1 **PRIMARY DIAGENETIC COPPER**
2 **CARBONATE AT THE MALBUNKA COPPER DEPOSIT, AMADEUS BASIN,**
3 **NORTHERN TERRITORY, AUSTRALIA**

4
5 **Erik B. Melchiorre^{a*}, Dehne McLaughlin^b, Ralph Bottrill^c, Jay Hight^a**

6
7 *^aDepartment of Geology, California State University, 5500 University Parkway, San*
8 *Bernardino, CA 92407, U.S.A.*

9
10 *^bMalbunka Copper Mine, 5 Tenth Avenue, West Moonah, Tasmania, 7009, Australia*

11
12
13 *^cMineral Resources Tasmania, PO Box 56, Rosny Park, Tasmania, 7018, Australia*

14
15
16
17 *Corresponding author. Tel.: +1 909 537 7754.

18 E-mail address: emelch@csusb.edu (E.B. Melchiorre).

19 dehne.mclaughlin@bigpond.com (D. McLaughlin).

20 ralph.bottrill@stategrowth.tas.gov.au (R. Bottrill).

ABSTRACT

The Malbunka copper deposit, located about 220 km west of Alice Springs, in the Northern Territory of Australia, may be a rare example of primary formation of copper carbonate mineralization. This deposit consists of unusual azurite disks up to 25 cm diameter, and lesser amounts of secondary azurite crystals and malachite. Carbon isotope values of the copper carbonate minerals are consistent with formation from groundwater-dissolved inorganic carbon. Oxygen isotope thermometry formation temperature estimates are 5 to 16°C above ambient temperatures, suggesting the copper carbonates formed at a depth between 0.3 and 1.6 kilometers in the Amadeus Basin. Azurite fluid inclusion waters are rich in boron, chlorine, and other elements suggestive of dilute oil basin formation fluids. In addition, presence of euhedral tourmaline with strong chemical zonation suggest that this was a low temperature diagenetic setting. The strong correlation of structures associated with hydraulic fracturing and rich copper carbonate mineralization suggest a strongly compartmentalized overpressure environment. It is proposed that copper carbonates of the Malbunka deposit formed when deep, copper-rich formation fluids were released upward by overpressure-induced failure of basin sediments, permitting mixing with carbonate-rich fluids above. This work bears directly upon exploration for a new type of primary copper deposit, through understanding of the conditions of genesis.

Abstract: 208 Words

KEYWORDS: azurite, malachite, carbon isotope, thermometry, diagenesis

1. INTRODUCTION

The Malbunka Copper Mine is located on Ljalaltuma Aboriginal Trust lands, approximately 220 kilometers west of Alice Springs, in the Northern Territory of Australia (Figure 1). Copper mineralization was discovered at Malbunka in the 1950s by the Aboriginal artist Albert Namatjira, and was originally known as the Namatjira Prospect. The deposit was prospected in the 1960s with bulldozer cuts and a 40 meter long adit driven at 5 degrees down the slope of the anticlinal axis. The deposit was deemed to be not economic at the time, because of a low grade and small tonnage. There were few who visited the site following exploration work, as the site is remote, difficult to drive to, is under tenure, and requires a travel permit from the Central Land Council. The site became noted in the 1970s for an unusual and attractive association of blue azurite disks on a white clay matrix. These mineral specimens were first reported in print by Sullivan (1979), where he describes azurite sun specimens from the mine that were sold at shows in Europe. The mine site is operated under Northern Territory Mineral Lease 29494 by Dehne McLaughlin, for production of mineral specimens, with the consent of the traditional Aboriginal owners. A detailed history and description of the operations is provided in McLaughlin and Grant (2012).

Deposit geology and mineralogy

The Malbunka copper deposit occurs in the Namatjira Formation; a mixed carbonate and clastic sequence with sandstone, carbonate mudstone and shale. The Namatjira formation is late Precambrian to early Cambrian in age, and is only known in the Gardiner Range of the Amadeus Basin. The Namatjira Formation is the lateral

equivalent of the Arumbera Sandstone, as described by Warren and Shaw (1995). Edgoose (2013) advises that the Eninta Sandstone is now mapped as Arumbera Sandstone. The Arumbera Sandstone can be up to 1300 metres thick and is copper-bearing over a wide area. In Ellery Creek, about 100 kilometers from the mine, the formation hosts malachite, covellite, chalcocite, and possibly chalcopyrite and cuprite (Freeman et al., 1987). Laurie et al. (1991) also point out the affinity of copper for the Arumbera Sandstone, and postulated that these deposits formed from copper-rich basin brines. Salt diapirism and associated halotectonics in the Amadeus Basin is likely to have a base metal association and should be considered in formulating exploration strategies (Dyson and Marshall, 2005).

The oil-bearing Amadeus Basin, of which the Arumbera Sandstone is a distinctive member, is a sequence of marine and terrestrial deltaic-fluvial sediments deposited from the late Precambrian to the Devonian. The Arumbera Sandstone is the key reservoir in the Dingo and Orange gas fields (e.g., Ambrose, 2006). It was uplifted starting in the late Devonian and faulted and folded in a major compressional event between 400 and 300 Ma (Haines et al., 2001). Seismites are common in the Arumbera Sandstone and are present in the mine site sandstone bounding the kaolinite lens (Girardi, 2012; McLaughlin et al 2012).

At the Malbunka copper deposit, disk-shaped azurite masses occur within a white to red kaolinite lens up to 2.75 meters thick and bounded below and above by grey clay-rich Arumbera Sandstone. The clay lens is fault-bounded with approximate lateral dimensions of 50 by 40 metres and has the appearance of a channel deposit with bedding structures. This kaolinite lens occurs at the crest of the Gardiner Range

Anticline and outcrops beside roadsides across the Central basin to the west and north in the West MacDonnell National Park (Cook, 1968; Figure 1).

Azurite is the most common copper mineral found in the deposit. Light to deep blue disks of azurite are normally from 2.5 to 13 cm in diameter and rarely reach 25 cm in diameter (Figure 2). These azurite specimens have a unique discoidal form, and are comprised of numerous small flat crystals of azurite arranged in radial and concentric forms (McLaughlin and Grant, 2012). They occupy bedding planes, relic thrust fault planes, and joints in the white and less commonly the red kaolinite host. The off white colour of the kaolinite in the azurite rich portions of the mineralized bed is probably due to bleaching of the clay by the mineralizing solutions (McLaughlin and Grant, 2012). Higher concentrations of iron oxide or lack of bleaching, gives the kaolinite a red colour for at least two thirds of the layer (Figure 3). In rare cases, azurite crystal clusters and 3-dimensional rounded to oblate malachite nodules are evident in bedding planes, clefts and channels in the hanging wall, soft sediment flow planes, and fractures in the kaolinite (Figure 4). The azurite is at its highest concentration within 30 cm of the upper sandstone in a series of up to five thin horizontal bedding planes. In the bedding plane closest to the upper sandstone large diameter azurite specimens are found, sometimes in direct contact with the sandstone. Azurite discs, exposed in mine entrance support pillars, are also present in the kaolinite within 30 cm of the contact of the kaolinite with the lower footwall sandstone, but are not persistent throughout the footwall area of the kaolinite lens. Azurite occurs occasionally as large light blue disks in iron oxide rich kaolinite throughout the kaolinite lens.

