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Relationship among metamorphic grade, vesuvianite “rod polytypism,” and vesuvianite composition

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ABSTRACT

Single-crystal X-ray study of different vesuvianite samples of known origin shows that different metamorphic grade results in different arrangements of structural rods oriented parallel to the vesuvianite **c** axis, interpreted as “rod polytypism.” There is a systematic dependence of space-group symmetry and rod arrangement on crystallization temperature: *P*4*nc*-dominant < 300 °C, *P*4/*n*-dominant ~300–500 °C, and *P*4/*nnc* > 500 °C. Partial occupancy of the T sites (B, Al, Fe^{3+}) and increased F-content seem to stabilize rod disorder causing *P*4/*nnc* space-group symmetry. All studied vesuvianites in calcsilicate rocks and marbles from regional- and contact-metamorphic upper amphibolite facies have disordered rods (*P*4/*nnc* symmetry). Electron-microprobe analyses of metamorphic vesuvianites from alpine and non-alpine occurrences, supported by structural investigation, showed that in addition to homo- and heterovalent substitution, partial occupancy of the commonly vacant T sites by B, Al, or Fe^{3+}, and the $(O_4H_4)^{4-} \rightarrow SiO_4^{4-}$ (hydrogarnet-type) substitutions are significant in nature. With few exceptions, T-site occupancy seems to be restricted to high-grade metamorphic rocks whereas the “hydrovesuvianite” substitution is only found in vesuvianites formed at very low metamorphic grade. The cell parameters of vesuvianite with empty T sites increase with increasing Ti + Mg → 2 Al substitution, and this increase is even more pronounced with increasing “hydrovesuvianite” component. An increase in boron on T sites leads to a decrease of *c* but an increase in *a*. Fluorine incorporation and T-site substitution (B, Al, Fe^{3+}) in vesuvianite are coupled with a decrease in hydroxyl groups. This causes vesuvianites to be stable under higher X_{CO_2} conditions, and in an assemblage with quartz at conditions above the experimentally determined upper stability of quartz + T site vacant, F-free vesuvianite. Optically anomalous vesuvianites have ordered rods and are generally characterized by an intergrowth of *P*4/*n* and *P*4*nc* domains. In addition to B-rich vesuvianite and wiluite, *P*4*nc*-dominant vesuvianites are also commonly optically positive.

Keywords: Analysis, chemical (vesuvianite), crystal structure, metamorphic petrology, polytypism

INTRODUCTION

Vesuvianite is a widespread rock-forming mineral originally described by Werner (1795) from dolomitic xenoliths in lavas of Mt. Vesuvius, Italy. The euhedral-shaped tetragonal crystals and their optical complexity attracted the interest of mineralogists, and led to detailed investigations of its chemical composition and optical properties (e.g., Gädeke 1938). The optical appearance of vesuvianite varies considerably. The mineral commonly displays green or brown hues, but it may be colorless or yellow, lilac, pink, red, blue-bluegreen, and nearly black. The mineral is found in zeolite- to granulite-facies rocks. It occurs in rodingite and metarodingite, contact aureoles and skarns, and in regional metamorphic calcsilicate rocks, but has not been reported in blueschist- or eclogite-facies rocks. Vesuvianite also characteristically forms under late-magmatic (or metasomatic) conditions in silica-undersaturated nepheline syenites (Kononova 1961; Arem 1973; Himmelberg and Miller 1980; Fitzgerald et al. 1987). Because its crystal structure can accommodate variable amounts of di- and trivalent cations, vesuvianite is stable under reducing and oxidizing conditions (e.g., Olesch 1979). A list of metamorphic minerals occurring in association with vesuvianite under different metamorphic conditions is given in Table 1.

CRYSTAL STRUCTURE AND “ROD POLYTYPISM” IN VESUVUVIANITE

The basic crystal structure of *P*4/*nnc* vesuvianite has been known since Warren and Modell (1931), and was later refined by Arem and Burnham (1969), Coda et al. (1970), and Rucklidge et al. (1975). The mineral formula of vesuvianite remained uncertain until the studies of Hoisch (1985) and Valley et al. (1985), who showed that one common natural end-member has the formula $Ca_{19}Mg_2Al_{11}Si_{18}O_{68}(O)(OH,F)_9$. Allen and Burnham (1992) discussed crystal-chemical factors why another theoretical end-member, $Ca_{19}MgAl_{12}Si_{18}O_{68}(O)_2(OH,F)_8$, cannot be stable. Groat et al. (1998) redefined a B-rich mineral isostructural with vesuvianite as *wiluite*, $Ca_{19}Mg_6Al_7B_5Si_{18}O_{68}(O)_{11}$ [hypothetical end-member assuming the substitutions: $^{T1}B + {}^{Y}Mg + 2{}^{W}O \leftrightarrow {}^{T1}\square + {}^{Y}Al + 2{}^{W}(OH)$ and $^{T2}B + 2{}^{W}O \leftrightarrow {}^{T2}\square + {}^{W}(OH)$]. Its structure contains 10 T sites per unit cell (5 per formula unit) occupied

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TABLE 1. Minerals associated with vesuvianite

Low grade (<300 °C)	Medium grade (~300–500 °C)	High grade (>500 °C)
hydrogarnet (CaAl-$CaFe^{3+}$ series)	**grossular** ("hessonite")	**grossular**
xonotlite (wollastonite)	**diopside**	**diopside**
natrolite-thomsonite	**Mg-chlorite**	**wollastonite**
pectolite	**prehnite**	**calcite**
calcite	**epidote**	**monticellite**
	calcite	**melilite**
		quartz
(±kirschsteinite, glaucochroite, aegirine, åkermanite, plombierite-tobermorite group, hydromagnesite, vuagnatite)	(±albite, titanite, apatite, dolomite, perovskite, zircon)	(±spinel, epidote, plagioclase, zoisite)
surrounding serpentinites consist of chrysotile/lizardite ± brucite	surrounding serpentinites contain antigorite	surrounding peridotites contain olivine, enstatite, anthophyllite, and spinel

TABLE 2. Common (bold) and less common (plain) site occupation in vesuvianite

X_{18}	X′	Y_{12}	Y′	T_5	${}^{O}Z_{10}$	${}^{D}Z_8$	O_{68}	$(W)_{10}$
Ca	**Ca**	**Al**	**Al**	□	**Si**	**Si**	**O**	**OH**
	Na	**Mg**	**Fe^{3+}**	**B**	**H_4**			**F**
	K	**Fe^{2+}**	**Cu^{2+}**	Al				**O**
	Ba	**Fe^{3+}**	**Mn^{3+}**	Fe^{3+}				Cl
	Sr	**Mn^{2+}**	Mg	Mn^{3+}?				
REE	REE	**Mn^{3+}**	Fe^{2+}	Mg?				
U	U	**Ti**	Mn^{2+}					
Th	Th	Zn	Ti					
Pb	Pb	Cr	Zn					
Bi	Bi		Cr					
Sb	Sb							
□	□							
[7-9]	[7-9]	[6]	[5]	[3-4]	[4]	[4]		

