BONDING STATE OF SODIUM IN AMPHIBOLE MINERALS STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY

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Abstract - The chemical state plot constructed from Na 1s photoelectron binding energy and KL23L3 Auger electron kinetic energy distinguishes Na in the 8-coordinate B site from Na in the large hollow A site in amphiboles. Sodium in the B site is characterized by the lower 1s binding and the higher KLL kinetic energies.

Key words XPS, amphibole, sodium, bonding state

Simultaneous determination of core electron binding energy and Auger electron kinetic energy of an element in various chemical environments by X-ray photoelectron spectroscopy (XPS) allows one to construct a chemical state plot which enhances the ability of XPS as a tool for bonding state analysis[1]. Recently, we have shown that the ion-exchangeable and non-exchangeable sodium in a synthetic tetrasilicic sodium fluor mica (Na-TSM) have significantly different 1s binding and KL23L3 Auger kinetic energies from each other[2]. The non-exchangeable Na shows characteristically low 1s binding and high KL23L3 kinetic energies. In this report, we have extended this approach to characterizing bonding states of Na in amphibole minerals.

Amphibole is a group of silicate minerals expressed by the standard formula A0.4B2C5T3O2(OH, F, Cl)2[3]. The tetrahedral site T is typically occupied by Si, but may be partly replaced by e.g. Al or Fe4+. The octahedral C sites correspond to the M1 + M2 + M3 sites occupied mainly by Mg and Fe4+. The B site represents the 8-coordinate M4 site and A represents the hollow site between the hexagonal rings formed by the double chain of the SiO4 tetrahedra. Sodium may occupy the B site and/or A site. Our main interest is to see whether XPS can distinguish Na in the B site from that in the A site.

EXPERIMENTAL

The amphiboles used for the XPS measurement are listed in TABLE 1 with their formal compositions and sources, and were kindly provided by the National Science Museum. When the original mass of a mineral apparently contained the undesired phase, the mass was crushed and the pieces of desired mineral were selected by inspection under a loupe. The minor crystalline impurities, still remained after the selection and detected by X-ray diffraction (XRD), are indicated in the last column of the table. The minerals were ground to powder for the XPS measurement.

To examine the effects of acid leaching of minerals on the electron spectra, 50 mg of each mineral was extracted by 5 cm3 of 0.1 mol dm-3 aqueous hydrochloric acid. The mixture was shaken for 12 h and separated by centrifugation. After removal of the extract, the residue was washed by deionized water, dried and subjected to the XPS measurement.

The electron spectra were recorded on a VG ESCALAB 5 apparatus with Al Ka and Mg Kα X-ray excitation sources operated at 12 kV x 5 mA. The measurement procedures have been previously described[4]. The analyzer pass energy was 50 V with the entrance slit width of 4 mm. The powdered mineral sample was fixed by double-sided sticky tape onto a stainless steel sample holder. The electron binding energies were determined using the Au 4f7/2 line (84.0 eV) of a gold film evaporated onto the sample as a standard.
RESULTS AND DISCUSSION

Fig. 1 shows the chemical state plot for Na in the six amphiboles obtained from the apparent peak binding energies and kinetic energies of 1s photoelectron and KL{23} Auger electron, respectively. The chemical state plot in some relevant Na containing systems is also included. The points of riebeckite and hastingsite represent two extremes in the amphiboles studied. The points for the remaining four amphiboles fall between them. In contrast to Na, the 1s binding energy and KL{23} kinetic energy of Mg in the amphiboles are almost constant, ranging ± 0.2 eV around their mean values of 1304.4 eV and 1180.4 eV, respectively. The Si 2s and O 1s binding energies are 153.6 ± 0.1 eV and 531.9 ± 0.1 eV respectively. Thus the distribution of points in the chemical state plots for Na in the amphiboles should be the manifestation of the different bonding states.

In riebeckite Na essentially occupies the B site, whereas in hastingsite it occupies the A site. Accordingly, we presume that 1s binding and KL{23} kinetic energies of Na in riebeckite and hastingsite are representative of bonding states of Na in the B and A sites, respectively. The point of hastingsite falls close to that of ion-exchangeable Na in layered silicate such as montmorillonite and TSM. This is reasonable since the A site in amphibole may be regarded as corresponding to the interlayer space of layered silicates between the hexagonal rings where the exchangeable Na occupies. Pargasite, in which Na is at the A site, gives the point close to that of hastingsite. Sodium in riebeckite exhibits the lower 1s binding and higher KLL kinetic energies. Notably for Mg-exchanged montmorillonite, the exchangeable Mg in the interlayer and the non-exchangeable Mg in the octahedral site behave similarly in the 1s-KLL chemical state plot[4]. In the octahedral site of montmorillonite Mg has 1s binding energy of 1303.8 eV and KL{23} kinetic energy of 1180.0 eV, slightly different from those of Mg in the octahedral site of the amphiboles.