Malachite is occasionally found in the deposit, and occurs in two forms. The first, and most common, is as disk or oblate spheroidal or ellipsoid forms which appear to be

unrelated to pseudomorphous replacement of azurite. These forms rarely exhibit crystal growth structures. The second, and rarer malachite occurrence, is pseudomorphous replacement of azurite disks. These often display faithful crystal replacement (Figure 5). Atacamite is abundant in the upper and lower sandstone, and rims the kaolinite-sandstone contact, and occurs as disseminated fine-grained crystals. Chrysocolla is rare in the deposit, and has only been reported from the lower sandstone in association with atacamite (McLaughlin and Grant, 2012). Traces of chalcocite, covellite, digenite, and cuprite are also reported. A highly mineralized and fractured zone which may have served as a primary fluid conduit is exposed below the clay unit.

The unusual occurrence of azurite as flattened disks was attributed by Sullivan (1979) to azurite replacement of marine life or algae. Warren and Shaw (1995) report that the lower Arumbera Sandstone has yielded specimens of the soft-bodied Ediacarian fauna and that there is a diversity of trace fossils in the upper Arumbera Sandstone. The Ediacarian organism *Dickinsoniacostata* does indeed bear a crude resemblance to the general size and shape of the azurite disks, as does *Aspidella terranovica* (Figure 6).

2. METHODS

2.1 Sample preparation and mineralogical characterization

Samples of azurite and malachite were collected and cleaned of white clay matrix. For each locality, a single disk or nodule was selected, then subdivided for analysis by different methods. Material for scanning electron microscope (SEM) and electron microprobe (probe) analysis was placed into a 1-inch round silicone mould, embedded in a low-volatile epoxy, ground flat, and polished, with the final polish using 0.2 µm grit, and employing the standard methodology of microanalysis laboratories around the world

(e.g., Goldstein et al., 2003; Reed, 2005). Samples for stable isotope analysis were crushed in an agate mortar to pass through a 100-mesh screen ($<0.147\text{mm}$). Resulting powders were scanned by x-ray diffraction (XRD) to check purity. The remainder of the sample was reserved for inclusion studies. Samples of white clay matrix were lightly crushed, washed, and panned to produce a sand-sized heavy mineral concentrate. The heavy sand fraction from the clay was studied by optical microscopy and mounted for electron microprobe chemical analysis. Clay was also examined by XRD to determine its mineralogy.

2.2 Geochemical analyses

Backscatter electron images and element analyses were generated using a CAMECA SX100 electron microprobe at the University of Arizona Lunar and Planetary Laboratory. The microprobe is equipped with five tunable wavelength dispersive spectrometers. Operating conditions were 40° takeoff angle, and beam energy of 15 keV. The beam current was 20 nA, and the beam diameter was 1 μm . Counting time was 60 s. Off-peak counting time was 20 s, using the LINEAR off-peak correction method. Well-characterized natural and synthetic minerals were used for in-house standards. Detection limits were better than 0.02 wt.% for all elements. Analytical sensitivity (at the 99% confidence level) ranged from 0.263% relative for Si Ka to 2.795% relative for S Ka. The matrix correction method was ZAF/Phi-Rho-Z calculations with an Armstrong/Love Scott algorithm (Armstrong, 1988).

Samples for fluid inclusion study were crushed under vacuum, with the liberated fluid collected in a liquid nitrogen trap. Samples were taken off-line in a break-seal, and

analysed for fluid chemistry by ICP-MS at Babcock & Sons Laboratories of Riverside, CA, with a split reserved for stable isotope analysis.

2.3 Isotope analyses and thermometry

Stable isotope analysis for carbon and oxygen was performed on azurite and malachite samples using the standard method of reaction with 100% orthophosphoric acid (H_3PO_4) at 50 °C to release CO_2 gas (e.g., McCrea, 1950; Walters et al., 1972). The resulting CO_2 gas was purified, and then analysed by continuous flow methods on a Finnigan Delta^{plus} isotope ratio mass spectrometer (Spötl and Vennemann, 2003). Detailed descriptions of malachite and azurite sample preparation, analysis techniques, data correction, and data reporting notation are outlined by Melchiorre et al. (1999) and Melchiorre et al. (2000). Carbon analyses are reported in the usual manner as per mil deviations from the VPDB standard. Results of oxygen analyses are reported as per mil deviation from the VSMOW standard. The precision of the $\delta^{13}\text{C}$ value is $\pm 0.09\text{‰}$, while for $\delta^{18}\text{O}$ the precision is $\pm 0.1\text{‰}$. Precision is based upon analysis of internal laboratory standards calibrated to the respective VPDB and VSMOW scales, and duplicate analyses performed for all unknown samples.

Fluid inclusion waters were prepared for oxygen isotope analysis using the standard CO_2 equilibration method (Epstein and Mayeda, 1953). Preparation of water for hydrogen isotope analysis used zinc shavings reacted at 500 °C for 30 min with water to yield hydrogen gas by reduction (Coleman et al., 1982). Precision for $\delta^{18}\text{O}$ is $\pm 0.2\text{‰}$, while the precision for δD is $\pm 1\text{‰}$.

Previous work by Melchiorre et al. (1999 and 2000) showed that for malachite and azurite, carbon isotope values may be used to determine the source of carbon in the mineral, and oxygen isotope values may be used to establish the temperature of mineral formation. With these two values, the possible environment of formation for the azurite veins and associated malachite can be determined. For example, the temperature dependence of malachite is given by the equation:

$$1000 \ln \alpha = 2.66 \cdot (10^6/T^2) + 2.66 \quad (\text{eq. 1, Melchiorre et al., 1999})$$

While for azurite the relationship is:

$$1000 \ln \alpha = 2.67 \cdot (10^6/T^2) + 4.75 \quad (\text{eq. 2, Melchiorre et al., 2000})$$

3. RESULTS

XRD analysis of the white clay matrix which hosts the azurite and malachite mineralization determined this was a well-crystallized kaolinite-dominated sandy clay with 2M1 illite(containing less than 3% expandable component). The clay contains a significant quantity of anhedral quartz, presumably inherited from the sedimentary source. Trace tourmaline was also identified in all samples. The red clay was of identical composition, but with the addition of fine grained hematite, an alunite-group mineral, and possible anatase.

The heavy mineral concentrates were found to be rich in fine euhedral, prismatic tourmaline crystals. Chemical analysis of the tourmaline reveals striking chemical zonation (Table 1). Magnesium in the tourmaline ranges from 1.1 to 3.3 wt% in cores, and 4.5 to 6.5 wt% in rims. Iron in the tourmaline ranges from 6.4 to 10.2 wt% in cores,

and 1.9 to 8.5 wt% in rims. The analyses indicate all cores are schorl and most rim compositions are dravite. Some minor Fe replacement of Al is confirmed for several rim analyses, suggesting higher oxidation in later growth zones. A few analyses have a deficiency in the octahedral cations, indicating a small Li content.

