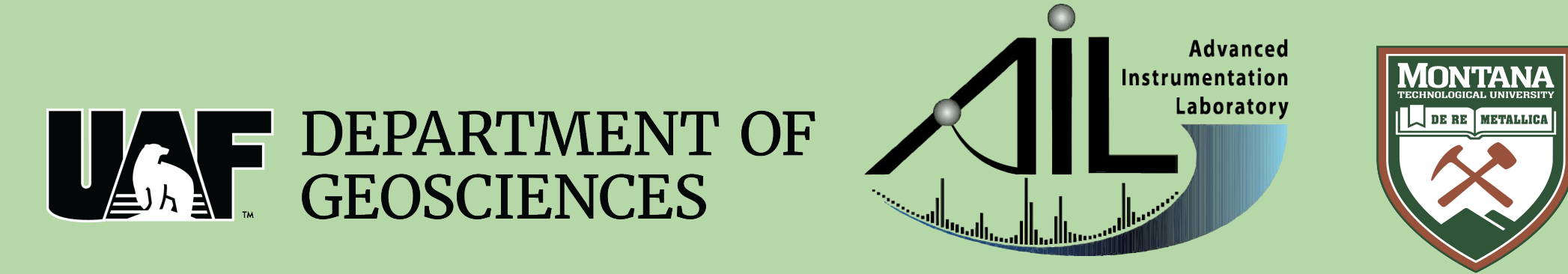


The Effect of Crystal Orientation on the Raman Spectra of K-Feldspar Polymorphs

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Abstract

As Al/Si site disorder increases, the character and number of K-feldspar Raman peaks systematically changes. However, similar peak widening effects are known to be caused by orientation differences, since molecular vibrations may be Raman “inactive” at certain orientations where they lack polarizability. Orienting samples so that the Raman beam is either parallel or perpendicular to the c-axis allows us to compare both Raman spectra between microcline, orthoclase, and sanidine along <100> and spectra from different directions in the same crystal. Analysis with a 514 nm laser at 50x magnification shows systematic differences both between the Raman spectra of different polymorphs at the same orientation and between those of similar polymorphs at different orientations.

