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Autor: Biino, Giuseppe G.

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X-ray photoelectron spectroscopy (XPS) evidence for interlayer phases in natural micas: effects on physico-chemical properties and geochronological consequences

by *Giuseppe G. Biino*[1]

Abstract

After cleaving, the chemistry of the (001) topmost layers of natural micas was experimentally investigated by X-ray photoelectron spectroscopy (XPS). There is evidence that phlogopite cleaves along very thin chlorite interlayers also including graphite-rich microinclusions. Muscovite cleavage exposes an aluminum-rich (gibbsite, kaolinite or pyrophyllite) interlayer as well as graphite-rich microinclusions planes. Cleavage occurs in these interlayered phases because they have the weakest bonds. These interlayered phases are also responsible for changes of the mechanical properties of micas (i.e.: lattice slip is enhanced). The investigated micas yield Rb–Sr, K–Ar and Ar–Ar ages that are unrelated to metamorphic or igneous events. The formation of the interlayered phases probably perturbed the Rb–Sr and K–Ar isotopic systems.

Keywords: mica, surface reaction, interlayer phase, photoelectron spectroscopy, isotopic systems.

Introduction

Micas are common rock-forming silicates. The mica lattice is a modular structure made up of two dimensional arrays of oxygen monolayers (not considering the presence of hydroxyl, F and Cl) alternating with cation monolayers (Fig. 1). On the other hand, considering the coordination polyhedra of cations, the mica structure can be described as octahedral sheet (o; mainly made up of Mg, Fe, Al) sandwiched between two tetrahedral sheets (t; mainly made up of Si and Al). In micas, Al substitutes for one Si every fourth atom and a charge imbalance appears in the tetrahedral sheet. The charge imbalance is compensated by interlayer cations like K (or Na, Ca) alternating with the t-o-t layer (i-sheet). Substitution of Al^{VI} Al^{IV} by $(Mg,Fe)^{VI}Si^{IV}$ in muscovite corresponds to the Tschermak vector leading to phengitic muscovite. In phengitic muscovite the charge imbalance is no more located in the tetrahedral sheets, but it is partitioned between tetrahedral and octahedral sheets. This partitioning of the net charge imbalance may destabilize the t-o-t structure due to alternation of negatively charged sheets. The net negative charge is no longer physically very close to K and the lattice slip should be affected. On the other hand, in phengitic muscovite the tilting of the hydroxyl group (PAVESE et al., 1997) reduces the coulombic repulsion between K and the proton of the OH group. Substitutions in the octahedral sheet are very complex, some producing vacancies in the lattice, which also play a role in changing the t-o-t bonding structure.

Natural surfaces of mica are mainly produced by cleavage since micas cleave perfectly and easily parallel to (001). Micas cleave parallel to (001) because bonding is strong within each sheet but weak between sheets. Octahedral edge-sharing leads to a continuous rigid network within each layer, in contrast to the more flexible linkages in the silicon and alkali-layer. The cleaved surface may correspond to four chemically different monolayers (i.e.: O, Si–Al, Mg–Fe–Al, K–Na–Ca; Fig. 1). It is generally believed that micas cleave along the plane housing the large cations (i.e.: K, Na or Ca), but this has not been experimentally investigated. GIESE (1974) suggested on a theo-

[1] Institut de Minéralogie et Pétrographie, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland. Present address: Materials Sciences Division, Lawrence Berkeley Nat. Lab., Berkeley California 94720 USA. <giuseppe.biino@unifr.ch>

retical base that muscovite cleave along the i-sheet, and that K is regularly partitioned on the two new surfaces. This interpretation relies on the assumption that the K sheet is weakly bonded (electrostaticly) to the basal oxygen of the t-sheet and also experiences electrostatic repulsion from other K atoms and from the OH present in the oxygen monolayer between the Si–Al and the Mg–Fe–Al monolayers. Substitution of OH by F in phlogopite increases hardness, specific resistivity, and dielectric constant (BLOSS et al., 1959; SHELL and IVEY, 1969). GIESE (1977) calculated the effect of F –> OH substitution on the strength of interlayer bonding. He concluded that K has stronger electrostatic bond with O in F-phlogopite than in OH-phlogopite. DAHL and DORAIS (1996) suggested that F –> OH substitution may alter the geometry of the i-sheet and prevents the slip of the lattice.

