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# Na-rich vesuvianite in jadeitite of the Tawmaw jade district, northern Myanmar

THET TIN NYUNT°, THOMAS THEYE and HANS-JOACHIM MASSONNE\*

Institut für Mineralogie und Kristallchemie, Universität Stuttgart, Azenbergstr. 18, D-70174 Stuttgart, Germany ° present address: Department of Geology, University of Yangon, 11041 Yangon, Myanmar

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ABSTRACT - In general, vesuvianite occurs in lowpressure environments such as contact aureoles, rodingite/metarodingites, and skarns. We describe a new occurrence of vesuvianite in a high-pressure metamorphic jadeitite. The composition of this phase is characterized by up to 1.5 wt.% Na<sub>2</sub>O. This content is higher than those of vesuvianite from elsewhere. Sodium is introduced into vesuvianite mainly by the substitution Ca + Al = Na + Ti. Electron microprobe measurements demonstrate an oscillatory growth zoning with Na and Ti showing the largest variation. The formation of vesuvianite and its zonation are explained by an interaction with a hydrous fluid phase that is characterized by a continuous increase of the chemical potentials of Ti and Ca. This fluid phase accounts for the simultaneous crystallization of vesuvianite + jadeite and the subsequent replacement of jadeite by vesuvianite.

RIASSUNTO - La vesuvianite si rinviene in generale in ambienti di bassa pressione, come nelle aureole di contatto rodingite/metarodingite e negli skarns. In questo lavoro viene descritto il ritrovamento di vesuvianite in una jadeitite metamorfica di alta pressione. La composizione di questa fase è caratterizzata da un contenuto di Na<sub>2</sub>O fino al 1,5 % in peso, il più alto finora riscontrato nelle vesuvianiti di diverse località.

E-mail: h-j.massonne@mineralogie.uni-stuttgart.de

Il sodio è introdotto nella vesuvianite principalemente tramite la sostituzione Ca + Al = Na + Ti. Le analisi alla microsonda elettronica evidenziano una zonatura di crescita oscillatoria e le maggiori variazioni composizionali riguardano il Na e Ti. Sia la formazione che la zonatura chimica della vesuvianite possono essere spiegate attraverso l'interazione con una fase fluida idrata, caratterizzata da un continuo aumento dei potenziali chimici di Ti e Ca. Questa fase fluida permette la cristallizzazione simultanea di vesuvianite + jadeite e la conseguente sostituzione di jadeite con vesuvianite.

KEY WORDS: vesuvianite, jadeite, jadeitite, jade, highpressure metamorphism, northern Myanmar.

### INTRODUCTION

Myanmar is famous for its wealth of high quality jade which is the trade term for rocks mainly composed of either jadeite or amphibole (nephrite). These almost monomineralic jade rocks have typically been formed close to tectonically emplaced ultrabasic bodies by fluidrock interaction (so-called wall-rock formation). The Myanmar jade is almost exclusively composed of Na-pyroxene such as jadeite. Jadeitite deposits in Myanmar are generally

<sup>\*</sup> Corresponding author,

associated with major strike-slip fault systems and hosted in serpentinite bodies which occur in blueschist or eclogite terrains related to subduction or transpression (Harlow *et al.*, 2007; Shi *et al.*, 2008). In the present paper, vesuvianite, found in a peculiar high-pressure metamorphic jadeitite from Myanmar, is characterized and its formation is discussed.

Vesuvianite [as end member Ca<sub>19</sub>Mg<sub>2</sub>Al<sub>11</sub>Si<sub>18</sub>O<sub>69</sub>(OH)<sub>9</sub>] is previously known to occur exclusively in relatively low-pressure contact aureoles, formations such as rodingite/metarodingites, skarns, zeolite to granulite facies metamorphic calc-silicate rocks (e.g., Gnos and Armbruster, 2006; Bogoch et al., 1997), and as late formation in igneous rocks such as nepheline syenites (e.g., Fitzgerald et al., 1987). The formation of vesuviante in the blueschist or eclogite metamorphic facies, however, has never been reported before. Only recently, vesuviante has been described as a late-stage vein mineral crosscutting jadeitite from Guatemala (Sisson et al., 2005; Harlow et al., 2006). A further peculiarity of the vesuvianite in the Myanmar jadeitite is a high Na content, which is significantly higher than in vesuvianite from elsewhere.

#### GEOLOGICAL SETTING

The study area belongs to the Indo-Burman Ranges and is located in the western part of the Sagaing fault zone within the Central Burma Basin in the Pharkant (also Hpakan or Hparkant) -Tawmaw area, Kachin state, Northern Myanmar. The Sagaing fault is a major active strike-slip fault of Myanmar extending more than 1200 km with the Andaman spreading centre being its southern termination (Bertrand and Rangin, 2003). The occurrence of ophiolite and tectonic slices of glaucophane-bearing high-pressure metamorphic rocks at this fault in the Central Burma Basin and Indo-Burman Ranges generally results from collision and subduction processes between India and Asia (Swe, 1981; Mitchell, 1993; Hall, 2002; Vigny *et al.*, 2003; Shi *et al.*, 2008).

