the Pleistocene deposits of Lake Magadi, Kenya, have been used as a model for Archean cherts. Pleistocene Magadi Cherts are interpreted to be purely chemogenic in origin (Eugster, 1967, 1969). Early work suggested that chemically precipitated hydrous sodium silicates such as magadiite (NaSi$_7$O$_{13}$(OH)$_3$·3H$_2$O) and kenyaite (NaSi$_{11}$O$_{20.5}$(OH)$_4$·3H$_2$O) dewatered to chert through the leaching of sodium in contact with groundwater (Eugster 1967, 1969, Sheppard and Gude 1986). Later, Eugster (1980) noted vertically oriented silicified plant fragments, relict tissues of grasses, fungi and other organic matter in chert, and hypothesized chert formation from an aluminosilicate gel. Wheeler and Textoris (1978) noted some Triassic cherts from the Deep River Basin in North Carolina had very fine crystalline quartz with some chalcedony but little else, suggesting a purely inorganic origin as well. Soft, gelatinous silica precipitates were noted in hydrothermal environments where thermal springs were submerged by lake water (Renaut et al., 2002).

Behr (2002) challenged these inorganically-formed precursors of Magadi cherts, noting the potential for biogenic chert formation based on coccoid cyanobacteria (Pleurocapsa, Gloecocapsa) in Magadi cherts. This interpretation suggested that the metabolic processes of cyanobacteria control pH and thereby influence the dissolution and precipitation of silica.

Peterson and von der Borch (1965) recorded silica precipitation in ephemeral lakes of Australia when pH (9.5 to 10.2) dropped (7.0 to 6.5). The initial siliceous phase
was gelatinous opal-CT with a weakly-crystalline structure that slowly converted to microcrystalline quartz (Peterson and von der Borch, 1965). Jones (1967) calculated that a drop in pH from 11 to 8.5 could precipitate up to 3000 ppm of SiO$_2$ in a 1.5 mm thick layer per meter of brine. This drop in pH could be caused by the retention of biogenic CO$_2$ in the hypolimnion of a stratified lake (Jones, 1967).

No one precursor for Magadi cherts has been agreed upon, yet, they have been used for paleoenvironmental interpretations of ancient cherts. Some cherts from the Eocene Green River Formation are interpreted to have formed following the decomposition of algal organic matter which lowered the pH of pore waters and precipitated silica (Kuma et al., 2019). Other mechanisms of chert formation in the Green River Formation are purely chemical and involve alkaline paleolake waters with elevated dissolved silica (Jagniecki and Lowenstein, 2015).

A deeper understanding of the formation of chert at Lake Magadi is needed for refinement of paleoenvironmental interpretations. Recent coring at Lake Magadi provided a stratigraphic sequence of Pleistocene and Holocene sediments, including chert, which added new material from which to assess the timing and mechanisms of chert formation.

### 3.2 Geological Background

Lake Magadi is a closed-basin, ephemeral, alkaline, hypersaline lake on the axial trough of the southern Kenya Rift, bounded by north-south normal faults (Fig. 1A); (Fazi, 2017). Perennial lake Nasikie Engida (referred to in older literature as Little Magadi) is north of Lake Magadi (Fig. 1B). Inflow waters to both lakes consist of ephemeral storm
runoff and perennial saline springs (Renaut et al., 2021). Evaporative concentration of lake water produces high pH, Na-CO$_3$-HCO$_3$-Cl-rich brines (Jones et al., 1977, Eugster, 1986). Salinities of ephemeral Lake Magadi range from 193,000 to 313,000 mg/kg with major solutes comprised of sodium, carbonate-bicarbonate, and chloride, and pH between 9.5 and 11.06 (Eugster, 1970).

The climate of the Lake Magadi region is semi-arid, characterized by annual potential evaporation (3500 mm/yr) exceeding precipitation (450-500 mm/yr). The wet season is biannual occurring February to April and October to November, correlating with the migration of the Intertropical Convergence Zone (ITCZ); (Nicholson, 2000). Mean air temperatures range between 19 and 35°C and rarely drop below 17°C at Lake Magadi townsite (Climate data from KNMI Climate Explorer https://climexp.knmi.nl/start.cgi and climate-data.org).

Trachyte flows (~ 1078.3 ± 3.6 ka) make up the basement rocks of the Magadi Basin (Fig. 1C), (Baker, 1958, 1963; Owen et al., 2019). Baker (1958) classified the outcrops and lithofacies of the Magadi Basin as: lacustrine Oloronga Beds in sharp contact with the underlying trachyte bedrock (~1.4 to 0.8 Ma, Owen et al., 2019). The Oloronga Beds are characterized by fossiliferous cherts, chert breccia and partially silicified limestone containing gastropods (*Viviparus, Melanoides tuberculata*), ostracods, and plant remains (Baker 1958, Herrick 1972, Behr 2002). The Oloronga Beds are capped by a calcrete layer (Eugster, 1980, 1986). Above this calcrete layer is laminated silt and silty clay, zeolitic tuff, and massive, thinly bedded and stromatolitic chert, containing coccoid cyanobacteria and filamentous microbial mat features, known as the Green Beds (Behr and Röhrich, 2000). Evaporite mineral pseudomorphs, dewatering
cracks, and tepee structures were recently documented in the Green Bed cherts (Brenna, 2016). Above the Green Beds, Baker (1958) described the late Pleistocene High Magadi Beds, which are noted for their magadiite deposits and finely laminated “paper” chert, laminated clay and a distinct layer with fish fossils. Finally, the uppermost Evaporite series, consists of abundant bedded trona (Baker, 1958, Eugster 1969, 1980, McNulty, 2017, Owen et al., 2019).

3.2.1 Chert

Chert, typically called “Magadi-type chert” has been documented from all the Pleistocene deposits described above. Magadi-type cherts commonly have evaporite molds and pseudomorphs along bedding surfaces (Schubel and Simonson, 1990; Behr, 2002). Some evaporite pseudomorphs are fine radiating needles, likely after trona crystals, and some evaporite pseudomorphs are tabular, likely after gaylussite crystals (Hay, 1967). Magadi-type cherts also possess internal fracturing in the form of v-cracks or fenestrae cracks (Schubel and Simonson, 1990). Chert bedding surfaces commonly show reticulate patterns and fracturing, interpreted to be dewatering features (Heaney and Post, 1992, Hattori, 1996, Bustillo 2001, Behr 2002). Most Magadi-type cherts are interpreted to have formed from magadiite or kenyaite (Eugster, 1967; Schubel and Simonson, 1990; Behr, 2002). Schubel and Simonson (1990) described these cherts as having a granular texture composed of a microcrystalline platy groundmass. Schubel and Simonson (1990) also noted chalcedony in Magadi cherts that filled voids and fractures and lined evaporite molds. Trace fossils along bedding planes of Magadi cherts were documented by Scott (2010) and interpreted as pock marks and ‘creeping’ by insects, possibly brine flies such as Diptera and Ephydridae. Beetle traces and burrows, 1 mm
wide to 1 cm deep, and creeping traces, were also described on surfaces of bedded cherts (Behr and Röhricht, 2000). Green Bed cherts contain Gloecocapsa, Pleurocapsa and Microcoleus indicative of hypersaline, sublacustrine habitats (Behr and Röhricht, 2000).