The results of stable isotope analyses are presented in Table 2. Carbon isotope values of azurite range between -9.88 and -7.74‰, while the malachite has a $\delta^{13}\text{C}$ value between -12.22 and -11.13‰. The oxygen isotope values of the azurite ranged from 27.66 to 29.54‰, with a value between 27.19 and 27.78‰ for the malachite. The oxygen isotope value of the water of formation, as determined from fluid inclusion extraction, is -5.3‰, and the δD value is -55‰. Using the $\delta^{18}\text{O}$ values of the fluid inclusion water and the copper carbonate minerals, it is possible to calculate the corresponding fractionation factors (α). These fractionation factors can then be used with the azurite and malachite thermometry equations (Eqs. 1 and 2) to determine a temperature of formation. The oxygen isotope thermometry results suggest that the azurite disks formed between temperatures of 32.2° to 37.9° C, azurite crystals formed between 26.8° to 30.0° C, while malachite formed at 24.3 to 28.6° C.

Results of chemical analysis of azurite-hosted fluid inclusions is presented in Table 3.

4. DISCUSSION

4.1 Geology and mineralogy

Copper carbonate minerals at Malbunkahave been divided into three groupings for the purpose of this study. The most common occurrence of azurite is a discoidal form, comprised of numerous small flat crystals of azurite arranged in radial and concentric forms. These disks occupy bedding planes, relic thrust fault planes, and joints in the white and less commonly in the red kaolinite-dominated clay host rock. These disks occasionally display inter-bedding relicts of the original clay host. Dark blue azurite disks are relatively free of solid-phase mineral inclusions, but do contain fluid inclusions. The colour of the light blue azurite disksis caused by incorporation of fine white clay interstitial to micro-azurite crystals during crystallization.

Azurite is also noted in lesser abundance as more equant or spheroidal crystal clusters. These clusters form from the radial growth of terminated azurite crystals from a central nucleation point. These clusters of azurite crystals are quite similar to the azurite disks, with the exception being coarser crystal size and more 3-dimensional form. Malachite is much less common, and is found as either finely-crystalline masses often with a lobate spheroidal todiscoidal form, or rarely as pseudomorphous replacements of azurite. The observed paragenetic sequence is microcrystalline azurite disks, followed by azurite crystal cluster nodules, followed by malachite.

The clay-rich sandstone which forms both the upper and lower boundary of the azurite-bearing clay, and even the clay bed itself, contain abundant sediment deformation features such as recumbent folds, slumping, micro-faulting, and flow structures (Figure 7) that may be injectites or seismites caused by earthquake shock during sedimentation

(e.g., Shi, Du, and Gong 2007). Many of these soft sediment injection structures are difficult to see in the field, due to a lack of contrast between the shades of off-white clay involved.

There is ample evidence that copper bearing fluids penetrated into the upper and lower layers of the kaolinite lens next to the sandstone, and to a lesser extent into the central thickest part of the kaolinite (Figure 7c). Azurite disks and other forms of copper carbonate are observed forming directly adjacent to fluid flow structures. Thrust planes are common in the hanging wall area of the kaolinite lens where imbrication structures are evident over distances of several meters. Thrusting preceded copper mineralisation and continued after the mineralising event, which along with the injectite events, demonstrates the dynamic environment under which most of the mineralisation took place.

4.1.1 Injectites

Three distinct over-pressure events, characterized by injectite structures, have been identified within the kaolinite lens (Figure 7). These events followed shock induced sediment slumping of sandstone and kaolinite (Figure 7a). The first event was characterised by eruption of streamers of white clay into higher levels of the kaolinite lens. Injectites from this event are difficult to see, due to the lack of contrast in the off-white layers (Figure 7b).

The second event is characterised by hydraulic fracturing of the kaolinite close to the hanging wall and the opening of vertical fractures in the clay followed closely by crystallisation of azurite (Figure 7c). Azurite cementation of hydraulically-fractured kaolinite is also noted (Figure 7d).

The third event consists of sandstone injectites penetrating into the kaolinite from the hanging wall (Figure 7e). Injectites associated with this event deform pre-existing azurite which has crystallised in the plane of relic thrust faults (Figure 7e, note azurite layer offset by the injectite near the tip of the pick). Late-stage micro faulting occurs during this phase (Figure 7f). Malachite is present along the edge of the sandstone injectite, suggesting formation late in the paragenetic sequence.

Structures associated with these events indicate that fluid pressures built up and were released explosively at least three times within the deposit. If the structures were purely a response to shearing or compressional forces, the kaolinite would have flowed and smeared like plasticine and not formed sharp vertical contacts with randomly-oriented clay and sandstone fragment inclusions. The hydraulic overpressure events required to produce these structures within a sedimentary sequence are not near surface phenomena suggesting azurite formation is not related to passive near surface copper sulphide oxidation events that normally precede azurite crystallisation.

These types of injection structures may be seismites, which record seismic activity associated with basin dewatering and compaction (e.g., Seilacher, 1969). These same structures are noted for deep sediments within petroleum basins around the world (e.g., Thompson et al., 2007; Kane, 2010).

4.1.2 Resemblance to fossils

The possibility of the azurite disks representing Ediacaran fauna (Figure 6) has been discounted by field evidence. While the rocks at the Malbunka deposit are of appropriate age, the form of the proposed fauna represented (*Dickinsoniacostata* and *Aspidellaterranovica*) is inconsistent with the azurite disks. For

example, while *D.costata* is often of appropriate size, it commonly displays an elongate form with bilateral symmetry unlike the uniformly round azurite disks. Similarly, *A.terrannovica* has superficial features that are similar to the azurite disks, such as concentric rings and centripetal rays. The inferred remnant of a holdfast stalk (e.g., MacGabhann, 2007) on *A.terrannovica*, evident as a raised central pimple, is also present on some azurite disks. However, the size of most *A.terrannovica* specimens is much smaller than the azurite disks, at only 0.4 to 1 cm (e.g., Narbonne, 2005). Population densities for these fauna are also inconsistent with observed densities of azurite disks (Figure 2d). There is also structural evidence that the azurite disks are not fossils, namely that they are occasionally observed to incorporate relict bedding structures, and cross-cut bedding along joints. And while an Ediacaran organism, *Arumberiabanksi*, has been reported for local rocks interpreted to be the lateral equivalents of the Namatjira Formation (Glaessner and Walter, 1975), it was later reinterpreted as having formed from the action of currents on a cohesive muddy substrate (McIlroy and Walter, 1997).

4.2 Carbon sourcing

Carbon isotope values of the azurite and malachite from the Malbunka deposit are quite light, and inconsistent with carbon from the local marine carbonate units or the atmosphere (Figure 8). Volcanic CO₂ carbon isotope values are also insufficient to explain the whole range of observed values in these copper carbonate minerals. The best fit for these values is carbon from deep groundwater basins, including carbonate minerals. However, there are many potential origins for carbon within these deep basins (e.g., Fontes, 1985). The closest match for the observed $\delta^{13}\text{C}$ values is for a source dominated by organic carbon (e.g., Jiráková et al., 2010), or soil CO₂ (e.g., Rose et al., 1996). Respectively, these potential carbon sources would be consistent with a deep or shallow sedimentary basin setting.

In addition, there is a positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for Malbunka copper carbonates (Table 2). Such positive correlations in carbonates have been interpreted by many as a record of diagenesis deep within a sedimentary sequence (e.g., Allan and Matthews, 1982).

