Exceptional datolite crystals from Albion Park, New South Wales: morphology, chemistry and likely origin

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Abstract

Large, well-formed, semi-transparent yellow–green crystals up to 5.6 cm were found in cavities within the Late Permian Bumbo Latite Member of the Gerringong Volcanics in the now abandoned Cleary Brothers Quarry, Albion Park, New South Wales. Although labelled by the collector as calcite, these were later identified as datolite, with two distinct habits, occurring on a matrix of crystallized quartz and prehnite. The datolite contains very low concentrations of elements other than the essential calcium, silicon, oxygen and boron. Its distinctive chondrite-normalized, positive europium anomaly, when compared with datolite data from elsewhere, suggests crystallization from post-diagenetic hydrothermal fluids in the temperature range of 200–250°C. These datolite crystals are the finest ever found in Australia and rank highly with those found elsewhere in the world.

KEYWORDS: datolite, Albion Park, Gerringong Volcanics, rare earth elements, hydrothermal, Bumbo Latite Member

Introduction

Only a few occurrences of datolite have been described from Australia and, although globally datolite is widespread, the only occurrences with large exceptional crystals are the Obersulzbach Valley in Austria; the Lower New Street Quarry in Paterson, New Jersey USA; the Roncari Quarry in Connecticut USA; Lane's Quarry in Massachusetts USA and the Boron Pit, Dal'negorsk, Primorskiy Kray Russia (www.mindat.org, accessed on 2 April 2018). Additionally, there are very few detailed studies on datolite occurrences. An opportunity to address this knowledge gap became available at a mineral sale of the Illawarra Lapidary Club at North Wollongong Beach in January 2006, where one of the authors (D Cendon) purchased a number of well-crystallized mineral samples that were labelled as calcite. These were acquired from a former quarry worker who had worked at the Cleary Brothers Quarry at Albion Park (Fig. 1) for over 30 years and, during that time, periodically collected mineral specimens. However, the crystals did not look like calcite due to their crystal morphology and lustre. As datolite has never been formally described from this site or from the more widespread host volcanic unit (Gerringong Volcanics), this occurrence has remained unknown to the mineralogical community. The specimens comprise well-formed datolite crystals to over 5 cm on a matrix of crystallized prehnite, quartz and laumontite. Some specimens have associated minor calcite and pyrite.

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The Cleary Brothers Quarry has been active for at least the past 50 years but the original quarry from which the datolite specimens were collected closed down in 2015. The company began to excavate a new quarry in late 2015, which may well have cut through the same datolite-bearing zone as in the old quarry, but access to the new quarry has not yet been made available.

Crystals of datolite in Australia have been reported from Colebrook Hill, Rosebery, Tasmania (as white to pale yellow crystals up to 1 cm); the Avebury mine, Zeehan, Tasmania; the Dookie Mineralogical Reserve near Shepparton, Victoria, and from Martins Fluorite (Speewah Prospect), in the east Kimberley region of Western Australia (www.mindat.org, accessed 2 April 2018). The datolite crystals from Albion Park exceed datolite from other Australian occurrences in terms of crystal size, colour, clarity and overall fine quality. They are thus the finest datolite crystals ever found in Australia and are equal to some of the best datolite crystals from the famous Paterson (New Jersey, USA) occurrences (Palache, 1935).

The aims of this paper are to: 1) confirm that the crystals are datolite and provide an overview of their crystal morphology, and 2) provide detailed geochemical analyses to offer insights into their formation and to compare them with other well-documented datolite occurrences. As a consequence of this study, we predict that similar conditions may have been present elsewhere (particularly within the various latite members of the Gerringong Volcanics), suggesting the existence of other sites in which datolite may have formed.

Local geology

The Cleary Brothers Quarry at Albion Park excavates basic volcanic rocks of the Permian Gerringong Volcanics (Joplin et al. 1952; Fig. 2). Traditionally, the Gerringong Volcanics have been considered to comprise nine latite members (all believed to be flows) of basaltic, basaltic andesite and andesitic compositions, along with three intercalated

Figure 1 Map showing the location of Cleary Brothers Quarry (150.802735°E, 34.58575°S) at Albion Park, New South Wales, and distribution of the Permian Bumbo Latite Member (Psgb; adapted from Bowman, 1974a,b).