All of these considerations on mica properties are only valid for ideal crystals. It is not clear whether natural micas which may have interlayers and lattice defects can be described by idealized models. Nevertheless, a better understanding of the (001) of natural mica is not a mere curiosity which concerns only mineralogists since micas surfaces are important for geochemical cycling of the elements (HOCHELLA and WHITE, 1990; FERRIS et al., 1996). In general, fluid-mica interactions are governed by the physico-chemical properties of the mica (001) surfaces. Lattice slip occurs on the (001) plane and is related to a cleavage mechanism. Due to lattice slip, micas have a low resistence to shear which is relevant in the definition of mechanical properties of crustal rocks. Any modification of mica (001) also modifies the mechanical properties of the mineral and of crustal rocks.

The aim of this paper is to experimentally characterize the surface chemical composition of freshly cleaved (001) natural micas. The surface chemical information provides experimental evidences for the cleaving mechanism, presence of interlayers and inclusions as well as a solid base to start to interpret geochronological data, mechanical properties of micas and to model fluid-mica interaction. Phyllosilicates commonly occur as regular or random intergrowths of layers or selective layer-replacement. Most methods of studying phyllosilicate involve measurements of properties

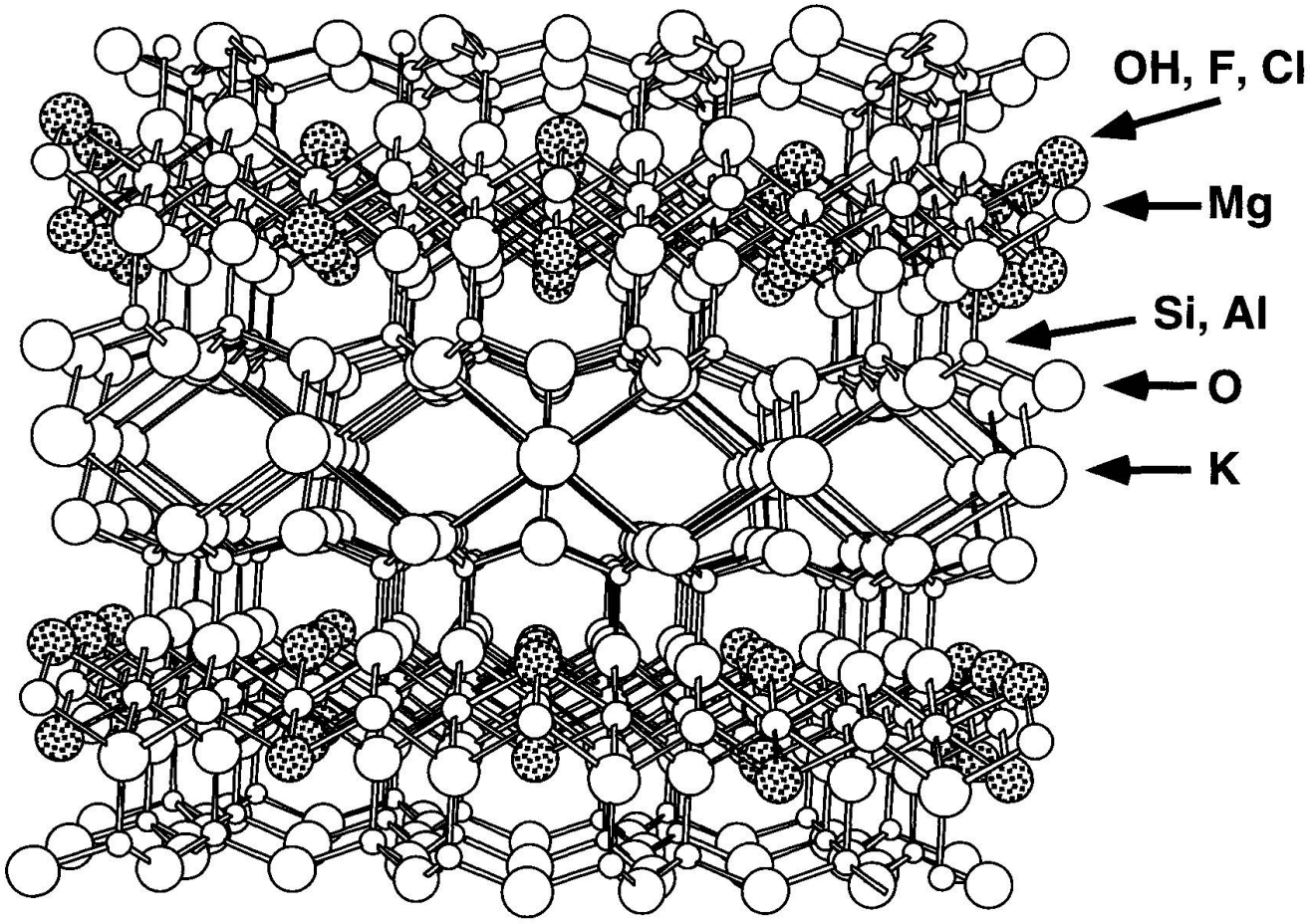

Fig. 1 Ideal crystal structure of phlogopite as shown in perspective along the **a** axis.

averaged over many grains or over many layers of the same grain. In case of fine scale intergrowths, most analytical techniques give an average over more than one phase, the interpretation of such data would therefore be subject to error. In this study the surface chemistry of mica (001) is investigated by means of X-ray photoelectron spectroscopy (XPS). XPS is probably the most reliable technique for quantitative surface chemical analysis, non-destructively providing information on both chemical composition and (via core binding energy changes) also chemical state.