4.3 Isotope thermometry

The geothermometers in Eq. 1 and 2 were used in conjunction with the results of oxygen isotope analyses for copper carbonate minerals to produce estimates of the temperatures at which the azurite and malachite formed (Table 2). A $\delta^{18}\text{O}$ value of -5.3‰, derived from fluid inclusion work, was used as the water of equilibration.

These isotope geothermometry temperatures are all well above the recorded ambient air temperatures, and often above even the seasonal extreme records (Australian Bureau of

Meterology, 2016). This suggests that the copper carbonate minerals formed in an environment with additional heat beyond the influence of the atmosphere. A volcanic source of heat is not likely, based upon local geology and carbon isotope evidence. Heat from exothermic geochemical or biological decomposition of sulfides is a possible source (e.g., Melchiorre and Williams, 2001), but would require a much larger body of massive sulfide proto-ore than would have been geologically possible for the deposit. A plot of malachite and azurite oxygen isotope temperature estimates from around the world (Figure 9) shows that samples from disseminated deposits have lower temperatures than samples from deposits where very large masses of sulfide minerals have been replaced by copper carbonate masses. It is presumed that heat from oxidation of concentrated sulfides produces this distribution. The range of temperature estimates for the copper carbonate minerals of the Malbunka deposit are consistent with azurite formation from a massive sulfide-type ore body, while malachite is consistent with a disseminated host. However, there is no geological evidence for a concentrated mass of sulfides at the Malbunka deposit. Quite the contrary, the copper carbonates show ample evidence of a disseminated distribution from a highly remobilized source (e.g., Figures 2d and 7c).

The most reasonable source of heat within the rocks of the Amadeus Basin is the geothermal heat related to the local ambient gradient. Cull and Conley (1983) state that major sedimentary basins in Australia have between 10-40°C of temperature increase per kilometer of depth in the basin. However, detailed study of the Amadeus Basin indicates a lower value of 10-25°C due to the thermal conductivity of the rocks (Beardsmore, 2007). Given this geothermal gradient, the isotope thermometry estimates which are 5 to 16°C above ambient temperatures would suggest the copper carbonates formed at a depth in this basin between 0.3 and 1.6 kilometers. These estimates are based on the assumption that the modern geothermal gradient is broadly similar to the gradient in the past, as the thermal properties of the rock have not changed significantly. This assumption is supported by fluid inclusion studies of halite from other units of the Amadeus Basin, which suggest early diagenesis occurred at temperatures of 60-100°C (Kovalevych et al., 2006).

4.4 Tourmaline qualitative thermometry

The kaolinite-dominated white and red clay associated with the Malbunka azurite deposit contains abundant, fine-grained tourmaline crystals (Figure 10). These euhedral to subhedral crystals range from 10 to 75 microns in length and have compositional, textural, and contextual geological data consistent with authigenic formation under oxidizing conditions at low temperature, similar to tourmaline reported from the cap rock of salt domes (Henry et al., 1999). Authigenic tourmaline has been widely reported to occur within clay, potash, halite, and anhydrite associated with evaporite deposits (e.g., Mügge, 1913; Popov and Sadykov, 1962; Hiller and Keller, 1965). There is no evidence

374 of fracturing or weathering of the tourmaline crystals from Malbunka that would suggest
375 a detrital or volcanic origin. Significant intracrystalline geochemical variation was noted
376 for Malbunka micro-tourmaline (Figure 10, 11; Table 1). The Malbunka crystals are
377 alkali-group tourmaline similar to tourmaline from Challenger Knoll caprock, and
378 evaporate and meta-evaporite deposits elsewhere in the world (e.g., Hawthorne and
379 Henry, 1999). Formula calculations indicate the tourmaline is largely Al-deficient,
380 suggesting replacement of Al by Fe^{3+} in tetrahedral sites. The Malbunka tourmaline
381 plots below the schorl-dravite join (Figure 11), and has compositional trends similar to a
382 solid solution between ferrian "oxy-dravite" and povondraite reported for salt dome cap
383 rock (Hawthorne and Henry, 1999). Substantial element zonation is noted in different
384 sectors of the tourmaline, but the most significant is high Fe with strong internal
385 variation. Elevated Fe content in tourmaline has been noted for oxidized evaporate
386 rocks (Walenta and Dunn, 1979; Mattson and Rossman, 1984; Grice et al., 1993; Jiang
387 et al., 1997). Significant compositional variation between tourmaline crystals has been
388 noted for some localities (e.g., Cavarretta and Puxeddu, 1990), but only salt dome cap
389 rock tourmalines exhibit this same range of variation within single grains (Henry et al.,
390 1999).

It is suggested by many that surface energies play a key role in chemical zonation within tourmaline and other minerals in the low temperature environment (e.g., Reeder and Prosky, 1986; Fouke and Reeder, 1992; Rakovan&Waychunas, 1996). However, the surface effects upon sector zoning decrease significantly with increasing temperature (Henry and Dutrow, 1992). Geochemical analysis of the micro-tourmaline from Malbunka reveal elemental abundances and chemical zonation consistent with low temperature authigenic formation from evaporite sources, consistent with formation ~1km deep within the Amadeus Basin.

4.5 Fluid inclusion chemistry

The use of fluid inclusion chemistry has been used by many to examine the potential origin of mineralizing fluids, especially within Mississippi Valley-Type deposits (e.g., Viets and Leach, 1990; Kendrick et al. (2002), Appold et al. (2004), Stoffelet al. (2008), Shelton et al. (2009), Wilkinson et al. (2009), Appold and Wenz (2011), and Wenz et al. (2012).

The liquid liberated by crushing of fluid inclusions has elevated element concentrations and light stable isotope values which are consistent with formation fluid from petroleum basins (Table 3). Given the nearly opaque nature of azurite, it was not possible to determine if the fluid inclusions are primary, secondary, or both. However, given the lack of evidence for metamorphism and textural relations consistent with formation during a period of high fluid flow, it is presumed that the majority of inclusions are primary.

The inclusion fluid is enriched in boron, and has key element ratios consistent with a seawater origin, and similar to values reported for evolved formation fluids that have experienced meteoric dilution through seismic pumping (e.g., Melchiorre et al., 1999). There is no evidence of a significant Ca excess or Na deficit in these fluids which would suggest albitization reactions within the basin (Davisson and Criss, 1996). Ratios of key elements in the inclusion waters are similar to seawater, with the exception of Na/Cl. The observed chlorine deficit for the inclusion waters is most likely influenced by precipitation of the copper chloride mineral atacamite within the distal portions of the deposit. The differences between the azurite inclusion water chemistry, and the halite inclusion water chemistry reported in Kovalevych et al. (2006), most likely results from the different host lithologies, and timing of mineralization.

The oxygen and hydrogen stable isotope values of the Malbunka azurite inclusion fluid are consistent with local meteoric dilution of formation fluid with a seawater origin, and subsequent water-rock interaction, similar to formation fluids from sedimentary basins around the world (e.g., Clayton et al., 1966; Wilson and Long, 1993; Moldovanyi et al., 1993).