In some serpentinite blocks of the corresponding ophiolitic mélange, jadeitite is found as vein or dyke-like body (Chhibber, 1934). The size of the jadeitite bodies ranges from 1-10 m in width and 10-20 m in length. The boundaries of these bodies to the hosting serpentinized peridotite are marked by chlorite and/or actinolite schist (Shi et al., 2003). The jadeitite partly shows a transition to albitite. The occurrence of kosmochlor within the jadeitite and albitite also indicates that this mineral has been formed in a specific Cr-rich chemical environment.

*P-T* conditions for the metamorphism of a garnet-bearing mica schist, representing the country rock close to the jadeitite bodies in Tawmaw, were derived from thermodynamic calculations resulting in a high-pressure stage (16-19 kbar) at 470-540 °C (Nyunt, 2009). These *P-T* conditions could be also verified for a glaucophane schist, sampled close to a jadeitite body (Nyunt, 2009). As discussed by Harlow et al. (2007), jadeitite may have been equilibrated at somewhat lower *T* and *P*, compared to other high-*P* metamorphic lithologies of ophiolitic mélanges throughout the world.

Shi *et al.* (2008) performed U-Pb dating on zircons from the Myanmar jadeitite. Inner zircon zones with oscillatory zoning and inclusions of Mg-rich minerals with an age cluster of  $163.2 \pm 3.3$  Ma are interpreted to be related to the formation of oceanic crust and/or hydrothermal overprint (serpentinization, rodingitization). Another zircon zone with a mean age of  $146.5 \pm 3.4$  Ma shows inclusions of jadeite/sodic pyroxene. This zone was interpreted to have been formed at high-pressure conditions possibly related to subduction of the eastern Indian oceanic plate. However, the invoked old subduction event seems to be in conflict with the

younger collisional history.

Vesuvianite has been detected in just one of the studied jadeitites samples (MJ11) which were collected on a dump in the Tawmaw ophiolitic zone, close the jade mine near Tawmaw village, Myitkyina district, Myanmar.

#### Petrography

The vesuvianite-bearing sample MJ11 belongs to an almost monomineralic jade variety. The rock contains about 97 % of jadeite showing medium to fine grained granoblastic texture with grain sizes ranging from 0.05 to 3 mm. This heterogeneous grain size distribution reflects deformation, localized along shear planes, and subsequent fine-grained dynamic recrystallization of stressed crystals. Uneven extinction observed under the microscope with crossed polarisers is a common feature for many of the larger grains of jadeite. Vesuvianite amounts to ~1 % of sample MJ11. This mineral forms aggregates up to 1 mm in diameter which are either roundish (Fig. 1a) or irregular (Fig. 1d) in shape.

The jadeite-vesuviante interface is, in some cases, characterized by euhedral crystal faces of jadeite. In back-scattered electron images, it can be observed that these faces correlate with growth zones of jadeite (Fig. 1c). Occasionally, euhedral inclusions of jadeite crystals enclosed in aggregates of prismatic vesuvianite (up to 0.5 mm in length) are present (Fig. 1b). In these cases, no indication for non-equilibrium between vesuvianite with fibrous outlines cut jadeite in an irregular manner (Fig. 1d) pointing to resorption of jadeite by vesuvianite. Rarely, the latter phase is intergrown with apatite.

Most vesuvianite is strongly altered along cracks and grain boundaries (Fig. 2b). Brownish alteration products are composed of smectitetype sheet silicates, limonite, and a TiO<sub>2</sub> phase. These products amount to ~2 % of sample MJ11. Because there is no albite or analcime replacing jadeite but limonite and smectite formed at the expense of vesuvianite, it is suggested that this alteration represents a very-low *T*, near-surface process involving oxidation of Fe<sup>2+</sup>.

Accessory minerals comprise albite, K-feldspar, apatite, pectolite, and grossular, altogether amounting to less than 1 % of sample MJ11. All these minerals are very small (< 20  $\mu$ m in most cases) and, except albite, in apparent textural equilibrium with jadeite. For instance, the observed grossular occurs as inclusion in jadeite.

## MINERAL CHEMISTRY AND SPECTROSCOPIC INVESTIGATION

## Methods

Because of the unusual occurrence of vesuvianite in a high-pressure environment, we verified the identity of this mineral by micro Raman spectroscopy using a high resolution Witec CRM200 spectrometer. This spectrometer was equipped with a frequency doubled Nd-YAG laser (523 nm). Scattered Raman light was collected in 180° backscattering geometry and dispersed with a grading of 600 groves/mm. A 100x objective lens with a numerical aperture of 0.9 was used.