Analytical techniques

A general introduction to XPS is given in articles and textbooks (FADLEY, 1978; BRIGGS and SEAH, 1990; HUFNER, 1996; TILININ et al., 1996). XPS directly measures the kinetic energy of the emitted photoelectrons and gives information on the energy of binding, oxidation state and coordination environment of an element as well as its concentration. It is well known that electrons excited by soft X-ray radiation have a short inelastic mean free path (λ) in solids (in the order of 1–3 nm). Thus, XPS only measures photoelectrons originated from the atoms in the topmost layers (Fig. 2). Since the probing depth (d_θ) is related to the distance that the electron can travel in a solid, tilting of the oriented sample reduces the probing depth according to the empirical formula $d_\theta = d_\theta \operatorname{sen} \theta$.

This investigation was carried out at the Department of Physics of the University of Fribourg with the VG ESCALAB 5. The (001) of mica was irradiated with non-monochromatized MgKα ($h\nu$ = 1253.6 eV) X-rays. The instrument was calibrated to the $4f_{7/2}$ peak of gold at E_B = 84.0 eV and the copper $2p_{3/2}$ peak at E_B = 932.7 eV. Spectra were taken with 20 eV pass energy in the constant analyser energy (CAE) mode. The X-ray source was operated at 10 kV, 20 mA. During measurement the pressure was in the range of 10^{-10} and 10^{-9} torr. Charge shift was corrected by using the Si2p peak position at 102.36 eV according to BIINO and GRÖNING (1998). XPS measurements were performed at normal emission and after a tilting of the polar (or take off) angle (θ angle) of the sample with respect to the mineral surface in order to modify the probing depth (Fig. 2). Sputtering by Ar^+ was done to test the thickness of Mg–Al silicate interlayered in phlogopite. Elemental concentrations were evaluated from experimental XPS peak areas obtained after Shirley background subtraction and Voigt peak shape fitting. The theoretical cross section and the energy dependent asymmetry parameter of the subshell were taken from YEH and LINDAU (1985). Accuracy should be better than 2 atomic percent.