Raman Spectroscopy

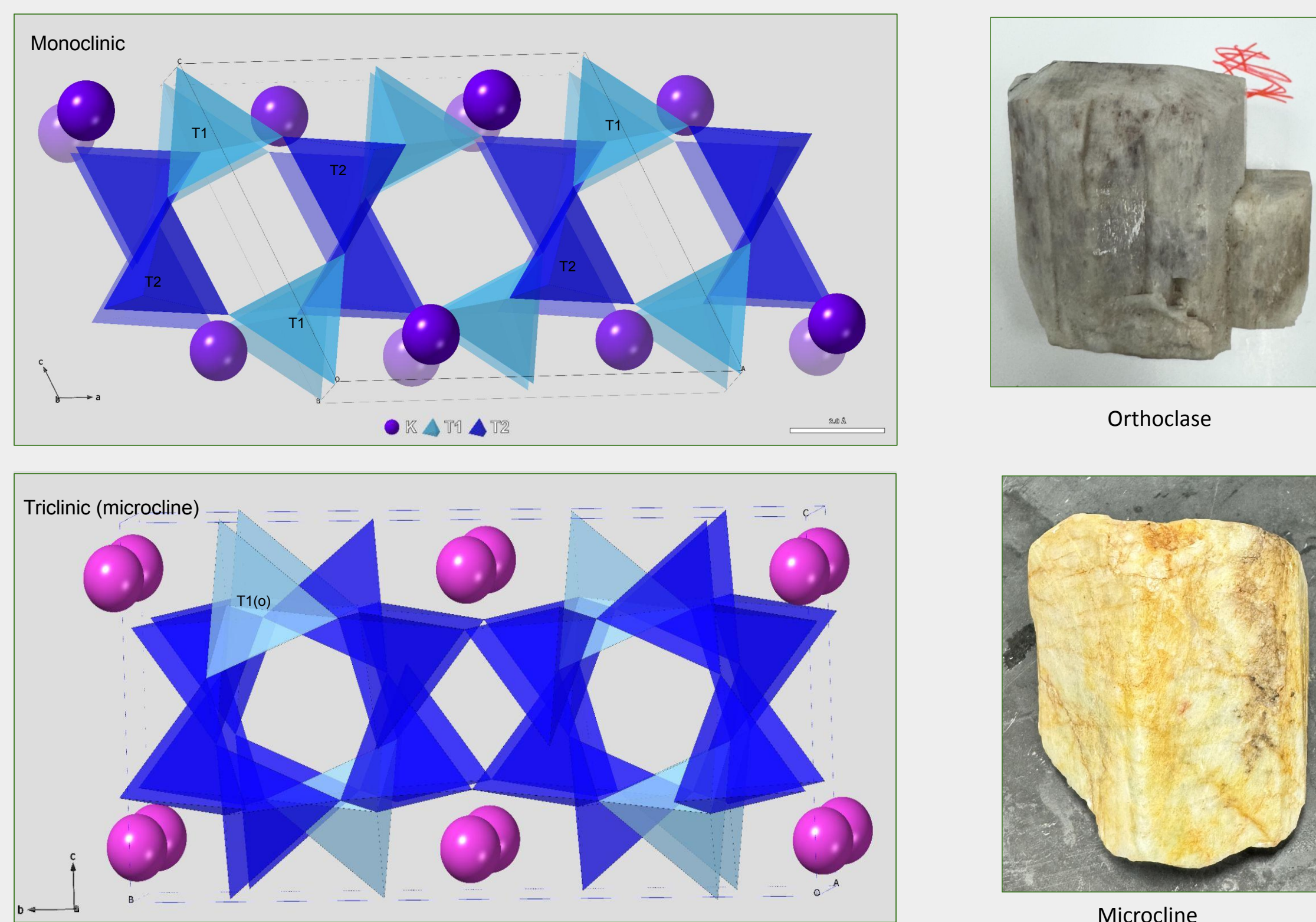
- Raman spectroscopy identifies molecular compositions and structures using vibrations
- The sample is illuminated with a laser and the scattered light is measured
- Molecular vibrations shift the energy of scattered light (“Raman shift”)
 - Different bonds → different shifts
- It is non-destructive and samples can be reused for further analysis (e.g., EPMA, SEM)