4.6 Environment of deposit formation

Following their deposition within the Amadeus Basin, these sediments were subjected to diagenetic processes that produced dewatering, lithification, and mineralization. It is not known what role, if any, the formation of the Amadeus aulacogen (Rutland, 1973) may have had on copper mineralization (Sawkins, 1976). During early diagenesis, halite was mobilized and recrystallized at temperatures of 60-100°C (Kovalevych et al., 2006). Water-rock interaction modified pore fluid composition and altered host lithology through

kaolinization with associated micro-tourmaline formation. During this time, compaction and associated dewatering elevated pore pressures to between hydrostatic and lithostatic. The highly-contrasting lithologies of the Amadeus Basin, and the discrete nature of their structures suggest that initial compaction produced compartmentalization and significant localized overpressure environments. Fluid flow through this type of poorly-connected system, with limited fluid mixing, is known to juxtapose fluids with significantly different chemistries (e.g., Rowland et al., 2008). When fluid pressures exceeded the failure envelope of the confining lithology, the result was very rapid fluid migration, recorded by a variety of dewatering structures such as injectites (Figure 7). These events permitted mixing of fluids with vastly different chemistries, and significantly altered local pressure. We propose that a copper-rich formation fluid from a deep source was released by these events to move upward and be trapped by the kaolinite-rich formation, where it mixed with a more dilute and CO₂-rich meteoric fluid. This mixing produced T-pH-p[CO₂] conditions which permitted azurite mineralization directly adjoining the fluid flow structures. However, at this time early in dewatering and depressurization, the compaction and fluid pressure dictated mostly 2-dimensional growth, similar to “pyrite dollars” which form as concretions during diagenetic conditions in some black shales elsewhere in the world. This population of azurite mineralization records isotopic equilibration temperatures 5 to 16°C above ambient temperatures which corresponds to a basin depth of 0.3 to 1.6 kilometers. As dewatering and depressurization progressed, azurite was able to crystalize under more equalized pressure as spheroidal crystal clusters with attendant lower isotope thermometry estimates. At some point, the depressurization and depletion of the CO₂ source produced lower p[CO₂] conditions which shifted into the malachite stability field. This

last phase of mineralization is recorded by discoidal malachite masses, some pseudomorphously replacing pre-existing azurite at near ambient surface temperatures.

A significant factor in the creation of this deposit is the occurrence of an impermeable clay unit. The association of kaolinite-dominated white and red clays with azurite formation has been noted in many other deposits (e.g., Grant, 1989; Melchiorre and Enders, 2003). It is suggested that the relatively impermeable clay enhances $p[\text{CO}_2]$ levels by creating a comparatively closed system that can reach the high levels above atmospheric required for azurite formation. The occurrence of impermeable clay units could provide a useful exploration tool in identification of economic copper targets. These clay-associated azurite deposits, such as the Northwest Extension at Morenci, Arizona, USA, can contain globally significant quantities of copper. The model in the Malbunka case has clay traps above fracture zones associated with halite-rich diapirs.

5. CONCLUSIONS

Azurite and malachite from the Malbunka deposit appear to form as primary ore minerals, rather than as secondary replacement of sulphides as is typical of other copper carbonate deposits around the world. Fluid flow structures and fluid inclusion data indicate formation of azurite and malachite occurred due to mixing between a deep basin formation fluid rich in copper, and more shallow meteoric-diluted fluids rich in carbonate. Stable isotope values of these minerals and micro-tourmaline chemistry suggest formation of copper carbonates occurred 0.3 to 1.6 kilometres deep with a sedimentary basin under conditions similar to diagenetic carbonates. The unusual

growth habit of the azurite disks is not due to fossil replacement, but rather an artefact of hydrostatic to lithostatic fluid pressure related to diagenesis. The paragenetic sequence of mineralization is azurite disks at higher P and T than later 3-dimensional azurite crystal clusters, followed by malachite formation at near ambient temperatures and near surface conditions. The role of clay in creating overpressured conditions, and retaining the high $p\text{CO}_2$ values required for azurite formation require additional investigation due to the potential importance in understanding the genesis of primary copper carbonate ore bodies.

Acknowledgements

Instrumentation was provided and supported by the National Science Foundation, EAR-0115884 and EAR-0941106. XRF instrumentation was provided by a grant from the W.M. Keck Foundation. Support was also provided by a NASA Astrobiology Institute Minority Institution Research Sabbatical (NAI-MIRS) program award to the lead author, and an institutional grant by CSUSB. We thank Ray Grant for valuable discussions of geology, and H. Albert Gilg for assistance with clay mineralogy. R. Bottrill publishes with the permission of the Tasmanian Director of Mines.

REFERENCES

- Allan JR, Matthews RK (1982) Isotope signatures associated with early meteoric diagenesis. *Sedimentology* 29:797-817.
- Ambrose G (2006) Northern Territory of Australia, onshore hydrocarbon potential, 2006. Northern Territory Geological Survey Record 2006-003.
- Appold MS, Numelin TJ, Shepherd TJ, Chenery SR (2004) Limits on the metal content of fluid inclusions in gangue minerals from the Viburnum Trend, southeast Missouri, determined by laser ablation ICP-MS. *Econ Geol* 99:185-198.
- Appold MS, Wenz ZJ (2011) Composition of ore fluid inclusions from the Viburnum Trend, Southeast Missouri district, United States: Implications for transport and precipitation mechanisms. *Econ Geol* 106:55-78.
- Armstrong JT (1988) Quantitative analysis of silicates and oxide minerals: comparison of Monte-Carlo, ZAF and Phi-Rho-Z procedures. In: Newbury DE (ed) *Proceedings of the Microbeam Analysis Society*. Microbeam Analysis Society, San Francisco, pp. 239-246.

516 Australian Bureau of Meteorology(2016)<http://www.bom.gov.au>. Accessed 20 February
517 2016.

518 Beardsmore G(2007) Geothermal energy potential of the Northern Territory. Northern
519 Territory Geological Survey Record 2007-004.

520 Cavarretta G, Puxeddu M (1990)Schorl-dravite-ferridravite tourmalines deposited by
521 hydrothermal magmatic fluids during early evolution of the Larderello geothermal field,
522 Italy. *Econ Geol*85:1236-1251.

523 Chester R, Jickells T (2012)Marine Geochemistry. Wiley-Blackwell Publishing,Hoboken,
524 NJ.

525 Clayton RN, Friedman I, Graf DL, Mayeda TK, Meents WF,Shimp NF (1966) The origin
526 of saline formationwaters: Isotopic composition. *J Geophys Res* 71:3869–3882.

527 Coleman ML, Shepard TJ, Rouse JE, Moore GR (1982) Reduction of water with zinc for
528 hydrogen isotope analysis. *Anal Chem* 54:993–995.

529 Cook PJ(1968)Henbury, Northern Territory 1:250,000 geological map series,
530 explanatory notes. Northern Territory Geological SurveySG53-01.

531 Cull JP, Conley D(1983)Geothermal gradients and heat flow in Australian sedimentary
532 basins. *J AustrGeolGeophys* 8:329-337.

533 Derry LA (2010) A burial diagenesis origin for the Ediacaran Shuram–Wonoka carbon
534 isotope anomaly. *Earth Planet Sci Lett*294:152-162.

535 Dyson IA, Marshall TR (2005) Neoproterozoic salt nappe complexes and salt-
536 withdrawal minibasin in the Amadeus Basin. In:Proceedings of the Central Australian
537 Basins Symposium (CABS), Alice Springs, Northern Territory, pp. 16-18.