3.2.2 Core Drilling at Lake Magadi

Coring of sediments beneath Lake Magadi provided a detailed stratigraphic sequence. Cores MAG 14-1A and 1C (composite) and MAG 14-2A, 137 m and 198 m long, respectively (Fig. 2), were drilled to trachyte basement rock in 2014 as part of the Hominin Sites and Paleolakes Drilling Project (HSPDP) (Cohen et al., 2016; Campisano et al., 2017; Owen et al., 2018). The HSPDP project aims to resolve the connection between climate and climatic variability, and human evolution and behavior. The one-million-year record at Lake Magadi parallels the change in early Hominin stone tool technology from Late Acheulean (615 to 499 ka) to Middle Stone Age (MSA) (~340 ka) at the nearby Olorgesailie Early-Late Pleistocene archeological site (Deino et al., 2018; Potts et al., 2018, Brooks et al., 2018). This transition in early Hominin tool technology corresponds to an intense period of prolonged aridity at Olorgesailie, ~500 to 300 ka (Potts et al., 2018).

Although core recovery was poor due to alternating mud and chert, (total recovery ~60%, Campisano et al., 2017), the HSPDP cores document progressive aridity during the basin history (Owen et al., 2018). A one-million-year chronology was obtained through radiocarbon, ⁴⁰Ar/³⁹Ar, paleomagnetic, and U-series dating, using Bacon 2.2 Bayesian geochronology (Owen et al., 2018). At the base of the cores, the Oloronga Beds indicate an early (~1,050 -750 ka), broad and shallow freshwater lake, with ostracod and gastropod grainstone, clast-supported gravel, silt/siltstone, and sand/sandstone with some
bedded chert (Owen et al., 2018). Faulting produced a narrowing of the Magadi basin and a stratified perennial saline lake existed between ~750-550 ka (Owen et al., 2019). The sediments from this interval are laminated mud, laminated and nodular chert, organic matter, and pyrite (Owen et al., 2018). Alluvial fan gravel, sandflat sand, and mudcracked mud, deposited between ~550-420 ka, indicate a period of desiccation and subaerial exposure (Owen et al., 2019). The laminated mud is followed by a 6 m thick zeolite-rich tephra sequence, with 4 dated horizons ranging in age from 354-316 ka (Owen et al., 2018). Above the tephra sequence, perennial lake mud alternates with mudflat mud and alluvial fan sand and gravel and a variety of nodular and bedded chert. Bedded trona and massive mud with trona and nahcolite, deposited in hypersaline conditions, first appear ~118.6 ka (Owen et al., 2019). Siliceous chemical sediments, particularly chert, but also zeolites, suggest alkaline conditions existed over much of the million-year basin history, but diatoms and mud with fish fossils suggest periods of fresher water existed over much of the lake history as well (Owen et al., 2018, Muiruri et al., 2021).

Mg-calcite and calcite are common in core 2A from the base to ~380 ka, but are rare above (Owen et al., 2018; 2019). Dolomite is rare anywhere in the core. Analcime is found throughout the core, but other zeolites such as erionite, mordenite, phillipsite, and clinoptilolite appear ~540 ka and are common to the top of core 2A (Owen et al., 2019).

3.3 Research Methods

Core Sampling & Collection

In the summer of 2015, more than 200 samples from the HSPDP cores were collected at the University of Minnesota National Lacustrine Core Facility (LACCORE) and sent to Binghamton University. Additionally, four core drives, MAG14-2A-29Y-2A,
MAG14-2A-30Y-2A, MAG14-2A-67Y-1A and MAG14-2A-81Q-2A, with laminated sediments were sent to Binghamton University for high resolution sampling and analysis. Chert samples and associated minerals such as magadiite were selected from the MAG-14 cores for thin section petrography, x-ray diffraction, scanning electron microscopy (SEM), and energy dispersive x-ray spectrometry (EDS) analysis.

Microscopy

Approximately 75 thin sections from chert were prepared for transmitted light microscopy. Some thick sections, greater than 20 µm, were prepared, and other thin sections were prepared from samples cut parallel to bedding. Selected chert and sediment samples were mounted for field emission scanning electron microscopy (SEM) on a Zeiss Supra 55 VP. Sediment and chips were carbon coated and analyzed under vacuum with back scattered electrons (BSE) and secondary electrons (SE). Energy-dispersive X-ray spectroscopy (EDS) was used for elemental analysis of samples.

X-ray powder diffraction

Powdered samples were prepared and analyzed on a Phillips Xpert PW3040-MPD diffractometer operated at 40 kV and 20 mA, using Cu-Kα radiation fitted with a diffracted-beam graphite monochromator. Powders were run at a continuous scan from 5° to 70° 2θ with a step size of 0.05° at 2 seconds per step.

3.4 Observations:

Several quartz textures were observed in the Magadi cherts and here we define three overarching types: (1) megaquartz, consisting of crystals greater than 20 µm; (2) microcrystalline quartz, commonly fibrous or radial chalcedony, consisting of quartz
crystals less than 20 µm and commonly 2-8 µm; and (3) cryptocrystalline quartz with submicron crystals, difficult to discriminate in thin section or SEM (Table 1).

Petrographic and SEM observations, along with XRD, EDS, and SIMS oxygen isotope analysis of chert in the Lake Magadi cores, distinguished four types of chert (Leet et al., in review). Type 1 chert is comprised primarily of cryptocrystalline quartz and formed from a siliceous gel precursor. Type 2 chert is composed of microcrystalline quartz with a hydrous sodium silicate precursor, such as magadiite or kenaite. Type 3 chert is cement and void filling chalcedony and megaquartz and Type 4 chert is compacted silicified mudstone.

3.4.1 Type 1 Chert Observations

Type 1 chert was the most common chert found in the Lake Magadi cores. Type 1 chert occurs in centimeter to decimeter thick beds with little to no evidence for compaction. Type 1 chert is composed primarily of cryptocrystalline quartz with minor chalcedony and megaquartz. Incorporated materials, such as evaporite crystals, plant fragments, bacteria, fungi, and diatoms, are not compacted or deformed and are not framework supported.

3.4.1.1 Evaporite Pseudomorphs:

Chert samples from the Lake Magadi cores have abundant evaporite crystal pseudomorphs within the cryptocrystalline chert matrix. Evaporite pseudomorphs in chert show a variety of relict crystal habits and growth fabrics. Evaporite pseudomorphs were found in cherts from core 2A at depths of 40 to 120 m and core 1A from 35 to 85 m, (~17.2 ka to ~477.8 ka), well below the deepest recovered evaporites.
Evaporite pseudomorphs are commonly 1-2 mm in size (Fig. 3F) with rare larger needles and blades surrounded by cryptocrystalline quartz (Fig. 3F) with fibrous chalcedony cement lining and filling pseudomorph pore spaces (Fig. 3F). Evaporite pseudomorphs are classified into two crystalline habits: (1) elongated bladed and acicular crystals, (Fig 3A-E), and (2) equidimensional tabular-prismatic crystals (Fig. 3F-H).

Remnants of trona were found in otherwise empty bladed pseudomorph crystals (Fig. 3B). Other bladed pseudomorphs occur in crystalline fining-upward sequences (Fig. 3C), or exhibit upward, shrub-like growth from a common surface (Fig. 3D, E).

Tabular-prismatic pseudomorphs, typically 1-2 mm in size, are randomly oriented and commonly segregated as single crystals in cryptocrystalline chert matrix (Fig. 3F, G, H). Pseudomorphs are commonly lined or filled with fibrous chalcedony cement (Fig. 3G).

**3.4.1.2 Pyrite:**

Pyrite is common in all chert types, but in Type 1 chert, it commonly clusters into reticulate patterns (Fig. 3I). Pyrite crystals are approximately 3µm. In other cases, pyrite crystals are evenly distributed in chert that is crosscut by chert-filled fractures (Fig. 3J).

