USING X-RAY DIFFRACTION AND RAMAN SPECTROMETRY TO HELP STUDENTS BETTER UNDERSTAND UNIT CELLS AND SOLID SOLUTIONS. AN ENGAGEMENT COMBINING NSF GEOPATH AND NSF MRI FUNDING

Jamie MacDonald
Alli Barbosa
&
Greg McManus

- **Unit cells and solid solutions are difficult concepts to demonstrate to students due to their intangibility.**

- **Unit cells will change size depending on the ionic radius of the major cation involved in a solid solution. There is a clear relationship between the two.**

- **To facilitate the students' understanding of unit cells and atomic substitutions, we utilized *powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SCXRD), and Raman spectrometry* of carbonate minerals as part of NSF sponsored GEOPATH student research experience.**

- **The SCXRD was acquired through the NSF Major Research Instrumentation Program (CHE #1919785).**

Florida Gulf Coast University NSF GEOPATH project:

New Environmental Geology BS program started in the Fall of 2019

A major goal of this GEOPATH project is to attract, retain, and graduate a diverse group of students in this new program.

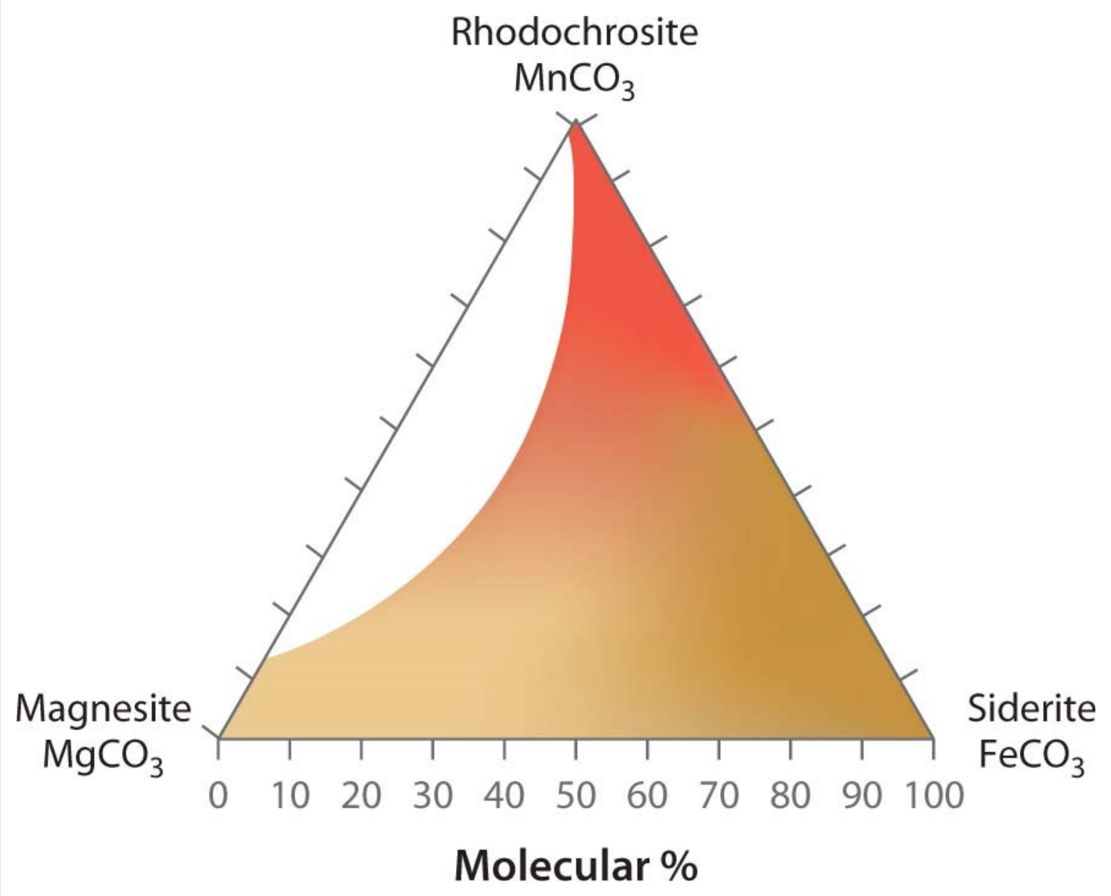
Targeting female and Hispanic students

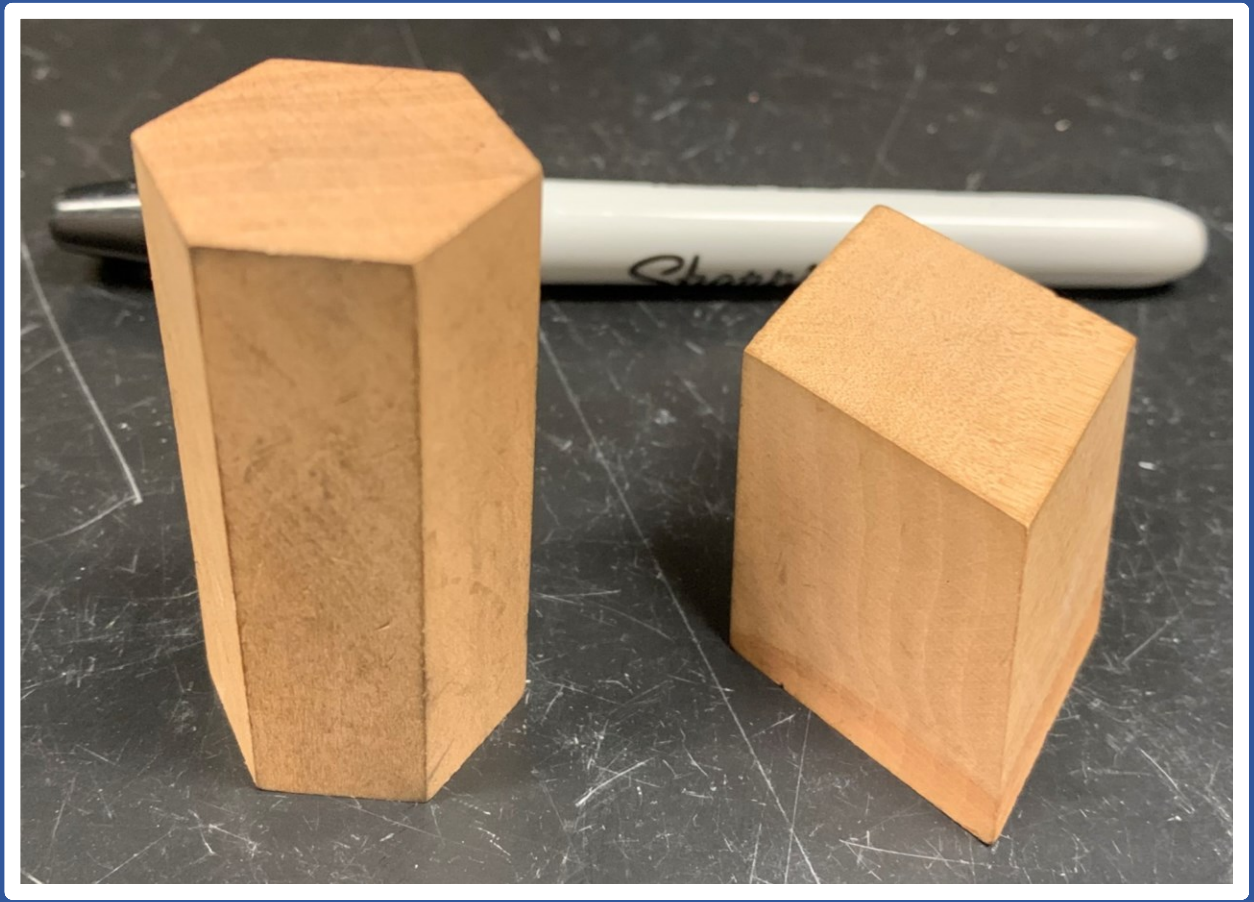
See Abercrombie et al. (2021), presented this past Sunday for more information.

Two week field-lab research experience where undergraduates investigated calcite.

Utilized PXRD, SCXRD, and Raman.

