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: \( P4nc \)-dominant < 300 °C, \( P4/n \)-dominant ~300–500 °C, and \( P4/nnc \) > 500 °C. Partial occupancy of the T sites (B, Al, Fe\(^{3+}\)) and increased F-content seem to stabilize rod disorder causing \( P4/nnc \) space-group symmetry. All studied vesuvianites in calcsilicate rocks and marbles from regional- and contact-metamorphic upper amphibolite facies have disordered rods (\( P4/nnc \) 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 \( \left[ O_5H_5 \right] \rightarrow SiO_4^4 \) 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 a 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 vesuvianite to be stable under higher \( X_{CO} \) 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 \( P4/n \) and \( P4nc \) domains. In addition to B-rich vesuvianite and wiluite, \( P4nc \)-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 disordered rods (~300–500 °C, and in an assemblage with quartz conditions, and in an assemblage with quartz non-ideal < 300 °C, dominant \( P4nc \)-dominant \( \left[ O_5H_5 \right] \rightarrow SiO_4^4 \) (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 a 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 vesuvianite to be stable under higher \( X_{CO} \) 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 \( P4/n \) and \( P4nc \) domains. In addition to B-rich vesuvianite and wiluite, \( P4nc \)-dominant vesuvianites are also commonly optically positive.

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CRYSTAL STRUCTURE AND "ROD POLYTYPISM" IN VESUVUINATE

The basic crystal structure of \( P4/nnc \) 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 \( \text{Ca}_{19}\text{Mg}_{6}\text{Al}_{7}\text{B}_5\text{Si}_{18}\text{O}_{68}(\text{O})_{11} \) [hypothetical end-member assuming the substitutions: \( ^{11}\text{B} + ^{11}\text{Mg} + 2^{0}\text{O} \leftrightarrow ^{11}\text{B} + ^{11}\text{Al} + 2^{0}\text{OH} \) (OH:F)\(_n\), Allen and Burnham (1992) discussed crystal-chemical factors why another theoretical end-member, \( \text{Ca}_{19}\text{Mg}_{12}\text{Al}_{11}\text{Si}_{18}\text{O}_{68}(\text{O})_{12} \) (OH,F)\(_n\), cannot be stable. Groat et al. (1998) redefined a B-rich mineral isostructural with vesuvianite as "wiluite," \( \text{Ca}_{19}\text{Mg}_{12}\text{Al}_{11}\text{Si}_{18}\text{O}_{68}(\text{O})_{12} \) [hypothetical end-member assuming the substitutions: \( ^{11}\text{B} + ^{11}\text{Mg} + 2^{0}\text{O} \leftrightarrow ^{11}\text{B} + ^{11}\text{Al} + 2^{0}\text{OH} \) (OH:F)\(_n\)]. Its structure contains 10 T sites per unit cell (5 per formula unit) occupied 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.