538 Edgoose CJ (2013)Geology and Mineral Resources of the Northern Territory. In: Ahmad
539 M, Munson TJ (eds) Amadeus Basin. Northern Territory Geological Survey Special
540 Publication 5.

541 Epstein S, Mayeda T (1953) Variation of ^{18}O content of waters from natural sources.
542 *GeochimCosmochimActa* 4:213–224

543 Fontes JC(1985) Some considerations on ground water dating using environmental
544 isotopes. *Hydrogeology in the Service of Man. Memoires of the 18th Congress of the*
545 *International Association of Hydrogeologists*, Cambridge, pp. 118–151.

546 Fouke BW, Reeder RJ (1992) Surface structuralcontrols on dolomite composition:
547 Evidence fromsectoral zoning. *GeochimCosmochimActa*56:4015-4024.

548 Freeman MJ, Shaw RD,Offe LA(1987)A field guide to geological localities in the Alice
549 Springs region. Northern TerritoryGeological Survey technical report GS 87/9.

550 Girardi O(2012) In-Situ Stresses and Palaeostresses around Salt Diapirs: a Structural
551 Analysis from the Gulf of Mexico and Amadeus Basin, Central Australia. Honours
552 Thesis, University of Adelaide.

553 Glaessner MF, Walter MR (1975) New Precambrian fossils from the Arumbera
554 Sandstone, Northern Territory, Australia. *Alcheringa*, 1:59-69.

555 Goldstein JI, Newbury DE, Echlin P, Joy DC, Lyman CE, Lifshin E, Sawyer LC, Michael
556 JR(2003) *Scanning Electron Microscopy and X-Ray Microanalysis: A Text for Biologists,*
557 *Materials Scientists, and Geologists*, 3rd ed. Plenum Press, New York.

558 Grant R(1989) The Blue Ball mine, Gila County, Arizona. *MinRec*20:447–50.

559 Grice JD, Ercit TS, Hawthorne FC (1993) Povondraite: a redefinition of the tourmaline
560 ferridravite. *Am Min*78:433-436.

561 Haines PW, Hand M, Sandiford M (2001) Palaeozoic synorogenic sedimentation in
562 central and northern Australia: a review of distribution and timing with implications for
563 the evolution of intracontinental orogens. *AustrJ Earth Sci* 48:911-928.

564 Henry DJ, Dutrow BL (1992) Tourmaline in low grade clastic metasedimentary rocks:
565 an example of the petrogenetic potential of tourmaline. *Contrib Min Petrol* 112:203-218.

566 Henry DJ, Kirkland BL, Kirkland DW (1999) Sector-zoned tourmaline from the cap rock
567 of a salt dome. *Europ J Min* 11:263-280.

568 Hiller JE, Keller P (1965) Untersuchungen an den Losern der
569 Kalisalzlagertstätte Buggingen. *Kali Steinsalz* 4:190-203.

570 Jiang SY, Palmer MR, Peng QM, Yang JH (1997) Chemical and stable isotopic
571 compositions of Proterozoic metamorphosed evaporites and associated tourmalines
572 from the Houxianyu borate deposit, eastern Liaoning, China. *Chem Geol* 135:189-211.

573 Jiráková H, Huneau F, Hrkál Z, Celle-Jeanton H, LeCoustumer P (2010) Carbon
574 isotopes to constrain the origin and circulation pattern of groundwater in the north-
575 western part of the Bohemian Cretaceous Basin (Czech Republic). *Appl*
576 *Geochem* 25:1265-1279.

577 Kane IA (2010) Development and flow structures of sand injectites: The Hind Sandstone
578 Member injectite complex, Carboniferous, UK. *Marine Petrol Geol* 27:1200-1215.

579 Kendrick MA, Burgess R, Leach D, Patrick RAD (2002) Hydrothermal fluid origins in
580 Mississippi valley-type ore districts: combined noble gas (He, Ar, Kr) and halogen (Cl,
581 Br, I) analysis of fluid inclusions from the Illinois-Kentucky fluorspar district, Viburnum
582 Trend, and Tri-State districts, midcontinent United States. *Econ Geol* 97:453-469.

583 Kovalevych VM, Marshall T, Peryt TM, Petrychenko Y, Zhukova SA (2006) Chemical
584 composition of seawater in Neoproterozoic: Results of fluid inclusion study of halite from
585 Salt Range (Pakistan) and Amadeus Basin (Australia). *Precam Res* 144:39-51.

586 Laurie JR, Nicoll RS, Shergold JH(1991)Ordovician siliciclastics and carbonates of the
587 Amadeus Basin, Northern Territory.Bureau of Mineral Resources, Australia record
588 1991/049.

589 MacGabhann BA (2007) Discoidal fossils of the Ediacaran biota: a review of current
590 understanding. Geological Society, London, Special Publication286:297-313.

591 Mattson SM, Rossman GR (1984) Ferric iron in tourmaline. Phys Chem Min 11:225-
592 234.

593 McIlroy D, Walter MR (1997) A reconsideration of the biogenicity of Arumberiabanksiof
594 Glaessner& Walter. Alcheringa21:79-80.

595 McCrea JM(1950) On the isotopic chemistry of carbonates and a paleotemperature
596 scale. J Chem Phys 18:849–858.

597 McLaughlin D, Grant R(2012) Azurite Suns from the Malbunka Copper Mine Northern
598 Territory Australia. Rock Min 87:490-501.

599 Melchiorre EB, Criss RE, Davisson ML (1999) Relationship between seismicity and
600 subsurface fluids, central Coast Ranges, California. J Geophys Res: Solid
601 Earth104:921-939.

602 Melchiorre EB, Criss RE, RoseTP(1999) Oxygen and carbon isotope study of natural
603 and synthetic malachite. Econ Geol 94:245–259.

604 Melchiorre EB, Criss RE, Rose TP(2000) Oxygen and carbon isotope study of natural
605 and synthetic azurite. Econ Geol 95:621–628.

606 Melchiorre EB, Williams PA (2001) Stable isotope characterization of the thermal profile
607 and subsurface biological activity during oxidation of the Great Australia deposit,
608 Cloncurry, Queensland, Australia. Econ Geol96:1685-1693.

609 Melchiorre EB, Enders MS (2003) Stable isotope geochemistry of copper carbonates at
610 the Northwest Extension Deposit, Morenci District, Arizona: implications for conditions
611 of supergene oxidation and related mineralization. Econ Geol98:607-621.

612 Moldovanyi EP, Walter LM, Land LS (1993) Strontium, boron, oxygen, and hydrogen
613 isotope geochemistry of brines from basal strata of the Gulf Coast sedimentary basin,
614 USA. Geochim Cosmochim Acta 57:2083–2099.

615 Mozley PS, Burns SJ (1993) Oxygen and carbon isotopic composition of marine
616 carbonate concretions: an overview. J Sed Res63:73-83.

617 Mügge O (1913) Über die Minerale im Rückstand des roten Carnallits von Stassfurt und
618 des schwarzen Carnallits von der Hildesia. Kali7:1-3.

619 Narbonne GM (2005) The Ediacara biota: Neoproterozoic origin of animals and their
620 ecosystems. Annu Rev Earth Planet Sci33:421-442.