Notes: Numbers in square brackets indicate coordination. Note that the T site is commonly vacant, and that only the 10 SiO_4 (orthosilicate) groups can be replaced by H_4O_4.

by B. These T sites are vacant in "common" vesuvianite but may contain minor Al, Fe^{3+}, or B (Groat et al. 1994a, 1994b). Armbruster and Gnos (2000a) and subsequently Galuskin et al. (2003a) showed that the orthosilicate groups in the vesuvianite structure may be partially replaced by H_4O_4, a substitution common in the garnet-hydrogarnet solid-solution series. A Mn-rich vesuvianite (Armbruster and Gnos 2000a; Armbruster et al. 2002) was defined as the new mineral species *manganvesuvianite* and Britvin et al. (2003) defined a new *fluorvesuvianite* end-member. Hence, the general formula for vesuvianite-group minerals can be written as $X_{18}X'Y_{12}Y'T_5{}^{O}Z_{10}{}^{D}Z_8O_{68}(W)_{11}$, where "O" and "D" stay for ortho- and disilicate groups. W sites represent (OH, F, O) positions not bonded to Si. Vesuvianites with empty T sites have 10 W, whereas vesuvianites with triangular-coordinated B on T2 have 11 W sites due to the substitution ${}^{T2}B + 2{}^{W}O \leftrightarrow {}^{T2}\square + {}^{W}(OH)$ (Groat et al. 1996). The sites X' and Y' denote positions within structural rods discussed below. A compilation of possible site occupancies for vesuvianite group minerals is given in Table 2.

The aberrant optical properties of some specimens (e.g., uniaxial and biaxial sectors in the same crystal), and the fact that some crystals are piezoelectric, led to speculations about the true symmetry of vesuvianite. Arem and Burnham (1969) noted symmetry-forbidden reflections indicating lower space-group symmetry than *P*4/*nnc* for some vesuvianites. Giuseppetti and Mazzi (1983), followed by many others, refined crystals successfully in space group *P*4/*n* and these authors also noted that vesuvianite apparently may crystallize with *P*4*nc* space-group symmetry (acentric, piezoelectric). Only recently have Ohkawa et al. (1994) and Armbruster and Gnos (2000b, 2000c) successfully refined vesuvianites with *P*4*nc* symmetry.

Critical to understanding the three different vesuvianite structures are channel-like rods oriented parallel to the **c** axis. The structure of vesuvianite may be envisioned as a polyhedral framework of simplified $[Ca_{18}MgAl_{11}Si_{18}O_{68}(OH,F)_8]^{1-}$ composition. This negatively charged framework has channels extending along the fourfold axes. The channel occupants (Ca, Mg, O, OH) are ordered to rods composed of eight-coordinated X' (Ca) and five-coordinated Y' (Mg) sites where O atoms on the channel wall act as coordinating anions. Extraframework O and OH are laterally fixed by Ca on X3, which is part of the polyhedral framework. In addition, the apex of the tetragonal Y' pyramid is formed by extraframework O. Due to the short distances between two adjacent X' or Y' sites, occupied sites alternate with vacant sites. Thus a rod has either $Y'\square X'\square$ or $\square X'\square Y'$ sequence. The topology of the polyhedral framework allows both varieties. Each rod represents a polar arrangement of X' and Y' coordination polyhedra, and each rod itself may be fully ordered. Adjacent rods follow either some specific order patterns leading to decreased symmetry (*P*4/*n* or *P*4*nc*) or they are long-range disordered (*P*4/*nnc*). These various arrangements can be described as "rod polytypism" (Armbruster and Gnos 2000b) following an extended definition of polytypism suggested by Angel (1986). Many vesuvianites have a mixed "rod polytype" structure. All "rod polytypes" have in common that they have identical next nearest neighbor distances. Theoretically, there is an indefinite number of possible different "rod polytypes" distinct either in space-group symmetry or in translation (super-structures). A simple way to visualize "rod polytypism" in vesuvianite is to trace the orientation of the apices of the tetragonal Y' pyramids within one rod (Armbruster and Gnos 2000b). These apices may point either all in the up or down direction. If all apices in adjacent rods point in the same direction the structure is acentric, and the space-group symmetry is *P*4*nc*. If apices in adjacent rods point in the opposite direction the structure is centro-symmetric, and the space group is *P*4/*n*. If adjacent rods have random polarity, the space-group symmetry becomes *P*4/*nnc*. One may easily imagine more complex "rod polytypes" by more complicated order patterns among adjacent rods, or domain formation of different "rod polytypes" (e.g., Veblen and Wiechmann 1991; Allen and

Burnham 1992; Groat et al. 1993; Groat and Hawthorne 1998). Rod arrangement does not alter with subsequent heat treatment of the crystal in lab experiments (Allen and Burnham 1992). The interstitial T2 site, which may be occupied by B, is also located in the rods (Groat et al. 1994b, 1996; Ohkawa et al. 1994).

Vesuvianites with space groups *P*4*nc* or *P*4/*n* are characterized by additional very weak X-ray single-crystal reflections occurring in addition to the basic *P*4/*nnc* reflections (e.g., Allen and Burnham 1992; Armbruster and Gnos 2000b, 2000c). In all low-symmetry vesuvianite structures studied by us (Armbruster and Gnos 2000a, 2000b, 2000c), *P*4*nc* and *P*4/*n* "rod polytypes" occur within the same crystal in different ratios. In rare cases, one "rod polytype" is dominant allowing structure refinement. Possible domains with random rod orientation (space group *P*4/*nnc*) intercalated with domains of ordered rods (space group *P*4/*n* or *P*4*nc*) cannot be identified by single-crystal X-ray experiments because disordered rods lack any distinctive diffraction characteristics. On the other hand, identification of pure *P*4/*nnc* vesuvianite is straightforward by single-crystal X-ray methods (no additional weak reflections). Standard powder X-ray diffraction is not an adequate tool to study "rod polytypism" in vesuvianite because the additional *P*4*nc* and *P*4/*n* characteristic reflections are too weak to be monitored (Arem and Burnham 1969; Armbruster and Gnos 2000b).