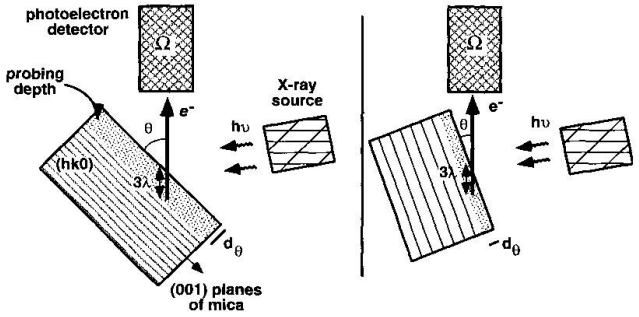

Fig. 2 Sample tilting: probing depth before and after 25° tilting. This investigation was carried out with the VG ESCALAB 5, and the geometry of XPS measurement is shown. The incoming X-ray on the (001) of micas has an energy $h\nu$ = 1253.6 eV. The detected photoelectrons leave the surface at an intersection angle θ (polar or take off angle). The inelastic mean free path is indicated by λ and is constant for each crystallographic direction of each substance. The probing depth (indicated by d) is reduced by tilting (θ angle) as evidenced in the right hand side of the figure. The tilting axes is perpendicular to the figure. During measurement the pressure was in the range of 10^{-10} and 10^{-9} torr.

Sample description

The (001) surface was produced by cleavage of natural single crystals in a high vacuum chamber (10^{-6} torr) or in air. The following samples were investigated: a muscovite from a pegmatite of the Locarno zone (Centovalli) in the central Alps (the locality corresponds to the sample WSπ33a after STERN, 1966), a phengitic muscovite from the coesite-pyrope whiteschist of Dora-Maira composite nappe (in the western Alps; CHOPIN, 1984; AMISANO et al., 1994), and a phengitic muscovite from the Sesia-Lanzo zone (in the western Alps; STÖCKERT et al., 1986). The mica from Dora-Maira exhibits ca. 60% of Tschermak substitution and the mica from the Sesia-Lanzo ca. 30%. Phlogopite was collected at two localities: Finero (in the western Alps; EXLEY et al., 1982) and Templeton (Ontario, Canada). Phlogopite from Finero is OH-, and that from Templeton is F-bearing. Phlogopite from Finero exposed to natural weathering (i.e.: the (001) face was parallel to the outcrop surface) was also investigated.

It is important to stress that in the investigated micas the presence of interlayered phases was not shown up by either powder X-ray diffraction

(PXRD) or single crystal X-ray diffraction (AMISANO et al., 1994). Indeed, powder neutron diffraction shows talc in the phengite from Dora Maira (PAVESE et al., 1997). Experimental investigation by transmission electron microscope of the phengite from Dora Maira evidences thin interlayered phases (C. FERRARIS, pers. comm.). The thicker interlayers (up to 70 Å) decompose under the electronic beam during transmission electron experiments before a high resolution picture can be collected in the proper orientation.

The investigated micas from the Alps provide Rb–Sr, K–Ar and Ar–Ar ages (JÄGER et al., 1967; OBERHÄNSLI et al., 1985; STÖCKERT et al., 1986; PAQUETTE et al., 1989; MONIÉ and CHOPIN, 1991; HUNZIKER et al., 1992) that are unrelated to metamorphic or magmatic events (SCAILLET et al., 1992; ARNAUD and KELLEY, 1995; RUFFET et al., 1996; REDDY et al., 1996; SCAILLET, 1996; INGVER et al., 1996; RUFFET et al., 1997).

Results

XPS is found to provide experimental evidence that micas cleaved in air are instantaneously coated by several ångstroms thick layers of adventitious material. The adventitious material is dominated by C (hydrocarbons?) that makes up to 80 wt% of the XPS analysis (H cannot be measured by XPS). Deconvolution of the Cls peak also may indicate the presence of a minor amount of graphite-like phase (in the following just named graphite) in all of the investigated samples. This graphite is practically the main carbon component in the Cls peak when micas are cleaved in high vacuum (Fig. 3). Therefore, graphite is interpreted as a primary solid inclusion, but it forms crystals below optical resolution.