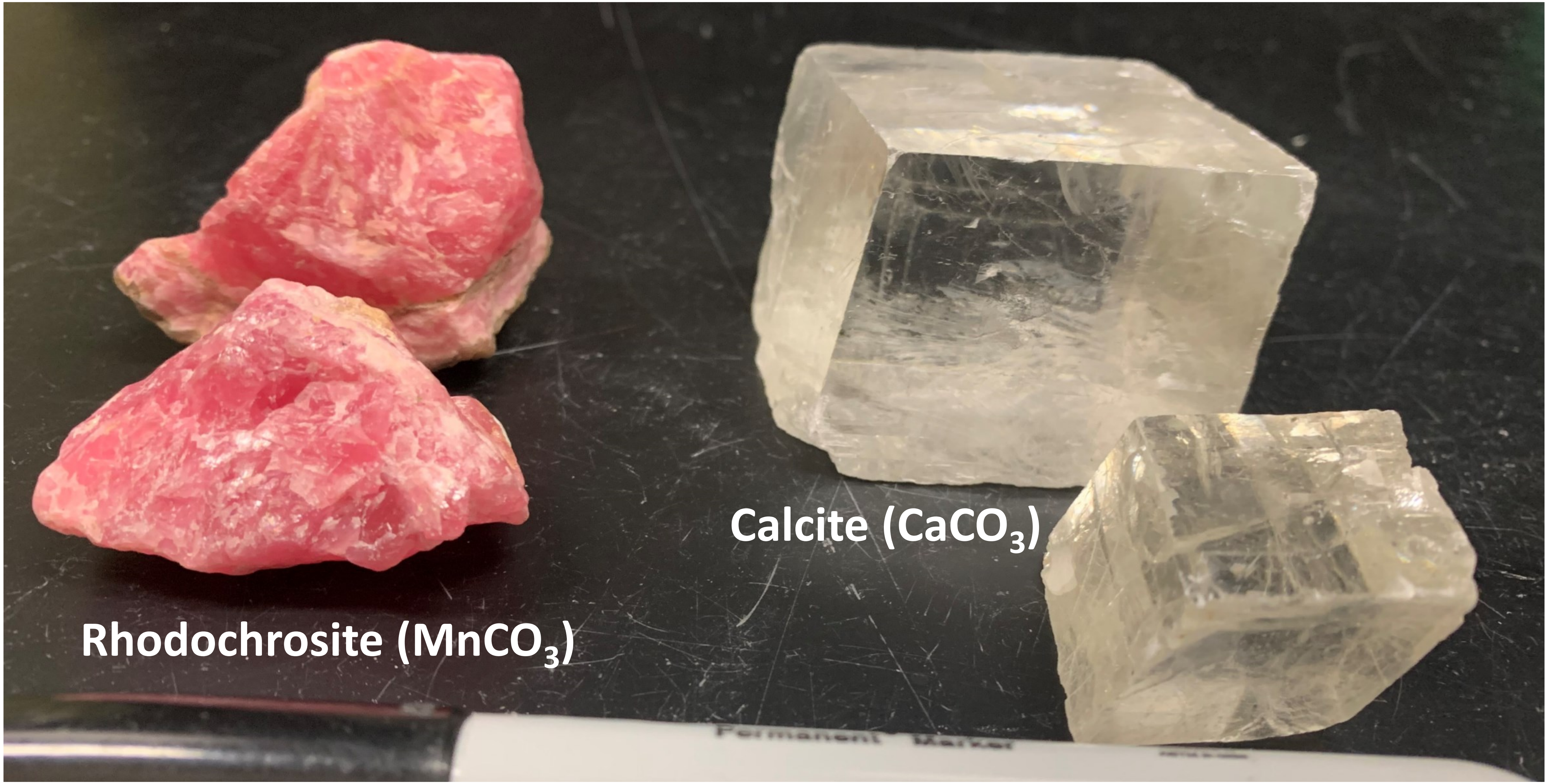
Learned about carbonate minerals including unit cell, atomic substitutions, and solid solutions