Mineral Polymorphs

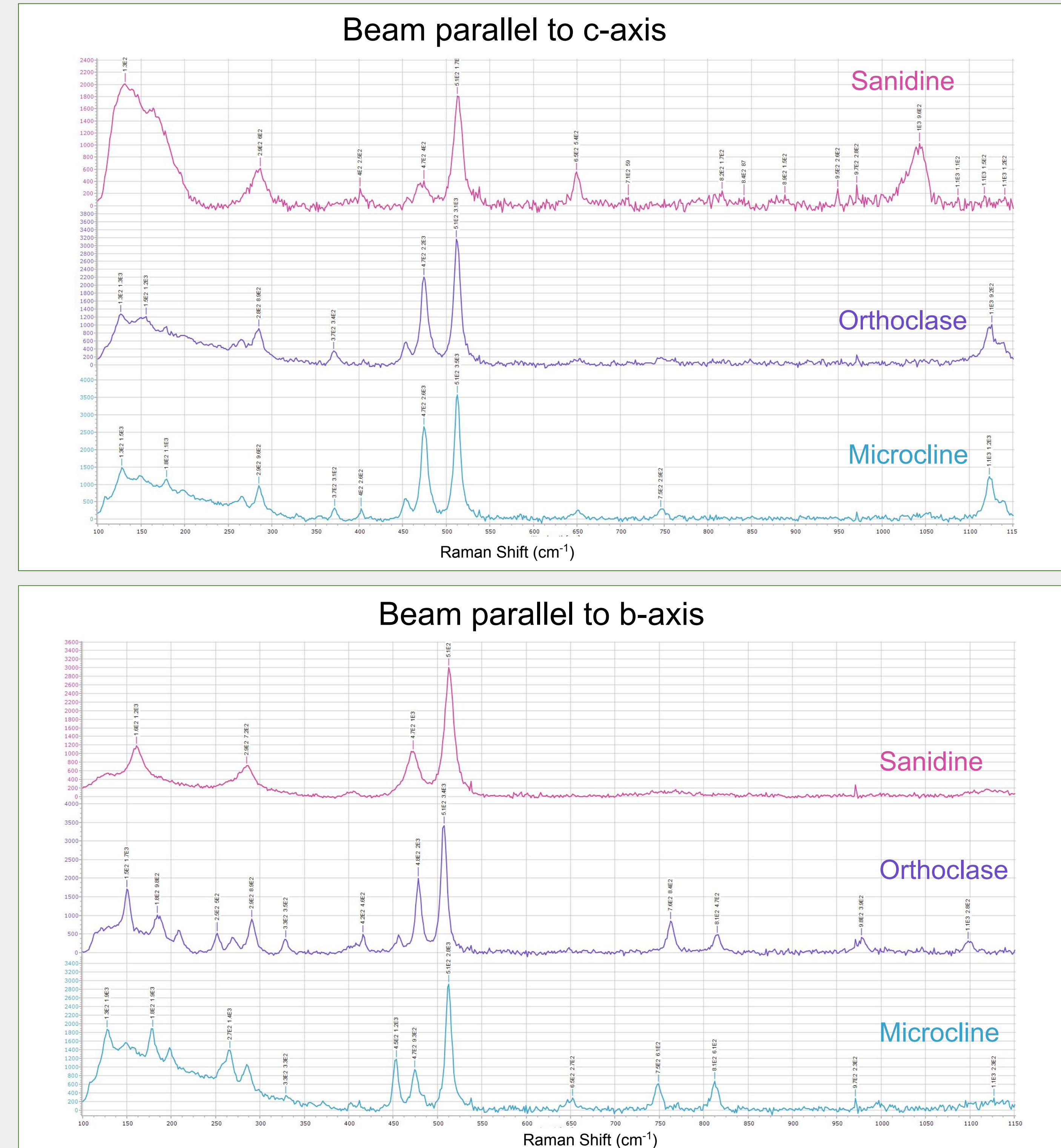
- Minerals with the same chemical formula but different molecular structures
- Cannot be distinguished by chemical analysis
- Indicates the environment during rock formation

Alkali Feldspar Crystal Structure

- K-feldspar crystal lattice is formed by four-membered tetrahedral rings
- Al/Si site disorder refers to the distribution of Al across tetrahedral sites
 - In triclinic feldspar (microcline) Al sits in T1(o) sites
 - Highly ordered in maximum microcline
 - In monoclinic feldspars (sanidine and orthoclase) Al and Si are distributed across all T1 and T2 sites
 - In orthoclase, Al has a slight preference for T1 sites



