

PHOSPHATE MINERALS IN ALTERED ANDESITE FROM MOUNT PERRY, QUEENSLAND, AUSTRALIA

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ABSTRACT

The Al-phosphate minerals augelite, $\text{Al}_2\text{PO}_4(\text{OH})_3$, trolleite, $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$, gatumbaite, $\text{CaAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, and lazulite, $(\text{Mg},\text{Fe})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$, occur in a suite of hydrothermally altered Triassic andesites at Mount Perry, eastern Queensland, Australia. This is only the second documented occurrence of gatumbaite worldwide, and the first reported Australian occurrence of augelite and trolleite. Associated minerals include quartz, andalusite, rutile, zircon and topaz. The Al-phosphates are considered to have formed initially by hydrothermal alteration of the volcanic rocks at relatively high temperatures (*ca.* 500°C), but later equilibrated at 380–450°C and 2 kbars $P(\text{H}_2\text{O})$. Small blebs of scorzalite, $(\text{Fe},\text{Mg})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$, included in lazulite may be exsolution features and suggest that a miscibility gap may exist in the lazulite–scorzalite series.

Keywords: phosphates, augelite, trolleite, gatumbaite, lazulite, scorzalite, Mount Perry, Queensland, Australia.

SOMMAIRE

Nous avons trouvé les phosphates d'aluminium augelite $\text{Al}_2\text{PO}_4(\text{OH})_3$, trolleite $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$, gatumbaite $\text{CaAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, et lazulite $(\text{Mg},\text{Fe})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$ dans une suite d'andésites triassiques altérées au mont Perry, dans le Queensland oriental, en Australie. C'est le deuxième exemple de la gatumbaite à l'échelle mondiale, et la première fois que l'augelite et la trolleite sont signalées en terre australienne. Leurs sont associés quartz, andalousite, rutile, zircon et topaze. Les phosphates se seraient formés d'abord par l'altération hydrothermale des roches volcaniques à température relativement élevée (500°C, environ), et auraient ré-équilibré entre 380 et 450°C à une pression d'eau de 2 kbars. Des petites inclusions de scorzalite, $(\text{Fe},\text{Mg})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$, dans la lazulite pourraient résul-

ter d'un phénomène d'exsolution, et indiqueraient la présence d'une lacune de miscibilité entre lazulite et scorzalite.

(Traduit par la Rédaction)

Mots-clés: phosphates, augelite, trolleite, gatumbaite, lazulite, scorzalite, mont Perry, Queensland, Australie.

INTRODUCTION

Augelite $\text{Al}_2(\text{PO}_4)(\text{OH})_3$ and trolleite $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$ are rare phosphate minerals characteristic of relatively high-temperature, Al-rich hydrothermal deposits, where they form by metasomatic replacement of aluminosilicate minerals (Wise 1975, Wise & Loh 1976). This paper describes an occurrence of augelite and trolleite, together with an even rarer Ca–Al phosphate, gatumbaite $\text{CaAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, near Mount Perry (Fig. 1), 75 km southwest of Bundaberg in eastern Queensland. This is apparently the first reported Australian occurrence of augelite and trolleite and only the second recorded occurrence of gatumbaite worldwide after the type occurrence in the Buranga pegmatite, Rwanda (von Knorring & Fransolet 1977).

OCCURRENCE

The phosphate occurrence is located within a hydrothermal alteration system in a sequence of Triassic andesites 7 km east of Mount Perry Township. The alteration belongs to the class termed "high-Al alteration" by Schmidt (1985), marked by central zones of extreme acid leaching consisting primarily of quartz (98%) and rutile (2%), with or without pyrite, andalusite, sillimanite and lazulite. At Mount Perry, accompanying zones of (adjacent) quartz–sericite and (outer) propylitic alteration have been recognized but not fully mapped. Andesites