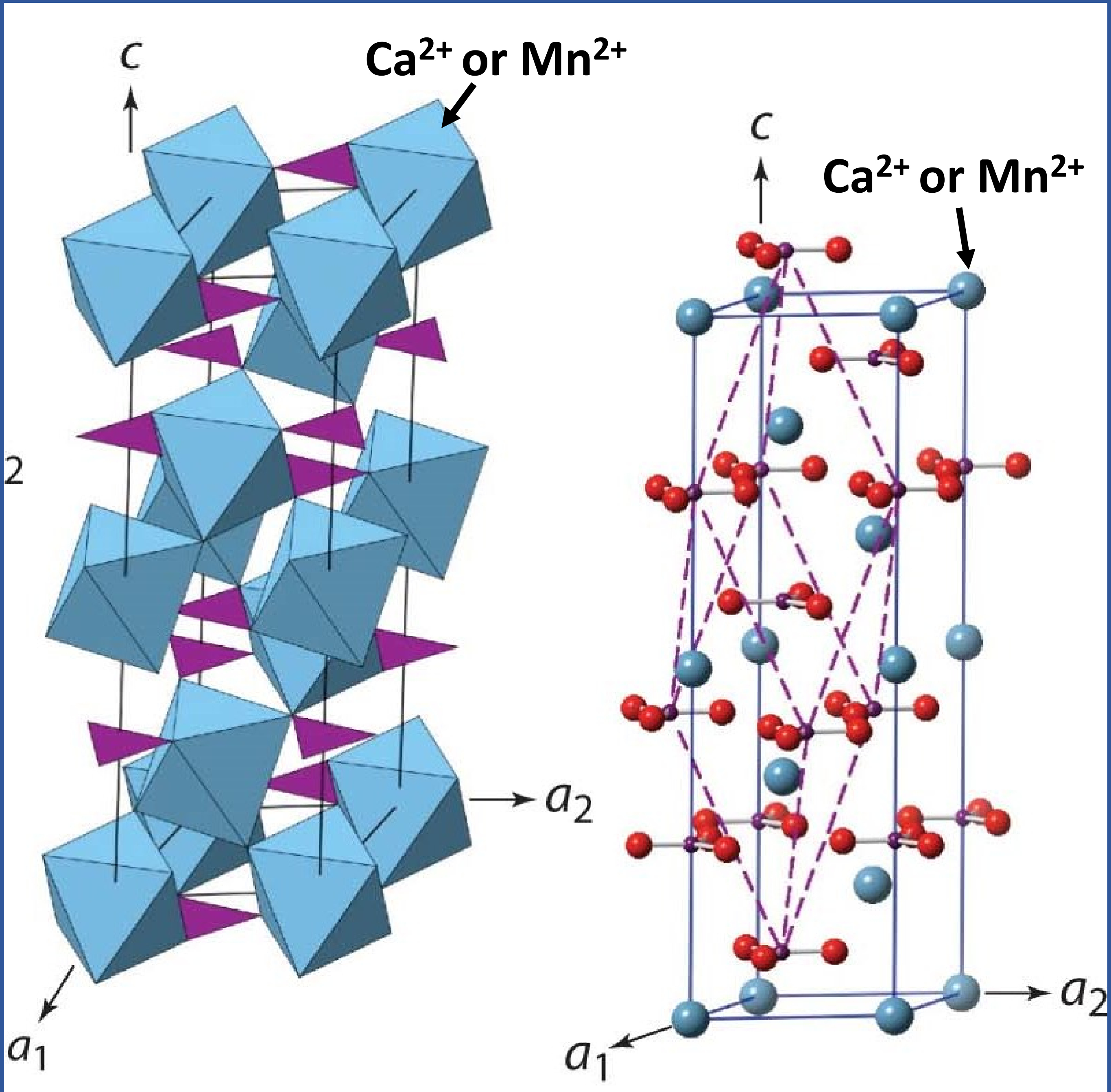


How do we teach unit cells, atomic substitutions, and solid solutions?

- **Normally only done in upper division classes**
- **The same way we were taught (mostly lectures and demos).**
- **As best as we can!**
- **Some examples from carbonates**



We chose calcite and rhodochrosite samples that are from Ward's Scientific to help the students with unit cells, atomic substitutions, and solid solutions.



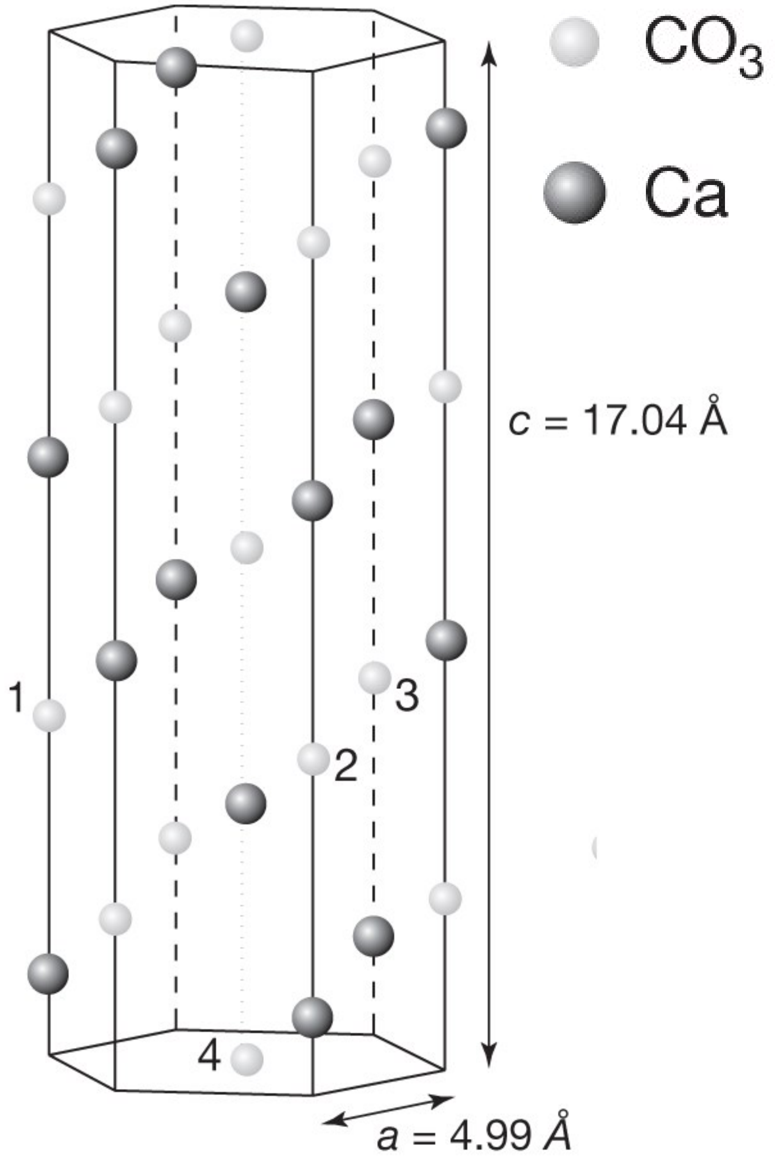
Start with size of the cations!

