

CHEMICAL AND STRUCTURAL STUDY OF ANIONIC AND CATIONIC SITES IN TRIOCTAHEDRAL MICAS AT RT AND HT TEMPERATURES

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INTRODUCTION

Micas are a group of minerals with a complex crystal chemistry, characterized by substitutional disorder that may involve tetrahedral (Si, Al, Fe, Ti), octahedral (Mg, Mn, Fe²⁺, Fe³⁺, Ti³⁺, Ti⁴⁺, Al, Cr, Li, □), interlayer (K, Ba, Ca, Na, NH₄, □, H₂O) sites, as well as the anion (OH⁻, O²⁻, Cl⁻, F⁻) site. Many of the mutually substituting atoms may enter more than one site of the mica structure and involve more than one substitution mechanism (Waters & Charnley, 2002; Righter *et al.*, 2002). In addition, some elements may be characterised by variable valence state (Fe, Ti, etc.).

The geological importance of these minerals depends on their occurrence in many geological environments and on their potentiality as petrogenetic indicators. More specifically micas from volcanic rocks could allow to infer pre-eruptive magmatic conditions and discriminate between processes that occurred during the igneous phase of mica crystallization and those due to post-crystallization events, provided that complete chemical analyses and detailed knowledge of the substitution mechanisms, are available (Laurora *et al.*, 2007; Scordari *et al.*, 2008). In addition, the knowledge of the biotite behaviour at high temperature has implications for the characterizations of petrologic and geological systems.

In this work, the crystal chemistry of Mt. Vulture trioctahedral micas has been extensively investigated at room and high temperature using a combination of several independent analytical techniques. In particular, Electron Probe Micro Analysis (EPMA), Secondary Ion Mass Spectrometry (SIMS), Single Crystal X-Ray Diffraction, (SCXRD), Mössbauer Spectroscopy (MS) and Fourier Transform Infrared (FTIR) spectroscopy analyses have been used, in order to:

- 1) investigate the crystal chemistry of trioctahedral micas with particular attention to substitution mechanisms and anionic site chemical composition that form the basis from which reliable activity-composition models may be developed;
- 2) examine in detail how the structure of trioctahedral micas of complex composition responds to heating;
- 3) use the crystal chemical data of micas to get an insight into the geological processes the host rock underwent.

The mica crystals considered here have been separated from deposits belonging mainly to the oldest (~ 740 ka) and to the intermediate (~ 720÷570 ka) volcanic episodes of Mt. Vulture activity. Detailed stratigraphic classification of these deposits is reported in Giannandrea *et al.* (2006). In the present work, mica samples (labelled Vut215, IgnA, IgnB, LCR, and Pg5) used for the room temperature analyses were collected from the oldest volcanic deposits belonging to the Foggianello Synthem. Specifically, Vut215 micas, selected from lava fragment of the Molara Ignimbrite, belong to the Campanile Subsynthem, whereas IgnA, IgnB, LCR, Pg5 samples belong to the Fara d'Olivo Subsynthem. For high temperature investigations, one sample labelled SA, from intermediate deposits (Barile Synthem, Rionero Subsynthems) has been considered.

CHEMICAL CHARACTERIZATION

The chemical results, obtained from EPMA, and, for some sample, from SIMS investigations, have shown that:

1) Pg5 and LCR biotites are characterized by significant intercrystalline chemical variations particularly regarding the Mg/Fe, Ti and F contents. Indeed, Pg5 samples are characterized by remarkable chemical inhomogeneity, as revealed by the generally large ranges in oxide wt.%: 32.8÷36.6 for SiO₂, 15.9÷22.0 for MgO, 6.1÷13.4 for FeO_{tot}, 0.38÷2.4 for TiO₂, 0.8÷3.3 for BaO, 0.7÷1.4 for F. LCR micas have shown inter-grain variability pronounced for TiO₂ (2.8÷5.0 wt.%), F (0.83÷2.73 wt.%, SIMS data), BaO (0.07÷1.8 wt.%) and H₂O (1.24÷3.37 wt.%, SIMS data). This trend is also documented by previous investigations on other Mt. Vulture micas selected both from different and from the same stratigraphic layer (Schingaro *et al.*, 2001, 2005; Mesto *et al.*, 2006);

2) IgnA, IgnB, Vut215 and SA samples turned out to be relatively homogeneous. However, for Vut215 micas were found higher TiO₂ (<4.6> wt.%), BaO (<2.2> wt.%) and Na₂O (<0.7> wt.%) contents than the other samples.

Finally, the Mg/(Mg+Fe_{tot}) ratio or “Mg number” ranges from ~ 0.60÷0.90, and generally it decreases with increasing Ti atoms p.f.u.

