

CRYSTAL CHEMISTRY AND SURFACE FEATURES OF MINERALS WITH SIX- AND EIGHT-MEMBERED TETRAHEDRAL RINGS

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INTRODUCTION

The study of mineral surface structures is very useful in understanding their reactivity toward surrounding environment. In fact reactions (*i.e.*, adsorption, desorption, precipitation, dissolution, etc.) occur only on few atomic layers.

Although studies on surface science are well established for some disciplines (*i.e.*, physics and chemistry), in mineralogy and related geosciences the study of surfaces has only recently begun (Hochella, 1995; Maurice, 2009).

In this work, the surface chemical composition and the atomic arrangement are compared with the crystal chemistry of the bulk in order to identify potential deviations from bulk to surface. In particular, this study is focused on the knowledge of the crystal chemical properties and their relationships between bulk and surfaces of silicates composed by a network of six-membered tetrahedral rings (osumilite and muscovite) and six- and eight-membered tetrahedral rings (vesuvianite). Only few results are available on the surface structure of these minerals (Kuwahara, 1999, 2001; Knyazev & Korsukov, 2004; Liu *et al.*, 2005; Elmi *et al.*, 2010, 2011); they were chosen for investigation because of: i) the presence of tetrahedral rings; ii) the large smooth surfaces, so that it was possible to conveniently study surfaces; iii) the different local stereochemistry; iv) the distinct occupancy of the cation site within the rings; v) some compositional similarities among selected crystals; vi) the differently-membered tetrahedral rings (from six to eight).

Because of their peculiar chemical composition and topology, the study of mineral surface is extremely complex and implicitly multi-disciplinary. For this reason, the osumilite, vesuvianite and muscovite samples were investigated, both at the bulk and at the surface, using many techniques (*e.g.*, single crystal X-ray diffraction, electron microprobe analysis, scanning probe microscopy, X-ray photoelectron spectroscopy, grazing incidence X-ray diffraction). All experimental analyses were carried out using fragments or powder which came from the same selected crystal.

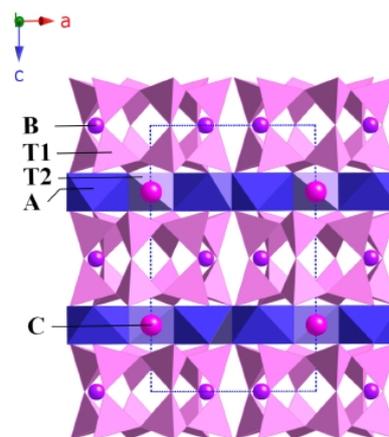


Fig. 1 - Schematic representation of the osumilite crystal structure, projection perpendicular to [010].

BULK AND SURFACE FEATURES OF OSUMILITE, VESUVIANITE AND MUSCOVITE

Osumilite

The osumilite from Mt. Arci (Sardinia) occurs in thin fissures and small cavities within a rhyolite from the volcanic massif of Mt. Arci, Sardinia. The mineral forms regular dark blue hexagonal prismatic-tabular crystals associated to trydimite and sporadic Fe-rich phlogopite crystals. The osumilite from Mt. Arci shows euhedral habit and, in particular, well defined surfaces on the basal pinacoid, and they are thus well suited to study the relationships between bulk and surface crystal chemistry.

Osumilite belongs to the osumilite group of minerals (Armbruster & Oberhänsli, 1988; Balassone *et al.*, 2008; Hawthorne *et al.*, 1991). This mineral has an ideal formula of $^{XII}C^VI A_2(T_2)_3^{IV}(T_1)_{12}O_{30}$ and it crystallizes

in the space group $P6/mcc$. The osumilite structure (Fig. 1) consists of double rings of six tetrahedra (T1), each sharing three vertices with the adjacent T1 tetrahedra. The [6]-membered tetrahedral double rings bond laterally and vertically, by sharing the fourth corner with either A octahedra or T2 tetrahedra, thus giving edge-sharing [12]-membered rings. T1 is mainly occupied by Si and by small amount of Al, T2 is usually occupied by Al with Fe and little Mg, whereas A octahedra mostly contain Mg and Fe. The ring arrangement defines structural channels occupied by the twelve-coordinated C site, which is characterized by the presence of the alkaline cations Na and K (Elmi *et al.*, 2010; Fig. 1).

