Characterization of Individual Chinese Soil Particles by the Combined Use of Low-Z Particle EPMA and ATR-FT-IR imaging Techniques

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Introduction

- **Airborne mineral dust**
  - The most abundant particulate matters in coarse atmospheric aerosols
  - Arid and semi-arid areas, such as Saharan desert and central China, are major sources of airborne mineral dust.
  - Mineral dust aerosols can react with atmospheric gaseous pollutants such as SOx and/or NOx → modified physicochemical properties of mineral dust
  - Mineral dust can influence global climate directly by scattering and absorbing solar radiations, and indirectly by serving as cloud condensation nuclei (CCN).
  - Airborne mineral particles – from soil minerals

- **Chinese soil particles at arid and desert areas**
  - Sources of Asian Dust particles
  - Asian Dust particles can experience chemical modification during long range transport to Korea.
  - Detailed characterization of Chinese soil particles is important to understand the characteristics of Asian Dust particles.
Objectives

- Characterization of Chinese soils on a single particle level by the combined use of two single particle analytical techniques such as quantitative low-Z particle EPMA and ATR-FT-IR imaging

  * **Low-Z particle EPMA** for the elemental concentration and morphology
    (It has limitation to clearly identify different mineral types having similar composition but different crystal structures)
  * **ATR-FT-IR imaging** for the functional groups, molecular species, and crystal structure

- 2 loess samples and 4 desert samples
<table>
<thead>
<tr>
<th>Type</th>
<th>Site</th>
<th>Locations (Altitude)</th>
</tr>
</thead>
<tbody>
<tr>
<td>loess</td>
<td>Luochuan</td>
<td>35.5°N, 109.2°E (1094 m)</td>
</tr>
<tr>
<td>loess</td>
<td>Ganquan</td>
<td>36.4°N, 109.2°E (1029 m)</td>
</tr>
<tr>
<td>desert</td>
<td>Shaptou</td>
<td>37.3°N, 105.0°E (1330 m)</td>
</tr>
<tr>
<td>desert</td>
<td>Minqin</td>
<td>38.3°N, 102.5°E (1378 m)</td>
</tr>
<tr>
<td>desert</td>
<td>Hungshan</td>
<td>42.1°N, 116.3°E (1266 m)</td>
</tr>
<tr>
<td>desert</td>
<td>Zhangbei</td>
<td>41.2°N, 114.5°E (1416 m)</td>
</tr>
</tbody>
</table>
Previous studies on these Chinese soil samples

- Single-particle characterization of soil samples collected at various arid areas of China, using low-Z particle electron probe X-ray microanalysis
  

  * Analysis using SEM/EDX
    - loess soils: aluminosilicates, CaCO$_3$
    - desert soils: aluminosilicates, SiO$_2$

- Bulk and single-particle mineralogy of Asian dust and a comparison with its source soils *(Jeong, JGR, 2007)*

  * Analysis using XRD
    - silt soil: rich-calcite, phyllosilicates
    - sandy soil: quartz, plagioclase, K-feldspar
Experimental

SEM/EDX and ATR-FT-IR imaging measurement

- Low-Z particle EPMA based on SEM/EDX
  - SEM (JEOL JSM-6390) equipped with Oxford SATW ultrathin window EDX detector
  - Condition
    - accelerating voltage : 10 kV
    - measuring time : 30 sec
    - beam current : 1.0 nA
    - substrate : Ag foil

- ATR-FT-IR imaging
  - Perkin Elmer Spectrum 100 FT-IR spectrometer
  - Spectrum Spotlight 400 FT-IR optical microscope
  - ATR accessory : Ge IRE crystal, diameter : 600 μm
  - Mercury Cadmium Telluride (MCT) array detector
  - pixel size : 1.56 μm
  - spectral resolution of 4 cm\(^{-1}\) at the range of 680 to 4000 cm\(^{-1}\)
Low-Z particle EPMA (Electron Probe X-ray Microanalysis) for single particle analysis

1. SEM-EDX (Scanning Electron Microscopy – Energy Dispersive X-ray Spectrometer)
   - Individual Particle Analysis
     * shape and size: secondary / backscattered electron images
     * chemical compositions: X-ray spectrum

2. Ultra-thin window EDX for low-Z elements detection (e.g., C, N, O, F)

3. Metallic collecting substrates for minimizing charging effect (e.g., Ag, Al)

4. Monte Carlo calculation for Quantification

5. Chemical speciation of aerosol particles – Expert System
Monte Carlo Calculation for Quantification

Measured and simulated spectra for a CaCO$_3$ standard particle on a Be substrate
ATR-FT-IR imaging for single particle analysis

- ATR-FT-IR (Attenuated Total Reflectance-FT-IR Spectrometry)
  - Individual Particle Analysis
    * location: optical image
    * functional groups, molecular species, and crystal structure: IR spectra