The chemical compositions of minerals in sample MJ11 were analysed with a Cameca SX100 electron microprobe equipped with five wavelength-dispersive spectrometers (WDS). The applied acceleration voltage and beam current were 15 kV and 10 or 20 nA depending on the stability of the analysed minerals under the electron beam. The beam diameter was normally set to 6  $\mu$ m, but in case of small grains reduced to 1  $\mu$ m. For vesuvianite, the concentrations of Si, Al, Ti, Mg, Mn, Fe, Ce, Ca, and Na were quantitatively determined using the following standards: albite (Na), wollastonite (Ca, Si),



Fig. 1 - (a) Roundish aggregate of vesuvianite crystals embedded in a colourless matrix of jadeite. The vesuvianite is partly replaced by yellowish smectite and brownish/black limonite. The black arrow points to an inclusion of jadeite in the vesuvianite aggregate. Sample MJ11, plane polarized light. (b) Inclusions of almost euhedral jadeite crystals (grey) in vesuvianite (bright) strongly altered to smectite (dark). Image is 0.5 mm across. (c) Euhedral jadeite crystal adjacent to vesuvianite aggregate. In the lower left, note the visible growth zoning in jadeite that is parallel to the crystal faces of this mineral against vesuvianite. Image is 0.5 mm across. (d) Strongly altered fibrous vesuvianite with irregular interfaces to matrix jadeite suggests a non-equilibrium replacement reaction. Image is 0.3 mm across.

periclase (Mg), synthetic corundum (Al), rutile (Ti), CePO<sub>4</sub> (Ce), rhodonite (Mn), and hematite (Fe). Counting times for full analyses were 20 s on peak and background of each element except Ce (40 s counting time). The PAP correction procedure (Pouchou and Pichoir, 1991) provided by Cameca was applied. With the selected analytical conditions, the following elements analysed on several vesuvianite grains were found to be below the detection limit of the applied conditions of the electron microprobe: Cl (detection limit: 0.04 wt.%), F (0.4), K (0.06), Sr

(0.3), Ba (0.05), Cr (0.04), Zr (0.26), Nb (0.15), V (0.10), Cu (0.11), Pb (0.10), Th (0.19) and U (0.08). WDS scans performed with the electron microprobe showed no discernable peak at the B K $\alpha$  position. Thus, it was concluded that boron, if at all, is only present in subordinate amounts in vesuvianite. The same major elements as determined for vesuvianite were also analysed in jadeite. Concentration maps for major elements were prepared by step-wise movement of the rock thin-section under the electron beam of the microprobe.



Fig. 2 – (a) Distribution of Ti in a vesuvianite aggregate (lower left of Fig. 1a). Two growth episodes can be distinguished: the core zones are characterized by a relatively low Ti content (dark in image) whereas the rims are higher in Ti (bright). Line A - B indicates the measured profile of Fig. 4. Small white grains are either limonite or TiO<sub>2</sub> left behind by the alteration of vesuvianite to smectite. Scale bar is 100  $\mu$ m. (b) Photomicrograph of the lower right portion of the Ti distribution image of Fig. 2a. The dots from A to B indicate the positions of the chemical analyses presented in Fig. 4. Low refractive indice or dark: smectite, partly stained by limonite; matrix of vesuvianite: jadeite.

## Verification of vesuvianite by Raman spectrometry

Raman spectra of vesuvianite have been acquired from several grains in sample MJ11. All collected spectra show the same peak positions and relative intensities. A representative spectrum is shown in Fig. 3. The peak positions of the acquired Raman spectra were compared with a reference vesuvianite spectrum (No. R060170 provided by the RRUFF<sup>™</sup> Project, http://rruff.info). As the coincidence of the measured peak positions with this reference spectrum is very good, the investigated mineral in sample MJ11 must be indeed vesuvianite (Fig. 3).

## Vesuvianite chemical composition

Representative mineral analyses of vesuvianite in sample MJ11 are given in TABLE 1. Concerning the major elements, the MJ11 vesuvianite corresponds to analyses of this mineral from elsewhere (*e.g.*, Gnos and Armbruster, 2006). However, the high Na<sub>2</sub>O content of up to 1.5 wt.% is a peculiar feature of the vesuvianite from the high-pressure jadeitite from Myanmar, which is higher than in this mineral from elsewhere. An even higher value of 1.75 wt.% Na was recently only measured in vesuvianite from Guatemala (pers. communication G. Harlow, 2009).