Figure 2 View of the western face of Cleary Brothers Quarry, Albion Park, New South Wales (taken on 12 January 2001), showing columnar-jointed latite with secondary mineralized zone (pale grey colour near centre of image) which contained crystals of quartz, calcite and laumontite. Photo Dioni Cendón.

volcaniclastic sandstone members (Joplin, 1964, 1965; Carr, 1985, 1998). An additional and lowermost latite member, the 'Coolangatta Latite Member', was subsequently described by Bann (1999).

The latite members of the Gerringong Volcanics are named, from base to top, Coolangatta, Blow Hole, Bumbo, Saddleback, Dapto, Cambewarra, Five Islands, Calderwood, Minnamurra and Berkely (Carr, 1983; Tye et al., 1996; Bann and Jones, 2000). These volcanic rocks can also be traced offshore and evidence suggests that they once extended from the southern end of the Sydney Basin near Batemans Bay to the north and northeast for at least 340 km. However, lavas are only known to outcrop in the Nowra–Wollongong region (Carr, 1998).

The main unit quarried within the old quarry at Albion Park was the Bumbo Latite Member (Psgb on Fig. 1). Both the Bumbo and Blow Hole Latite Members represent remnants of moderate-sized compound lava flows that have flowed at least 10 from their source vent into a shallow marine environment (Campbell et al., 2001). Immediately underlying the Blow Hole Latite is the Budgong Sandstone, which is at the top of the Shoalhaven Group (Bowman, 1974a). This Early Permian sandstone contains abundant volcanic-derived particles and in places near the top, relatively abundant marine fossils including brachiopods, pelecypods, gastropods, crinoids and bryozoans. These fossils have also been collected at the quarry. The Bumbo Latite Member is up to 150 m in thickness and contains relatively abundant pillow structures, columnar joints, breccia zones and intrusive basal contacts (Bowman, 1974a).

The primary minerals within these volcanic rocks are plagioclase, potassium-feldspar, clinopyroxene, olivine, iron–titanium oxides and apatite (Carr, 1998). The main secondary minerals within the Blow Hole Latite Member identified by Raam (1964) are quartz, microcrystalline silica (chalcedony and agate), calcite, chlorite and laumontite. In addition, and for the Gerringong Volcanics as a whole, Carr (1998) recorded the occurrence of zeolites, prehnite, pumpellyite and epidote, while Campbell et al. (2001) also recorded clays and hematite.

Methods

The crystal morphology study focused on two of the largest crystals of datolite with well-developed crystal faces. These were compared to computer-generated drawings made using unit cell data given in Anthony et al. (2001). The faces were identified by matching the angles between adjacent faces to a template cut from thin cardboard having angles calculated from the unit cell data.

For the X-ray diffraction analysis (XRD), a transparent fragment was taken from the sample crystal used for the ICP–MS analysis and analysed with a Phillips PW1349 diffractometer using copper Kα radiation with a scan range of 5–70° 2θ.

A small (29 milligrams), cleaned crystal fragment of datolite was analysed for trace elements using a Varian quadrupole Inductively Coupled Plasma – Mass Spectrometer (ICP–MS) at the School of Earth Sciences, University of Melbourne. The digestion, analytical and instrumental drift correction procedures followed a protocol modified from Eggins et al. (1997). A total of four replicates of 100 scans per replicate were measured for each isotope. Dwell time was 10 milliseconds, with the exception of beryllium, which was 30 milliseconds. The datolite dilution factor was 10400. Two digestions of USGS standard reference material W-2 were used for calibration and BHVO-2 was run as an unknown. A second, 14-milligram crystal fragment from a different specimen was later analysed at a lower dilution factor of 3200 for replication and to improve detection limits. This produced very similar results.

Powder XRD data

The powder XRD data (Table 1) clearly show that the mineral analysed is datolite and closely matches ICDD 11-70, datolite from St Andreasburg, Germany.

Mineralogy

Datolite $CaB(SiO_4)(OH)$

All of the images of datolite provided are of specimens obtained from Cleary Brothers Quarry. Datolite occurs as very sharp, well-terminated, semi-transparent, pale yellow–green crystals up to 5.6 cm in length (Figs 3 and 4) that are moderately fractured in places. They occur on a matrix of radial aggregates of small transparent, short prismatic quartz crystals and appear to have formerly occurred within quartz veins or quartz-lined amygdules. The quartz itself commonly overlies opaque white bladed laumontite. Associated species include widespread prehnite and calcite and rarer pyrite. The smaller crystals of datolite (< 10 mm) and similar-sized portions of the larger crystals are suitable for faceting. The larger crystals are partially etched near their base, suggesting the possibility of some post-depositional partial dissolution by later fluids. Most of the larger crystals are crazed and have slightly dull crystal faces, possibly the result of some exposure to weathering, though this is difficult to confirm given that their exact depth within the quarry is unknown.