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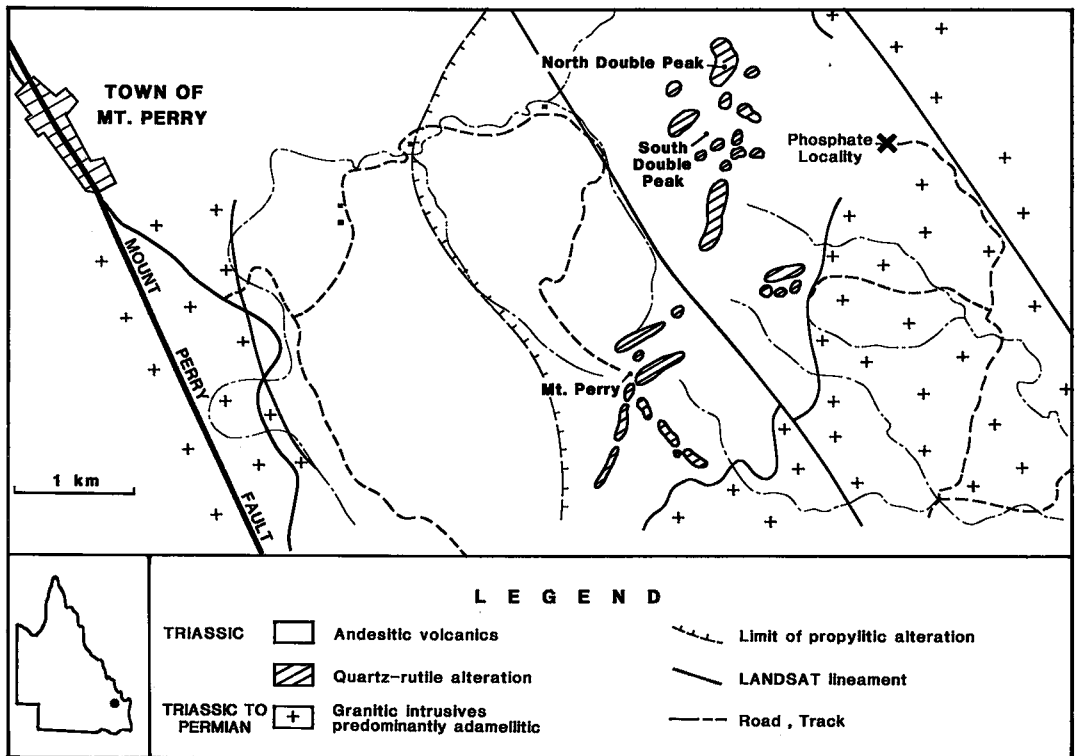


FIG. 1. Simplified geological map of the Mount Perry area.

showing propylitic and quartz-sericite alteration retain all the textural features of the igneous precursors, including abundant relict plagioclase phenocrysts up to 1.5 mm in length. By contrast, rocks in the zone of high-Al alteration retain no textural evidence of igneous parentage, which is predicated wholly on the basis of relationships in the field, where partial replacement of individual flows may be observed. The contact between replaced and unreplaced zones is quite sharp, and intermediate textural variants have not been recorded.

The phosphate-bearing specimens studied contain quartz, andalusite, augelite, trolleite, gatumbaite, rutile, zircon and, in one specimen, abundant topaz (> 50 vol. %). Small amounts of lazulite occur sporadically throughout the rock as irregular patches and thin veins. Traces of berlinite AlPO_4 are included in quartz.

There is no unequivocal textural evidence of replacement phenomena among these phases, apart perhaps from the rather ragged anhedral appearance of some grains of gatumbaite. However, there is some alteration of the phosphate phases to variscite $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, which seems to have occurred much later and at a lower temperature than the main assemblage.

MINERALOGY

Results of microprobe analyses of the phosphate minerals are given in Tables 1 and 2. Analyses were carried out by wavelength-dispersion methods with a Camecax Camebax Microbeam electron-probe microanalyzer using an accelerating voltage of 15 kV, a take-off angle of 40° and a beam current of 0.034 mA. Volatilization of structurally combined water in the phosphates was minimized by using a rastered electron beam. The following primary standards were used: pure metal (Fe) and synthetic phases TiO_2 (Ti), MnO (Mn), MgO (Mg), $\text{Ca}_2\text{P}_2\text{O}_7$ (P), CaAl_2O_4 (Al) and CaSiO_3 (Ca, Si). Secondary standards included natural apatite, pyroxene and garnet. In all phosphates, Na, K, Cr, As, Ni, Ba, Sr, Cu and Zn are below the limit of detection (typically 100–200 ppm).

Augelite

Augelite typically forms stumpy prismatic grains, up to 6 mm but usually less than 2 mm in length. The grains generally consist of a turbid core (owing to abundant microscopic to submicroscopic inclusions) surrounded by a water-clear rim. Small

amounts of Ti detected in augelite (Table 1, No. 1) may substitute for Al or may represent sub-microscopic inclusions of rutile, which is an abundant associated mineral.