The general formula of vesuvianite is  $X_{19}Y_{13}T_5Z_{18}O_{68}(W)_{10}$  with the most common cations being (Ca, Na) in X, (Al, Mg, Fe, Mn, Ti) in Y, and Si in Z. Anions in W are (OH, O, F, Cl). The T-site is vacant in common vesuvianite, but may occasionally contain some Al, Fe<sup>3+</sup>, and B (Groat *et al.*, 1994). For the calculation of the structural formulae, it is generally proposed to normalize vesuvianite analyses to 50 cations (e.g., Groat *et al.*, 1992; Gnos and Armbruster, 2006), not considering a partial occupancy of the T-site. For our vesuvianite, this procedure resulted in average Z-site and X-site occupancies



Fig. 3 – Raman spectrum (raw data, upper line) of vesuvianite from jadeitite sample MJ11 in comparison with a vesuvianite reference spectrum (lower spectrum, No. R060170, provided by the RRUFF<sup>™</sup> Project, http://rruff.info). The reference spectrum is corrected for background intensity.

of 17.75 and 18.73 cations, respectively, being below the ideal values of 18 and 19. In contrast, the Y-site cations are above the ideal value of 13, showing a mean value of 13.32 cations. Therefore, it is obvious that the T-site is partially filled, as it is the case for high-grade metamorphic vesuvianite from elsewhere ("Excess-Y"; Groat et al., 1994; Gnos and Armbruster, 2006). Accordingly, we normalized Si to 18 cations as proposed by Gnos and Armbruster (2006). The assumption to restrict the Z site to Si as sole cation may be particular appropriate for vesuvianite from a high-pressure metamorphic environment at elevated temperature as the potential tetrahedral site element Al generally prefers higher coordinated sites in high-pressure minerals. The resulting cation total of the X-site is 18.89 as mean value and, thus, close to ideality with a slight deficiency only. Assuming that the Y-site contains 13 cations in total, an average value of 0.26 cations can be assigned to the T-site. Because we did not find boron in vesuvianite, it is assumed that the T-site cations mainly consist of Al. The OH content is calculated from charge balancing (H = 156 - F - Cl - valencies of cations). The resulting mean value of 7.6 is relatively low compared to the ideal value of 9 per formula unit (pfu).

A peculiar feature of MJ11 vesuvianite is the relatively high content of Na up to about 1.5 wt.% Na<sub>2</sub>O. In most published analyses of vesuvianite from elsewhere, the content of this element (as oxide) is below 0.4 wt.%, or even below the detection limit. In contrast, compared to common vesuvianite, FeO and MgO are present only in low concentrations averaging 2.2 and 0.7 wt.%, respectively. The analysed TiO<sub>2</sub> content of 1.0 to 3.3 wt.% is in the range of analyses of vesuvianite from elsewhere.