**3.4.1.3 Fossils:**

Type 1 cherts contain abundant uncompacted biological material including plant fragments, insect fragments, diatoms, and microorganisms. Plant fragments in Type 1 chert are randomly oriented (Fig. 3K) and may show vague cellular structure (Fig. 3L). Rare possible insect remains also occur in Type 1 chert (Fig. 3M). Diatoms found in Type 1 chert are sparse and surrounded by cryptocrystalline quartz (Fig. 3N). Diatom
structure is not well defined in thin section, but some are probably Anomoeoneis sphaerophora (Fig. 3O) and Rhodalodia gibberula (Fig. 3P).

Silicified plants and microorganisms were observed in cryptocrystalline quartz from core 1A at ~ 75 m (Fig. 4). SEM images from a broken, unpolished chert surface revealed several life stages of fungi near silicified filamentous plant material (Fig. 4A). Fungal morphologies include spherical blastospores (Fig. 4B), arthrospores, or segmented hyphae (Fig. 4C). Some hyphae have ~5µm diameter silicified, spherical conidium (asexual spores) (Fig. 4D). Due to silicification, connected hyphae segments comprising the intertwined mycelium of fungi were difficult to identify (Fig. 4C, D). Dispersed, silicified fungal germination features, such as conical heads with segmented tails, were observed (Fig. 4E). Coccoid bacteria and chains of streptococci occur in close association with silicified fungi (Fig. 4F).

**3.4.1.4 Shrinkage Features:**

Shrinkage features identified in Type 1 chert include granular patterns and cracks. Granular patterns, such as labyrinth (Fig. 3Q) and bubble stick patterns (Fig. 3R), are types of viscous fingering that form during the invasion of air into a granular fluid (Leet et al., 2021). Internal fracturing in the form of v-cracks or fenestrae cracks (Fig. 3S), some partially- to fully- filled with chalcedony, occur in Type 1 chert (Fig. 3T). Cracks originating from a common surface in regularly-spaced intervals are visible where sediment layers meet cryptocrystalline quartz (Fig. 3U). Cracks are filled with sediment, commonly from the layer directly above. Fractures and other shrinkage features comprise <10% of the area of Type 1 cherts studied in thin section.
3.4.2 Type 2 Chert Observations

Type 2 chert is comprised of microcrystalline quartz with evidence for lepisphere structure and little to no incorporated material. These cherts formed from a hydrous sodium silicate such as magadiite or kenyaite. Primary magadiite is made of ~20 µm spherical rosettes of platy crystals, known as lepispheres, (Fig. 5A); (Schubel and Simonson, 1990; Muraishi, 1995; Ma et al., 2010).

Soft, deformed magadiite, was recovered from a 3-cm thick layer in Core 1A at 49 m (Fig. 8A). The magadiite layer contains compressed lepispheres composed of layered crystals resembling stacked plates (Fig. 5B). EDS and XRD confirm magadiite in this sample and no other siliceous phases (Fig. 5C and D). No kenyaite was found in XRD analyses of sediments in the Magadi cores.

Type 2 chert is composed of granular microcrystalline quartz with platy groundmass textures and little incorporated material (Fig. 5E, K and L). The groundmass shows vague curvilinear accumulations of microcrystals and spherulitic textures (Fig. 5F). Circular shapes (Fig. 5G) are approximately 20 µm in diameter (Fig. 5H). Under SEM, the circular textures are spherical balls composed of microcrystalline quartz, ~25 µm in diameter (Fig. 5I). EDS analysis confirms that these spheres are comprised entirely of quartz (Fig 5J).

Type 2 chert commonly contains dewatering features, primarily external v-cracks. Internal fractures and fenestrae are less common than in Type 1 chert. More commonly, type 2 chert has v-shaped cracks that point inward to the center of the chert layer (Fig. 5K). V-cracks can be partially filled with sand and mud (Fig. 5L). No granular labyrinth patterns were observed in Type 2 chert.
3.4.3 Type 3 Chert Observations

Type 3 chert is pore filling cement, composed of chalcedony and megaquartz, that crystallized in dissolved evaporite crystals, fossil shell interiors, dewatering and shrinkage voids, and fractures. Chalcedony is a generic term for microcrystalline quartz with individual crystals less than 20 µm. Chalcedony is separated into two types, length-fast and length-slow. Length-fast, also known as fibrous chalcedony, is characterized by the horizontal stacking of microcrystals that give it the characteristic fibrous texture under cross-polarized light. Crystalline fibers can also form radiating spherical patterns, called radial chalcedony. Length-slow chalcedony, also known as quartzine, consists of microcrystals stacked vertically along the long axis, (Flörke et al., 1991). Megaquartz describes large crystals >20 µm in size (Folk and Pittman, 1971; Knauth, 1994; Table 1).

3.4.3.1 Chalcedony

Chalcedony in Lake Magadi chert fills pore spaces left by dissolved evaporites (Fig 6A) or internal fractures (Fig. 3T). Some evaporite pseudomorphs are completely replaced with fibrous chalcedony (Fig. 6B).

Chalcedony lines the margins of voids (Fig. 6C and D); radial chalcedony occurs in the void interiors (Fig. 6C and D). Gastropod shell fragments in cryptocrystalline quartz matrix are connected by a fracture network and filled with fibrous chalcedony (Fig 6F). Voids within shells are lined by fibrous chalcedony (Fig. 6F). Under SEM, void-filling chalcedony shows well defined quartz microcrystals, >1 µm in size, surrounded by cryptocrystalline quartz <<1 µm (Fig. 6G).
3.4.3.2 Megaquartz

Megaquartz forms cement, especially in cherts of the Oloronga beds, where it fills ostracod and gastropod shells (Fig. 6H). Megaquartz only occurs in the deepest cores from the Oloronga bed cherts. Radial chalcedony was also observed in fractures, crystals, ~0.1 mm, (Fig. 6E).

3.4.4 Type 4 Chert Observations

Type 4 chert occurs in laminated silicified mudstone marginal to Type 1 and Type 2 chert layers (Fig. 7B). The silicified mudstone is comprised of dark, millimeter thick detrital and/or zeolitic laminae (Fig. 7A) alternating with millimeter to centimeter thick lighter, purer, chert laminae. Plant fragments in detrital layers are highly compacted and horizontally aligned (Fig. 7A). Cellular structures in plant fragments have been destroyed by compaction. Associated Type 1cherts contain v-cracks, evaporite pseudomorphs (Fig 7C), and uncompacted plant material (Fig. 7D) or are composed of pure microcrystalline quartz, in places, finely laminated (Type 2) (Fig. 7B).

3.4.5 Observations of Types 1-4 Chert from core MAG14-1A-34Y-1:

Virtually all the chert types in the Lake Magadi Basin were observed in one 40 cm-thick section of core from a depth of 49.21 m (Fig. 8A). The bottom of the sequence, ~37 cm, is laminated mud composed of clay and zeolite, primarily erionite (Fig. 8A:1 and Fig. 8F). Above, from 35 to 26 cm, mud is laminated with magadiite. XRD patterns of some of the magadiite layers show broad peaks indicating moganite may occur along with magadiite. Moganite is interpreted to form during the transition from magadiite to quartz (Heaney, 1995). Deformed magadiite layers between 26 and 28 cm are soft, putty-like, and composed of lepispheres (Fig. 5, 8E), and minor detrital material (Fig 8A:2).
Laminated mud above the magadiite (Fig. 8A:3) contains erionite “cement” between grains (Fig. 8D), and minor fluorite. The chert layer at 14 cm (Fig. 8A:4) is Type 1 with uncompacted plant fragments and other incorporated material in microcrystalline quartz (Fig. 5I, 7C, D). Highly compacted silicified mudstone (Type 4 chert) occurs above and below the primary chert bed from 50 mbs to the bottom of core. The Type 1 chert at 3-6 cm (Fig. 8A:5) contains rare plant fragments and abundant evaporite pseudomorphs lined with fibrous chalcedony (Type 3 chert). Immediately above this core drive is a decimeter thick bedded trona deposit.

