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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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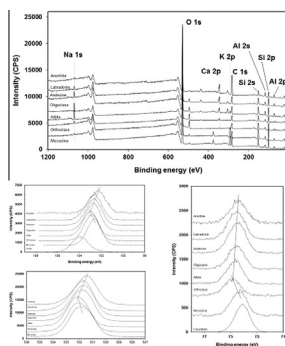
## Chemical bonding and electronic structures of microcline, orthoclase and the plagioclase series by X-ray photoelectron spectroscopy

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### HIGHLIGHTS

- XPS showed the effect of symmetry on Si 2p and Al 2p for microcline and orthoclase.
- XPS showed the effect of coupled substitution on Si 2p, Al 2p and O 1s in plagioclase.
- The Si 2p, Al 2p and O 1s binding energies decrease from albite to anorthite.
- The bonding character for microcline is more covalent than Al<sub>2</sub>O<sub>3</sub> but less than SiO<sub>2</sub>.
- Plagioclase shows two distinct bonding characters comparable to SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 30 May 2014

Received in revised form 11 August 2014

Accepted 24 August 2014

Available online 10 September 2014

#### Keywords:

Microcline

Orthoclase

Plagioclase

X-ray photoelectron spectroscopy

Albite

Anorthite

### ABSTRACT

A detailed analysis was undertaken of the X-ray photoelectron spectra obtained from microcline, orthoclase and several samples of plagioclase with varying Na/Ca ratio. Comparison of the spectra was made based on the chemical bonding and structural differences in the Al- and Si-coordination within each specimen. The spectra for Si 2p and Al 2p vary with the change in symmetry between microcline and orthoclase, while in plagioclase an increase in Al–O–Si linkages results in a small but observable decrease in binding energy. The overall shapes of the O 1s peaks observed in all spectra are similar and show shifts similar to those observed for Si 2p and Al 2p. The lower-VB spectra for microcline and orthoclase are similar intermediate between  $\alpha$ -SiO<sub>2</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in terms of binding energies. In the plagioclase series increasing coupled substitution of Na and Si for Ca and Al results in a change of the overall shape of the spectra, showing a distinct broadening associated with the presence of two separate but overlapping bands similar to the 21 eV band observed for quartz and the 23 eV band observed for corundum. The bonding character for microcline and orthoclase is more covalent than that of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, but less than that of  $\alpha$ -SiO<sub>2</sub>. In contrast, the plagioclase samples show two distinct bonding characters that are comparable with those of  $\alpha$ -SiO<sub>2</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

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### Introduction

Feldspars belong to the most abundant minerals in the earth's crust and form a major component in almost all igneous rocks and many metamorphic rocks. The feldspar minerals are

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aluminosilicates whose structures are composed of corner sharing  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra linked in an infinite three-dimensional array (Fig. 1). Charge balancing cations such as  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  with ionic radii larger than  $1.0 \text{ \AA}$  occupy large, irregular cavities in the tetrahedral framework [1].

Reactions comprising feldspars are of major importance in the environment, influencing geochemical cycles in different ways. Feldspar dissolution has been extensively studied in the laboratory, in order to reproduce and gain a better understanding of the processes involved in “weathering” and clay formation as seen in the environment. A good review of this topic is given by Chardon et al. [2]. XPS has been extensively used to study the changes in

feldspar surfaces. Early studies on feldspar dissolution have indicated that under low temperature and pressure conditions (from room temperature up to  $100 \text{ }^\circ\text{C}$ , 1 atm. pressure, pH from 2 to 8), no leached layer is detectable and the dissolution appears to be stoichiometric. This advocates a surface reaction mechanism instead of one comprising the formation of a leached layer depleted in alkali ions. More recent studies have focussed on the dissolution of feldspars at higher temperatures ( $>200 \text{ }^\circ\text{C}$ ) and pressures ( $>300$  bars). The existence of a leached layer up to 100 nm thick (depending on the particular feldspar mineral studied), and depleted in Al, Na and O but enriched in Si, has been detected by XPS. The top few atomic layers are drastically depleted in Al and Na, emphasizing the incongruent nature of the dissolution. However, the real strength of XPS measurements is in their capacity to give both species information and elemental composition of the material at the surface [2].

Other studies focussed on the absorption of other compounds on the surfaces of feldspars. Vidyadhar et al. [3] for example looked at the absorption of long-chain primary amines on albite and microcline with, among other techniques, XPS. Pelte et al. [4] studied the changes in cadmium removal by heat treated feldspars. The XPS spectra of an albite and an orthoclase were compared with their reference samples in good agreement with XPS spectra collected by other authors [5]. The binding energies of O 1s, Si 2p  $3/2$  and Al 2p  $3/2$  photoelectron peaks, located respectively at  $532.8 \pm 0.2 \text{ eV}$ ,  $102.6 \pm 0.2 \text{ eV}$  and  $74.1 \pm 0.2 \text{ eV}$  are characteristic of the chemical environments which were reported for these three elements in silica, alumina oxides and tectosilicates [5,6]. Graveling et al. [7] examined the adsorption of partially hydrolyzed polyacrylamide (HPAM) to kaolinite, feldspar, and quartz. The survey XPS spectra of the HPAM-free control minerals showed bands in the O 1s, Si 2p, Al 2p, and C 1s regions. Again, additional peaks in the C 1s and N 1s regions appeared following treatment with HPAM. When the HPAM level was progressively raised for quartz, kaolinite, and feldspar, the O 1s signal from the minerals was so large that the weak signal from the polymer was masked. Consequently, the intensity of the N 1s peak was used to track levels of surface-bound HPAM. Unfortunately, in all of these studies no attention has been paid to the effects of the crystal structures of the feldspars studied and how changes in these structures affect the high resolution Si 2p and Al 2p spectra.