The aim of this study is to show (1) how vesuvianite "rod polytypes" and metamorphic grade and/or vesuvianite composition are related, and (2) why vesuvianite in metacarbonates should not be used as an index mineral for high H_2O-activity but rather as an indicator for partial T-site occupancy (B, Al, Fe^{3+}) and/or significant F → OH replacement. Both substitutions are coupled with a reduced OH content.

SAMPLE DESCRIPTION

For this study, we mainly selected rock-forming vesuvianites from the Alps to have a control on the conditions reached during regional-scale metamorphism (e.g., Frey et al. 1999). In addition to samples from our private collection, we used material from the collections of the former Mineralogical Institute, University of Berne, and the Natural History Museum-Berne. Our set contains assemblages covering a range from very low metamorphic grade to upper-amphibolite facies, and it also includes samples from alpine fissures (e.g., Stalder and Aufdenblatten 1995; Keusen 1972). For additional tests we selected vesuvianite from other areas, including samples from contact aureoles, and a wiluite sample from the Siberian type locality. Sample localities and assemblages are listed in Table 3[1] and grouped into vesuvianites from (1) serpentinites and metaserpentinites, (2) metacarbonates and calcsilicate rocks, (3) contact aureoles and skarn deposits, (4) hydrothermal deposits, and (5) samples without X-ray data.

EXPERIMENTAL METHODS

Cell parameters of vesuvianite were determined with an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer with graphite monochromatized Mo$K\alpha$ X-radiation. Cell dimensions were refined from the angular settings of 18 reflections with $18 < \Theta < 29°$. The accuracy of cell dimensions refined from high-angle reflections collected with a four-circle diffractometer with point detector is superior to measurement with an area-detector although the precision may be similar (Herbstein 2000).

A Siemens SMART three-circle diffractometer (Mo$K\alpha$ X-radiation) with a CCD detector was used for collection of intensity data. Special care was taken for weak reflections and systematic absences sensitive to the three different "rod polytypes." A listing of reflections used for estimating the amount of each "rod polytype" present in a crystal is given in Armbruster and Gnos (2000b, 2000c).

Vesuvianite fragments from the same crystals as used for the single-crystal experiment were analyzed on a Cameca SX-50 microprobe using beam conditions of 15 kV and 20 nA, a spot size of ca. 10 μm, wavelength-dispersive spectrometers, and natural or synthetic mineral standards. Analysis conditions are the same as reported by Armbruster and Gnos (2000a, 2000b).

RESULTS

"Rod Polytypism"

The amount of each "rod polytype" present in a vesuvianite crystal is estimated from the weak reflections characteristic for each rod stacking-variety (Armbruster and Gnos 2000b) and listed in Table 3. Generally more than one fragment of the same crystal was investigated. *P*4*nc* and *P*4/*n* domains are coexistent in all low-temperature vesuvianites. For the alpine occurrences (Fig. 1), we plotted our results as "polytype cakes" on the metamorphism map of the Alps (Frey et al. 1999) where the cake sectors represent the relative concentrations of different "rod polytypes." Note the correlation of *P*4*nc*-dominant vesuvianites with very low-grade metamorphic areas, *P*4/*n*-dominant vesuvianites with greenschist-facies parts, and *P*4/*nnc* "rod polytypes" with amphibolite-facies areas.

Alpine fissures may form over a range of metamorphic conditions. This is reflected by the samples (4, 6, 7, 8, 14) from Zermatt-Saas and Fleschalp (Table 3). Part of these hydrothermal vesuvianites formed during a late stage of alpine metamorphism and thus at lower-grade metamorphic conditions than the peak-metamorphic condition depicted by the map. The Fleschalp fissure sample (8) has a *P*4/*n*-dominated structure in an area where peak alpine temperatures suggest *P*4/*nnc* vesuvianites (Fig. 1 and discussion below). Vesuvianite found in upper amphibolite-facies gabbroic metarodingites displaying a flaser texture at Alpe Albion (9 in Table 3) could not be studied by single-crystal X-ray techniques because this material is very fine-felted ("californite") suggesting pseudomorphs after an undetermined mineral. This is apparently the same material as was described by Gannser and Dal Vesco (1962). The anomalous interference color in thin section and comparison with similar occurrences suggest a *P*4/*n* or *P*4*nc* "rod polytype" formed at temperatures below ~500 °C.

Out of the *P*4/*nnc* "rod polytypes" in Figure 1, only the sample from Claro (17) formed during alpine metamorphism. The Innertkirchen (18) and Erstfeldertal (16) vesuvianites belong to prealpine assemblages. Moreover, most *P*4/*nnc* vesuvianites in high-grade metamorphic carbonates contain B or other trivalent cations on the T1 and T2 sites, and many show increased F content (Table 4)[1]. In particular, the *P*4/*nnc* samples from the Alps (16, 17, and 18) have about 1 wt% F. Combining our results with

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[1] Deposit item AM-06-017, Tables 3 and 4. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