3.5 Interpretations of Chert Formation

3.5.1 Type 1 Chert Interpretations

Type 1 chert is interpreted to form from amorphous hydrated siliceous gel. Translucent siliceous gels precipitate and accumulate today in the shoreline waters of Nasikie Engida during dry seasons (Renaut et al., 2021). Along the northern shore of Nasikie Engida, subaerially exposed gelatinous layers are commonly overlain by microbial mats (where water temperature is less than 65°C) and efflorescent crusts, up to 1.5 cm thick (Renaut et al., 2021, Eugster and Jones, 1968, Eugster, 1986). In shallow waters at the southern end of Nasikie Engida, patches of siliceous gel occur around trona rafts and crystals (Renaut et al., 2021). Subaqueous gels also occur along the eastern and western margins of Nasikie Engida. There, the gels contain dispersed sediment and plant fragments but lack microbial mats (Renaut et al., 2021). The gels incorporate plant and insect fragments, microbial exopolymers, zeolites, and other detritus (Renaut et al., 2021).
Type 1 chert contains acicular crystal pseudomorphs likely after trona (Fig. 3A, B). Trona precipitating today at Lake Magadi and Nasikie Engida commonly forms upward and downward radiating crystal shrubs composed of acicular crystals, nucleated from sunken rafts (Fig. 9C) (McNulty, 2017). Bottom growth trona crystals show competitive upward and outward radiative bladed crystal growth (McNulty, 2017, Renaut et al., 2021). Trona rafts from the southern end of Nasikie Engida may contain patches of siliceous gel surrounding crystals (Renaut et al., 2021). This association is similar to the evaporite pseudomorphs surrounded by cryptocrystalline quartz in Type 1 chert. Elongate, bladed evaporite pseudomorphs exhibiting competitive growth from a planar surface have right-angle terminations characteristic of nahcolite (Fig. 9B). Tabular, prismatic and randomly oriented evaporite pseudomorphs have the flattened wedge-shaped crystal habit of gaylussite (Fig. 3G). Gaylussite crystals <3 mm in diameter occur in silts along modern fan-deltas at Nasikie Engida (Renaut et al., 2021) and are common in the subsurface deposits of Searles Lake, California (Olson and Lowenstein, 2021).

Trona, nahcolite, and gaylussite pseudomorphs indicate hypersaline environments concurrent with gel formation. Evaporite pseudomorphs also provide clues on the timing of conversion of gel to chert. First, cryptocrystalline chert with evaporite pseudomorph shrubs (Fig. 3D), raft-like textures (Fig. 9D), and graded crystals (Fig. 3C) indicate that the trona and/or nahcolite formed prior to precipitation of the gel and then dissolved after the gel solidified to quartz. This sequence is necessary in order to preserve well-defined crystal pseudomorphs (Brenna, 2016). Second, randomly oriented, isolated crystals (Fig. 3 F-H), in cryptocrystalline chert suggest incorporation of pre-existing crystals in gel or growth within a gelatinous layer prior to conversion to quartz. Third, trona casts observed
along the upper bedding planes of bedded cherts (Brenna, 2016) suggest efflorescent precipitation of trona on the siliceous gel surface. Conversion to quartz must have been early in order to preserve delicate trona needles (Brenna, 2016). Evaporite pseudomorphs were not observed on bedding surfaces in cores but are well documented from outcrops in the Lake Magadi region, especially from the Green Beds (Scott et al., 2021).

Pyrite is common in the Magadi cores (Owen et al., 2019). Pyrite is abundant in deltaic muds on the southern shore of Nasikie Engida where brines are most concentrated (Renaut et al., 2021). At Nasikie Engida and Lake Magadi, early loss of sulfate from brines has long been acknowledged (Jones et al., 1977) but is not well understood. Some depletion in sulfate in brines is due to bacterial sulfate reduction (Renaut et al., 2021). The sulfur isotope composition of pyrite from the Magadi cores has been interpreted as a paleosalinity proxy (Wynn et al., 2018). As salinity increases there is a net loss of $^{32}\text{S}$-enriched sulfate from microbial sulfate reduction. Pyrite formed from brines in which sulfate reduction has occurred is therefore enriched in $^{34}\text{S}$ (Wynn et al., 2018). This suggests some pyrite precipitated in the water column under evaporative conditions, associated with microbial sulfate reduction. Abundant fine pyrite crystals occur within cryptocrystalline quartz (Fig. 3I, 3J). This pyrite precipitated in the water column and became incorporated in gels at the lake bottom, or it formed in situ within the gel. Invasion of air into the gel (Fig. 3I) displaced evenly distributed fine pyrite crystals into a reticulate pattern. Reticulate patterns defined by pyrite suggest early pyrite formation (water column or gel) and depletion of sulfate in surface waters noted by Jones (1977), Wynn et al. (2018), and Renaut et al. (2021). They also indicate invasion of air and/or
volume changes when gels dried, which must have occurred near the surface in order to
preserve such delicate patterns.

Microorganisms discovered in bedded chert from core 1A at 75 m resemble
Ascomycetes fungi, Sodiomyces tronii and Sodiomyces magadii, which have been
identified in Lake Magadi sediments less than 5 cm below the lake surface (Bondarenko
et al., 2018). The genus Sodiomyces is thermotolerant, growing at temperatures up to
40ºC, with optimal growth at 32ºC (Grum-Grzhimaylo et al., 2016). Sodiomyces is
alkaliphilic, growing best at pH ~10 (Grum-Grzhimaylo et al., 2016). Sodiomyces are
associated with the decay of plants and may contain bacteria on their mycelium
(Bondarenko et al., 2018). Life cycle features of ascomycetes fungi preserved in Type 1
chert include spores (Fig. 4B) and yeast-like germination structures (Fig. 4E). The
preservation of fungi in situ suggests (1) the environment was alkaline with temperatures
between 32 and 40 ºC and (2) silicification occurred rapidly, preserving the delicate
microbial features. Salinity is more difficult to interpret from these Sodiomyces fungi as
they are halotolerant but grow best in low salinity. The preservation of Sodiomyces fungi
at various stages of their life cycle, along with plant material, indicate incorporation into
gels formed on the lake floor. The complete preservation of delicate plant fragments and
fungal material in Type 1 chert (Fig. 9F), which resembles organic material in modern
gels (Fig. 9E), indicates early, constant volume conversion of gel to chert.

Diatoms in chert are not in grain contact, as in diatomite, but occur isolated in
cryptocrystalline quartz (Fig. 3 N). The diatoms identified in Type 1 chert, Anomoeoneis
sphaerophora (Fig. 3O) and Rhopalodia gibberula (Fig. 3P) are found in modern
environments, primarily in shallow water. Anomoeoneis sphaerophora lives in shallow
alkaline-saline waters, such as springs, commonly at pH near 9.5 and salinities ~18,000 TDS (Gasse, 1995). *Rhopalodia gibberula* has a wider salinity tolerance and is also commonly found in marshes surrounding hot springs (Owen et al., 2008). Diatoms, preserved in chert, may have been transported from marginal springs and local environments to the lake during periodic flood events (Muiruri et al., 2021, Owen et al. 2019).