The Mt. Arci osumilite crystal, refined by single crystal X-ray diffraction (SC-XRD) confirms the hexagonal space group $P6/mcc$ (unit cell parameters $a = 10.1550(6)$ Å; $c = 14.306(1)$ Å). The structural formula is $(K_{0.729})_C (Na_{0.029})_B (Si_{10.498} Al_{1.502})_{T1} (Al_{2.706} Fe^{2+}_{0.219} Mg_{0.075})_{T2} (Mg_{0.660} Mn_{0.091} Fe^{2+}_{1.258})_A O_{30}$ (Elmi *et al.*, 2010).

The main characteristic of osumilite from Mt. Arci is the presence of Fe^{2+} , in octahedral coordination, in higher amounts (1.478 apfu) than those reported in literature (Hesse & Seifert, 1982; Schreyer *et al.*, 1983; Armbruster & Oberhänsli, 1988; Balassone *et al.*, 2008; Seryotkin *et al.*, 2008). Also the experimental results by X-ray absorption spectroscopy (XAS) in the $L_{2,3}$ -edge confirmed that iron is present under its divalent form on the surface, as well.

The comparison between Mt. Arci osumilite and literature data, shows that the a cell parameter is mostly related to Fe content, which is usually greater in samples of igneous origin; its variation leads to topological modifications involving the entire cell, unlike the c cell parameter, which is less evidently related to chemical and topological variables. Nevertheless, it shows different values depending on host rock genetic conditions, thus possibly depending on the intensive variables acting during crystallization (*e.g.*, T, P, and fluid activities).

The atomic force microscopy (AFM) investigations performed on osumilite surface confirm the well-defined hexagonal tetrahedral ring network (Elmi *et al.*, 2010).

Structural and chemical information acquired by SC-XRD and electron microprobe analysis (EMPA) are also confirmed by X-ray photoelectron spectroscopy (XPS), thus suggesting that the surface crystal chemistry closely corresponds to the bulk one, except for the presence of the Si^{1+} component (about 10%) on the surface, which can be caused by Si-O bonds breaking, but it is still related to tetrahedrally coordinated Si.

Vesuvianite

Vesuvianite is a complex tetragonal silicate (Warren & Modell, 1931) having an ideal formula of $X_{19}Y_{13}Z_{18}O_{68}W_{10}$, with $X = Ca, Na, Ln^{3+}, Pb^{2+}, Sb^{3+}$; $Y = Al, Mg, Fe^{3+}, Fe^{2+}, Ti^{4+}, Mn, Cu, Zn$; $Z = Si$; $W = (OH, F, O)$. The sample studied came from the Vesuvius volcano skarns (Mt. Somma) and it was generated during contact metamorphism of limestones ejected during the highly explosive phases (Plinian eruptions) of the Somma-Vesuvius volcano. The vesuvianite samples form brown crystals variable in habit from short-pyramids to elongated-prisms. Unlike osumilite, the morphology of vesuvianite is more complex to study because some crystal faces are not perfectly flat and/or chemical zoning can be present; hence, surface crystal chemical study must be restricted to planes showing the best features. For this reason, preliminarily observations by scanning electron microscope (SEM) were necessary in order to verify both surface flatness and chemical homogeneity. The secondary electron images highlighted the complexity of the surfaces, but the backscattered ones did not reveal any chemical zoning. For this reason, the XPS study was performed on this specific crystal face.

On the basis of the cation arrangements in the partially occupied X' and Y' sites, it is possible to distinguish "low vesuvianites" formed at $T < 300^\circ C$, generally with symmetry $P4/n$, from "high vesuvianites" formed at $T > 500^\circ C$, with symmetry $P4/nnc$. The classification of the vesuvianite from Mt. Somma (either low- or high-temperature) was suggested both by X ray powder diffraction at non ambient conditions ($25 \leq T \text{ } ^\circ C \leq 1250$) and by differential thermal analysis, coupled with mass spectrometry on evolved gas phases. The dehydroxylation of the crystal occurred at about $1000^\circ C$, when vesuvianite was completely replaced by grossular, gehlenite and wollastonite. These results confirmed that our sample is a high temperature vesuvianite (Elmi *et al.*, 2011).