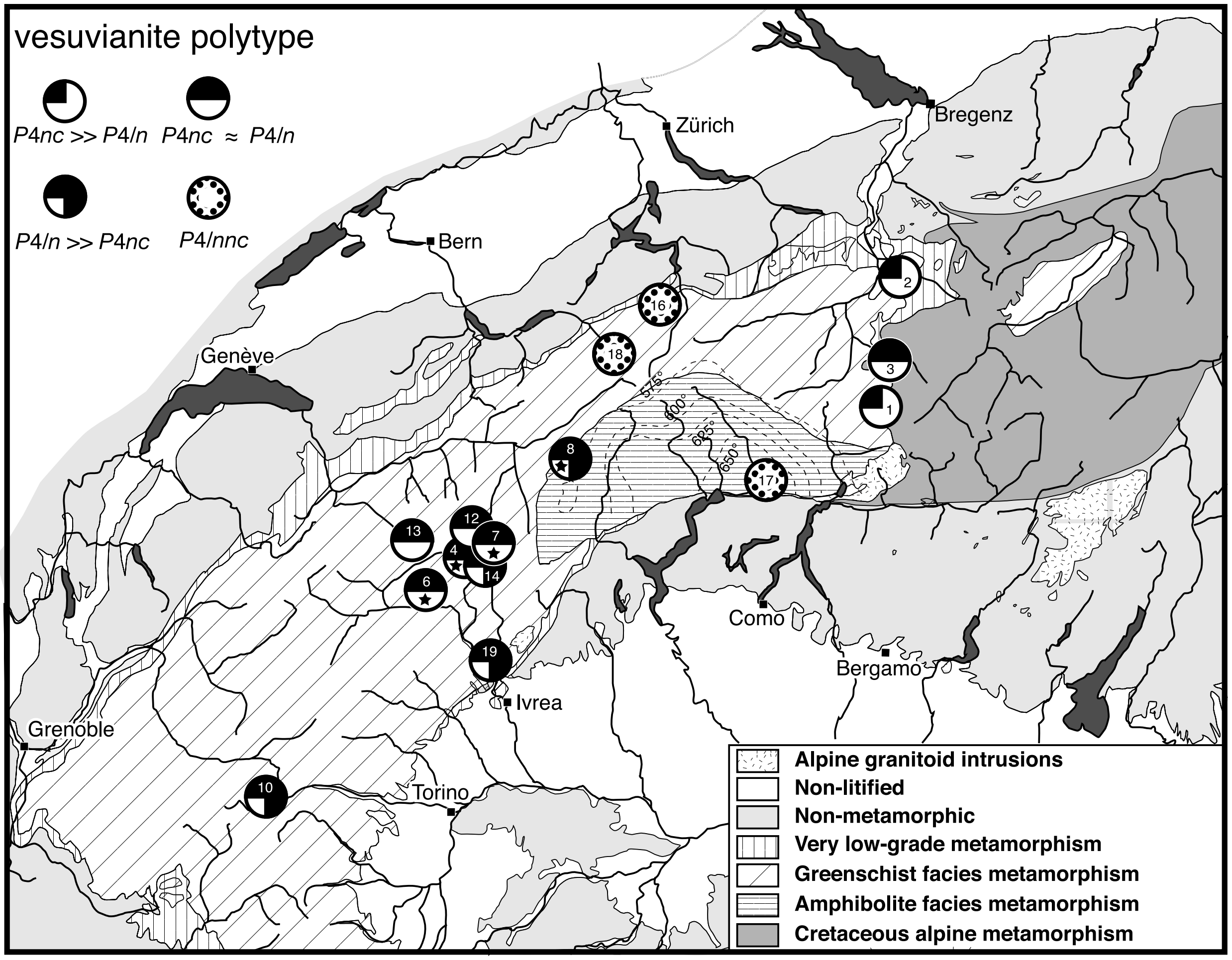

FIGURE 1. Metamorphic map of the Alps based on Frey et al. (1999) with vesuvianite polytypes obtained in this study displayed. Note the trend from *P4nc* to *P4/n* and *P4/nnc* polytype dominance with increasing alpine metamorphic grade. Number 16 and 18 are located in pre-alpine upper amphibolite-facies areas. Number 19 represents a skarn deposit where the metamorphic grade is not well known. The samples marked with a star are from alpine fissures. All numbers as listed in Table 3.

the data from Groat et al. (1994a, 1994b), it becomes clear that occupancy of T sites at crystallization temperatures below ~500 °C seems very rare (but see Galuskin et al. 2003a). Occupancy of T sites favors rod disorder resulting in space group *P4/nnc*. Although pure *P4/nnc* "rod polytypes" are widespread in nature, pure *P4/n* or *P4nc* vesuvianites are very rare (Table 3).

Vesuvianite composition

Deer et al. (1982) suggested normalization of wet-chemical analyses including (H_2O, Cl, and F) to 78 (O,OH,F). However, vesuvianite commonly shows zoning and, in such cases, wet-chemical analyses yield averages. Microprobe analyses of vesuvianite are usually normalized to 50 cations (Valley et al. 1985; Groat et al. 1992). The problem with this normalization is that H, B, and the oxidation state of Fe and Mn remain undetermined. In the case of H_4O_4 replacing SiO_4 (Armbruster and Gnos 2000b; Galuskin et al. 2003a), a normalization to 50 cations will statistically result in X cations > 19 apfu. If vesuvianites with a partial T-site occupany (B, Al, Fe^{3+}) (Groat et al. 1992, 1994a, 1994b) are normalized to 50 cations, it results in X < 19, Si < 18, and >13 Y-cations pfu. Low-grade metamorphic *P4nc* and *P4/n* vesuvianites have all 19 X sites occupied. Thus, in cases where H_4O_{4-} replacement in *P4nc* vesuvianites is indicated, analyses can be normalized to 19 X cations. High-grade metamorphic *P4/nnc* vesuvianites may have vacant X sites (e.g., Groat et al. 1994a) if interstitial T sites are partially occupied ("excess-Y"). For this reason, we normalized our *P4/nnc* vesuvianites to 18 Z sites (Table 4). All other analyses were normalized to 50 cations pfu.

In vesuvianite with vacant T sites ("ophiolitic" vesuvianites), the 13 Y sites available in the structure (e.g., 2 Mg and 11 Al) are occupied with cations having a total charge of 37 (or 2.85 average valence per cation). Titanium substitutes in the Y site by ${}^{Y}Ti + {}^{Y}M^{2+} \leftrightarrow 2\,{}^{Y}M^{3+}$, which leaves the total charge on the Y site unaffected. The total charge on the 13 Y sites may vary if the X sites are partially occupied by Na^+ or REE^{3+} (in addition to Ca). If the total charge on the 13 Y sites is 37, it is possible to estimate the amount of di- (*a*) and trivalent (*b*) iron pfu from