Shrinkage features (internal fractures, fenestrae, and V-shaped cracks) (Fig 3. S,U) are common in Type 1 chert, but constitute only a small fraction, less than 10%, of the total area of thin sections examined. Shrinkage features are interpreted to form from the loss of water during the conversion from the precursor material to chert (Eugster 1969, Schubel and Simonson, 1990). Well-preserved granular drying patterns, such as labyrinth (Fig. 3Q) and bubble stick (Fig. 3R) features, indicate the chert formed near the air-water interface prior to burial and compaction (Leet et al., 2021).

SIMS microanalysis of oxygen isotopes indicate that Type 1 chert has high $\delta^{18}O$, from +42 to +47‰ (Leet et al., in preparation). The oxygen isotope composition of chert can be used to determine the temperature and $\delta^{18}O$ of the water involved at the time of formation (Fig. 10). High $\delta^{18}O$ values, > + 42‰, from most Type 1 chert, shows that concentrated brines were involved in their formation.

In order to preserve evaporite pseudomorphs and other delicate features, the conversion from gel to chert must be a near constant volume process. This occurs by reordering the amorphous silica and oxygen arrangement in the gel to a crystalline $\alpha$-quartz lattice. But to maintain constant volume, additional silica is needed to replace the water lost in the conversion of amorphous silica gel to quartz. Cracks, reticulate
structures, and labyrinth patterns indicate addition of external silica, from water, not gel, during chert formation. These processes occurred near the surface prior to burial and compaction.

3.5.2 Type 2 Chert Interpretations

Type 2 chert is interpreted to form from a hydrous sodium silicate precursor, such as magadiite or kenyaite. Chert layers, 1 mm to 10 cm thick, contain little to no incorporated material, which suggests the precursor material was homogeneous. Magadiite layers in outcrops around Lake Magadi are similarly pure. The purity of Type 2 chert suggests subaqueous chemical precipitation and deposition of magadiite in a lake, similar to the magadiite laminae from Lake Kitagata, Uganda (Ma et al., 2011).

Type 2 chert contains microcrystalline quartz arranged as spherical balls identical in size to magadiite lepispheres (Fig. 5I). This spherical arrangement of microquartz suggests quartz replaced magadiite lepispheres, and supports the volume for volume replacement proposed by Schubel and Simonson (1990). Preservation of lepisphere structure in chert also suggests that conversion of magadiite to quartz did not involve intermediate stages. Conversion of magadiite to quartz occurred prior to burial because soft magadiite in core 1A at depths of 49 m contains compacted and deformed lepispheres.

Type 2 chert has v-cracks along the edges of some layers but few to no internal fractures such as those found in Type 1 cherts. These v-cracks represent a minor volume decrease.

Oxygen isotope values of Type 2 chert, obtained by SIMS microanalysis, are +38 to +40‰, (Fig. 10). These values are lower than the δ18O from Type 1 chert and are
interpreted to indicate formation from brines, but less concentrated than those from which Type 1 chert formed (Leet et al., in review).

3.5.3 Type 3 Chert Interpretations

Type 3 chert forms cement in voids and fractures of Type 1 and Type 2 chert. Fibrous chalcedony lines evaporite pseudomorphs which shows that the chalcedony postdates chert formation and dissolution of evaporites. Fractures in cryptocrystalline chert, lined with fibrous chalcedony, again indicate that chalcedony formed subsequent to the chert (Fig. 6D). The close association between voids and fractures suggests pore fluids involved in the formation of Type 3 chert flowed through interconnected networks (Fig. 6F). These pore filling fluids were undersaturated with respect to gaylussite, nahcolite, and trona, which allowed dissolution of evaporites and formation of cavities in which chalcedony and megaquartz cement formed (Fig. 6A and 6B).

$\delta^{18}O$ isotopic compositions of Type 3 chert from SIMS microanalysis revealed much lower $\delta^{18}O$ values for megaquartz, +24 to +32‰, compared to Type 1 and Type 2 chert. These low values were interpreted to reflect precipitation from waters at elevated temperatures that have not undergone evaporation, similar in composition to modern warm and hot springs in the Magadi basin (Leet et al., in review). The textures and oxygen isotope composition of Type 3 chert supports formation of chalcedony and megaquartz via migration of warm, silica rich waters through fractures and pore spaces of chert.
3.5.4 Type 4 Chert Interpretations

Type 4 chert is interpreted to form by silicification of mudstone. Type 4 chert only occurs in mudstone directly in contact with Type 1 and Type 2 chert. In contrast to adjoining Type 1 and Type 2 chert, plant fragments in Type 4 silicified mudstone are rotated parallel to layering and highly compacted. Type 4 chert therefore formed later than Type 1 and Type 2 chert. The shallowest silicified mudstone was identified at a depth of 61 m in core 2A (Fig. 2, ~100 ka), which suggests that significant compaction of mud was achieved at depths less than 60 m.

SIMS microanalysis of siliceous mudstone showed a wide range of $\delta^{18}O$ values, from +37 to +46‰, similar to the oxygen isotope composition of Type 1 and Type 2 chert. This indicates that subsurface brines were involved in the silicification process. Variable isotopic values of Type 4 chert are due to silicification involving pore waters at different temperatures and oxygen isotope compositions.

3.5.5 General Discussion on the formation of Lake Magadi Cherts

Chert is polygenetic, implying there is no one single method of formation. Not all cherts in Lake Magadi form from chemically deposited layers of magadiite and kenyaite as originally proposed by Eugster (1967). In fact, Type 2 chert formed from magadiite and kenyaite is not the dominant type of chert found in the cores from Lake Magadi. Most of the cherts, especially bedded cherts, formed from a siliceous gel precursor, Type 1. Type 1 and Type 2 chert, however, both indicate saline-alkaline paleoenvironments. Type 1 and Type 2 chert correspond to chert outcrops of the Chert Series and High
Magadi Beds (Baker, 1958); the Lower, Middle and Upper High Magadi Beds (Eugster 1969, 1980); and the Green Beds (Behr, 2002).

Bedded Type 1 chert with evaporite pseudomorphs, between 110 to 130 m (core 2A), suggest saline-alkaline conditions existed ~533 to 422 ka. This interval correlates with a period of intense aridity and large mammalian extinctions from ~528 to 392 ka (Muiruri et al., 2021). Cores from nearby Olorgesailie contain an erosional gap over a similar time period, ~499 to 320 ka (Lupien et al., 2021).

### 3.5.6 Paleoenvironments of the High Magadi Cherts

Cherts formed from siliceous gels and magadiite are indicative of saline-alkaline environments. One core drive, MAG 14 Core 1A-34Y-1, 49.21 m, demonstrates an evaporative sequence (Fig. 8). This core drive contains a progression from Type 2 chert (lithified paper-thin chert laminae after magadiite) (Fig. 8A between layers 1, 37 cm and 2, 27 cm) to Type 1 chert (centimeter thick beds after siliceous gels) (Fig. 8A, layers 4 and 5). The upper chert bed (Fig. 8A, layer 5) contains abundant evaporite pseudomorphs, possibly gaylussite, and lies just below the first appearance of bedded trona in core 1A. \( \delta^{18}O \) values from chert can be used to infer paleosalinity of the parent waters, as high \( \delta^{18}O \) in chert has been shown to correlate to high \( \delta^{18}O \) values in the waters from which the chert formed (Fig. 10) (O’Neil and Hay; Leet et al, in review). In 1A-34Y-1, 49.21 m, \( \delta^{18}O \) in chert increases up section, with the mean value of \( \delta^{18}O \) equal to 40.9‰, (Fig. 8 layer 4) for the Type 2 chert formed from magadiite (with silicified mudstone, Type 4 chert) and the mean \( \delta^{18}O \) value of the chert formed from gel with evaporite pseudomorphs equal to 42.7‰, (Fig. 8 layer 5). The high oxygen isotope
values for Type 1 chert indicate that gels formed from highly evaporated brines (Leet et al., in review).