Trolleite

Trolleite usually occurs as small, equant, anhedral grains typically less than 0.5 mm in diameter, commonly included in augelite, and rarely in quartz or gatumbaite. A microprobe analysis (Table 1, No. 2) indicates the presence of minor Fe (0.29–0.60 wt. % Fe_2O_3), presumably substituting for Al, and a trace of Mg (0.08–0.16 wt. % MgO).

Gatumbaite

Gatumbaite, which is less abundant than augelite and trolleite, occurs as bladed, anhedral prismatic crystals up to 5 mm in length. This coarsely crystalline habit contrasts markedly with the fine-grained, radiating fibrous habit of gatumbaite from the only other known locality, in the Barunga pegmatite, Rwanda (von Knorring & Fransolet 1977). At Mount

TABLE 1. CHEMICAL COMPOSITION OF AL-PHOSPHATES

	1	2	3	4
P_2O_5 Wt. %	34.68	48.13	41.95	58.43
SiO_2	0.07	—	—	0.13
TiO_2	0.08	—	0.13	—
Al_2O_3	50.33	45.45	30.16	41.88
Fe_2O_3 *	—	0.40	0.04	0.04
MgO	—	0.12	—	—
CaO	—	—	16.22	—
Total	85.16	94.10	88.50	100.48
	Cation proportions [#]			
P	0.993	3.008	2.001	0.999
Si	0.002	—	—	0.002
Al	2.008	3.955	2.003	0.997
Fe^{3+}	—	0.022	0.002	0.001
Mg	—	0.013	—	—
Ca	—	—	0.979	—

1. Augelite. 2. Trolleite.
3. Gatumbaite 4. Berlinite

* Total Fe calculated as Fe_2O_3

Cation proportions based on 5.5 (augelite), 13.5 (trolleite), 9 (gatumbaite) and 4 (berlinite) atoms of oxygen anhydrous.

TABLE 2. CHEMICAL COMPOSITION OF LAZULITE AND SCORZALITE

	1	2	3	4	5	6	7	8	9	10
P_2O_5 Wt. %	46.29	45.60	45.71	42.61	43.36	42.95	45.53	46.48	43.05	44.53
TiO_2	0.08	0.03	0.06	—	—	—	—	—	—	—
Al_2O_3	32.76	31.92	32.55	31.17	31.60	31.16	31.67	32.94	30.52	31.19
FeO	5.74	8.27	6.48	18.74	15.48	17.35	4.80	1.71	17.16	11.72
MnO	0.05	0.25	0.13	0.57	0.38	0.47	—	—	0.05	0.03
MgO	10.18	8.59	9.35	0.57	3.16	1.78	11.23	12.69	2.98	7.16
Total	95.10	94.66	94.28	93.66	93.98	93.71	93.23	93.82	93.77	93.21
	Cation proportions based on 9 atoms of oxygen (anhydrous)									
P	2.004	2.009	2.002	2.000	1.995	2.001	2.004	2.001	2.001	1.996
Ti	0.003	0.001	0.002	—	—	—	—	—	—	—
Al	1.974	1.958	1.985	2.037	2.024	2.021	1.941	1.975	1.975	1.946
Fe^{2+}	0.245	0.360	0.280	0.869	0.704	0.798	0.209	0.073	0.788	0.519
Mn	0.002	0.011	0.006	0.027	0.018	0.022	—	—	0.002	0.001
Mg	0.776	0.666	0.721	0.047	0.256	0.146	0.870	0.962	0.244	0.565
100Mg/(Mg+Fe)	76.0	64.9	72.0	5.1	26.7	15.5	80.6	92.9	23.6	52.1

1. Lazulite, Mount Perry. Most Mg-rich grain analyzed. R29677.[#]

2. Lazulite, Mount Perry. Most Fe-rich grain analyzed. R29677.

3. Lazulite, Mount Perry. Average of 6 analyses.

4. Scorzalite in lazulite, Mount Perry. Most Fe-rich grain analyzed. R29677.

5. Scorzalite in lazulite, Mount Perry. Most Mg-rich grain analyzed. R29677.

6. Scorzalite in lazulite, Mount Perry. Average of 8 analyses.

7. Lazulite, Rapid Creek, Yukon, Canada. R29619.

8. Lazulite, Werfen, Salzburg, Austria. R24426.

9. Scorzalite, Victory mine, Sth Dakota, USA. R24427.

10. Lazulite in scorzalite, Victory mine, Sth Dakota, USA. R24427.

* Total Fe calculated as FeO.