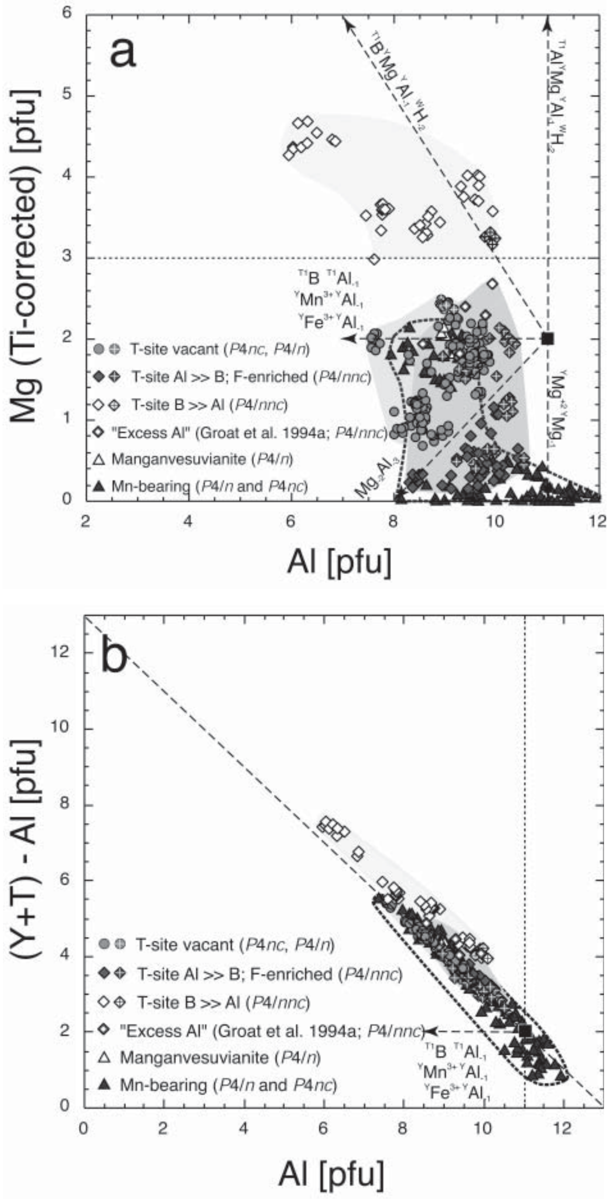

FIGURE 2. Discrimination diagrams allowing for separation of different vesuvianite groups. The black square marks $Ca_{19}Mg_2Al_{11}Si_{18}O_{68}(O)(OH,F)_9$ vesuvianite. Data points with plus signs indicate analyses for which no structural data are available in Table 3. See text for discussion. (**a**) Al–Mg diagram. All data are corrected for Mg necessary to charge balance Ti on the Y sites. Note the clear separation of B-rich (>1 B pfu) from B-free or B-poor vesuvianites. One group of Mn-rich vesuvianites plotting near the base of the diagram contains Mn^{2+} instead of Mg on the Y sites. The $Mg_{-2}Al_{-3}$ vector is for visual help only. (**b**) Al vs. (Y + T except B) – Al diagram allowing separation of T-site B-dominant from other *P4*/*nnc* vesuvianites.

the total charge $(M^{2+} + a) \times 2 + (M^{3+} + b) \times 3 + (Ti \times 4) = 37$ where $a(Fe^{2+}) + b(Fe^{3+}) = Fe_{tot}$ pfu. In case of Mn-bearing vesuvianites, the amount of Mn^{3+} can be estimated in a similar way if Fe^{3+} is not sufficient to charge balance the Y positions. T-site vacant vesuvianites show chemical ranges between 7–10 Al and 0.5–2.5 Mg pfu (Fig. 2a). Some Mn-rich vesuvianites plot near the base in this the diagram because they contain Mn^{2+} instead of Mg on the Y sites. Notice that Figure 2a does not account for Fe^{2+} replacing Mg.

Estimates of Fe^{2+} or Fe^{3+} are not possible from microprobe data for *P4*/*nnc* vesuvianites with partial T-site occupancy. Single-crystal structure refinements showed that two of three of our specimens from amphibolite or granulite-facies metacarbonates of the Alps (*P4*/*nnc* "rod polytypes"; Table 3) contain minor trivalent cations (commonly Al or B) on the T sites (Table 5).

Boron enters the T1 site of the vesuvianite structure by the coupled substitution $^{T1}B + {}^{Y}Mg + 2^{W}O \leftrightarrow {}^{T1}\square + {}^{Y}Al + 2^{W}(OH)$ (Groat et al. 1994b) and $^{T2}B + 2^{W}O \leftrightarrow {}^{T2}\square + {}^{W}(OH)$ (Groat et al. 1996). There are four tetrahedral T1 and one triangular T2 sites pfu, and only the larger T1 sites can also accommodate Al or Fe^{3+}. Boron-bearing vesuvianites can be easily recognized by plotting Al^{3+} vs. Mg^{2+} (Fig. 2a) as suggested by Groat et al. (1992). Plotting Al vs. (Y + T) – Al (Fig. 2b) also allows for a distinction of B-bearing and B-free vesuvianites from microprobe data because the more important B substitution on the four T1 sites is coupled with decrease of Al on the Y sites. Groat et al. (1994b) showed that the upper limit for M^{2+} on Y sites is 3 apfu if nine W sites are occupied by OH groups or F. All our B-dominated *P4*/*nnc* vesuvianites and wiluites [Laguna de Jaco (20) is a wiluite] plot above the Mg = 3 line indicating that the B substitution is coupled with replacement of OH by O on the W sites, and hence more than 3 M^{2+} on the Y sites are possible. To our knowledge, no B-rich vesuvianites (>1 B pfu) with Mg < 3 apfu is reported. This indicates that M^{2+} on the Y sites must be at least 3 apfu before more B can be incorporated. Thus, recognition of vesuvianites with B-dominated T-site occupancy (>1 B pfu) is straightforward.

Our electron-microprobe analyses of the samples with excess Y cations (>13) do not support the assumption of Groat et al. (1994a) that these vesuvianites with Al or Fe^{3+} as T1-site cations commonly show less than 19 X sites by normalizing the formula to 18 Si (Table 4). Our three basically B-free *P4*/*nnc* vesuvianites from the Alps (16, 17, 18) that contain little or no Al on the T1 sites (Table 5) plot below the virtual $Mg_{-2}Al_{-3}$ vector. The low Mg content of these samples in Figure 2a is balanced by Fe^{2+}. Essentially all Fe in these high-temperature vesuvianites is Fe^{2+} and all three samples have about 1 wt% F. Thus, recognition of such vesuvianites using microprobe results

TABLE 5. Boron and aluminium concentrations on the T sites in P4/nnc vesuvianites

No.	Sample	T1 (epfu)	T2 (epfu)	Sum T1 + T2 (epfu)	B_{max} X-ray (pfu)	B_{meas} spec (pfu)	Al_{diff} X-ray (pfu)
17	Claro 1, 2	–	–	0.0	–	0.02	–
18	Innertkirchen	5.0(2)	1.8(1)	6.8	1.36	0.08	0.52
16	Erstfeldertal	2.5(2)	–	2.5	0.50	0.05	0.17
20	Laguna de Jaco	8.5(2)	5.1(3)	13.6	2.72	2.63	0.03
21	Xalostoe	15.2(2)	4.8(2)	20.0	4.00	1.69	0.89
11	Sierra de los Cruces	12.9(1)	3.0(1)	15.9	3.18	1.33	0.71
23	Wiluy	15.3(2)	4.1(1)	19.4	3.88	3.69	0.07

Notes: Electrons per formula unit (Ca_{19})—if only B is considered the sum has to be divided by 5 to obtain B pfu (B_{max}X-ray). If only Al is considered as excess Y cation the sum has to be divided by 13. Al_{diff}X-ray is the calculated Al concentration on the T site per formula unit by difference to the spectrophotometrically obtained B concentration (B_{meas}spec) listed in Table 4. The numbers of the first column refer to Table 3.