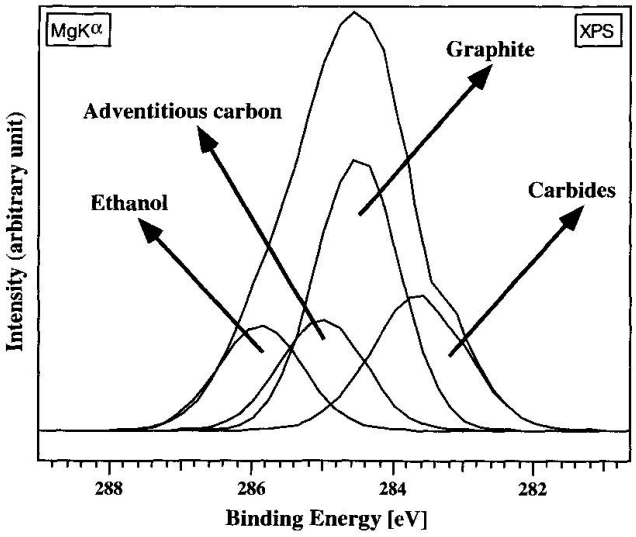

Fig. 3 Deconvolution of the Cls peak (sample from Centovalli, locality WSπ33a after STERN, 1966). The muscovite was measured after cleaving in vacuum (10^{-6} torr). Charge correction was done according to BIINO and GRÖNING (1998). All the fitting parameters were let free during the last step of the fitting procedure. One of the resulting peak is at 285.0 eV (binding energy) as expected for the adventitious carbon. The adventitious carbon and ethanol peaks are due to contamination in the preparation chamber (after cleaning the sample holder was not baked to prevent thermally induced modification of the mica).

The surface composition of phlogopite cleaved in vacuum suggests that the cleavage occurred along interlayers of MgAl silicate (chlorite). The MgAl silicate forms interlayers at least a few tens of ångstroms thick. Graphite-rich microinclusions planes were also exposed by cleaving. When MgAl silicate (chlorite) interlayered phase was absent or minor, K was not the top monolayer but cleavage occurred in the brucite-like sheet or more properly in the Mg monolayer (Fig. 4). No difference was observed between the (001) surface of F- and OH-bearing phlogopite. In all experiments of phlogopite surfaces exposed to natural weathering the topmost layers consisted of a MgAl silicate (chlorite). In these layers Fe, K and Ti are completely leached away.

The (001) topmost layer of phengitic muscovite (from both localities) consists mainly of Al (Fig. 4). This surface chemistry corresponds to a gibbsite sheet or better to the Al monolayer (kaolinite, gibbsite or pyrophyllite phase ?).

Muscovite cleaved in high vacuum shows a topmost layer consisting of a mixture of o- and t-sheets (this may also be interpreted as along an Al-rich interlayered phase) in 75% of the experiments and in the remaining 25% of the experiments K dominates the crystal termination.

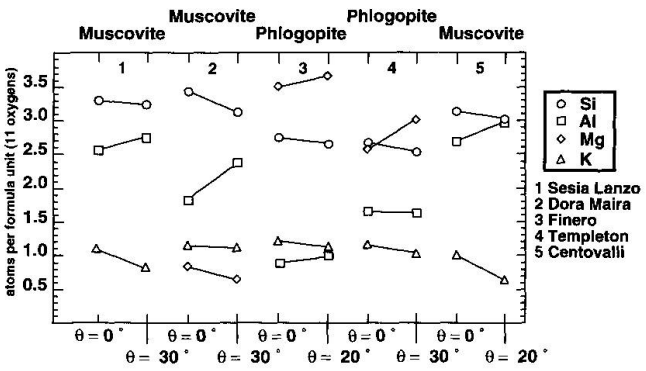

Fig. 4 Representative chemical composition of mica (001) surfaces before and after tilting (θ). The surface analyses corresponding to chlorite are not plotted since they were not tilted.

Discussion

The surface composition of micas cleaved under vacuum suggests that the cleavage is controlled by interlayers of chlorite, graphite, and an Al-rich phase (pyrophyllite, kaolinite or gibbsite). With the exception of chlorite, the scale of the intergrowth is in the order of a few ångstroms and even XPS cannot, in every experiment, resolve a single interlayered phase. Surface chemistry clearly points out an irregularity in the stacking of a monolayer sequence with absence of the interlayer cation sheet. Micas with deficiency in interlayer cations may be derived from the theoretical pure end member by the exchange vectors $K_{-1}Al_{-1}$ Sivac (vac = site vacancy) or $K_{-1}(H_3O)$. The absence of an i-sheet (001) surface (i.e.: K monolayer) in phengitic muscovite is surprising but the structure is significantly different from muscovite since in phengitic muscovite the apical oxygen is underbonded, whereas the basal oxygen atoms are overbonded. The observed interlayers which are only a few ångstroms thick may also compensate this disequilibrium generating a random stacking sequence with monolayers very weakly bonded along [001]. The presence of these interlayered phases has important implications in mechanical properties of micas, geochronology and modelling interaction between micas and fluids or organic molecules.