Specimen numbers refer to the Bureau of Mineral Resources Museum mineral collection.

Perry, gatumbaite (Table 1, No. 3) contains traces of Fe (up to 0.08 wt. % Fe_2O_3) and Ti (0.05–0.18 wt. % TiO_2), but is otherwise close to the ideal composition. In contrast, von Knorring & Fransolet (1977) reported significant Fe (2.2 wt. % Fe_2O_3), Mn (0.3 wt. % MnO) and Na (0.3 wt. % Na_2O) in the type gatumbaite. However, these differences can probably be attributed to analysis by electron microprobe, which excludes impurities, in contrast to the standard wet-chemical analysis performed on

the fibrous type specimen, with attendant problems of sample purity of the separate. A detailed optical and single-crystal X-ray study of the Mount Perry gatumbaite is in progress and will be presented in a separate paper.

Berlinite

Berlinite is restricted in occurrence to rare sub-spherical blebs up to 0.05 mm in diameter included

in quartz. Microprobe analytical results indicate little substitution and a close approach to stoichiometry (Table 1, No. 4).

Lazulite

Lazulite occurs as small, irregular polycrystalline patches and veins throughout the rock. It is relatively Fe-rich (Table 2, Nos. 1-3), with measured $100\text{Mg}/(\text{Mg} + \text{Fe})$ values in the range 65-76 (av. 72). Trace amounts of Ti (0.03-0.09 wt. % TiO_2) and Mn (0.05-0.25 wt. % MnO) also are present. Included in the lazulite are small blebs of scorzalite up to 0.03 mm in diameter, which have variable $100\text{Mg}/(\text{Mg} + \text{Fe})$ values in the range 4.0-26.7 (av. 15.5; Table 2, Nos. 4-6). These blebs may be exsolution features and strongly suggest, contrary to previous suggestions (Abernathy & Blanchard 1982), that there is a miscibility gap in the lazulite - scorzalite solid-solution series. To further test this possibility, specimens of lazulite-scorzalite from three other localities were examined with the electron microprobe. The compositions of lazulite from Rapid Creek, Yukon (Table 2, No. 7) and Werfen, Austria (Table 2, No. 8) are homogeneous in terms of Fe and Mg, but fall outside the proposed miscibility gap. However, microprobe data on a specimen of scorzalite from the Victory mine, South Dakota (Table 2, Nos. 9, 10) again appear to support a miscibility gap. In this case, very pale blue and faintly pleochroic scorzalite [$100\text{Mg}/(\text{Mg} + \text{Fe})$ in the range 20.6-24.2] is the major phase, but it contains small inclusions and outgrowths up to 0.1 mm across of deeper blue and strongly pleochroic Fe-rich lazulite [$100\text{Mg}/(\text{Mg} + \text{Fe})$ in the range 52.1-57.5]. The boundary between the Mg-rich and Fe-rich phases is extremely sharp, and intermediate compositions are not resolvable even with a finely focused electron beam.

Experimental data on intermediate members of the series apparently are unavailable, but equivocal support for the presence of a gap is offered by available analyses of lazulite and scorzalite (Meyers 1948, Pecora & Fahey 1950, Palache *et al.* 1951, Campbell 1962, Fransolet 1975, Abernathy & Blanchard 1982), which show a paucity of intermediate $100\text{Mg}/(\text{Mg} + \text{Fe})$ values. Indeed, the data of Abernathy & Blanchard (1982) show a clear gap in $100\text{Mg}/(\text{Mg} + \text{Fe})$ over the range 33-63. Furthermore, all previously published data have been obtained by wet-chemical methods, and the possibility of fine-scale heterogeneity being more widespread cannot be discounted. The presence of separate Mg-rich and Fe-rich phases is easily overlooked in thin section, in spite of moderate differences in index of refraction and possibly pleochroism. Further data on intermediate members of the series are clearly desirable, especially since, if con-

firmed, such miscibility in an Fe^{2+} -Mg isomorphous series is highly unusual, if not unique.