|                     | Prc    | ofile rim | $(A) \rightarrow$ | core (E | (2)    |        |        |        |        |        |        |        |        | (dar   | Relic c<br>k in BS | ores<br>E image |        |
|---------------------|--------|-----------|-------------------|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------------------|-----------------|--------|
| wt.%                | #1     | #3        | #5                | L#      | #8     | #10    | #12    | #13    | #15    | #17    | #19    | #20    | #26    | #1     | #2                 | #4              | #5     |
| $SiO_2$             | 36.87  | 36.55     | 36.88             | 36.95   | 37.01  | 36.94  | 36.94  | 37.00  | 37.05  | 37.22  | 36.59  | 36.70  | 36.57  | 36.90  | 36.79              | 37.01           | 36.69  |
| $TiO_2$             | 2.81   | 2.65      | 2.64              | 2.38    | 2.45   | 1.81   | 1.33   | 1.26   | 1.23   | 3.07   | 3.17   | 3.13   | 2.74   | 1.53   | 1.48               | 1.41            | 1.29   |
| $AI_2O_3$           | 19.45  | 19.48     | 19.65             | 19.89   | 19.50  | 20.04  | 20.43  | 20.37  | 20.41  | 19.17  | 18.99  | 19.03  | 19.31  | 20.25  | 20.31              | 20.51           | 20.36  |
| FeO                 | 1.73   | 1.90      | 1.88              | 1.77    | 1.88   | 1.96   | 1.85   | 1.77   | 1.90   | 1.84   | 1.73   | 1.81   | 1.71   | 1.74   | 1.82               | 1.81            | 1.82   |
| MnO                 | 0.15   | 0.16      | 0.19              | 0.17    | 0.17   | 0.19   | 0.17   | 0.21   | 0.15   | 0.15   | 0.10   | 0.12   | 0.13   | 0.15   | 0.22               | 0.21            | 0.16   |
| MgO                 | 0.59   | 0.56      | 0.57              | 0.51    | 0.58   | 0.56   | 0.56   | 0.56   | 0.60   | 0.66   | 0.67   | 0.68   | 0.60   | 0.28   | 0.31               | 0.26            | 0.41   |
| $Ce_2O_3$           | lbdl   | lbd       | lbd               | lbdl    | lbd    | lbdl   | lbdl   | lbd    | lbdl   | 0.11   | 0.07   | 0.17   | 0.15   | lbd    | lbd                | lbdl            | bdl    |
| CaO                 | 33.89  | 34.09     | 34.13             | 34.16   | 34.28  | 34.36  | 34.71  | 34.59  | 34.96  | 33.38  | 33.79  | 33.88  | 33.71  | 33.70  | 33.45              | 33.72           | 33.69  |
| $Na_2O$             | 1.25   | 1.20      | 1.28              | 1.30    | 1.28   | 1.14   | 1.12   | 1.15   | 1.09   | 1.31   | 1.26   | 1.28   | 1.33   | 1.45   | 1.49               | 1.44            | 1.40   |
| $\rm H_2O$          | 2.23   | 1.98      | 2.09              | 2.16    | 2.29   | 2.24   | 2.17   | 2.33   | 2.21   | 2.57   | 2.11   | 2.10   | 2.14   | 2.54   | 2.47               | 2.51            | 2.39   |
| Total               | 99.01  | 98.57     | 99.31             | 99.29   | 99.46  | 99.30  | 99.32  | 99.22  | 99.62  | 99.48  | 98.49  | 98.91  | 98.38  | 98.55  | 98.35              | 98.88           | 98.21  |
| Si                  | 18.000 | 18.000    | 18.000            | 18.000  | 18.000 | 18.000 | 18.000 | 18.000 | 18.000 | 18.000 | 18.000 | 18.000 | 18.000 | 18.000 | 18.000             | 18.000          | 18.000 |
| Ti                  | 1.030  | 0.981     | 0.968             | 0.871   | 0.897  | 0.664  | 0.488  | 0.460  | 0.449  | 1.116  | 1.173  | 1.157  | 1.014  | 0.563  | 0.546              | 0.516           | 0.476  |
| Al                  | 11.191 | 11.305    | 11.300            | 11.422  | 11.177 | 11.508 | 11.733 | 11.681 | 11.686 | 10.930 | 11.009 | 11.003 | 11.205 | 11.642 | 11.713             | 11.758          | 11.773 |
| $\mathrm{F}e^{2^+}$ | 0.705  | 0.783     | 0.766             | 0.722   | 0.765  | 0.800  | 0.754  | 0.720  | 0.770  | 0.746  | 0.710  | 0.741  | 0.703  | 0.708  | 0.744              | 0.736           | 0.746  |
| Mn                  | 0.060  | 0.066     | 0.080             | 0.068   | 0.070  | 0.078  | 0.070  | 0.086  | 0.062  | 0.062  | 0.042  | 0.050  | 0.055  | 0.064  | 0.092              | 0.085           | 0.065  |
| Mg                  | 0.427  | 0.411     | 0.411             | 0.370   | 0.422  | 0.405  | 0.408  | 0.407  | 0.435  | 0.477  | 0.491  | 0.501  | 0.437  | 0.201  | 0.224              | 0.191           | 0.298  |
| $\Sigma \; Y{+}T$   | 13.414 | 13.547    | 13.524            | 13.453  | 13.332 | 13.455 | 13.453 | 13.353 | 13.402 | 13.331 | 13.426 | 13.452 | 13.413 | 13.179 | 13.319             | 13.286          | 13.358 |
| Ce                  | 0.007  | 0.000     | 0.002             | 0.000   | 0.000  | 0.009  | 0.006  | 0.000  | 0.003  | 0.019  | 0.013  | 0.030  | 0.026  | 0.000  | 0.000              | 0.000           | 0.000  |
| Са                  | 17.728 | 17.986    | 17.844            | 17.834  | 17.863 | 17.937 | 18.125 | 18.031 | 18.200 | 17.299 | 17.811 | 17.807 | 17.779 | 17.613 | 17.535             | 17.573          | 17.709 |
| Na                  | 1.185  | 1.149     | 1.212             | 1.229   | 1.211  | 1.080  | 1.061  | 1.081  | 1.031  | 1.230  | 1.199  | 1.214  | 1.266  | 1.376  | 1.412              | 1.355           | 1.335  |
| ΣΧ                  | 18.962 | 19.152    | 19.070            | 19.090  | 19.103 | 19.062 | 19.219 | 19.141 | 19.265 | 18.599 | 19.033 | 19.073 | 19.092 | 18.997 | 18.963             | 18.955          | 19.071 |
| НО                  | 7.257  | 6.517     | 6.810             | 7.033   | 7.426  | 7.273  | 7.057  | 7.550  | 7.171  | 8.290  | 6.932  | 6.861  | 7.039  | 8.271  | 8.076              | 8.136           | 7.808  |

TABLE 1

Na-rich vesuvianite in jadeitite of the Tawmaw jade district, northern Myanmar

# Chemical zoning in vesuvianite

Chemical mapping with the microprobe was applied to record chemical zonation. The most obvious zoning concerns the Ti content (Fig. 2a). The core zone of a vesuvianite aggregate is characterized by a relatively high and constant Ti content. Towards the rims, the Ti content decreases and then again continuously increases in the outer rim. On the basis of the Ti distribution image, a profile was selected perpendicular to the zoning (line A-B in Fig. 2). Along the profile (Fig. 4), the strong Ti zoning is discernable as in the distribution map: a high