Crystal morphology

The morphology and size of crystals relate to their conditions of formation, kinetics of crystal growth and effects of later fluids such as etching. There are numerous distinct faces present in the datolite specimens acquired for this study, some with a frosted surface and some slightly undulating.

Datolite crystals display quite a variety of habits as illustrated in Dana (1892) and Palache (1935). Two main habits dominate the Albion Park datolites and two well-formed crystals representing these different habits were selected for detailed examination of their morphology. Clinographic drawings of the two crystal habits studied in detail are illustrated in Figures 5a and 5b. Figures 6–8 illustrate these datolite crystals along with their crystallographic interpretation.

Datolite is monoclinic with *2/m* symmetry and unit cell parameters, *a* = 4.832 Å, *b* = 7.608 Å, *c* = 9.636 Å and β =90.4° (Anthony et al. 2001). Although the β angle is very close to 90° it is still sufficiently different to give a noticeable asymmetrical appearance to the crystals. The crystals from the Albion Park quarry resemble those illustrated in figure 142 of Palache (1935, p. 97) which are dominated by four forms:

M {110} m {011} *v* {103} *v*' $\{10\bar{3}\}$

The faces corresponding to these forms were identified by the following method. Edges of the crystal were identified where faces having the same form met. A set of templates was then cut from thin cardboard corresponding to the theoretical angles calculated from unit cell data. The templates were then fitted to the crystal with a 'match' identifying the pair of faces. Three templates were made using the following data.

M $(110) \wedge (1\bar{1}0) = 64.84°$ and $(\bar{1}\bar{1}0) \wedge (\bar{1}10) = 64.71°$ (Template angle 115.29°)

(blue dot on actual crystal faces in Figure 7). These faces meet at the positive and negative ends of the *a* axis respectively.

m $(011) \wedge (01\bar{1}) = 76.59°$ and $(0\bar{1}\bar{1}) \wedge (0\bar{1}1) = 76.59°$ (Template angle, 103.41°)

(orange dot on actual crystal faces in Figures 7 and 8). These faces meet at the positive and negative ends of the *b* axis respectively.

v $(103) \wedge (\bar{1}03) = 67.36°$ and $(10\bar{3}) \wedge (\bar{1}0\bar{3}) = 67.36°$ (Template angle, 112.64°)

(green dot on actual crystal faces in Figures 7 and 8). These faces meet near the positive and negative ends of the *c* axis respectively.

Faces having the 'M' {110} are larger than those having the 'm' {011} form. Once these faces were identified the other smaller faces could subsequently be identified by inspection. Other forms identified are, *v*, $\{0\bar{1}3\}$; *L*, $\{11\bar{3}\}$; *n*, {111}; *u*, {123}; x, {013} and t, {113}.

Trace and rare earth element chemistry

The ideal chemical formula for datolite is $CaB(SiO_4)(OH)$ (Anthony et al., 1995). The ICP-MS analyses (Table 2) show that the datolite from the Cleary Brothers Quarry is extremely pure compared to other published analyses. Although there are abundant data on the major element chemistry of datolite (e.g. Deer et al., 1963), there are very few analyses of minor, trace and rare earth element concentrations. The exception is from Zaccarini et al. (2008), who conducted a very detailed geochemical and fluid inclusion study of datolite from a number of localities within the Northern Apennine ophiolites of Italy.

Compared to a mean composition of the Bumbo Latite Member from Carr (1984), the datolite from the Albion Park quarry is highly depleted in all reported trace elements, though unfortunately Carr (op.cit.) did not analyse for beryllium and lithium. Although a wide range of elements from the host volcanic rocks should be able to partition into the datolite via substitution for calcium (e.g. Fe, Mg, Mn, Sr and Ti) this does not seem to have occurred and would suggest that the host latite had little to do with datolite formation other than providing the necessary space for crystallization from the hydrothermal solutions.