MÖSSBAUER AND FTIR INVESTIGATIONS

Mössbauer investigation evidenced that in all samples Fe was in octahedral coordination. Indeed, all spectra showed three absorption bands at approximately -0.2, 1.0 and 2.3 mm/s which corresponded respectively to i) the sum of low energy lines of ^{VI}Fe²⁺ and ^{VI}Fe³⁺ doublets, ii) the high energy line of the ^{VI}Fe³⁺ doublet, and iii) high energy component of the ^{VI}Fe²⁺ doublet. There was no clear evidence for tetrahedral Fe³⁺ (whose high energy component occurs at ~ 0.5 mm/s) in the samples. The fitting according to the QSD method yielded the following results:

- 1) Fe²⁺ (%) = 42.3(34), Fe³⁺ (%) = 57.7(34) for IgnA;
- 2) Fe²⁺ (%) = 65.7(21), Fe³⁺ (%) = 34.3(21) for IgnB;
- 3) Fe²⁺ (%) = 61.5(69), Fe³⁺ (%) = 38.5(69) for Pg5.

For samples Vut215 and SA the results of previous Mössbauer investigations were used, which provided Fe²⁺ (%) = 11.21(35), Fe³⁺ (%) = 88.79(35) for Vut215 (Matarrese, 2007) and Fe²⁺ (%) = 11.21(35), Fe³⁺ (%) = 88.79(35) for SA (Scordari *et al.*, 2006).

The FTIR investigations were carried out in order to characterize the local environment of the anionic site O4. Measurements were performed on single crystals in the range 4000-600 cm⁻¹. The OH-stretching region for most of the analysed samples extended in the range ~ 3740-3600 cm⁻¹ and consisted of normal and impurity bands associated only to fundamental vibrations of the OH groups. On the contrary, for three out of the five investigated LCR samples (LC6_R7, L6_R29 and LC7_R2), the OH stretching region was affected by overlapping of bands that extends up to ~ 2500 cm⁻¹. The results of fitting have shown:

1) a prominent band at ~ 3540 cm⁻¹ assigned to OH with two Fe³⁺ and a vacancy, whereas a shoulder at ~ 3621 cm⁻¹ is attributed to OH bonded to two Al and a vacancy (Libowitzky & Beran, 2004, and reference therein);

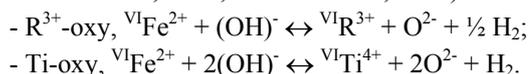
2) a series of overlapping band arising from about 3400 to 2800 cm^{-1} due to the ammonium ion (NH_4^+) and water (H_2O) normal modes of vibration.

Therefore, for LCR samples the total hydrogen content determined by SIMS encompasses different species, *i.e.* OH groups but also NH_4^+ groups and H_2O molecules, both of which substitute for K^+ at the interlayer site (Sadofosky & Bebout, 2000; Cesare *et al.*, 2003). It can be concluded that in this work FTIR analyses have significantly contributed to investigate the hydrogen speciation, the occurrence of octahedral vacancies, Fe-oxy substitution mechanism and, in general, to assess the correct structural formula of the analysed samples.

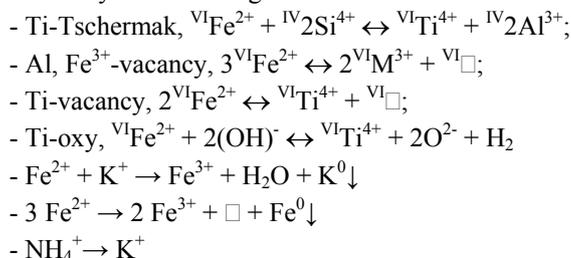
STRUCTURAL AND CRYSTAL CHEMICAL CHARACTERIZATION

Micas studied here belong to the 1M polytype. About 30 single crystal structure refinements have been performed in space group $C2/m$.

The samples Vut215, IgnA, IgnB, Pg5 and SA showed structural details (short c cell parameter, bond distances and distortion parameters such as t_{int} , t_{oct} , and $t_{\text{K-O4}}$; high value of shift_{M2}) which were consistent with the following occurrence of oxy-type substitutions (Cesare *et al.*, 2003; Matarrese *et al.*, 2008; Scordari *et al.*, 2006; Ventruti *et al.*, 2008):



On the basis of the cell parameters (especially the c -cell parameters) the LCR samples could be divided into two groups: the first one, characterized by $c \sim 10.23 \text{ \AA}$, encompasses three samples (LC6_R7, LC6_R29 and LC7_R2); the other two samples (LC7_R4, LC7_R5) constitute the second group, which has $c \sim 10.14 \text{ \AA}$. These differences pointed to different extents of substitutions at the O4 hydroxyl site (Cesare *et al.*, 2003, and references therein; Matarrese *et al.*, 2008). Micas of the Group 1 were affected by the following substitution mechanisms:



In Group 2 micas VITi^{4+} and VIFe^{3+} enter the structure through oxy-type substitution mechanisms involving deprotonation at O4 as see above.