is also easy. However, *P*4/*nnc* vesuvianites with high Al, Fe^{3+}, and B occupancy on the T1 sites may partially overlap with the field of "ophiolitic" *P*4*nc* and *P*4/*n* vesuvianites (Figs. 2a and 2b). Such vesuvianites commonly show nil to little X site vacancies. The dominant substitution, equivalent to the case for B, is $^{T1}Al + {}^{Y}Mg + 2^{W}O \leftrightarrow {}^{T1}\square + {}^{Y}Al + 2^{W}(OH)$ (Fig. 2a). All these vesuvianites are from contact aureoles in metacarbonates or regionally metamorphic metacarbonates or calcsilicate rocks. Although the chemical range of such vesuvianites may overlap in the diagrams shown in Figure 2 analyses normalized to 18 Si yield Y cation sums significantly above 13. Thus, knowledge of the provenance will additionally help to recognize them as vesuvianites with increased T1-site occupancy.

Boron contents of a few *P*4/*nnc* vesuvianites were also determined spectroscopically by Ruth Mäder, Institute of Geological Sciences, Berne, using the method of Fleet (1967). Results are listed in Table 5. Maximum B values for some vesuvianites were estimated from single-crystal structure refinements (Table 5). Our data corroborate the findings of Groat et al. (1992, 1994b) that B-bearing vesuvianites are common in nature.

Not all vesuvianite analyses listed in Tables 3 and 4 have structural data available. These analyses are also included in Figure 3 and we conclude that the samples Miask (30) and Egeran (27) are *P*4/*nnc* vesuvianites with low T-site occupancy. The samples Monzoni (25) and Vesuvius (22) are also *P*4/*nnc* vesuvianites with increased Al content on the T1 sites, and the sample Monzonialp (28) is a *P*4/*nnc* vesuvianite with increased Al on T1 and additionally >1 B pfu on the T sites. Vesuvianites (24, 26, 29) are considered having *P*4/*n*-dominant structures. Chemical analyses (Table 4) show that the samples Sierra de los Cruces (11), Xalastoe (21), and Monzonialp (28) have ca. 14 Y cations (1 Y excess).

Optical observations

Our microscopic study of the analyzed samples confirm that Fe^{2+} [e.g., Totalp (2), Stalvader (3), Val d'Ala (10)] or Fe^{3+} (e.g., Bela) (Armbruster and Gnos 2000b) in B-free or B-bearing vesuvianites produces green hues, Fe-poor Mg-Al vesuvianite is yellowish-olive or colorless, and Mn^{2+} or Mn^{3+} produce pink, orange, and red to black hues (Kalahari; Armbruster et al. 2002). A little Cu^{2+} causes a blue color (Fitzgerald et al. 1986; Groat et al. 1992) that is commonly masked by the Mn color (Armbruster and Gnos 2000a). In combination with Fe, the blue color changes to blue-green. Vesuvianites containing Ti and a little Fe^{3+} show brown hues [e.g., Pollux (6), Brosso (19), Claro (17), Innertkirchen (18)] whereas an emerald color is probably produced by small amounts of Cr [e.g., Miask (30)].

During this study we found that not all optically positive vesuvianites are B-rich (Groat et al. 1994b, 1998). Careful orthoscopic studies on the Totalp (2) samples confirmed the observation by Peters (1961) that this B-free material is optically positive. Moreover, the Bela vesuvianite (Armbruster and Gnos 2000b) is optically positive. Both crystals formed under low-temperature metamorphic conditions and are dominated by domains of space group *P*4*nc* (Table 3). Additionally, Giuseppetti and Mazzi (1983) also described another *P*4*nc* vesuvianite from Predazzo as optically positive. Interesting to note in this context is that in early studies on vesuvianite (e.g., Gädeke 1938; Winchell and Winchell 1951; Tröger 1952), the change in the optical character to positive was linked to an increased H_2O content (>2.5 wt%, according to Gädeke 1938). Unfortunately, such optically positive vesuvianites were called wiluit(e) or viluit, too. The mineral name wiluite is now correctly reserved for optically positive, B-rich vesuvianites (Groat et al. 1998) as characteristic for the Siberian type locality and other occurrences in contact aureoles.

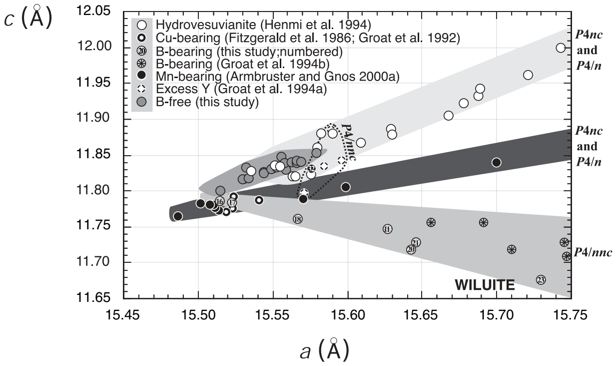

FIGURE 3. Vesuvianite cell parameters showing three main substitution trends. Note that Mn-bearing vesuvianites are similar to common vesuvianites unless a hydrogarnet substitution (32) is present. B-bearing vesuvianite and wiluite cell parameters clearly separate from vesuvianites containing only Al of Fe^{3+} on the T site. The B-rich vesuvianites (wiluite) and some of the *P*4*nc*-dominant vesuvianites are optically positive (see Table 3). Cell data defining the hydrovesuvianite trend (Henmi et al. 1994) were obtained by powder diffraction and need confirmation by single-crystal anlysis.

Many *P*4/*n*-dominated vesuvianites are optically anomalous showing interference colors varying from blue to brown. To our knowledge, such vesuvianites are always optically negative. Boron-poor *P*4/*nnc* varieties are optically negative, whereas B-rich varieties are optically positive (Groat et al. 1994b, 1998). Manganese-rich vesuvianites are also optically negative (e.g., Armbruster and Gnos 2000a; Armbruster et al. 2002).