When compared to the range in trace element chemistry of datolites from the Northern Apennine ophiolites (Zaccarini et al., 2008), the datolite from Albion Park is significantly depleted in almost all of the trace elements with the exception of beryllium and lithium, which show enrichment. Significantly, the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) are far more depleted (by at least an order of magnitude). Zaccarini et al. (2008) suggested that these elements are substituting for calcium in the datolite crystal lattice.

On a chondrite-normalized REE diagram (Fig. 9), the datolite from Albion Park has a very prominent positive europium anomaly, whereas those for the northern Apennine datolites lack europium anomalies or have small negative or positive anomalies. Both the Albion Park and Northern Apennine datolites have similar positive lanthanum anomalies. The unusual saw-tooth, heavy rare earth element pattern for the Northern Apennine datolite is unlikely to represent the true mineral composition.

Figure 3 Datolite crystals with prehnite on quartz crystals. Specimen dimensions are 4 × 3 × 4 cm and largest crystal is 3 × 2.5 × 2 cm. Collection Ian Graham, photo Angela Lay.

Table 1. **X-ray diffraction data for Albion Park datolite**

Albion Park Datolite		*ICDD 11-70*	
D-spacing (A)	*Relative Intensity (%)*	*D-spacing (A)*	*Relative Intensity (%)*
5.94	1.6	5.98	8
4.81	16.6	4.83	16
3.75	25.6	3.76	45
3.40	25.2	3.40	30
3.11	100	3.11	100
		2.99	35
2.89	15.6		
2.85	78.3	2.86	65
2.52	20.2	2.52	30
2.40	7.9	2.41	10
2.30	6.1	2.30	10
2.24	36.8	2.24	35
2.19	33.0	2.19	60
2.16	16.1	2.16	14
2.07	5.8	2.07	10
2.04	1.5	2.04	8
1.99	11.6	1.99 (2 peaks)	35
		1.91	4
1.87	18.1	1.87	40
1.87	14.7		
1.77	5.4	1.77	10
1.74	3.7	1.75	8
1.72	33.0	1.72	14
1.71	17.6	1.71	10
1.66	7.7	1.66	18
1.64	11.1	1.64	40
1.62	3.4	1.62	6
1.61	10.8	1.61	6
1.56	1.6		
		1.53	20

Figure 4 Datolite crystals with minor laumontite (white) on quartz crystals. Specimen dimensions are 5.3 × 4.4 × 6.9 cm and largest crystal is 4.3 × 2.5 × 5.6 cm. Australian Museum specimen No. D54379, photo Angela Lay.

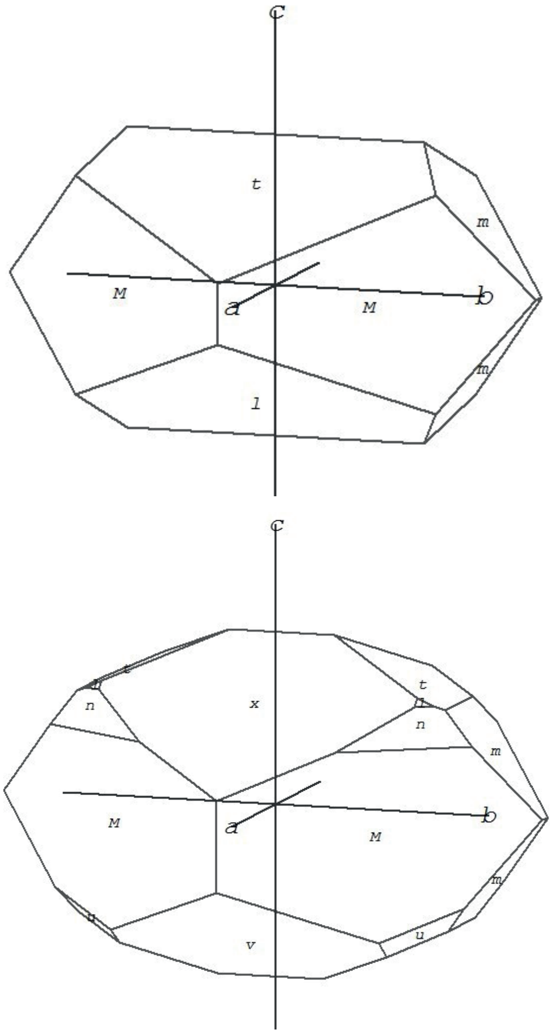

Figure 5 Crystal drawings in clinographic projection showing the two main habits of datolite crystals from Cleary Brothers Quarry: top) simplest habit; bottom) more complex habit with many more crystal facets. Notice faces having the M form meet at the *a* axis, while faces having the m form meet at the *b* axis.