Variscite

Turbid areas of commonly fibrous variscite comprising up to 30 vol. % of the phosphate-bearing rocks appear to replace earlier Al-phosphates (augelite and trolleite). For example, embayments and fractures in some large augelite grains are infilled with the fine-grained variscite. Elsewhere, several ragged patches of optically continuous augelite are totally enclosed in the variscite. On the basis of this textural evidence and the usual low-temperature paragenesis of variscite, it is assumed to be of later, lower-temperature origin than the other phosphates.

Rutile

Rutile is widespread in the phosphate-bearing rocks as a minor phase, but is also concentrated in small, highly irregular veinlets and occurs as euhedral inclusions in quartz. The specimens studied here are less quartz-rich than those described from Mount Perry by Putnis & Wilson (1978), but analyses confirm the iron-rich compositions they reported and also indicate that a small but consistent amount of Nb (av. 0.08 wt. % Nb_2O_5) is present. However, the analyses failed to reproduce the high levels of Si and V reported by Putnis & Wilson (1978). Their analyses were obtained by energy-dispersion microprobe analysis, and the reported high V contents (0.28-1.25 wt. % V_2O_5) almost certainly result from overlap of the $\text{TiK}\beta$ and $\text{VK}\alpha$ peaks. The superior resolution of wavelength-dispersion analysis allows better correction for this overlap. The new data suggest that the high levels of V reported by Putnis & Wilson (1978) are in error. Similarly, failure to reproduce the high reported Si contents (up to 1.28 wt. % SiO_2) supports their suggestion that these are the result of fluorescence from surrounding quartz grains.

Zircon

Zircon is relatively common in the phosphate-bearing rocks as small euhedral prisms up to 0.1 mm in length, usually associated with rutile or included in quartz.

Topaz

Topaz is irregularly distributed but locally very abundant as a fine-grained (<0.1 mm) granoblastic aggregate with minor rutile, quartz and phosphates.

DISCUSSION

The silicate-phosphate assemblage at Mount Perry

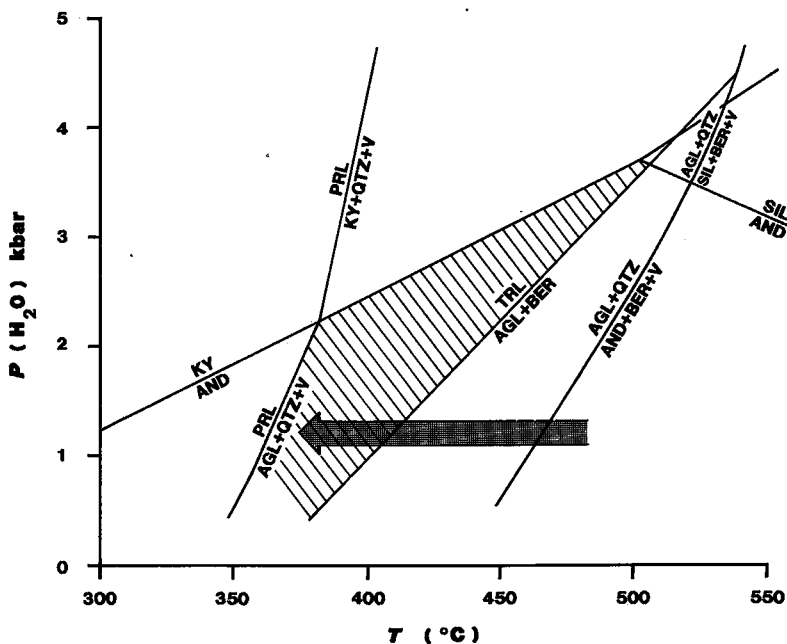
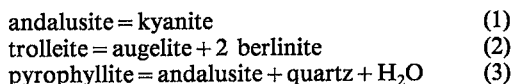


FIG. 2. $P(\text{H}_2\text{O})$ - T diagram for the system Al_2O_3 - SiO_2 - AlPO_4 - H_2O with excess SiO_2 , modified from Wise & Loh (1976) and incorporating data from Robie *et al.* (1978) and Bass & Sclar (1981). Mineral abbreviations: And andalusite, Agl augelite, Ber berlinite, Ky kyanite, Prl pyrophyllite, Qtz quartz, Sil sillimanite, Trl trolleite, V vapor. Univariant curves for $\text{And} = \text{Ky}$, $\text{And} = \text{Sil}$ and $\text{Ky} = \text{Sil}$ are from Holdaway (1971); the $\text{Prl} = \text{And} + \text{Qtz} + \text{V}$ and $\text{Prl} = \text{Ky} + \text{Qtz} + \text{V}$ curves are from Haas & Holdaway (1973).