The Na 1s and KL{23} spectra of arfvedsonite with Na both in the A and B sites did not show apparently separated peaks. However, as compared with the spectra of riebeckite, the full width at half maximum (FWHM) of Na 1s spectrum of arfvedsonite is slightly broader (2.7 eV vs 2.5 eV, Al Kα excitation) due to the slight asymmetric broadening towards high binding energy side, and KL{23} spectrum is significantly broader (FWHM, 3.25 eV vs 2.7 eV) with the less clear satellite at the low kinetic energy side. Leaching arfvedsonite with 0.1 mol dm⁻³ hydrochloric acid resulted in the decrease in the FWHMs and the shift of the peak position of Na 1s and KLL to the lower binding energy and higher kinetic energy respectively to approach to those of riebeckite. This change was accompanied with the decrease in the intensities of Na 1s and KLL lines relative to that of Si 2s line. Those observations suggest that the Na spectra in arfvedsonite consist of composite peaks due to the existence of

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Source</th>
<th>Impurity**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riebeckite</td>
<td>South Australia, Australia. NSM-M7310</td>
<td>ND***</td>
</tr>
<tr>
<td>Crossite</td>
<td>Nishinoiri, Saitama, Japan. NSM-M24147</td>
<td>Feldspar</td>
</tr>
<tr>
<td>Barroisite</td>
<td>Higashiakaishi, Ehime, Japan. NSM-M118993</td>
<td>Chlorite, Feldspar</td>
</tr>
<tr>
<td>Arfvedsonite</td>
<td>Mont Saint Hilaire, Canada. NSM-M8149</td>
<td>Aegirine</td>
</tr>
<tr>
<td>Pargasite</td>
<td>Kasuga, Gifu, Japan. NSM-M24569</td>
<td>Calcite, Chlorite</td>
</tr>
<tr>
<td>Hastingsite</td>
<td>Sanpo-mine, Okayama, Japan. NSM-M19630</td>
<td>(Chlorite)****</td>
</tr>
</tbody>
</table>

* National Science Museum
** As determined by XRD
*** Not detected
**** Trace, if present

TABLE 1 Amphibole minerals used for the XPS measurements
the different bonding states of Na. An attempt showed that the Na 1s and KLL spectra were separable to the B and A site components with 2 : 1 intensities. The A-site Na is suggested to be more susceptible to the leaching by dilute hydrochloric acid than the B-site Na.

Crossite gave the result similar to that of arfvedsonite. That is, the Na spectra showed the FWHMs broader than those in the riebeckite and after the treatment with dilute hydrochloric acid decreased their FWHMs and shifted to the positions closer to those of riebeckite. The result is unexpected from the formal composition of crossite which requires Na to occupy the B site only as in riebeckite. We tentatively attribute those behavior to the coexistence of Na-containing feldspar, e.g. albite (TABLE 1), rather than to partial occupation of the A site by Na.

The point of barroisite in which Na should share the B sites with Ca, falls intermediate between hastingsite and riebeckite, but closer to hastingsite. Since the structure of barroisite has been documented less than that of the other amphiboles and our barroisite sample is less pure than the samples of other amphiboles, we cannot be sure whether the XPS result is attributed to the structure of barroisite or other factors.

In conclusion, XPS can distinguish between Na in the B and A sites of amphiboles and hence provide supplementary informations about the site occupation by Na in amphiboles. Compared with the present chemical state plot for Na in amphiboles, the point of the non-exchangeable Na in TSM, as shown in Fig. 1, still remains to be exceptional with its low 1s binding energy and high KL23L23 kinetic energy.

We are grateful to Drs. Yasuji Saito and Satoshi Matsubara of National Science Museum for providing the amphibole samples and instructions about them.

![Fig. 1. Chemical state plot for Na in the amphibole minerals (Q) and in the reference systems (C): (1) riebeckite, (2) crossite, (3) barroisite, (4) arfvedsonite, (5) pargasite, (6) hastingsite, (7) NaF, (8) NaCl, (9) NaBr, (10) analcite, (11) montmorillonite, (12) albite, (13) TSM, exchangeable, (14) TSM, non-exchangeable.](image-url)
REFERENCES