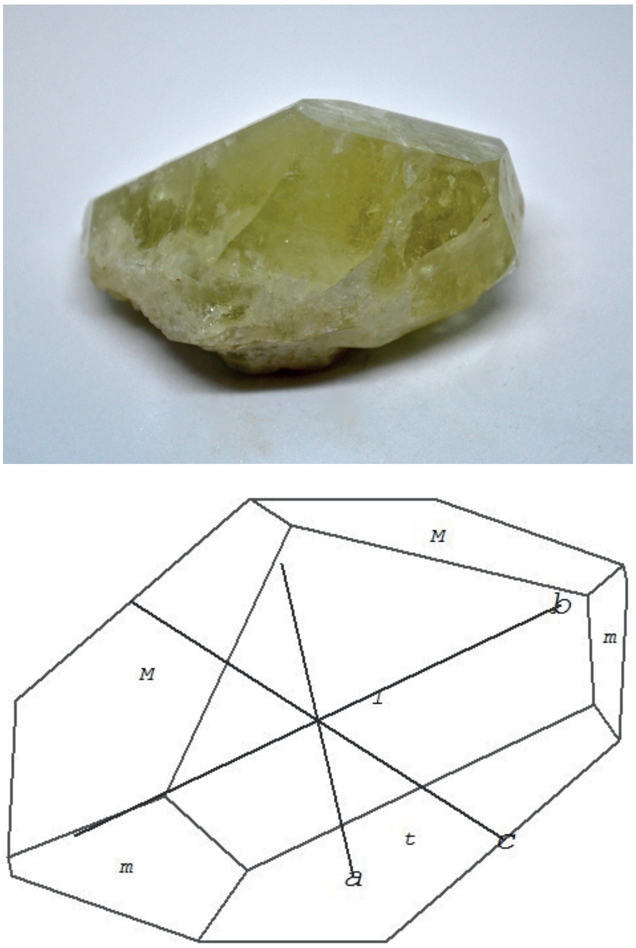

Figure 6 Datolite crystal (top) and crystallographic drawing (bottom) in the same orientation identifying the crystal faces of a relatively flat yellow-green crystal. Crystal is 3.5 × 2 × 2 cm. Collection Dioni Cendón, photo Angela Lay.

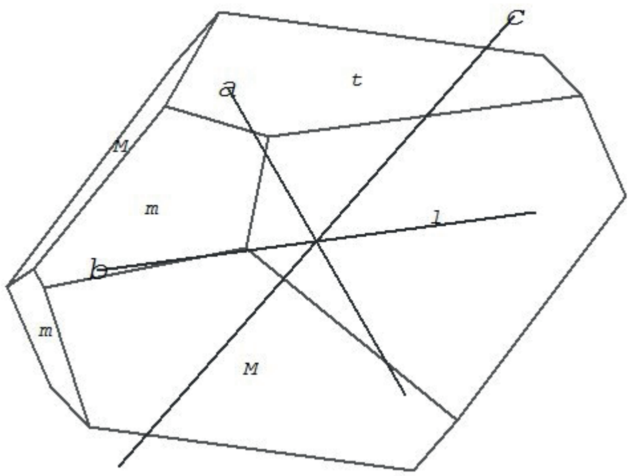

Figure 7 Datolite crystal (left) and crystallographic drawing (above) in the same orientation identifying the crystal faces of a relatively equant-shaped yellow-green crystal. Specimen is 5.5 × 4 × 4 cm and largest crystal is 3 × 2 × 1.5 cm. Stickers mark prominent crystal faces. Collection Dioni Cendón, photo Angela Lay.

