A CLOSER LOOK AT PHLOGOPITE BY ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)

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Micas are very common in crustal rocks but several aspects are poorly understood and therefore their full utilisation in petrology, geochronology and technology is limited. For example their crystal chemistry is complex and numerous set of linearly independent exchange components can describe their composition. Traditional chemical analytical techniques as electron-probe microanalysis (EPMA) cannot solve ambiguities since some elements may be present in different oxidation states and there is not an unique way to define the linearly independent exchange components.

Electron Spectroscopy for Chemical Analysis (ESCA) allows to analyse the composition of the outermost (down to 50 Å) volume of the sample by direct measurement of the energy of electrons. At least 70% of the signal is emerging from the first few Å. ESCA also gives information on the energy of binding, oxidation state and coordination environment of an element. ESCA allows to access at new information and reduces the scale of observation of several orders of magnitude if compared to EMPA.

We used ESCA to investigate phlogopite from the peridotite of Finero (Ivrea-Verbano Zone, Italy, western Alps). Phlogopite monocrystals were cut away from the altered and unaltered (freshly cut in the laboratory) surfaces with a sharp cutter. The phlogopite flake to analyse was loaded on a copper holder and the top flakes removed mechanically by cleavage to produce a new (001) surface (old surfaces are usually very dirty, see the photo at www.unifr.ch/mineral/tech.html). Phlogopite books from the weathered surfaces were directly fixed on the copper holder (up-side up) without any manipulation. After a first analysis of the surface, Ar^+ plasma flushed on the biotite surface for 1 to 60 minutes at 1 keV and the surface was measured again. We also investigated the effects of Ar^+ erosion on the phlogopite surface.

The observation and general implications can be summarised as in the following:

1) surface of phlogopite exposed to natural weathering is transformed into an Al-Mg silicate (chlorite?)

2) in the region in which phlogopite cleaves (i.e. the (001) plane) the composition is not stoichiometric.

3) phlogopite statistically cleaves along ultrathin chloritisation plane.

4) ESCA evidences chlorite ultrathin (cryptic) layers (few ten of Å) in phlogopite that results to be unaltered when observed with the electron microscope (and probably at TEM too, but research is in progress).

5) these cryptic chlorite planes are probably responsible for the young Rb-Sr and Ar-Ar ages defined by the Finero phlogopite. The discovery of cryptic chlorite planes has self-evident implications in geochronology.

6) C has been identified. It is probably related to mantle metasomatism. Therefore the chemical composition of the metasomatic fluid should include C too (K, Ti, Ba, Fe, REE, H_2O, Cl and F are more obvious component).

7) the oxydation state of Ti is (III). Ti^{3+} is usually not considered in natural terrestrial silicates. Indeed, this finding is not inconsistent with the general opinion that the redox state of the mantle is nearer to iron-wüstite buffer than to quartz-fayalite-magnetite buffer. Implications for crystal chemical and mantle petrology are evident.

At the beginning of the century, several physicists stressed that in first approximation mechanics well works at macroscopic scale and is closely connected with the intuitive common logic, but at atomic scale the world is rather different and sometimes even in disagreement with macroscopic observation (and intuitive conclusion). A huge amount of work is necessary before the full characterisation of micas at atomic scale is achieved, and there are no doubts that a lot of surprises are waiting for us.