Brine evolution simulations using modern Nasikie Engida hot spring brines, (discharged at 83° Na⁺-HCO₃⁻-CO₃²⁻-Cl⁻-rich composition), Table 2, were run using the EQL/EVP computer program, which is based on Pitzer’s ion-interaction model (Risacher and Clement, 2001). Simulations were at modern pCO₂ (400 ppm: modern atmospheric composition) in a closed system at hot spring temperatures and average lake temperatures, 83°C and 25°C, respectively (Fig. 11). Closed conditions allows evaporating brines to back react with earlier formed minerals. At 83°C, simulations produced the mineral sequence calcite-gaylussite-thermonatrite-amorphous silica with amorphous silica precipitating at evaporative concentration factors of 122 and 127, respectively. At 25°C, simulations produced the mineral sequence amorphous silica-calcite-gaylussite-pirssonite-trona with amorphous silica precipitating immediately with no evaporative concentration of the waters. These simulations show the strong temperature control over precipitation of siliceous phases at Lake Magadi.

At average lake temperatures of 25°C, gaylussite precipitates at ~ 220,000 ppm total dissolved solids (TDS) and trona at 322,200 ppm TDS, which shows that high salinity is necessary for the precipitation of these salts.

3.6 Conclusions

Chert has multiple precursors but here we classify Magadi cherts as those formed in saline-alkaline environments, Type 1 and Type 2 cherts. Most cherts of Lake Magadi are Type 1 cherts formed after an amorphous siliceous gel precursor. These gels preserve paleoenvironmental information such as plant and insect fragments, microorganisms and
evaporite pseudomorphs. This evidence supports the gels and thereby cherts formed in hypersaline environments. Type 2 cherts forming after precipitation of a hydrous sodium silicate, such as magadiite, show pure quartz with very little incorporated material in contrast with the Type 1 cherts formed after gels. The preservation of lepispheres-like textures in Type 2 cherts shows the conversion to quartz occurs near surface and early in the diagenetic history. Type 3 cherts form by the precipitation of quartz by pore fluids after the initial chert formation. Finally, Type 4 cherts forming from the silicification of laminated muds are the latest diagenesis phase.
Table 3.1. Quartz Varieties of the Lake Magadi Cherts:

<table>
<thead>
<tr>
<th>Variety</th>
<th>Sub-Variety</th>
<th>Secondary Terms</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Megaquartz</strong></td>
<td></td>
<td></td>
<td>Quartz crystals, greater than 20 µm (Folk and Pittman, 1971; Knauth, 1994)</td>
</tr>
<tr>
<td><strong>Microcrystalline</strong></td>
<td></td>
<td></td>
<td>Individual granular crystals in thin section, &lt;20 µm (Flörke et al., 1991), typically between 2-8 µm in Magadi cherts</td>
</tr>
<tr>
<td><strong>Chalcedony</strong></td>
<td>Length-fast</td>
<td></td>
<td>Horizontally stacked microcrystals in fibrous bundles or radiating spherulites, referred to as radial chalcedony (Flörke et al., 1991)</td>
</tr>
<tr>
<td></td>
<td>‘fibrous’</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Length-slow</td>
<td></td>
<td>Vertically stacked microcrystals (Flörke et al., 1991)</td>
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<tr>
<td></td>
<td>‘quartzine’</td>
<td></td>
<td></td>
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<tr>
<td><strong>Moganite</strong></td>
<td></td>
<td></td>
<td>Platy crystals grown at random orientations; common lepispheres. Identified by XRD, often found with other quartz varieties in chert. Cherts formed in evaporitic environments may contain up to 20-75% moganite (Heaney, 1995)</td>
</tr>
<tr>
<td></td>
<td>Water content 0.5 to 2.5 wt. %, highest for moganite, water content decreases with increasing crystal size (Flörke et al., 1991)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cryptocrystalline</strong></td>
<td></td>
<td></td>
<td>Individual crystals are submicron scale (&lt;1 µm), not visible in thin section and difficult to identify individual crystals in SEM, (Brenna, 2016)</td>
</tr>
<tr>
<td><strong>Amorphous Silica</strong></td>
<td></td>
<td></td>
<td>No crystalline structure, gelatinous (Renaut et al., 2021)</td>
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</table>
Table 3.2. Chemical composition of hot spring (83°C) inflow water, north-west of Nasikie Engida, in mg kg\(^{-1}\) and mmol kg\(^{-1}\) H\(_2\)O, pH 9.44.

<table>
<thead>
<tr>
<th></th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>Na(^+)</th>
<th>K(^+)</th>
<th>HCO(_3^-)</th>
<th>CO(_3^{2-})</th>
<th>Cl(^-)</th>
<th>SO(_4^{2-})</th>
<th>SiO(_2)</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg kg(^{-1})</td>
<td>0</td>
<td>0</td>
<td>10,500</td>
<td>198</td>
<td>10,400</td>
<td>4,450</td>
<td>4,890</td>
<td>168</td>
<td>85</td>
<td>28,945</td>
</tr>
<tr>
<td>Mmol kg(^{-1})</td>
<td>0</td>
<td>0</td>
<td>471</td>
<td>5.2</td>
<td>176</td>
<td>76.5</td>
<td>142</td>
<td>1.8</td>
<td>1.5</td>
<td>-</td>
</tr>
</tbody>
</table>

From Jones et al. (1977).
**Figure 3.1. Geological Setting** A. East African Rift Map. B. Geological map of the Lake Magadi and Nasikie Engida region. Red stars are locations of the drill cores; black stars are the locations of hot spring inflow. C. Major lithofacies as defined by Baker (1958), Eugster (1969, 1980) and Owen et al. (2019).
Figure 3.2. Stratigraphic column of MAG-14 2A core and MAG-14 1A and 1C composite core; drill site locations shown on Fig. 1B. Cherts are indicated by red wavy
lines for continuous chert beds and red ovals for nodules. Age model dates (Owen et al., 2019) given for Core 2A. Major lithologies, paleoenvironments and chert features are plotted. M: mud/mudstone, S: sand/sandstone, G: gravel/conglomerate, E: evaporite.
Figure 3.3. Images of features associated with Type 1 Cherts, interpreted as cherts formed from siliceous gels.