Fig. 4 – Profile from rim (A) to core (B) in vesuvianite. The location of the profile is indicated in Fig. 2.

and relatively constant Ti content in the core is dropping at a sharp boundary from about 1.1 to 0.4 pfu and, then, increasing up to 1.2 Ti pfu in the outer rim. The sodium zoning is roughly parallel to that of Ti, but not as strong. Particularly Al and to a lesser degree Ca show an opposite zoning compared to Ti. Iron and Mg are almost constant along the profile. Cerium is present in minor amounts in the core of the vesuvianite aggregate whereas the rim is devoid of Ce. Similar zoning patterns can also be observed in other vesuvianite aggregates of the same sample.

The described zoning pattern can be interpreted as a (oscillatory) growth zoning. In Fig. 2, two growth cycles are present. In addition, there is another type of intra-crystalline zoning discernable in BSE images (Fig. 5): a darker core occasionally occurs in individual crystals. In contrast to the aforementioned zoning pattern, this zoning seems to be due to an incomplete equilibration of newly grown vesuvianite with an earlier vesuvianite composition. Actually, if plotted in a diagram Ti vs. Na (Fig. 6), it can be recognized that these few relic compositions analyzed follow a different trend compared to all othevvr analyses. These relic vesuvianite compositions are characterized by relatively low Ti and high Na contents.

## Cation substitution mechanism in vesuvianite

The major cation in the X site and Y site of vesuvianite is Ca and Al, respectively. The replacement of Al by Ti,  $Fe^{2+}$  and Mg, and of Ca by Na and Ce (and probably further rare earth elements with contents at and below the detection limit) requires charge balance considerations. A mechanism commonly proposed for the incorporation of Ti into vesuvianite is the coupled substitution (see Hoisch, 1985; Fitzgerald *et al.*, 1992; Groat *et al.*, 1992; Gros and Armbruster, 2006)

# (1) $Ti + (Mg, Fe^{2+}, Mn^{2+}) = 2 Al.$

However, in sample MJ11, the amount of Mg +  $Fe^{2+}$  +  $Mn^{2+}$  is almost constant at a value of c. 1.3 cations pfu except in the relic cores which contain c. 1.0 Mg +  $Fe^{2+}$  +  $Mn^{2+}$  pfu. Accordingly, substitution mechanism (1) can be ruled out as a major one for Ti incorporation. However, substitution of Al by Ti is strongly suggested by a good negative correlation of Al and Ti with a slope close to -1. The required charge balance can be provided by Na-Ca substitution (Groat *et al.*, 1992):

(2) Ti + Na = Al + Ca.

Actually, a significant cluster of compositions show an equal amount of Na + Ti of about 1.2 cations pfu (Fig. 6). However, in case of Tipoorer compositions, the amount of Na is too high to be exclusively explained by substitution mechanism (2). This is particularly true for the relic core compositions. A further mechanism is required to account for the too high Na content. A possible substitution to keep charge balance despite Na incorporation is

 $(3) \qquad Na + O = Ca + OH.$ 

A plot of Na pfu versus the calculated OH content, however, shows no correlation ruling



Fig. 5 – BSE image of vesuvianite, sample MJ11. Occasionally, in vesuvianite, dark cores are discernable in BSE images. These cores are interpreted as relic of an early formed vesuvianite. Black: alteration phases. Scale bar is 20µm.

out mechanism (3) for the studied vesuvianite. The correlation of Na versus Fe + Mg + Mn of about -1 suggests that, despite some scatter, the substitution

(4) Na + Al = Ca + (Fe+Mg+Mn)

is of importance. Vacancies in the T site may also be considered for the charge balance, for instance, by:

(5) Na + 0.33 Al<sub>T-site</sub> = Ca + 0.33  $\Box_{T-site}$ 

However, a negative correlation was found for the total of cations in the (Y + T) sites and Na also ruling out this substitution for Na incorporation.

Summarizing, substitution (2) is important to understand the incorporation of Na and Ti into vesuvianite, but also substitution (4) should be considered for Na incorporation into this mineral.

## Alteration of vesuvianite

The alteration phases of vesuvianite are limonite and a brownish sheet silicate. Microprobe analyses reveal that the latter mineral has the chemical composition and anhydrous total of  $\sim 85$  wt.% typical for smectite (TABLE 2).

## Composition of jadeite

The jadeite analyses have been normalized to 4 cations and 6 oxygen. The resulting cation distribution corresponds to near end-member jadeite with jadeite contents ranging from  $Jd_{94}$  to  $Jd_{99}$  (TABLE 2). A minor oscillatory growth zoning may be present in the core portion of jadeite with a slight Ca enrichment at the end of each oscillation zone.