- 621 Popov V, Sadykov T (1962) Authigenic tourmaline from rock salt deposits of Khodja-
622 Mumyn. Doklady Akademii Nauk USSR 145:1121.
- 623 Rakovan J, Waychunas G (1996) Luminescence in minerals. Mineral Rec 27:7-19.
- 624 Reed SJB (2005) Electron Microprobe Analysis and Scanning Electron Microscopy in
625 Geology, 2nd ed. Cambridge University Press, Cambridge.
- 626 Reeder RJ, Prosky JL (1986) Compositional sector zoning in dolomite. J Sed
627 Petrol 56:237-247.
- 628 Rose TP, Davisson ML, Criss RE (1996) Isotope hydrology of voluminous cold springs in
629 fractured rock from an active volcanic region, northeastern California. J Hydro 179:207-
630 236.
- 631 Rowland JC, Manga M, Rose TP (2008) The influence of poorly interconnected fault
632 zone flow paths on spring geochemistry. Geofluids 8:93-101.
- 633 Rutland RWR (1973) Tectonic evolution of the continental crust of Australia, In: Tarling
634 DH, Runcorn SK (eds) Implications of continental drift to the earth sciences. Academic
635 Press, London, pp. 1011-1033.
- 636 Sawkins FJ (1976) Metal deposits related to intracontinental hotspot and rifting
637 environments. J Geol 84:653-671.
- 638 Seilacher A (1969) Fault-graded beds interpreted as seismites. Sedimentology 13:155-
639 159.
- 640 Sharp Z (2007) Principles of stable isotope geochemistry. Upper Saddle River, NJ,
641 Pearson Education.
- 642 Shelton KL, Gregg JM, Johnson AW (2009) Replacement dolomites and ore sulfides as
643 records of multiple fluids and fluid sources in the Southeast Missouri Mississippi
644 Valley-type district: Halogen- $^{87}\text{Sr}/^{86}\text{Sr}$ - $\delta^{18}\text{O}/\delta^{34}\text{S}$ systematics in the
645 Bonnetterre Dolomite. Econ Geol 104:733-748.
- 646 Shi GR, Du YS, Gong YM (2007) Soft-sediment deformation structures interpreted as
647 seismite from the Middle Permian of the southern Sydney Basin, southeastern Australia.
648 Austr J Earth Sci 54:861-74.
- 649 Spötl C, Vennemann TW (2003) Continuous-flow isotope ratio mass spectrometric of
650 carbonate minerals. Rapid Com Mass Spect 17:1004-1006.
- 651 Stoffell B, Appold MS, Wilkinson JJ, McClean NA, Jeffries TE (2008) Geochemistry and
652 evolution of Mississippi Valley-type mineralizing brines from the Tri-State and northern
653 Arkansas districts determined by LA-ICP-MS microanalysis of fluid inclusions. Econ Geol
654 103:1411-1435.
- 655 Sullivan B (1979) Letter from Europe. Min Rec 10:121-24.

- 656 Thompson BJ, Garrison RE, Moore JC (2007) A reservoir-scale Miocene Injectite near
 657 Santa Cruz, California, In: Hurst A, Cartwright J (eds) Sand injectites: Implications for
 658 hydrocarbon exploration and production. AAPG Memoir 87:151-162.
- 659 Viets JG, Leach DL (1990) Genetic implications of regional and temporal trends in ore
 660 fluid geochemistry of Mississippi Valley-type deposits in the Ozark region. Econ
 661 Geol 85:842-861.
- 662 Walenta K, Dunn PJ (1979) Ferridravite, a new mineral of the tourmaline group from
 663 Bolivia. Am Min 64:945-948.
- 664 Walters WJ, Claypool GE, Choquette PW (1972) Reaction rates and $\delta^{18}\text{O}$ variation for
 665 the carbonate-phosphoric acid preparation methods. Geochim Cosmochim Acta 36:129-
 666 140.
- 667 Warren RG, Shaw RD (1995) Hermannsburg, Northern Territory 1:250,000 geological
 668 map series, explanatory notes. Northern Territory Geological Survey SF53-13.
- 669 Wenz ZJ, Appold MS, Shelton KL, Tesfaye S (2012) Geochemistry of Mississippi Valley-
 670 type mineralizing fluids of the Ozark Plateau: A regional synthesis. Am J Sci 312:22-80.
- 671 Wilkinson JJ, Stoffell B, Wilkinson CC, Jeffries TE, Appold MS (2009) Anomalous
 672 metal-rich fluids from hydrothermal ore deposits. Science 323:764-767.
- 673 Wilson TP, Long DT (1993) Geochemistry and isotope chemistry of Ca-Na-Cl brines in
 674 Silurian strata, Michigan Basin, USA. Appl Geochem 8:507-524.

675 FIGURES AND TABLES

676 **Figure 1.** Index map of the study area, showing extent of the Amadeus Basin (grey),
 677 and locations of major geological structures.

678 **Figure 2.** Examples of azurite disks showing a). radial growth habit and detail, b). typical
 679 disk size, c). intergrowth relationships, and d). population density and distribution.

680 **Figure 3.** Typical relationship of red and white clay types.

681 **Figure 4.** Example of 3-dimensional azurite crystal habit. Specimen is 10 cm wide, with
 682 largest crystal cluster 2.5 cm diameter.

683 **Figure 5.** Examples of a) Malachite ellipsoids in association with azurite disks.
 684 Specimen is 11.5 cm across, and largest malachite disk is 1.5 cm diameter. b)
 685 pseudomorphous replacement of a 2.5 cm azurite disk by malachite.

686 **Figure 6.** Morphological comparison of a). typical azurite disk form, and b).
 687 *Aspidella terranova* (photo courtesy ML Droser).

Figure 7. Sediment deformation structures a) Sediment bed slumping (approximately 2 m field of view, wheelbarrow for scale). b) White injectites cut off-white clay matrix. Specimen is 12 cm long. c) Cross-sectional view of azurite disks forming directly adjacent to a fluid pathway joint. Photo is 50 cm across. d) Azurite-cemented breccia specimen (9 cm long) from fluid conduit zone beneath clay unit. e) Sediment injection structure, cross-cutting bedding (black arrow above rock hammer). f) Late stage injectites and associated faulting cut azurite mineralization (specimen is 10 cm).

Figure 8. Carbon isotope values of Malbunka deposit azurite and malachite, relative to potential carbon sources. Data fields other than azurite and malachite are from Sharp (2007) and references therein.

Figure 9. Distribution of oxygen isotope thermometry estimates for malachite (Melchiorre et al., 1999) and azurite (Melchiorre et al., 2000) samples from around the world, showing relative temperatures for samples from the Malbunka deposit.

Figure 10. Scanning Electron backscatter images of mirco-tourmaline crystals, showing locations of probe analyses in Table 1.

Figure 11. Chemical classification of mirco-tourmaline from the Malbunka deposit.

Table 1. Probe data for chemistry and formulae of mirco-tourmaline.

Table 2. Stable isotope data for malachite and azurite samples used in this study.

Table 3. Chemical and isotopic composition of azurite-hosted fluid inclusions from the Malbunka deposit, with comparison to average seawater values from Chester and Jickells (2012).