The differences in the chemical bonding and electronic structures of the feldspars are fundamental to the understanding of their thermodynamic properties and stability relations. X-ray photoelectron spectroscopy (XPS) is a technique to probe the chemical bonding of specific elements. However, application of the XPS technique to minerals, like the feldspars, can be difficult due to sample charging during the analysis. The advantage of XPS over Auger is that in XPS the area under the photoelectron peak (which is used to calculate Atom %) is easily estimated whereas in Auger the peak–peak of the differential of the peak is used. This p–p of this differential is a function of the peak shape which, with Auger, can change significantly from compound to compound of the same element. Also, for Auger the surface needs to be reasonably conducting and Auger on insulators poses problems. There is also sample degradation which can be problem with the highly focused electron beam uses for Auger emission. Degradation by the soft Al K alpha X-rays used for XPS is only experienced by a very few compounds. The only advantage for Auger is you can get analysis from a very small area as it uses a focussed electron beam as in a SEM. Detailed analyses of photoelectron spectra obtained from aluminosilicate glass have been reported [8,9]. In glass form, however, Al and Si polyhedra are all corner linked, therefore the present study can give further insight into the chemistry and electronic structure of the potassium, sodium and calcium feldspars.

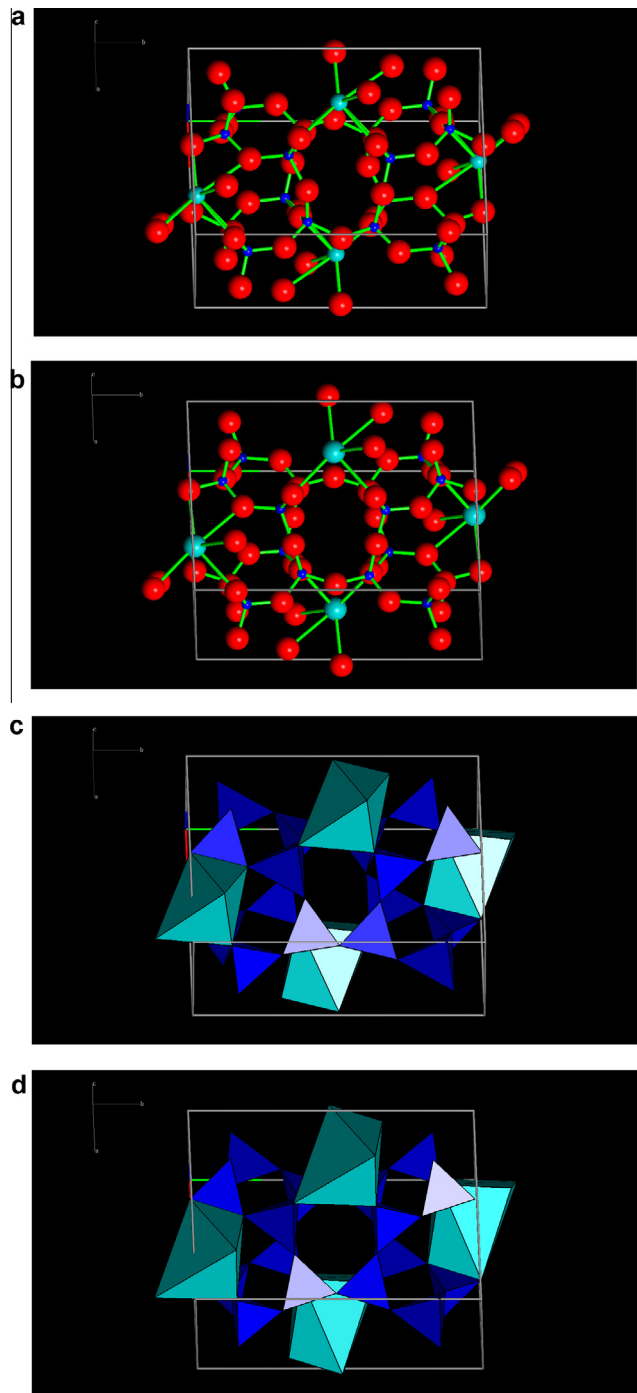


Fig. 1. Ball and stick models of (a) albite and (b) microcline, and polyhedral models of (c) albite and (d) microcline.

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