## PETROLOGICAL SIGNIFICANCE OF VESUVIANITE IN JADEITITE JADE

The formation of jadeitite is generally interpreted as due to extensive serpentinite – Narich hydrous fluid interaction along channelized



Fig. 6 – Element correlations in vesuvianite from jadeitite sample MJ11. Oblique lines have a slope of 1 or -1. Filled symbols: early formed vesuvianite; open circles: lately formed vesuvianite.

fluid flow zones (*e.g.*, Harlow and Sorensen, 2004; Sorensen *et al.*, 2006). The Na-rich environment leading to the formation of jadeite is also reflected by the high Na content of coexisting vesuvianite. The largest chemical variation in vesuvianite, however, concerns Ti. It can therefore be speculated that this element was, in our case, of significance for the formation of vesuvianite as it can be introduced in jadeite only in subordinate amounts. In addition, it has to be considered that vesuvianite contains Ca as major element, in contrast to jadeite.

Based on the above observations, it is suggested that the formation of vesuvianite is the

TABLE 2 Representative analyses of jadeite and smectite. bld = below detection limit.

| wt.%                        |       | Jadeit | e      | Sme   | ectite |
|-----------------------------|-------|--------|--------|-------|--------|
| SiO <sub>2</sub>            | 58.52 | 58.79  | 59.55  | 49.02 | 49.05  |
| TiO <sub>2</sub>            | bdl   | bdl    | bdl    | 0.30  | 0.57   |
| $Al_2O_3$                   | 25.30 | 25.53  | 23.93  | 12.86 | 12.37  |
| $Cr_2O_3$                   | bdl   | bdl    | bdl    | bdl   | bdl    |
| FeO                         | 0.06  | 0.05   | 0.18   | 7.34  | 10.55  |
| MnO                         | bdl   | bdl    | 0.02   | 0.09  | 0.10   |
| MgO                         | 0.07  | 0.08   | 0.92   | 12.43 | 11.75  |
| CaO                         | 0.20  | 0.07   | 1.54   | 0.81  | 0.72   |
| Na <sub>2</sub> O           | 15.00 | 15.09  | 14.11  | 0.23  | 0.24   |
| $K_2O$                      | bdl   | bdl    | bdl    | 0.66  | 0.72   |
| Total                       | 99.14 | 99.60  | 100.27 | 83.08 | 85.34  |
| Si                          | 1.987 | 1.986  | 2.0040 | 3.656 | 3.628  |
| Al                          | 0.013 | 0.014  | 0.000  | 0.344 | 0.372  |
| S                           | 2.000 | 2.000  | 2.004  | 4.000 | 4.000  |
| Al                          | 1.000 | 1.003  | 0.949  | 0.787 | 0.706  |
| Ti                          | 0.000 | 0.000  | 0.000  | 0.017 | 0.032  |
| Cr                          | 0.000 | 0.000  | 0.000  | 0.000 | 0.000  |
| $\mathrm{F}\mathrm{e}^{3+}$ | 0.000 | 0.000  | 0.000  | 0.000 | 0.000  |
| $Fe^{2+}$                   | 0.001 | 0.001  | 0.005  | 0.458 | 0.653  |
| Mn                          | 0.000 | 0.001  | 0.001  | 0.006 | 0.006  |
| Mg                          | 0.004 | 0.004  | 0.046  | 1.382 | 1.296  |
| Ca                          | 0.007 | 0.003  | 0.056  | 0.064 | 0.057  |
| Na                          | 0.987 | 0.988  | 0.920  | 0.033 | 0.034  |
| Κ                           | 0.000 | 0.001  | 0.000  | 0.062 | 0.068  |
| S                           | 2.000 | 2.000  | 1.9760 | 2.809 | 2.852  |

result of a specific chemical environment. Obviously, mineral reactions leading to the formation of vesuvianite have not been isochemical reactions but involved a (hydrous) fluid phase. Considering the ideal composition of vesuvianite, such a reaction involving a Ti mineral such as titanite, CaTiSiO<sub>5</sub>, may be (for simplification, fluid species are not considered as ions but as oxide components):

 $\begin{array}{ll} (R1) & 19 \mbox{ titanite} + 2(MgO)_{fluid} + 11(AlO_{1.5})_{fluid} \\ + 4.5(H_2O)_{fluid} \end{array}$ 

= vesuvianite +  $19(TiO_2)_{fluid}$  +  $1(SiO_2)_{fluid}$ . Rocks influenced by extensive hydrothermal infiltration are usually composed of a few minerals or a single phase only, reflecting that chemical variables (chemical potentials or activities) of most or of all components are externally controlled by the fluid phase, in the sense of Korzhinskii (1959). In the studied rock with vesuvianite, this was probably also the case for CaO and TiO<sub>2</sub>. Thus, these two chemical parameters may be used as monitor in an isothermal-isobaric chemical potential diagram (Fig. 7). In addition to jadeite and vesuvianite, titanite and rutile are considered in this diagram, because these Ti-minerals occur as secondary phases in jadeitite (Harlow et al., 2007).