The lattice of the silicate interlayered phases do not strongly disturb the mica lattice. However, the mica lattice does not match the graphite lattice. It was experimentally shown that K is bonded on the graphite surface on top of the cavity of the hexagonal ring as shown in figure 5 (BENNICH, 1996). The distance between K is not matching that in the i-sheet of micas. A slightly better fit exists between graphite and the o- and t-sheets; nevertheless chemical bonds at mica-graphite interfaces should be significantly distorted. The presence of graphite in the phlogopite collected at Finero is consistent with the mantle metasomatism (characterized by CO_2 rich fluids) of the Finero peridotite. Graphite microinclusions in the other micas may also be related to mica-CO_2 rich fluid interactions (CO_2-rich fluid inclusions in quartz or pyrope associated with the investigated micas were observed).

Considering now the adventitious component of the C1s peak, it is not clear how C from the atmosphere can be adsorbed as C on a mica surface. Atomic force microscopy (AFM) images of mica surfaces produced in air should also show adventitious material. AFM images are generally interpreted as a view of the basal oxygen lattice and cations are never in evidence (LINDGREEN et al., 1991; SHARP et al., 1993; EBY et al., 1993; HENDERSON et al., 1994). Indeed, it is not clear whether the scanning tip pushes cations and the C coating away from the surface and detects oxygen from the true mineral lattice or the observed surface is made up of adventitious materials that mimicks the mineral surface structure (i.e.: pseudomorphic in the surface physics literature). Similar pseudomorphic layers are commonly described at the quartz-aqueous solution interface. Alternatively, C molecules sorbed on mineral surfaces have a to weak tunneling current and a relative surface mobility to be detection by AFM.

Studies on the mechanical strength of micas are contradictory (WILSON and BELL, 1979; BELL et al., 1986; KRONENBERG et al., 1990; MARES and KRONENBERG, 1993). WILSON and BELL (1979) showed that muscovite has stronger mechanical strength than biotite but biotite investigated by KRONENBERG et al. (1990) has stronger mechanical strength than muscovite investigated by MARES and KRONENBERG (1993). DAHL and DORAIS (1996) suggested that F –> OH substitution is responsible for experimental inconsistencies. The mechanisms controlling cleavage and mechanical properties are related and the presence of very thin interlayered phases may help to

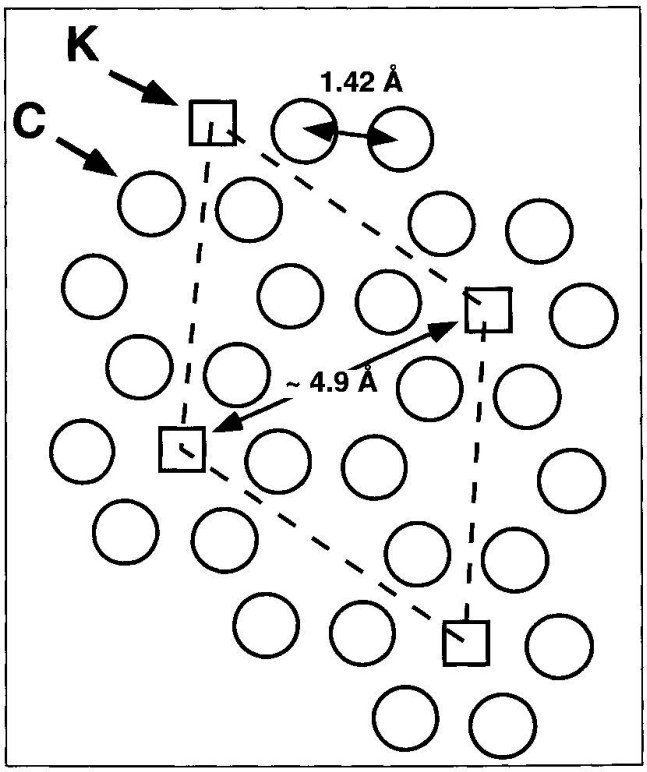

Fig. 5 Mineralogical relationship between the (001) mica surface and the (001) in graphite The unit cell for K sorbed on graphite (indicated in the figure) was experimentally determined by BENNICH (1996).

re-interpret the experiments on the mechanical properties of micas. My experience in investigating Alpine metamorphic rocks suggests that when muscovite and biotite occur in the same shear zone, muscovite flakes show less basal slip than biotite. Indeed, we should keep in mind that most Alpine shear zones recrystallized in the stability field of chlorite, talc, serpentine and muscovite. It may follow that during deformation biotite underwent a breakdown reaction and interlayered phases were newly formed. Mechanical strength is probably modified by very thin interlayered phases already before these interlayers can be observed with an optical microscope.