The crystal structure of vesuvianite was refined by SC-XRD (Ohkawa *et al.*, 1992; Groat *et al.*, 1992). The sample studied belongs to the space group $P4/nnc$ with unit cell parameters $a = 15.633(1) \text{ \AA}$, $c = 11.834(1) \text{ \AA}$ and chemical formula $(\text{Ca}_{18.858} \text{Na}_{0.028} \text{Ba}_{0.004} \text{K}_{0.006} \text{Sr}_{0.005} \square_{0.098})_{19.000} (\text{Al}_{8.813} \text{Ti}_{0.037} \text{Mg}_{2.954} \text{Mn}_{0.008} \text{Fe}^{2+}_{0.114} \text{Fe}^{3+}_{1.375} \text{Cr}_{0.008} \text{B}_{0.202})_{13.511} \text{Si}_{18.000} (\text{O}_{0.261} \text{F}_{0.940} \text{OH}_{7.799})_{9.000}$. The chemical formula identifies an occupancy excess for Y sites at values exceeding 13 apfu. As discussed by Groat *et al.* (1992), this excess can be associated with the presence of atoms in the T1 and T2 sites. Structure refinement demonstrates a strong positional disorder down the four-fold axes, thus indicating that Y1 site is splitted into two positions (Y1A and Y1B) alternatively occupied. However, because of the proximity of the sites X4, Y1B and Y1A, the site X4 cannot be occupied if Y1B or Y1A are (Fig. 2). Moreover, T1 position, partially occupied, accommodates the excess of cations generally related to Y position.

A little quantity (0.202 apfu) of boron is sited at T2 site, which is poorly occupied (Elmi *et al.*, 2011).

Unlike osumilite surface, in vesuvianite significant differences between the bulk- and surface- concentration of specific elements were found. In fact, the quantity of each element on the mineral surface revealed by XPS evidenced that a greater Al- and a smaller Ca-amounts characterize the surface with respect to the bulk. The Al increase can be related to the preferential orientation of Al-rich sites (Y2) on the (100). Furthermore, the structure of the (100) vesuvianite suggests that Al, Ca and Mg cations maintain similar coordination features from bulk to the surface. Silica, however, despite presenting four-fold coordination on vesuvianite surface, as in osumilite, shows also a [1]-fold small coordinated component, due to the broken of the Si-O bonds at the surface. The presence of eight- and nine-coordinated Ca cations is suggested by a large XPS feature peak resulting from the merging of $\text{Ca}_{2p_{3/2}}$ and $\text{Ca}_{2p_{1/2}}$ peaks at binding energy of 348.45 eV and 352.05 eV, respectively. Besides, XAS analyses at $L_{2,3}$ edge contributed to confirm the presence of iron in both its valence state also on the surface.

Muscovite

The muscovite considered in this study came from Antarctica; it is monoclinic, $2M_1$ polytype, with symmetry $C2/c$. Dioctahedral $2M_1$ micas in $C2/c$ symmetry show two independent tetrahedral sites, T1 and T2. In muscovite from Antarctica these two sites present similar distances thus reflecting a $^{[IV]}\text{Si}$ and $^{[IV]}\text{Al}$ disordered distribution in T1 and T2. The tetrahedral parameters, such as the τ angle (tetrahedral flattening angle), the α angle and the Δz , reflect the complex crystal chemistry of the 2:1 layer. In fact, they change not only the topology of the cleavage plane but also the bond strength between interlayer cations (which are represented by K and Na) and oxygen atoms in the uppermost plane.

While in osumilite and vesuvianite a very little Si component was found as Si^+ due to broken bonds at the surface, in muscovite Si always maintains four fold coordination, both at the surface and in the bulk.

A peculiarity of the studied muscovite is a limited Na for K interlayer substitution, which was found in the bulk as well as on the mineral surface. It is well known that in micas the coordination of the interlayer cations can vary from twelve to six, depending on the distortion of the hexagonal tetrahedral ring, as measured by α , as well observed and predicted by Weiss *et al.* (1992). The binding energy values of K_{2p} are consistent with an eight-fold coordination, whereas the binding energy values of Na_{1s} indicate a six-fold coordination. The six-fold coordination presented by Na is consistent with $\alpha \approx 16^\circ$, which is typical for paragonite, whose interlayer is completely occupied by Na.