Possible scenarios to explain the presence of vesuvianite in jadeitite comprise either a local source of Ca and Ti or an externally controlled variation of the composition of the fluid phase. On the basis of Fig. 7, it can be speculated that locally high chemical potentials of TiO<sub>2</sub> and CaO were active during dissolution of a Ti mineral such as titanite which could represent a relic in the rock being metasomatized and transformed to jade. Dilution of a local fluid by an externally compositionally controlled fluid phase leads to a decrease of the chemical potentials of TiO<sub>2</sub> and CaO which can result in the formation of vesuvianite (path  $B \rightarrow A$  in Fig. 7). In case of complete equilibrium with the externally controlled fluid phase. а monomineralic rock (jadeitite) would finally

result. A further parameter to be considered is the chemical variation of vesuvianite coexisting with jadeite. A decrease of the activity of the end member  $Ca_{19}Mg_2Al_{11}Si_{18}O_{69}(OH)_9$  by variable incorporation of Ti (and Na for charge balance) would enlarge its stability field (Fig. 7). In case of chemical equilibrium between jadeite and vesuvianite, the latter mineral would get continuously richer in Ti during progressive dilution of the local fluid which is influenced by the dissolution of a precursor mineral such as titanite. Instead of titanite, other Ti minerals such as Ti-rich spinel, rutile or ilmenite could have been formerly present.

In many cases in sample MJ11, however, vesuvianite crystallized at the expense of jadeite suggesting an alternative process which is more probable. This process is related to an externally



Fig. 7 – Schematic chemical potential diagram at constant P and T (components in the fluid phase simplified to oxide components). The chemical potentials of the other components of the phases are considered to be externally controlled. (1) is the stability limit for end-member vesuvianite, (2) for low Ti vesuvianite, and (3) for high Ti vesuvianite. Path A  $\rightarrow$  B indicate the mineral sequence with increasingly higher chemical potentials of CaO and TiO<sub>2</sub>.

controlled increase of the chemical potentials of Ca (and of Mg, Fe, Ti) of the fluid phase (path  $A \rightarrow B$  in Fig. 7). At first, at the two-phase boundary jadeite-vesuvianite of Fig. 7, the latter mineral crystallized in equilibrium with jadeite. This was probably the case in Fig. 2d, where euhedral jadeite coexists with vesuvianite. Afterwards, higher Ca contents of the fluid phase resulted in vesuvianite replacing jadeite (Fig. 2e). Still higher chemical potentials of TiO<sub>2</sub> and CaO would result in the crystallization of a Ti mineral such as titanite, being a common secondary mineral in jadeitite from elsewhere (Harlow et al., 2007). The chemical variation of vesuvianite as oscillatory zoning would have been caused by pulses of external fluids. The formation of other Ca minerals such as grossular or pectolite could probably be related to a compositionally different (Ti-poorer?) fluid phase compared to the one responsible for vesuvianite formation.

For jadeitite in general, a temporal sequence can be observed from Na-rich (jadeite) to Ca-rich minerals, e.g., vesuvianite, grossular, pectolite, titanite, and actinolite (cf., Harlow et al., 2007) which can be interpreted in terms of geologic processes. The chemical environment during jadeite formation is mainly controlled by fluids in chemical equilibrium with the host peridotite/serpentinite that acts as a sink particularly for elements such as Ca, Fe, Mg, Ti due to formation of, e.g., serpentine, talc, magnetite, and carbonate minerals. During exhumation, such an environment is progressively disturbed by the dismembering of an ophiolite resulting, for instance, in an ophiolitic mélange. Thus, rock types other than serpentinite such as blueschist, mica-schist, or eclogite are getting in contact with jadeitite. These basic to acidic rock types are a Ca source for fluids becoming chemically different compared to the original serpentinite-controlled fluids.

A quantitative calculation of the invoked

processes does not seem to be possible because of the poor knowledge of the thermodynamic properties of vesuvianite. There are only a few experimental data available on the P-T stability of vesuvianite (Plyusnina et al., 1994; Hochella et al., 1982). Moreover, all experiments have been performed at low pressure, and, thus, no data are available for high-P conditions. For instance, variations in P-T conditions might be responsible for omphacite with high TiO<sub>2</sub> content of up to 7.5 wt.%, described by Harlow (2003) from Guatemala and Japan, formed instead of jadeite + vesuvianite. At least, an important conclusion of the presented observation is that vesuvianite is stable under high pressure condition, for instance, in the stability field of jadeite.

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