XPS does not provide any experimental evidence for chemical difference in the topmost surface layers between F- and OH-bearing phlogopite (i.e.: no modification of the cleavage mechanism). While GIESE (1977) and DAHL and DORAIS (1996) are probably correct in considering that F-bearing ideal phlogopite has a stronger K–O bond because there is no repulsion between K and H, this observation may not be relevant in natural micas since interlayered phases change the mechanical properties of micas significantly.

Micas are extensively used in geochronology. Phengitic muscovite is stable at high-pressure and it is the only mineral that can be dated in low temperature eclogite (at this P-T conditions isotopic disequilibrium prevents the use of Nd–Sm isotopic geochronology and zircons may not recrystallize). A better understanding of the recrystallization dynamics in the phengitic muscovite lattice and of the resetting of the isotopic systems will help to define the time of subduction. Unfortunately, several evidences suggest that the K–Ar isotopic system of the phengite could be heavily disturbed by excess Ar (SCAILLET et al., 1992; TONARINI et al., 1993; LI et al., 1994; ARNAUD and KELLEY, 1995; RUFFET et al., 1996; REDDY et al., 1996; SCAILLET, 1996; RUFFET et al., 1997). A few interpretations of the excess Ar were proposed, for example, RUFFET et al. (1995) suggested that the excess Ar incorporation was related to limited flow of the fluid phase conveying the excess Ar under the high pressure metamorphic conditions, but more recently, RUFFET et al. (1997) failed in providing any convincing experimental evidences for fluid flow, and they abandoned their former hypothesis. After a close look at articles on the geochronology of Alpine micas, a very confusing model arises (JÄGER et al., 1967; OBERHÄNSLI et al., 1985; STÖCKERT et al., 1986; SCAILLET et al., 1990; PAQUETTE et al., 1992; MONIE and CHOPIN, 1991; HUNZIKER et al., 1992; SCAILLET et al., 1992; ARNAUD and KELLEY, 1995; RUFFET et al., 1996; REDDY et al., 1996; SCAILLET, 1996; INGVER et al., 1996; RUFFET et al., 1997). Rb–Sr, A–Ar and K–Ar ages from micas are traditionally interpreted following an empirical rule that relates the open system behavior of micas to temperature. For example in the case of muscovite, isotopic age determinations are considered as formation ages when the muscovite formed below ca. 550 °C, or as cooling ages when formation occurred at higher temperatures. Phengitic muscovite defies this empirical rule and often gives ages that are too old (e.g.: TONARINI et al., 1993; LI et al., 1994; ARNAUD and KELLEY, 1995; RUFFET et al., 1996; REDDY et al., 1996; SCAILLET, 1996; RUFFET et al., 1997). The radiogenic isotopic systems in biotite are normally considered to be reset at low temperature (ca. 350 °C), but there is experimental evidence showing resetting at higher temperatures (ARNOLD and JÄGER, 1965; VERSCHURE et al., 1980; VILLA and PUXEDDU, 1994). It is necessary to conclude that the isotopic systems of micas are not influenced by temperature, since in the Alps a large spread in ages is documented for closely spaced samples and even in the same crystal. Solid state diffusion of radiogenic isotopes in homogeneous phases is unlikely to be governed by temperature in the range of 300 to 500 °C (even considering defects migration). On the other hand, formation and/or presence of interlayered phases provides lattice dynamics and discontinuities in the lattice. The new surfaces are fast diffusing pathways allowing both partial resetting and/or trapping from external source of parent and/or daughter isotopes as discussed in the following.