A. Photomicrograph of elongated, needle-like evaporite pseudomorphs, (v) void space. Depth 122.35 m, core 2A. Scale 0.5 mm. B. Photomicrograph (cross-polarized light) of elongated needle-like evaporite pseudomorphs. Trona in sample was dissolved during thin section preparation; interior is open void (v). Pseudomorphs are surrounded by cryptocrystalline (cc) quartz. Chalcedony (ch) replaced smaller crystals on the periphery of the image (arrow). Dark circles are air bubbles and polishing grit from thin section.
preparation. Depth 49.0 m, core 1A. Scale bar 0.5 mm. C. Photomicrograph of elongated evaporite pseudomorphs. Crystals decrease in size toward top, surrounded by cryptocrystalline quartz. Depth 63.83 m, core 2A. Scale 2 mm. D. Photomicrograph (cross-polarized light) of shrub-like, vertical growth (arrow) of evaporite pseudomorphs. Pseudomorphs are replaced by chalcedony (ch) and surrounded by cryptocrystalline(cc) and microcrystalline (mc) quartz. Depth 67.3 m, core 1A. Scale bar 1 mm. E. Photomicrograph of vertical columnar evaporite pseudomorphs surrounded by cryptocrystalline quartz and small pseudomorphs in chert matrix, (v) void. Depth 87.05 m. Scale 5 mm. F. Photomicrograph (cross-polarized light) of rectilinear evaporite pseudomorphs with chalcedony (ch) lining pseudomorphs and interior void (v), filled with epoxy. Cryptocrystalline (cc) quartz surrounds pseudomorphs. Dark circles are air bubbles and/or polishing grit from thin section preparation. Depth 89.1 m, core 2A. Scale bar 0.5 mm. G. Photomicrograph (cross-polarized light) of rectilinear evaporite pseudomorphs, now chalcedony (ch), surrounded by cryptocrystalline (cc)/microcrystalline quartz (~1µm). Chalcedony has not completely replaced pseudomorphs; dark areas are void (v) and round dark circles are air bubbles and/or polishing grit from thin section preparation (arrow). Depth 91.0 m, core 2A. Scale bar 0.05 mm. H. Photomicrograph of prismatic evaporite pseudomorph surrounded by cryptocrystalline quartz. Depth 84.18 m. Scale 0.2 mm. I. Photomicrograph (cross-polarized light) of dark reticulate pattern with pyrite accumulation between pattern (pyrite, arrows) in cryptocrystalline quartz (cc) with internal crack (x). Depth 87.7 m. Scale bar 0.1 mm. J. Photomicrograph of reticulate pattern with pyrite crystals (1-3 µm) accumulating and highlighting pattern. Depth 161.65 m. Scale 0.1 mm. K. Photomicrograph of uncompacted plant fragment surrounded by cryptocrystalline quartz. Depth 70.6 m, core 2A. Scale bar 0.2 mm. L. Photomicrograph of randomly-oriented plant fragments, with vague cellular structures, and other incorporated material, in chert. Depth 70.6 m, core 2A. Scale bar 0.15 mm. M. Photomicrograph of uncompacted insect? fragment. Depth 49.3 m, core 1A. Scale bar 10 µm. N. Photomicrograph of region with diatoms (arrows) surrounded by cryptocrystalline quartz. Depth 85.6 m. Scale bar 150 µm. O. Photomicrograph of diatom surrounded by cryptocrystalline quartz, possibly Anomoeoneis sphaerophora. Depth 85.6 m. Scale bar 20 µm. P. Photomicrograph of diatom surrounded by cryptocrystalline quartz, possibly Rhopalodia gibberula. Depth 85.6 m. Scale bar 20 µm. Q. Photomicrograph of labyrinth pattern in cryptocrystalline (cc) quartz, individual quartz crystals are not distinguishable on SEM or under cross-polarized light. Depth 84.1 m. Scale bar 50 µm. R. Photomicrograph of bubble stick drying pattern, in cryptocrystalline (cc) quartz. Depth 84.1 m. Scale bar 20 µm. S. Photomicrograph of dewatering (?) fracture in chert (arrow), surrounded by quartz. Interior of fracture is void space and grit from thin section preparation. Depth 70.6 m. Scale bar 0.5 mm. T. Photomicrograph (cross-polarized light) of internal dewatering fracture with chalcedony lining interior of fracture. Depth 70.6 m, core 2A. Scale bar 0.5 mm. U. Photomicrograph of cross section of reticulate pattern cracks in cryptocrystalline quartz (arrow) along chert boundary with silicified mudstone. Depth 84.2 m. Scale bar 80 µm.
Figure 3.4. SEM images of silicified microorganisms, possibly fungi, in chert. A. Secondary electron (SE2) SEM image of silicified plant material, electron high tension (EHT) = 5.00 kilovolts (kV). Scale bar 40 µm. B. SE2 SEM image of silicified microorganisms, possibly blastospores and pseudomycelium of Sodiomyces fungi, EHT = 5.00 kV. Scale bar 20 µm. C. SE2 SEM image of thread-like material, possible arthrospospores and segmented hyphae, EHT = 5.00 kV. Scale bar 10 µm. D. SE2 SEM
image of hyphae with silicified, spherical conidium of *Sodiomyces*, ~5µm, EHT = 5.00 kV. Scale 2 µm. E. SE2 SEM image of yeastlike fungal features, including conical heads with segmented tails, possible germination stage, EHT = 5.00 kV. Scale bar 2.5 µm. F. SE2 SEM image of silicified microorganism, possibly streptococci bacteria, EHT = 5.00 kV. Scale bar 2.5µm. A-F. Sample Depth 74.64 m, core 1A.
Figure 3.5. Selected photomicrographs, SEM and XRD and EDS analysis of Type 2 cherts and magadiite.

A. SE2 SEM image of magadiite lepisphere, EHT = 5.00 kV. Depth 49.59 m, core 1A. Scale bar 5 µm. B. Immersion lens (In-lens) SEM image of magadiite from deformed magadiite layer, EHT = 10.00 kV. Depth 49.44, core 1A. Scale 4 µm. C. EDX analysis of magadiite lepispheres from 49.4 m core 1A. D. XRD analysis of magadiite layer from 49.44 m core 1A. E. Photomicrograph (cross-polarized light) of microcrystalline quartz exhibiting circular groundmass pattern. Depth 77.34, core 1A. Scale bar 40 µm. F. Photomicrograph (cross-polarized light) of microcrystalline quartz, as in E with circular groundmass pattern highlighted. Depth 77.34, core 1A. Scale bar 40 µm. G. Photomicrograph (cross-polarized light) of microcrystalline quartz with circular groundmass pattern, enlarged. Depth 77.34. Scale bar 10 µm. H. Photomicrograph (cross-polarized light) of microcrystalline quartz as in G, with circular groundmass pattern highlighted. Depth 77.34. Scale bar 10 µm. I. SE2 SEM image of microcrystalline quartz with radial/spherical texture; crystals are ~ 5µm or less, EHT = 15 kV. Sample depth 49.36 cm, core 1A. Scale bar 10 µm. J. EDX analysis of Type 2 microcrystalline quartz. K. Photomicrograph of microcrystalline quartz in small nodule showing cross-section of reticulate crust crack pattern. Note lack of plant fragments and other detrital material. Depth 144.04 m. Scale bar 200 µm. L. Photomicrograph of Type 2 chert layer, showing inward-directed v-shaped fractures. Some fractures are filled with dark brown detrital material (sand and clay). Depth 79.33 m, core 1A. Scale bar 0.5 mm.
Figure 3.6. Selected photomicrograph and SEM images of features associated with Type 3 Cherts and EDS pattern.

A. Photomicrograph (cross-polarized light) of rectilinear evaporite pseudomorphs, now chalcedony (ch), surrounded by microcrystalline/microcrystalline (cc) quartz (crystals ~1µm). Elsewhere in sample, quartz is cryptocrystalline. Chalcedony does not completely replace all pseudomorphs; dark areas are void space (v) and round dark circles are air bubbles and/or polishing grit from thin section preparation. Depth 91.0 m, core 2A. Scale bar 0.05 mm. B. Photomicrograph (cross-polarized light) of elongate evaporite pseudomorphs filled with fibrous chalcedony and surrounded by microcrystalline quartz. Dark circles are trapped air bubbles and grit from thin section preparation. Depth 90.99 m, core 2A. Scale bar 0.15 mm. C. Photomicrograph of fibrous and radial chalcedony in void and evaporite pseudomorph with organic matter (o), surrounded by cryptocrystalline quartz (cc), dark circles are air bubbles and polishing grit trapped from thin section preparation. Depth 77.24 m, core 1A. Scale bar 0.1 mm. D. Photomicrograph (cross-polarized light) of fibrous (f) and radial (r) chalcedony in fracture and around organic matter, surrounded by cryptocrystalline quartz, (same view as C). Depth 77.24 m, core 1A. Scale bar 0.1 mm. E. Photomicrograph (cross-polarized light) of radial chalcedony filling fracture in siliceous mudstone. Depth 124.5 m, core 1A. Scale bar 0.1 mm. F. Photomicrograph (cross-polarized light) of gastropod shell fragment replaced with chalcedony (ch), and megaquartz (MQ) partially filling shell interior. (v) is void inside shell fragment. Depth 179.09 m, core 2A. Scale bar 1 mm. G. SE2 SEM image of microcrystalline quartz (chalcedony). Largest crystal (4 µm) fills void space surrounded by cryptocrystalline (cc) quartz (crystals < 1 µm) EHT = 5.00 kV. Sample depth 49.35 m, core 1A. Scale bar 4µm. H. Photomicrograph (cross-polarized light) of ostracod shell filled with megaquartz (MQ), individual crystals are 50 to 100 µm. Depth 179.09 m, core 2A. Scale 0.05 mm.
Figure 3.7. Selected photomicrograph images of features associated with Type 4 Cherts