Raman Spectra Orientation Dependence

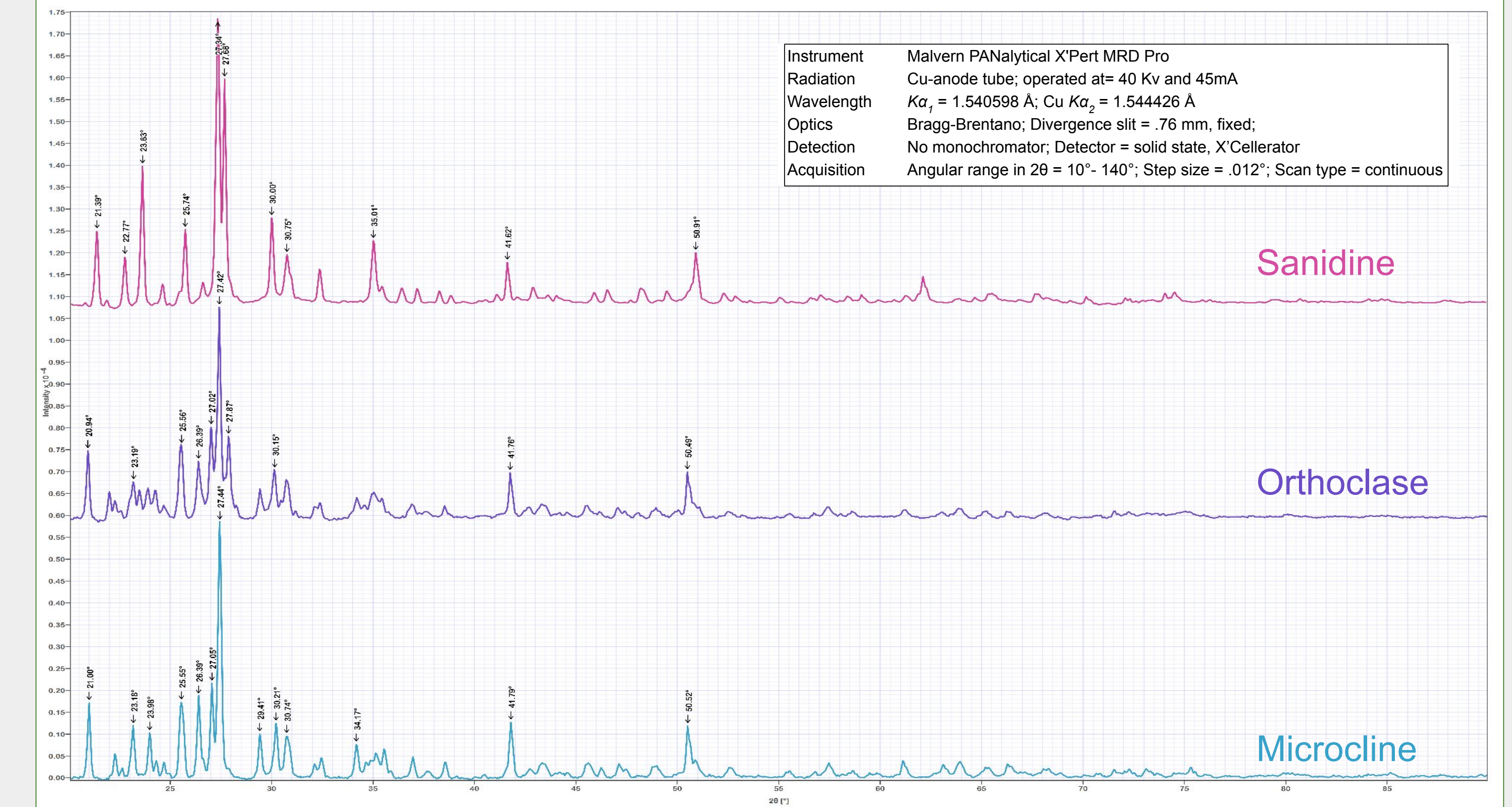


Raman Peak Correlations

Peak Position	Structural Equivalencies
<400 cm ⁻¹	rotation-translation of rings and cage-shear modes
450-520 cm ⁻¹	deformation modes of tetrahedra
700-900 cm ⁻¹	ring breathing modes of four membered tetrahedral rings
900-1200 cm ⁻¹	vibrational stretching modes of tetrahedra

- The multiplicity of 450-520 cm⁻¹ peaks and location of the highest peak above 500 cm⁻¹ are most important to differentiate polymorphs from each other and other feldspars
- The widths of peaks systematically increase as Al/Si disorder increases