The isotopes in the Rb–Sr and K–Ar isotopic systems are located in the i-sheet (this may not be correct for radiogenic Ar) and the formation of thin interlayers in the (001) perturbs this sheet both adding and leaching elements. It was experimentally shown that volume diffusion of isotopes along the (001) plane is faster than along other directions (FORTIER and GILETTI, 1991; ONSTOTT et al., 1991). On one hand, the formation of interlayered phases will tend to enhance diffusion of Ar and Sr, which do not fit the lattice either of micas or of interlayered phases, and therefore it opens the isotopic systems at low temperature. On the other hand, the formation of interfaces between micas and interlayered phases may also trap daughter isotopes in the grain boundaries. Sorption of radiogenic isotopes at the interfaces can account for to old isotopic ages. The presence of graphite may cause an excess in radiogenic Ar because Ar adsorption on graphite surface is governed by Henry's law. This states that the number of atoms adsorbed per unit area is proportional to the Ar partial pressure with a proportionality constant (SAMS et al., 1960; STEELE, 1978), and it is

evident that during metamorphism the pressure of radiogenic Ar is not zero.

If the nucleation and growth of interlayered phases occurs at any temperature below ca. 500 °C it is unprobable that the isotopic systems remain closed. Non pervasive alteration may be responsible for observed anomalies in the retentivity of radiogenic isotopes. It is interesting to note that biotite investigated by ARNOLD and JÄGER (1965) and by VILLA and PUXEDDU (1994) were not collected in outcrops. The biotite from ARNOLD and JÄGER (1965) was from an ultramafic lens crosscut during the construction of a tunnel and a metasomatic rim sealed the ultramafic lens from fluid infiltration. The sample of VILLA and PUXEDDU (1994) was from a drillhole and biotite was very carefully hand picked. It may be suggested that in both cases biotite was not altered. KAMBER and BIINO (1995) observed interlayered phases in micas from the high grade rocks of the Limpopo belt and the isotopic systems (Rb–Sr and Ar–Ar) turned out to be perturbed (KAMBER et al., 1997). The case of the Limpopo belt is not a simple anomaly of a paradigm, but the macroscopic evidence for a process.

It is important to stress that a second possible explanation exists for the presence of Al-rich interlayers in phengitic muscovite and the incomplete isotopic resetting during high-pressure metamorphism. It is well documented that the investigated phengitic muscovite from the Sesia-Lanzo zone crystallized as muscovite before the Alpine cycle, and it re-equilibrated during the prograde in pressure Alpine metamorphism to a phengite-richer muscovite. Considering a phase equilibrium diagram, it is reasonable to assume that the phengitic muscovite from the Dora-Maira composite nappe nucleated at low to middle pressure and was re-equilibrated to a phengite-richer muscovite at the peak pressure condition. If Al was not transported out of the lattice an Al-rich exsolution must have formed. The radiogenic isotopes may also migrate in these exsolution and therefore the isotopic systems in the mica are only partially reset. Argon laser extraction on crystal faces perpendicular to (001) reduces the volume of the analyzed sample, but it may only mitigate the effect of interlayered phases since too much sample volume is vaporized.

Conclusion

XPS experiments on cleaved micas are able to evidence a few ångstroms thick layer that is selectively exposed by cleaving. In the ideal mica structure the i-sheet is the weaker part of the lattice, but as soon as interlayered phases are present physical and chemical properties of micas are altered. In the interlayered phases and at the interface micas/interlayered phases the strength of the bonds is even lower than the van der Waals bonds between K and O in micas. The interlayered phases control the cleavage mechanism, dictate the mechanical properties, perturb the isotopic system and define the physico chemical properties of the (001) surfaces.

During exhumation of metamorphic terranes, rock units cross temperature ranges in which micas are unstable. Retrograde reactions involving micas generate interlayered phases. Indeed, the interlayered phases are not only the result of retrograde metamorphism, since prograde evolution of high pressure muscovite may also be responsible for interlayered phases.

Any quantitative description of mineral surface phenomena implies the characterization of atomic identities, atomic position, bond length, and bond directions within 3 to 5 atomic monolayers. In this work only the identification of atoms was carried out, indeed it is already possible to conclude that apparently fresh micas are often interlayered with other phases. The evidence of thin interlayered phases in micas is not new and it is well known that chloritization proceeds along (001) but the beginning of this process is difficult to be evidenced using other techniques.

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