Cell parameters

The cell dimensions of analyzed vesuvianites are listed in Table 3 and displayed graphically in Figure 3. Within the investigated data set, three different trends become obvious: (1) The titanium substitution ($^{Y}Ti + {}^{Y}M^{2+} \leftrightarrow 2^{Y}M^{3+}$; common vesuvianite trend in Fig. 3) on the Y sites causes the cell parameters to increase due to the coupled introduction of the larger Mg^{2+} and Fe^{2+} cations. This trend overlaps with the trend observed by Henmi et al. (1994) for vesuvianite showing "hydrovesuvianite"-type substitution. (2) Boron substitution [$^{T1}B + {}^{Y}Mg + 2^{W}O \leftrightarrow {}^{T1}\square + {}^{Y}Al + 2^{W}(OH)$ and $^{T2}B + 2^{W}O \leftrightarrow {}^{T2}\square + {}^{W}(OH)$] results in a decrease in the *c* cell dimension, but an increase of the cell volume (Groat et al. 1992; Fig. 3). We have additionally plotted cell parameters for vesuvianites containing Al and Fe^{3+} on the T1 sites (Groat et al. 1994a) to show that they can be distinguished from B-bearing varieties. (3) Manganese- and "hydrovesuvianite"-substituted vesuvianites (Armbruster and Gnos 2000a) define a separate "hydromanganese" trend. Manganese vesuvianites without "hydrovesuvianite" subsitution overlap with the trend for common vesuvianites (Fig. 3). However, the cell parameters for Cu-substituted vesuvianites (Fitzgerald et al. 1986; Groat et al. 1992) also overlap with the manganvesuvianite trend. This finding suggests that Jahn-Teller atoms with anisotropic electron configuration (e.g., Cu^{2+} and Mn^{3+}), occupying the five-coordinated Y' site (tetragonal pyramid), have a similar effect on unit-cell dimensions. U-Th-REE-rich vesuvianites commonly show metamictization, which renders cell-parameter interpretation difficult and hence such data are not included in Figure 3.

If the calculated formula from microprobe analyses is close to 50 cations or 19 X sites pfu (within analytical error), determination of accurate cell parameters is the most powerful approach to obtain indirect chemical information on vesuvianites, especially to estimate the B occupancy on the T sites.

DISCUSSION

Morphology and optical data

Vesuvianite crystals found in low-grade metamorphic assemblages tend to be long prismatic or fibrous. Probably all material called "californite" or vesuvianite "jade" belongs to the *P*4/*n* or *P*4*nc* "rod polytype." Pointed crystals as reported from rodingites in the Muslimbagh (Arem 1973; Ohkawa at al. 1994) and Bela ophiolites (Armbruster and Gnos 2000b) in Pakistan belong to the *P*4*nc*-dominated "rod polytype."

All known *P*4/*n* and *P*4*nc* vesuvianites have a mixed "rod polytype" structure, macroscopically expressed by striations parallel to **c** (domain boundaries?) on freely grown mineral surfaces, and show a complex habit. Freely grown *P*4/*nnc* vesuvianites, on the other hand, have simple first- and second-order unstriated prism and pyramid faces.

*P*4*nc* and *P*4/*n*-dominant "rod polytypes" tend to be optically anomalous and some *P*4*nc* vesuvianties may be optically positive, whereas *P*4/*n* vesuvianites are optically negative. Among *P*4/*nnc* vesuvianites, B-poor varieties are optically negative, but B-rich varieties and wiluites are positive.

Composition and normalization of electron-microprobe analyses

A larger set of microprobe data is generally needed to recognize statistically weakly "hydrogarnet"-substituted vesuvianites (Si < 18). The 50 cation normalization scheme can be used for common *P*4/*n* and *P*4*nc* vesuvianites (rodingite, metarodingites, some skarns, hydrothermal formation). Where formation conditions below 300 °C are expected (*P*4*nc*-dominant "rod polytype"), microprobe analyses should additionally be normalized to 19 X sites to recognize a possible "hydrovesuvianite" substitution (Si < 18). Significant Al replacing Si in vesuvianite has not yet been demonstrated (Groat et al. 1992). Vesuvianites from high-grade metamorphic rocks (>~500 °C; Fig. 4) have *P*4/*nnc* symmetry and commonly have >50 cations pfu due to partial occupancy on the T sites by B, Al, or Fe^{3+}. If T site occupany is mainly by B, this substitution, however, remains undetected in some cases if the mineral formula is normalized to 50 cations. Moreover, *P*4/*nnc* vesuvianites may also have vacancies on their X sites (Groat et al. 1994a). It is thus suggested that vesuvianite microprobe analyses from high-grade metamorphic rocks (metacarbonates and calcsilicate occurrences) always be normalized to 18 Si pfu to reveal vacancies on the X sites and Al, Fe^{3+}, B occupancy on the T sites. This procedure allows vesuvianites with >1 B pfu, Y-excess vesuvianites, and even vesuvianites with low T-site occupancy to be recognized (Fig. 2). T1 site Al, Fe^{3+}-rich vesuvianites show less than 3 Mg pfu whereas B-dominated vesuvianites (wiluite) show >3 Mg pfu. The major reason for this relationship is that the maximum Al occupancy on T1 in our data set is ca. 1 Al pfu whereas the samples Laguna de Jaco (20) and Wiluy (23) have 2.6 and 3.6 B pfu on T1 and T2.

"Hydrovesuvianite"-substituted vesuvianites seem to be restricted to low-temperature (<300 °C) rodingites and hydrothermal deposits, and to alterations where hydrogarnets are also common. They characteristically belong to the *P*4*nc*-dominated polytype and may be optically positive. Determination of high-accuracy vesuvianite cell dimensions (or volume) allows the B content of vesuvianite in metacarbonates to be estimated (Groat et al. 1992). For this purpose, unit-cell refinement from powder X-ray data is also suitable.

"Rod polytypes"

Allen and Burnham (1992) heated low-symmetry vesuvianite fragments up to 50 days at 1000 °C and concluded that rod order ("rod polytypism") is frozen in during growth and does not alter with the heat treatment. Tribaudino and Prencipe (2001) found no change in cation order or rod arrangement of a *P*4/*n* vesuvianite after prolonged heating at 1070 K and confirmed this observation. The systematic correlation between "rod polytype" predominance and metamorphic conditions under which they formed (Fig. 4) confirms that the "rod polytype" will not change.

Vesuvianite is not stable under blueschist to eclogite-facies conditions. For the vesuvianite formation of the Zermatt-Saas Fee and Val D'Ala areas, this finding implies that the vesuvianite-bearing calcsilicate assemblages and veins in the neighboring serpentinites containing vesuvianite may have formed during metasomatization (hydrothermal activity) under greenschist-facies conditions (post eclogite/blueschist) although the occurrences may represent recrystallized meta-rodingites.