ATR imaging accessory

Ge crystal – sample contact surface

Ge crystal for imaging
Images for Luochuan loess soil particles

(a) Secondary electron image
(b) Optical image
(c) PCA image
(d) Transmission signal Image at single wavenumber of 1000cm$^{-1}$
X-ray spectra and elemental concentrations of typical loess soil particles

(a) Quartz/Calcite
(b) Calcite
(c) Montmorillonite/Calcite
(d) Montmorillonite/MgCO\(_3\)/Fe
(e) Muscovite/Calcite
(f) Na-feldspar/Calcite
ATR-FT-IR spectra of typical loess soil particles

(a) Quartz/Calcite (Ganquan)
(b) Calcite (Luochuan)
(c) Montmorillonite/Calcite (Luochuan)

1383: CO$_2^-$
1062: Si-O
1176: Si(Al)-O (Heulandite)
871: CO$_2^-$
797, 779: Si-O
834: AlMg-O
1398
1008: Si-O
ATR-FT-IR spectra of typical loess soil particles

(d) Montmorillonite/MgCO$_3$/Fe (Ganquan)

(e) Muscovite/Calcite (Luochuan)

(f) Na-feldspar/Calcite (Ganquan)
X-ray spectra and elemental concentrations of typical desert soil particles

(a) Cristobalite

Elemental Concentration (at. %)

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Al</th>
<th>O</th>
<th>Si</th>
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<td>2.5</td>
<td>2.6</td>
<td>63.5</td>
<td>28.5</td>
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(b) Montmorillonite/Fe

Elemental Concentration (at. %)

<table>
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<th>Element</th>
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<th>O</th>
<th>Si</th>
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<th>Fe</th>
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<td>5.5</td>
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(c) Montmorillonite

Elemental Concentration (at. %)

<table>
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<th>Mg</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
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</thead>
<tbody>
<tr>
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<td>17.4</td>
<td>1.5</td>
<td>46.3</td>
<td>5.9</td>
<td>12.4</td>
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(d) Na-feldspar

Elemental Concentration (at. %)

<table>
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<tr>
<th>Element</th>
<th>C</th>
<th>Al</th>
<th>O</th>
<th>Si</th>
<th>Mg</th>
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<td></td>
<td>9.4</td>
<td>11.7</td>
<td>54.9</td>
<td>17.8</td>
<td>1.3</td>
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(e) K-feldspar

Elemental Concentration (at. %)

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<tr>
<th>Element</th>
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<th>Al</th>
<th>O</th>
<th>Si</th>
<th>Mg</th>
<th>K</th>
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</thead>
<tbody>
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<td>2.6</td>
<td>21.2</td>
<td>54.9</td>
<td>17.8</td>
<td>1.3</td>
<td>3.7</td>
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(f) Muscovite

Elemental Concentration (at. %)

<table>
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<tr>
<th>Element</th>
<th>C</th>
<th>Al</th>
<th>O</th>
<th>Si</th>
<th>Mg</th>
<th>K</th>
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<td>2.6</td>
<td>21.2</td>
<td>40.7</td>
<td>25.4</td>
<td>1.1</td>
<td>7.5</td>
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ATR-FT-IR spectra of typical desert soil particles

(a) Cristobalite (Shaptou)

(b) Montmorillonite/Fe (Hungshan)

(c) Montmorillonite (Zhangbei)
ATR-FT-IR spectra of typical desert soil particles

(d) Na-feldspar (Shaptou)
(e) K-feldspar (Minqin)
(f) Muscovite (Minqin)

- 3605 : OH
- 1152, 1093 : Si-O
- 1026, 974 : Si(Al)-O
- 916 : AlAl-OH
- 810 : Al-O-Si
- 735, 728 : Si(Al)-Si
- 795, 760 : Si-Si
- 1112 : Si-O
- 1031, 1003 : Si(Al)-O
- 1026, 974 : Si(Al)-O
- 980 : Si-O
- 916 : AlAl-OH
- 852 : AlMg-OH (montmorillonite)

- 3700, 3200, 2700, 1700, 1200, 700 wavenumber (cm⁻¹)
Relative abundances of mineral types observed in Chinese soils

Loess

Desert

Calcite
$\text{SiO}_2$/Calcite
Montmorillonite/Calcite
Montmorillonite species
Feldspar species
Vermiculite species
Apatite species
Muscovite species
Fe-containing species
Others

Relative abundances (%)

Mineral types

Ganquan
Luochuan
Minqin
Shanptou
Hungshan
Zhangbei
Conclusions

- In loess soils, the most abundant particles are observed to be silicates minerals mixed with calcite.
- Desert soils have higher content of SiO$_2$ than the loess soils do.
- Low-Z particle EPMA and ATR-FT-IR imaging techniques provide complimentary information on the physicochemical characteristics of the same individual soil particles.
- Low-Z particle EPMA for the information on the morphology and elemental concentrations
- ATR-FT-IR imaging for the information on the functional group, molecular species and crystal structure