Figure 1.

Figure 2.

Figure 3.

2.5 cm

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
(wt%)	Rim	Core	Core	Core	Rim	Rim	Rim	Rim	Rim	Core	Core	Rim	Rim	Rim	Rim	Rim	Rim	Core	Core
SiO₂	37.14	35.66	35.66	35.56	36.88	36.10	36.09	37.59	38.24	34.59	34.33	36.72	38.60	36.19	36.26	35.85	37.92	34.39	34.40
TiO₂	0.07	0.44	0.92	0.59	0.12	0.10	0.09	0.07	0.09	0.81	0.73	0.38	0.03	0.77	0.21	0.49	0.07	0.47	0.84
Al₂O₃	33.00	34.14	33.69	33.96	33.62	31.76	33.78	34.17	31.57	34.18	34.42	31.90	34.86	27.01	32.12	28.94	34.18	34.76	34.42
Cr₂O₃	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.00	0.01	0.68	0.01	0.01	0.02	0.00	0.02
FeO	4.06	8.64	8.29	8.55	4.31	6.46	5.45	4.20	5.97	12.38	12.50	5.58	1.68	10.94	7.12	9.81	2.52	12.17	13.06
MgO	9.41	5.44	5.60	5.52	9.07	8.97	8.39	9.01	8.43	2.16	2.19	9.62	10.77	7.39	8.20	7.83	9.58	2.32	1.82
CaO	0.03	0.34	0.45	0.35	0.06	0.05	0.06	0.04	0.05	0.35	0.30	0.38	0.02	0.27	0.07	0.14	0.04	0.25	0.29
MnO	0.00	0.04	0.03	0.01	0.02	0.03	0.00	0.00	0.00	0.06	0.08	0.00	0.02	0.00	0.02	0.00	0.01	0.10	0.10
Na₂O	2.69	1.87	1.84	1.88	2.65	2.94	3.03	2.82	3.12	1.76	1.78	2.62	2.01	3.07	2.47	2.91	1.80	1.75	1.75
K₂O	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.02	0.02	0.04	0.04	0.02	0.02	0.04	0.02	0.11	0.01	0.04	0.04
B₂O₃	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76	9.76
Total:	96.18	96.35	96.28	96.20	96.51	96.22	96.69	97.67	97.26	96.11	96.15	96.98	97.78	96.11	96.26	95.85	95.92	96.02	96.48
Formulae, based on 15 cations excluding Ca, Na, K																			
Si	5.96	5.84	5.85	5.84	5.90	5.86	5.82	5.95	6.00	5.82	5.77	5.89	5.96	6.00	5.88	5.96	6.00	5.77	5.78
Al	6.04	6.16	6.15	6.16	6.10	6.07	6.18	6.05	6.00	6.18	6.23	6.02	6.04	5.35	6.12	5.67	6.00	6.23	6.22
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00
Fe⁺³	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.56	0.00	0.37	0.00	0.00	0.00
Tet	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Ti	0.01	0.05	0.11	0.07	0.02	0.01	0.01	0.01	0.01	0.10	0.09	0.05	0.00	0.10	0.03	0.06	0.01	0.06	0.11
Al	0.20	0.43	0.37	0.40	0.24	0.00	0.24	0.31	0.00	0.60	0.59	0.00	0.30	0.00	0.02	0.00	0.38	0.64	0.59
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe⁺²	0.54	1.18	1.14	1.17	0.58	0.81	0.73	0.56	0.80	1.74	1.76	0.66	0.22	0.97	0.97	1.00	0.33	1.71	1.83
Mg	2.25	1.33	1.37	1.35	2.16	2.17	2.02	2.12	2.03	0.54	0.55	2.30	2.48	1.85	1.98	1.94	2.26	0.58	0.45
Mn	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Oct	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	2.84	3.00	3.00	3.00	3.00	2.92	3.00	3.00	2.99	3.00	3.00
Ca	0.00	0.06	0.08	0.06	0.01	0.01	0.01	0.01	0.01	0.06	0.05	0.07	0.00	0.05	0.01	0.02	0.01	0.05	0.05
Na	0.84	0.59	0.59	0.60	0.82	0.93	0.95	0.86	0.98	0.57	0.58	0.81	0.60	1.00	0.78	0.94	0.55	0.57	0.57
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.02	0.00	0.01	0.01
Vacancy	0.15	0.34	0.33	0.34	0.16	0.06	0.04	0.13	0.01	0.35	0.36	0.12	0.39	-0.06	0.20	0.01	0.44	0.38	0.37
A	0.85	0.66	0.67	0.66	0.84	0.94	0.96	0.87	0.99	0.65	0.64	0.88	0.61	1.06	0.80	0.99	0.56	0.62	0.63
total:	15.85	15.66	15.67	15.66	15.84	15.94	15.96	15.87	15.83	15.65	15.64	15.88	15.61	15.98	15.80	15.99	15.56	15.62	15.63
Mg/Mg+ 	0.805	0.529	0.546	0.535	0.790	0.727	0.733	0.793	0.716	0.237	0.238	0.778	0.920	0.655	0.672	0.661	0.871	0.254	0.199
Li	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.162	0.000	0.000	0.000	0.000	0.079	0.000	0.000	0.008	0.000	0.000

Sample Number	Mineral	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Oxygen Isotope
		(VPDB) (‰)	(VSMOW) (‰)	Thermometry Temperature of Formation Estimate (°C)
A3	Azurite Disk	-8.28	28.13	34.0
A4	Azurite Disk	-8.58	28.13	34.0
A7	Azurite Disk	-8.90	28.27	33.2
A8	Azurite Disk	-8.58	27.85	35.5
A9	Azurite Disk	-8.91	28.32	33.0
A10	Azurite Disk	-7.74	28.12	34.0
A11	Azurite Disk	-9.28	27.66	36.5
A12	Azurite Disk	-7.94	28.21	33.5
A13	Azurite Disk	-8.74	28.13	34.0
A15	Azurite Disk	-7.96	28.46	32.2
A14	Azurite Disk	-9.23	27.84	35.5
EM4	Azurite Disk	-10.06	27.40	37.9
EM1	Malachite Nodule	-12.22	27.78	24.3
EM2	Malachite Nodule	-11.59	27.55	25.5
M5	Malachite Nodule	-11.13	27.19	28.6
EM3	Azurite Crystals	-9.25	29.08	29.1
EM4	Azurite Crystals	-9.49	28.89	30.0
A6	Azurite Crystals	-9.88	29.54	26.8

	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	SO ₄ (ppm)	Ba (ppm)	B (ppm)	Sr (ppm)	TDS (ppm)
Azurite Inclusion Water	45	20	1100	17	1000	18	0.19	42	6.4	2700
¹ Seawater	411	1250	10800	392	19400	940	0.021	4.45	8.1	35000

	δ ¹⁸ O ‰ (VSMOW)	δD ‰ (VSMOW)	Na/Cl	SO ₄ /Mg	B/Ba	Na/Ca
Azurite Inclusion Water	-5.3	-55.0	1.1	0.9	221	24
Seawater	² 0.0	² 0.0	0.6	0.8	212	26

¹Chester and Jickells, 2012

²Assumed by definition, VSMOW

Figure 14.