All three vesuvianite "rod polytypes" can be present within the same contact aureole, as reported for Canzoccoli near Predazzo, Italy (Giuseppetti and Mazzi 1983; optical observations of Vogel 1888). The samples from thermal aureoles used

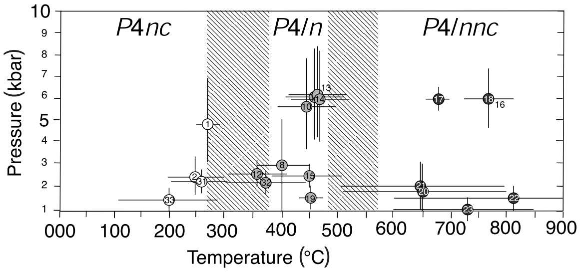

FIGURE 4. Vesuvianite polytypes plotted as functions of independent pressure-temperature estimates form the metamorphic map of the Alps (Frey et al. 1999) or from the literature listed in Table 3. Note the systematic change from *P*4*nc*-dominant to *P*4/*n*-dominant and *P*4/*nn*c structures with increasing temperature. 31, 32, and 33 are from Armbruster and Gnos (2000a, 2000b), all other numbers as in Table 3.

in this study do not allow reconstruction of the distance to the pluton. Based on results obtained for regional metamorphic occurrences, it seems likely that with increasing distance from the contact *P*4/*nnc*, *P*4/*n*-dominant and finally *P*4*nc*-dominant vesuvianites should be found. Retrograde vesuvianite replacing melilite in the highest-grade metamorphic part in contact aureoles is common.

It remains unclear whether rod disorder, as observed for high-temperature *P*4/*nnc* vesuvianite, is solely due to the elevated temperature or also due to the more complex chemical composition characteristic of this condition (partial T-site occupancy, increased F content). One may speculate that an inhomogeneous charge distribution within the polyhedral framework reduces cooperative interactions among adjacent rods. Corresponding arguments also hold for rods of variable composition (partial F substitution for OH, partial B occupancy on T2). Galuskin et al. (2003b) discussed the case of intra-rod disorder caused by partial F → OH substitution within the rods. Such vesuvianites have space group *P*4/*nnc* even though they formed below 350 °C.

The predominance of the acentric *P*4*nc* structure in which all rods show the same polarity observed for samples formed at the lowest metamorphic condition is not understood. We would rather expect equal probability of the *P*4*nc* and *P*4/*n* "rod polytypes" because of the very low energy differences between the two stacking variants. However, there is no doubt that at certain low-temperature vesuvianite-occurrences, the acentric *P*4*nc* "rod polytype" clearly prevails whereas for other occurrences, for which we estimate slightly higher metamorphic conditions, the centro-symmetric *P*4/*n* "rod polytype" is dominant.

Implications for metamorphism

Chatterjee (1962) and Braitsch and Chatterjee (1963) proposed the use of metamorphic assemblages containing vesuvianite as an index for metamorphic grade. Trommsdorff (1968) later discussed why the mineral reactions and assemblages proposed by the above authors were violating thermodynamic rules, and hence did not represent stable assemblages. Trommsdorff (1968) and Rice (1983) considered H_2O-rich fluids necessary for the formation of vesuvianite and wollastonite in calcsilicate assemblages. This is the reason why vesuvianite-bearing assemblages were commonly used as an indicator of fluids containing nil or very little CO_2. Experimental equilibrium data on Mg-Fe substituted vesuvianite (Olesch 1978, 1979; Hochella et al. 1982) and thermodynamic calculations (Valley et al. 1985; Plyusnina et al. 1992) have underlined its restriction to H_2O-dominated systems. The experimentally formed vesuvianites were probably all *P*4/*n* or *P*4*nc* "rod polytypes," similar to the natural material used by Tribaudino and Prencipe (1999, 2001) to obtain compressibility data. However, B (wiluite component) and Al or Fe^{3+} on the T sites (excess Y cations) are an important constituent in many vesuvianites (Groat et al. 1992, 1994a, 1994b, 1998). In particular, the fact that all our vesuvianites in metacarbonates have partially occupied T sites and/or high F contents (Table 5) needs discussion.

The critical vesuvianite-quartz association is known in amphibolite to granulite-facies calcsilicate rocks [780 ± 30 °C at 8 ± 1 kb (Valley and Essene 1979), 750 °C at 6 kbar (Bogoch et al. 1997), 650 ± 15 °C at 6 ± 0.5 kbar (Trommsdorff 1968)]. All these occurrences are well above the experimentally determined upper stability of ca. 480 °C for this assemblage. Quartz-free, upper amphibolite-facies occurrences associated with diopside, grossular, calcite, and wollastonite are know from regionally metamorphic migmatic terranes (e.g., Innertkirchen basement, Hügi 1955), contact aureoles (e.g., Predazzo-Monzoni), and xenoliths in volcanic rocks (e.g., Mt. Vesuvius). Vesuvianite in association with clintonite-monticellite (± åkermanite ± wollastonite) is also not uncommon (Larsen and Goranson 1932; Joesten 1974; Adams and Anderson 1979; Valley and Essene 1979). Because Mg-Fe vesuvianites break down to monticellite + melilite at temperatures below 750 °C (Christie 1961; Hochella et al. 1982), the stability field of many naturally occurring vesuvianites in metacarbonates probably is strongly enlarged by the presence of cations on the T sites, coupled with reduction of hydroxyl groups, and also by F replacing OH on the W sites. Notice that recently a new fluorvesuvianite end-member has been defined (Britvin et al. 2003).

Although natural metarodingite occurrences containing vesuvianite are compatible with the available experimental results, our data set suggests that vesuvianite solid-solutions with partially occupied T sites and/or increased F content may be responsible for an important enlargement of the stability field of vesuvianite and vesuvianite+quartz. Moreover, as the T-site occupancy is coupled with $^{W}O \rightarrow {}^{W}(OH)$ substitution, such vesuvianites are also stable under much lower X_{H_2O} conditions (higher X_{CO_2}). Attempts to estimate the effect of partial T-site occupancy by B, Al (or Fe^{3+}) on the stability of vesuvianite in the system CaO-MgO-Al_2O_3-SiO_2-B_2O_3-H_2O-CO_2 are presently hampered by the lack of thermodynamic data for non-stoichiometric *P*4/*nnc* and F-bearing vesuvianites. All investigated vesuvianites from metacarbonates have *P*4/*nnc* symmetry and have either excess Y cations (Al, Fe^{3+}), or B on the T sites, and/or are F-enriched. Experimental and solid-solution data for T site occupied and F-bearing *P*4/*nnc* vesuvianites seem thus necessary for calculating equilibria involving vesuvianite in metacarbonates and calcsilicate rocks.

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