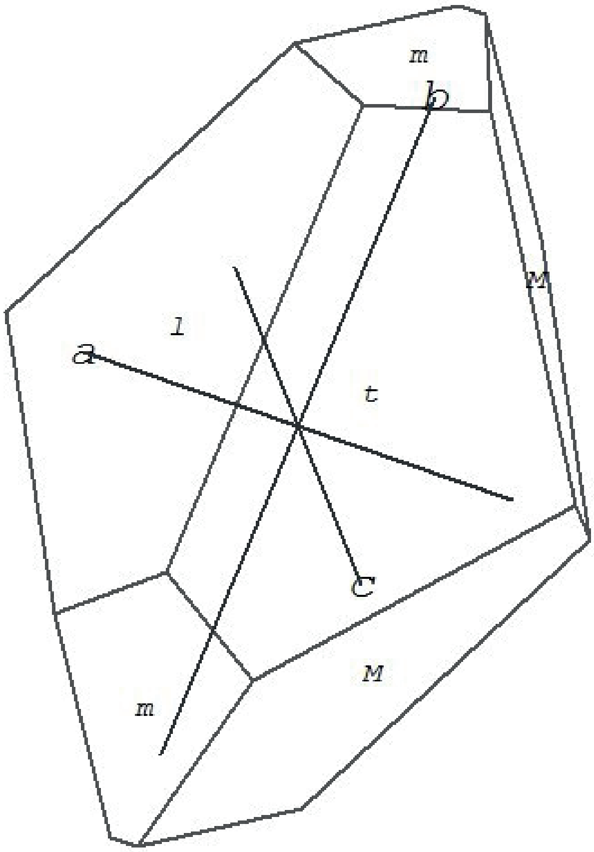

Figure 8 Datolite crystal (top) and crystallographic drawing (bottom) in the same orientation identifying the crystal faces of a slightly elongate equant-shaped yellow-green crystal (with faces marked) on a matrix of well-crystallized prehnite and quartz. Specimen is 4.5 × 3 × 3 cm and largest crystal is 3 × 2 × 1.5 cm. Collection Dioni Cendón, photo Angela Lay.

Table 2. ICP-MS analyses for selected trace elements (ppm) and rare earth elements including yttrium (ppb) of Albion Park datolite in comparison to datolites from the Northern Apennine ophiolites of Italy (ppm; data from Zaccarini et al., 2008).

Element	*Datolite 1 (ppm)*	*Datolite 2 (ppm)*	*Northern Apennine range (ppm)*
Li	1.50	1.33	0.00–0.84
Be	2.31	1.37	0.04–2.69
Ca	252 804	235 869	na
Ti	0.39	0.36	na
V	0.29	0.76	0.66–5.89
Cu	0.12	0.26	0.35–111.90
Zn	0.52	1.52	0.00–101.70
Ga	0.14	0.17	0.57–1.25
Rb	0.007	0.001	0.08–0.63
Sr	2.35	2.45	6.41–48.08
Ba	0.038	0.049	0.69–3.12
	(ppb)	(ppb)	(ppm)
Y	11.5	8.48	0.03–1.00
La	207.8	194.86	0.82–6.42
Ce	132.3	101.94	0.09–1.24
Pr	9.84	7.39	0.01–0.11
Nd	27.59	19.81	0.00–0.53
Sm	3.45	1.97	0.01–0.11
Eu	8.34	6.89	0.00–0.07
Gd	2.16	1.72	0.01–0.14
Tb	0.30	0.21	0.01–0.02
Dy	1.62	1.16	0.00–0.10
Ho	0.31	0.22	0.01–0.03
Er	0.68	0.65	0.00–0.05
Tm	0.08	0.08	0.00–0.01
Yb	0.47	0.34	0.00–0.03
Lu	0.05	0.05	0.00–0.01

na = not analysed

These authors employed a different ICP–MS technique (with ppm detection limits) in acquiring their trace-element data and the apparent saw-tooth pattern for the heavy rare earth elements is most likely due to their concentration being below or close to the detection limit of their analytical technique.

Prehnite $Ca_2Al(Si_3Al)O_{10}(OH)_2$

Prehnite usually occurs as radial aggregates (to 1 cm) of opaque, dull, pale yellow–green, interpenetrating tabular crystals with sharp chisel-like terminations (Fig. 10). Bow-tie aggregates are also relatively common. Prehnite also occurs as individual sharp tabular crystals up to 5 mm.

Less common are semi-transparent radial botryoidal aggregates (to 6 mm) of pale apple-green, interpenetrating tabular crystals, though these are not as sharp as the form mentioned above (Fig. 11). These commonly carry a sprinkling of minute (<0.5 mm) brassy pyrite cubes and, in places, are partially coated by platy calcite, itself partially coated in minute pyrite crystals.