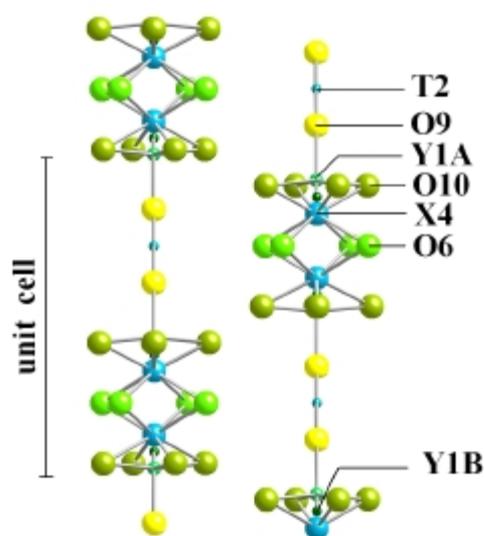


Fig. 2 - Arrangement of atoms in X4 and Y1 sites in vesuvianite from Mt. Somma.

The chemical composition at the surface was compared to the bulk chemical composition evidenced by EMPA data. This comparison highlights a close similarity in chemical composition between bulk and surface for Si and Al, but an increase of Na and a decrease of K were also observed. The decrease in K content can be explained by its location on the cleavage surface, since the cation is expected to be distributed equally along the two surfaces generated after cleavage; moreover, the increase in Na can be related to Na domains close to the cleavage surface.

The Grazing Incidence X-ray Diffraction (GIXRD) results suggest that this surface is very similar to a simple termination of the bulk structure; however, there are evidences that the surface structure exhibits slight lateral relaxation (*i.e.*, distortion from the bulk structure) owing to modest shifts of surface atoms.

CONCLUSIONS

This work was focused on studying the crystal chemical properties of osumilite, vesuvianite, and muscovite and the relationships between their bulk and surfaces crystal chemistry. In osumilite and vesuvianite, the tetrahedra are centred by Si, whereas in muscovite the Al ions, which are also present in the octahedral site, substitute silica in a 1:3 ratio. The results obtained gave a detailed surface characterization of these minerals, considering: i) the influence of bulk crystal-chemistry and cation ordering on the surface structure; ii) the geometry of the tetrahedral rings on the surface, where they would be expected to undergo relaxation or reconstruction effects; iii) both oxidation state of the cations and element coordination, which can vary at the surface with respect to the bulk structure.

Chemical characterization of the un-reacted freshly cleaned surface of natural phases by direct measurements is of greatest importance for describing the mechanism of surface reaction on the outermost atomic layers. Despite a mineral surface reconstructs only if it is heated to a few hundred degrees or more, relaxation is a common feature for minerals with a low-symmetry structure, *e.g.* for feldspar. On the other hand, higher symmetry structure may not show lateral relaxation at all, but some relaxation perpendicular to the surface would be expected. These aspects were also confirmed in the studied minerals. In fact, in osumilite and vesuvianite, which present a high symmetry, a relaxation was not evidenced; in contrast, the atomic structure of muscovite surface relaxed from an equivalent plane in the bulk, as evidenced by GIXRD results.

Moreover, the atomic arrangement in the surface can be also influenced by the physical properties of the minerals. In fact, osumilite and vesuvianite are not readily altered in nature and they have both high hardness (6-7); on the other hand, muscovite has lower hardness (2.5-3) and may be converted to clay minerals by weathering. Considering the experimental data collected, these physical aspects can clarify why in osumilite and vesuvianite the relaxation of the outermost layers is not really evident, whereas in muscovite it occurs.

While the Si and Al contents of osumilite and muscovite surfaces were very close to the mineral bulk composition, significant differences between the concentration of specific elements in the bulk and surface were found in vesuvianite and muscovite. In particular, a greater amount of Al and a smaller amount of Ca characterize the surface with respect to the bulk. In particular, the Al increase may be related to the preferential orientation of Al-rich sites (Y2) on the cleavage plane; on the other hand, in muscovite surface, while K content decrease, Na amount increase due to the stronger Na-O bond. The decrease of K content in muscovite can be explained by its location on the cleavage surface, since the cation is expected to be distributed equally along the Na-rich and K-rich surfaces generated after cleavage.

The lower Ca content observed at the vesuvianite surface, together with a lowering of Si coordination, observed in osumilite and vesuvianite surfaces (from 4⁺ to 1⁺), may be ascribed as the root cause for surface negative charging, as demonstrated by XPS data. Considering the results obtained by XPS, it could be claimed that in osumilite and vesuvianite, the tetrahedral network of the bulk is maintained also at the surface, thus, although a break of Si-O bonds at the surface of both minerals, a relaxation is not so evident.

The results reached in this project pave the way to a large variety of interesting studies, which have either already been started or will be approached in the future; moreover, they would be a benchmark, as well as a

reference values, for comparison with recent and future experimental findings on silicates, aluminosilicates and other materials.

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