KINETICS OF FE-OXYDATION/DEPROTONATION PROCESS

Recent investigation have ascertained that oxy substitution mechanisms involving deprotonation at O(4) site play a major role in phlogopites (Virgo & Popp, 2000; Righter *et al.*, 2002; Scordari *et al.*, 2006). Feeley & Sharp (1996) pointed out that the H_2 released by these reactions can combine with the O_2 in the melt, thus increasing the volatile components and the explosive nature of volcanism.

In the second part of this work, the kinetics of the Fe-oxidation/deprotonation process at $T = 600$ and 700°C in SA samples (labelled SA_14 and SA_9) with composition analogous to those submitted to thermal investigation by Ventruti *et al.* (2008) has been studied. These authors observed the Fe-

oxidation/deprotonation reaction in an *in situ* high temperature X-ray single-crystal diffraction experiment in the temperature range -173-750°C. Ventruti *et al.* (2008) found that the process take place starting from $T > 550^\circ\text{C}$ and causes a shortening of the unit cell parameters and, consequently, of the cell volume. In that paper, it was demonstrated that the process is irreversible. It remained questionable, however, whether it was a one-step or a multi-step reaction.

Under isothermal condition the unit-cell parameters decrease following an exponential law and the most pronounced variations occur along the *c* axis. Equilibrium was reached in a time scale of $\sim 10^4$ and $\sim 10^3$ min at 600 and 700°C, respectively. The reversal experiment in the temperature range 950-25°C has shown:

- 1) the irreversibility of the Fe-oxidation/deprotonation process;
- 2) the superimposition of the linear expansion curves obtained for the two crystals, suggesting a same degree of deprotonation achieved at the two temperatures.

Therefore, the process occurs in an unique step. Structural modifications were also observed by comparing FTIR spectra in the OH stretching region collected before and after heating at 700°C. The most pronounced variations occur to normal and impurity OH stretching bands associated to $^{\text{VI}}\text{Fe}^{2+}$ and $^{\text{VI}}\text{Fe}^{3+}$ local environments. Relationships among the amount of Fe^{2+} that is oxidized, the amount of deprotonation, and the *b* and *c* parameters shortening have also been quantitatively estimated. They were found to be consistent with variation of crystal chemical formula before and after heating.

CONCLUSION

1) On the basis of their mineral chemistry, the analysed samples were “biotites” in the sense of the IMA classification of micas (Rieder *et al.*, 1998). Among the analysed micas, two samples (Pg5 and LCR) displayed significant intercrystalline chemical variations, whereas the others (IgnA, IgnB, Vut215 and SA) turned out to be relatively homogeneous.

2) Typical structural features of dehydrogenated micas were generally present in the analyzed biotites. The *c* parameter was reduced with respect to those measured in close-to-end-member annite (10.3235(4) Å, Redhammer & Roth, 2002) and phlogopite (10.310(5), synthetic sample Phl#2 in Redhammer & Roth, 2002).

3) Most of analysed samples are characterized by prevalence of oxy-type substitutional mechanisms that involve deprotonation at O4. On the contrary, some LCR micas show prevalence of vacancy-bearing substitutions and the occurrence of H_2O and NH_4^+ at the interlayer. These samples features were likely the result of the hydrothermal alteration of brown micas (the most common in Vulture deposits), which started their crystallization at high temperature (about 900°C) and low pressure (about 2 Kbar) conditions.

4) For IgnA, IgnB, Pg5 and SA samples were found $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios similar to other Vulture samples and likely very close to magmatic values (Matarrese, 2007). On the contrary, for Vut215 micas were obtained $\text{Fe}^{3+}/\text{Fe}^{2+} \gg 1$. Therefore, Vut215 biotites, selected from lavas, very likely underwent post-magmatic thermal oxidation processes.

5) The study of trioctahedral mica SA in the temperature range 25-950°C showed the occurrence of an irreversible deprotonation process with a consequent $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation starting from about 600°C and a phase transition implying no symmetry change. Kinetics of Fe-oxidation/deprotonation followed an exponential law, as shown by the trend of the lattice parameters and the volume measured at 600 and 700°C as a function of time. The results obtained in the present study confirmed the occurrence

of the Fe-oxidation/deprotonation process in a unique step, as previously found in other high temperature studies on micas (Tutti *et al.*, 2000; Chon *et al.*, 2006). The effects of the Fe-oxidation/deprotonation process were also observed on some OH stretching bands in the FTIR spectrum of an SA sample before and after heating.

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