A. Photomicrograph of aligned plant fragments and organic material in silicified mudstone. Gray circles are air bubbles trapped during thin section preparation. Depth 63.83 m, core 2A. Scale bar 0.2 mm. B. Photomicrograph of pure chert (Si) layer (Type 2), with compacted and aligned plant fragments below and detrital material above. Depth 63.83 m, core 2A. Scale bar 0.2 mm. C. Photomicrograph of laminated mudstone (bottom) grading into chert with uncompacted organic matter. Depth 49.35 m, core 1A. Scale bar 0.5 mm. D. Photomicrograph of laminated mudstones. Overlying chert contains evaporite pseudomorphs. Depth 86.91 m. Scale bar 2 mm.
Figure 3.8. Selected images and analyses from Core Drive 1A-34Y-1. Depth top of drive: 49.21 m.

A. Core drive 1A-34Y-1 with selected layers marked, (1) ~37 cm mud, (2) ~26-28 cm deformed soft magadiite layer, (3) ~23 cm finely laminated green mud, (4) ~14 cm, 1-3 cm thick chert with abundant plant fragments, (5) ~3-5 cm thick chert with abundant
evaporite pseudomorphs. B. Photomicrograph of layer (5) showing evaporite pseudomorphs. Scale bar 0.1 mm. C. Photomicrograph of layer (4) showing microcrystalline quartz after magadiite and abundant uncompacted plant fragments. Scale bar 0.1 mm. D. SE2 SEM image of zeolites, possibly erionite, formed between detrital grains. Scale bar 4 µm. E. SE2 SEM image of magadiite lepispheres from layer (2). Scale bar 10 µm. F. SE2 SEM image of clays and detrital material from layer (1). Scale bar 10 µm.
Figure 3.9. Modern evaporites and gels compared to chert.
A. Photomicrograph of upward growth of bladed nahcolite crystals from modern Nasikie Engida. Scale 0.25 cm. B. Photomicrograph of upward growth evaporite pseudomorphs from Lake Magadi cores. Depth 92.03 m, core 2A. Scale 0.5 mm. C. Photomicrograph of upward and downward growth of needle-like crystals of trona from trona rafts, modern Nasikie Engida. Scale 0.5 cm. D. Photomicrograph of upward and downward needle-like evaporite pseudomorphs in chert from Lake Magadi cores. Depth 113.95 m, core 2A.
Scale 2 mm. **E.** Photograph of modern siliceous gel from Nasikie Engida, placed in clear plastic bag. Scale 1 cm. **F.** Photomicrograph of chert formed after siliceous gel from Lake Magadi core, with plant material and abundant detritus. Depth 70.63 m. Scale 0.1 mm.
Figure 3.10. Formation water $\delta^{18}O$ vs. Temperature.
Curves show $\delta^{18}O$ values calculated for equilibrium precipitation of quartz as a function of water $\delta^{18}O$ value and water temperature, using fractionation factors from Vho et al. (2019). Curves bracket the range of measured $\delta^{18}O$ values from Lake Magadi cherts, from $+24\%$ to $+48\%$, at $4\%$ intervals. Modern Magadi water $\delta^{18}O$ values and temperatures are shown as colored dots. Red dots are modern hot springs, temperatures above $50^\circ C$. Yellow dots are modern warm springs, temperatures between $20$ and $50^\circ C$ and blue dots represent modern lake brines. The $\delta^{18}O$ values of type 1 chert with cryptocrystalline quartz and evaporite pseudomorphs formed from siliceous gels, ranges from $+41\%$ to $+47\%$. Light purple area shows range of modern lake brine $\delta^{18}O$ values, $\sim +5\%$ to $+15\%$, and temperatures, $23$ to $47^\circ C$, from which cherts with relatively high $\delta^{18}O$ values ($+41$ to $+47\%$) are interpreted to have formed. The $\delta^{18}O$ of type 2 chert with microcrystalline quartz and relict magadiite lepispheres ranges from $+38\%$ to $40\%$. Purple area shows $\delta^{18}O$ values, from $+2\%$ to $+7\%$, and temperature range, $23$ to $47^\circ C$, of the lake waters from which type 2 cherts are interpreted to have formed. The waters are less evaporated than modern lake brines. The $\delta^{18}O$ in type 1 chert from $179.09$ m and with cryptocrystalline quartz surrounding gastropod and ostracod shells, ranges from $+26\%$ to $+35\%$. This chert is interpreted to have formed from waters with $\delta^{18}O$ values from $-5\%$ to $0\%$ and temperatures from $34$ to $49^\circ C$, consistent with modern warm springs (blue area). The $\delta^{18}O$ of type 3 chert, megaquartz, ranges from $\sim +23\%$ to $+30\%$. The red area shows the range of modern hot springs water $\delta^{18}O$ values and modern hot spring temperatures, $60$ to $85^\circ C$ which represents the type of water from which megaquartz
cements are interpreted to have formed. The $\delta^{18}O$ values of type 4 cherts, siliceous mudstones, range from (+37‰ to +46‰). The brown shaded area shows the range of water $\delta^{18}O$ values and borehole brine temperatures, 33 to 38°C, from which burial cherts are interpreted to have formed.

**Figure 3.11.** Brine evolution from Nasikie Engida hot spring waters using the EQL/EVP computer program (Risacher & Clement, 2001) under closed system conditions at 25°C and 83°C at modern $pCO_2$ concentration of $10^{-3.4}$ (400 ppm). Top panels show major ion evolution in millimols per kg of H$_2$O. Bottom panels show the sequence and amount of salts precipitated, in moles per kg of H$_2$O. Concentration factor increases to the right.
Conclusions

Cherts from Lake Magadi show a variety of chemically precipitated precursors including formation after amorphous siliceous gels and hydrous sodium silicates, such as magadiite. Detailed petrographic and scanning electron microscopy reveal that both of these precursors alter to chert near the surface, prior to burial or compaction. The discovery of branching labyrinth patterns in cherts formed after siliceous gels provided key evidence for near surface diagenesis. Precision secondary ion mass spectrometry showed that the majority of cherts formed from highly evaporated waters. Nearly all cherts from the Lake Magadi cores exhibit high $\delta^{18}O$ values, ranging from +41 to +46‰, indicating hypersaline environments for much of the basin history, from 750 ka to today. These cherts preserve key paleoenvironmental information such as evaporite pseudomorphs, plant fragments, diatoms, microorganisms, and dewatering features. This work enhanced our understanding of the paleoenvironments in the Lake Magadi basin over the last one million years and improved our understanding of chemically-formed cherts. Planned future work involves studying modern environments in which siliceous gels form and further resolving the geochemical conditions needed to convert the siliceous gel to chert.
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