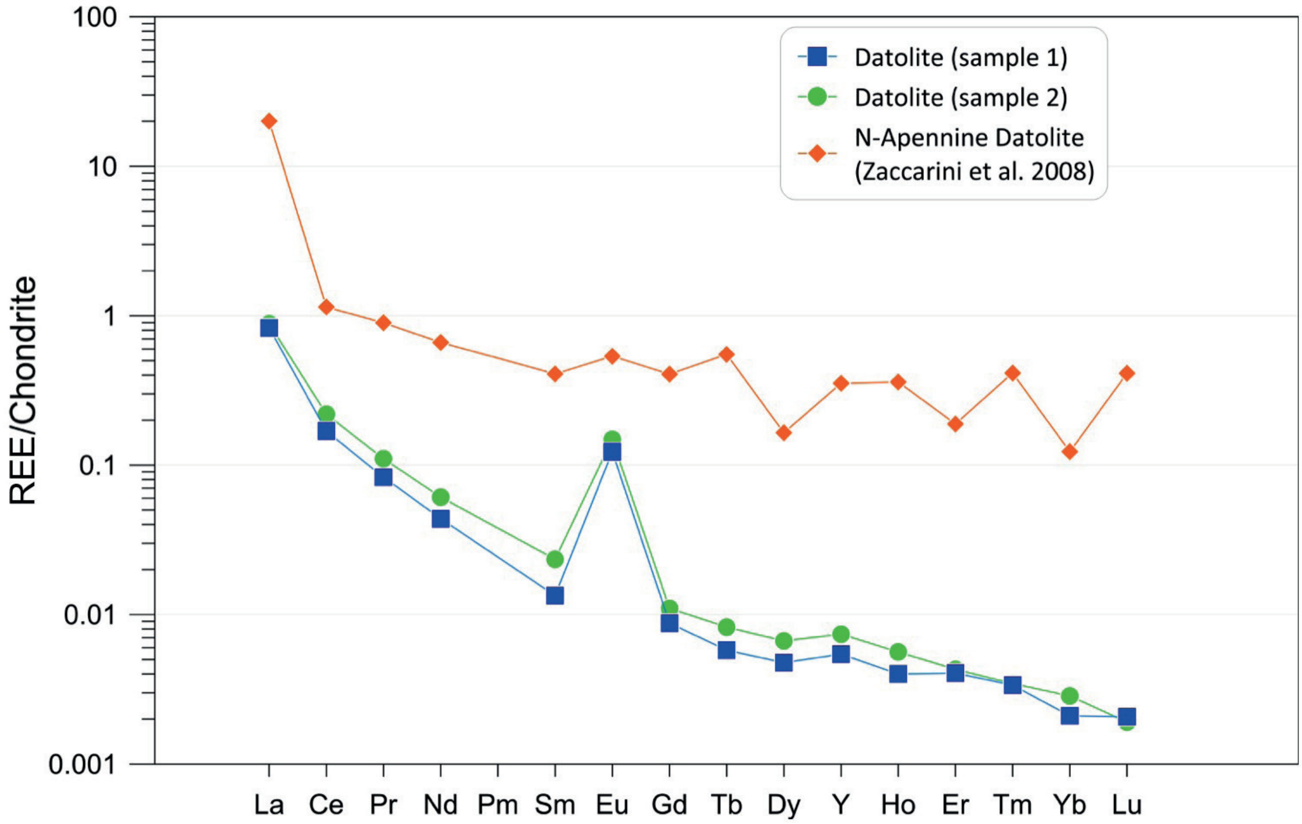

Figure 9 Chondrite-normalized rare earth element plot for two datolite analyses from Clearly Brothers Quarry (chondrite values used are those of Sun and McDonough, 1989).

Figure 10 Botryoidal aggregates of pale yellow–green prehnite and minor calcite and laumontite on quartz crystals. Specimen size is 5 × 3.5 × 2 cm and largest prehnite aggregate is 7 mm across. Collection Ian Graham, photo Angela Lay.

Figure 11 Well-crystallized pale yellow-green prehnite. Specimen is 5 × 5 × 3.5 cm, largest prehnite crystal is 3 mm. Collection Ian Graham, photo Angela Lay.