Powder X-ray diffraction pattern



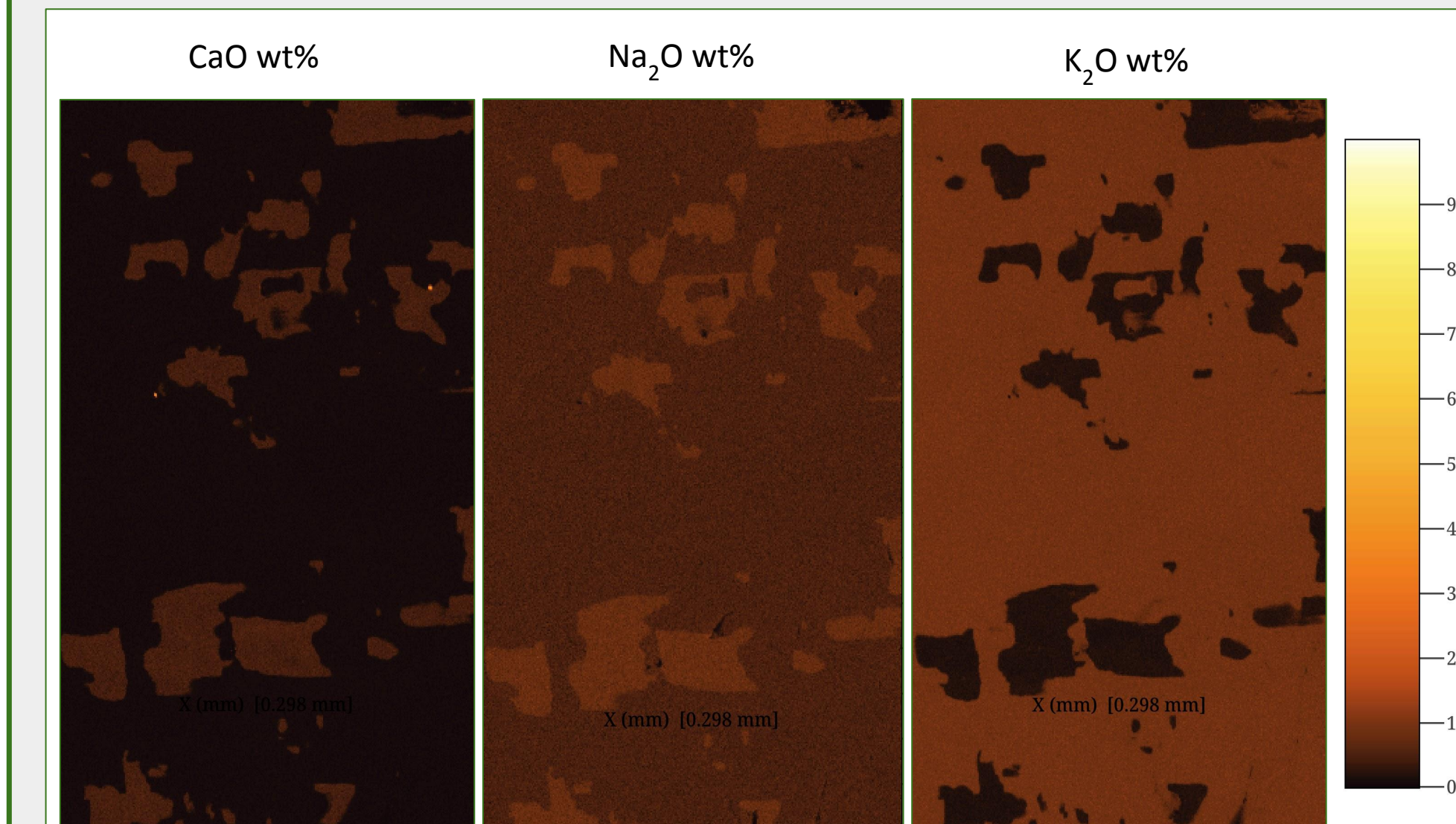
Z-factor equations for calculating Al/Si disorder

For triclinic feldspars: $\Sigma t_1 = t_1 o + t_1 m = \frac{b-21.5398+53.8405c^*}{2.1567-15.8583c^*}$

For monoclinic alkali feldspars: $\Sigma t_1 = 2t_1 = \frac{b-24.8095 + 74.90540c^*}{-3.3261 + 195.012c^*}$

$\Delta t_1 = t_1 o - t_1 m = \frac{\gamma^*-44.778-0.50246\alpha^*}{6.646-0.0561\alpha^*}$

b = length of b axis of unit cell α^* = reciprocal angle between b and c axes
 c^* = reciprocal c-axis γ = angle between a and b axes



- Sanidine is heterogeneous at microscale
 - albitic crystals
- Problematic for XRD Rietveld refinements
- Quantitative electron microprobe maps to constrain composition for Rietveld refinement initial parameters

Preliminary Conclusions

- There is a clear orientation dependence to Raman peak intensities and widths
- Peaks >600 cm⁻¹ are more affected by orientation. There is also significant change in the 100-350 cm⁻¹ range
- There appear to be systematic changes in Raman spectra due to Al/Si site disorder

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