is strikingly similar to that described from the Champion mine, White Mountains, California, where the minerals also occur in faulted and hydrothermally altered metavolcanic rocks (Wise 1977). Such unusual concentrations of Al-silicates (andalusite, pyrophyllite, topaz) and Al-phosphates (lazulite, augelite, trolleite) are believed to form by the action of voluminous highly acidic fluids (hydrogen metasomatism: Wise 1975). This proposal is consistent with the geological setting of the Mount Perry deposit, which occurs in hydrothermally altered andesites intruded by Triassic high-level granites and microgranites.

If the silicate-phosphate association represents an equilibrium assemblage, then experimental data can constrain the P - T regime under which it formed. Stability relations in the system Al_2O_3 - P_2O_5 - H_2O were determined by Wise & Loh (1976), but reactions involving excess silica have not been studied experimentally. However, Wise & Loh (1976) calculated a P - T diagram for the relevant portion of the system Al_2O_3 - SiO_2 - AlPO_4 - H_2O using available thermodynamic data and their data on the system Al_2O_3 - P_2O_5 - H_2O . A revised version of this diagram is presented in Figure 2. The position of the univar-

iant curves has been determined using thermodynamic data from Wise & Loh (1976), Bass & Sclar (1979) and Robie *et al.* (1978) by solving equation (8) of Fisher & Zen (1971) for P at various values of T . The stability field of the assemblage augelite-trolleite-andalusite-quartz is restricted to the hatched area of the diagram, *i.e.*, the area bounded mainly by the reactions



Preservation of traces of berlinite as inclusions in quartz suggests that the P - T regime initially involved somewhat higher temperatures (to the right of the univariant curve for reaction 2). The common occurrence of trolleite as small round granules closely associated with augelite is consistent with its formation by reaction of berlinite and augelite during (isobaric?) cooling from these higher temperatures. However, textural evidence does not discount conclusively the possibility that augelite and trolleite formed simultaneously during the main metasomatic episode.

A lower-temperature limit of the assemblage may be deduced from the presence or absence of pyrophyllite, which breaks down to andalusite + quartz + H₂O above 360–380°C (Haas & Holdaway 1973). Pyrophyllite is not present in the specimens studied here but does occur elsewhere in the phosphate-bearing zone at Mount Perry (Putnis & Wilson 1978), so that final equilibration of the assemblage probably involved temperatures not much above that of pyrophyllite breakdown. A best estimate of the temperature of formation is therefore in the range 380–450°C. Total pressure and $P(\text{H}_2\text{O})$ are more difficult to estimate, but the presence of andalusite and absence of kyanite provide an upper limit of about 3.8 kbars (Holdaway 1971). However, given the relatively high-level nature of the associated intrusive activity, the products of which are dominated by porphyries and high-level granites, $P(\text{total})$ and $P(\text{H}_2\text{O})$ were probably substantially less than this value and are unlikely to have exceeded about 2 kbars.

No data are available on the stability of gatumbaite, but the type occurrence in a pegmatite and its close association with augelite and trolleite at Mount Perry indicate that it is also a relatively high-temperature phosphate. Note that its presence is not recorded in experiments at 200°C and about 17 bars $P(\text{H}_2\text{O})$ in the water-saturated portion of the system CaO–Al₂O₃–P₂O₅–H₂O (Yuh & Rockett 1981).

Members of the lazulite–scorzalite series are stable to relatively high temperatures. At 2 kbars, and an $f(\text{O}_2)$ controlled by the Ni–NiO buffer, lazulite breaks down at 635°C and scorzalite at 515°C (Wise & Loh 1976).

In summary, field and petrographic data on the Mount Perry silicate–phosphate assemblage, and published experimental data on the system Al₂O₃–P₂O₅–H₂O, are consistent with an origin by hydrothermal alteration of volcanic rocks, initially at relatively high temperatures (450–500°C), followed by (isobaric?) cooling along a P – T path such as that indicated by the broad arrow in Figure 2. The hydrothermal solutions were highly acidic and apparently carried relatively high concentrations of P and F, leading to development of the Al-phosphates and topaz. Lower-temperature alteration of the assemblage was restricted to limited breakdown of the high-temperature phosphates to variscite.

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