Discussion

As with datolite recently described by England (2017) from Allandale in the Hunter Valley of New South Wales, the datolite from the Cleary Brothers Quarry is associated with laumontite, calcite, pyrite and quartz but, in contrast, is also intimately associated with prehnite. This association of datolite with quartz, calcite, laumontite and prehnite is typical of most basalt-hosted datolite occurrences worldwide (www.mindat.org, accessed 2 April 2018). The zeolites heulandite-Ca and stellerite occur at Allandale but were not identified with datolite at the Cleary Brothers Quarry. In the world-famous Paterson prehnite occurrences (New Jersey, USA), Laskowich and Puffer (2016) noted that datolite was restricted to large partially filled vesicles related to volcanic diapirs. In these vesicles, zeolites and quartz are generally absent whereas carbonate minerals are relatively abundant.

Given that the specimens in this study were purchased from a previous quarry employee who had collected them over a period of 30 years, and the upper exposures in the quarry have long since been worked-out, our interpretation of datolite formation presented below is largely derived from an understanding of the regional geology, the examination of exposures visited by the authors in 2001, and the study of literature pertaining to datolite occurrences elsewhere.

For the Paterson occurrences (New Jersey, USA), Laskowich and Puffer (2016) concluded that datolite crystallization was related to hydrothermal fluids from a post-extrusive heating event driven by later magma pulses. Similarly, for the Northern Apennine ophiolite-hosted datolite, Zaccarini et al. (2008) concluded that post-magmatic hydrothermal fluids were responsible for datolite precipitation. These fluids were more saline than seawater and were more akin to diagenetic fluids which evolved from initial trapped seawater due to changing physicochemical conditions brought about by burial. In other words, after the Bumbo Latite Member had formed within a submarine environment, a later underlying magma provided a heat source for circulating hydrothermal fluids, which would have interacted with highly saline pore waters within the underlying sediments. These then migrated upwards into the overlying latite, depositing the datolite and associated minerals.

The interpretation of homogenization data from the analyses of primary fluid inclusions within the datolite (i.e. fluids trapped at the time of formation) is that temperatures of 173–236°C prevailed during datolite formation (Zaccarini et al., 2008). Similarly, in a fluid inclusion study of datolite (once again associated with quartz and prehnite) from crosscutting veins within Jurassic pillow basalts of northeastern Hungary, Kiss et al. (2012) suggested that the datolite crystallized at temperatures of 160 to 210°C. They also suggested that the datolite and associated minerals crystallized subsequent to pillow basalt formation during low-grade metamorphism. In an earlier study of datolite and associated minerals from the active Larderello–Travale geothermal field (~80 km southwest of Florence, Italy), Cavarretta et al. (1982) showed that the assemblage datolite–prehnite–quartz co-existed at temperatures of 250–270°C but that datolite was stable down to 220°C.

The positive europium anomaly for the Albion Park datolite provides some additional constraints on the datolite formation conditions. Such positive europium anomalies occur in hydrothermal vein systems (Bau, 1991; Michard and Albarede, 1986) and lend support to the hypothesis that the datolite and associated minerals precipitated from post-magmatic hydrothermal fluids, as suggested by Laskowich and Puffer (2016) for the New Jersey's occurrences. Such conditions of formation would also be in agreement with the Northern Apennine, northeast Hungary and Larderello geothermal field datolite occurrences. Based on experimental evidence and studies of active hydrothermal mineralizing fields (Sverjensky, 1984; Michard and Albarede, 1986; Bau and Moller, 1992), the very strongly positive europium anomaly for the Albion Park datolite suggests temperatures of crystallization of 200–250°C.

From the limited number of samples available for this study the paragenetic sequence is: quartz → prehnite → datolite → calcite → pyrite.

Conclusions

Mineral specimens collected from the Cleary Brothers Quarry at Albion Park over a period of 30 years have been confirmed to be datolite and probably represent the best crystallized specimens for this species from Australia. The quality of these specimens is comparable to some of the best datolite crystals from the world-renowned historic Paterson locality in New Jersey (USA). Two dominant habits are present in the Albion Park occurrence and the crystals are inferred to be chemically pure as they contain very low trace element concentrations. On a chondrite-normalized REE diagram both datolite samples display a prominent positive europium anomaly and this, combined with studies elsewhere, is consistent with datolite crystallization from a hydrothermal fluid around 200–250°C. This study suggests that datolite should be more widespread within the Gerringong Volcanics than the single occurrence described in this paper.

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