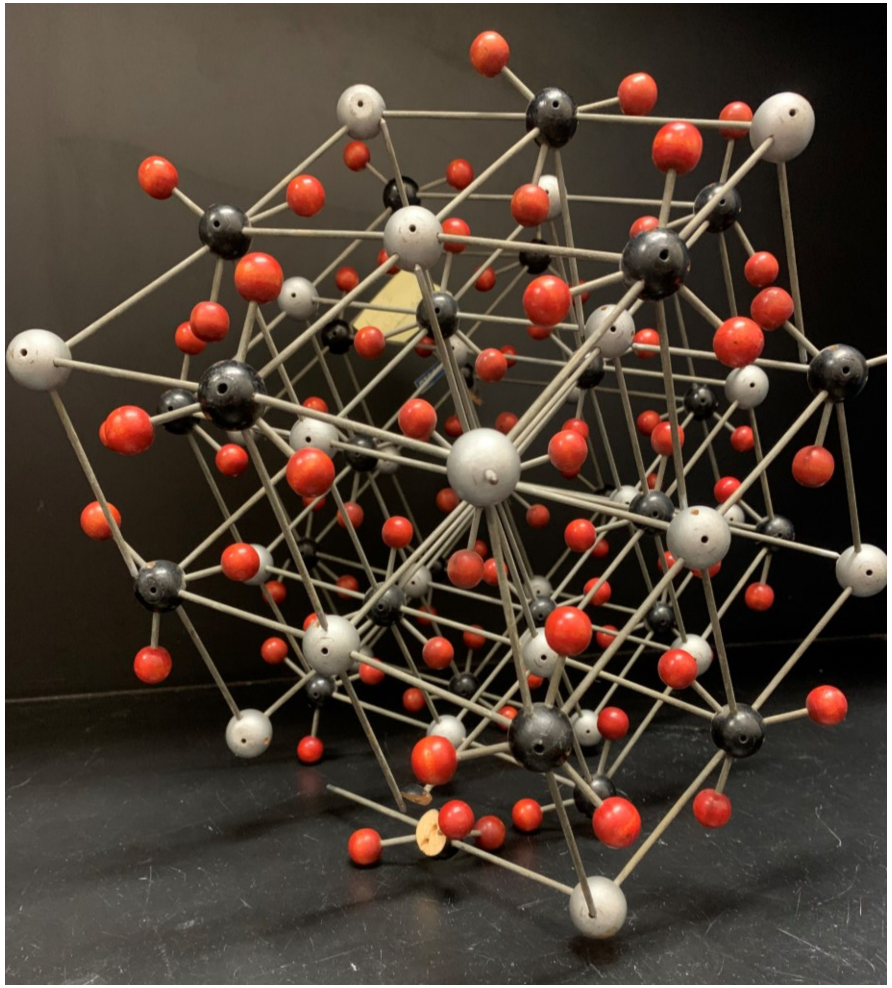
Ca^{2+} and Mn^{2+} are surrounded by 6 oxygen in an octahedral coordination polyhedron.

Ca^{2+} effective ionic radius in a 6 fold octahedron is 1.08 Å in calcite.

Mn^{2+} effective ionic radius in a 6 fold octahedron is 0.83 Å in rhodochrosite.

Mn^{2+} is smaller!

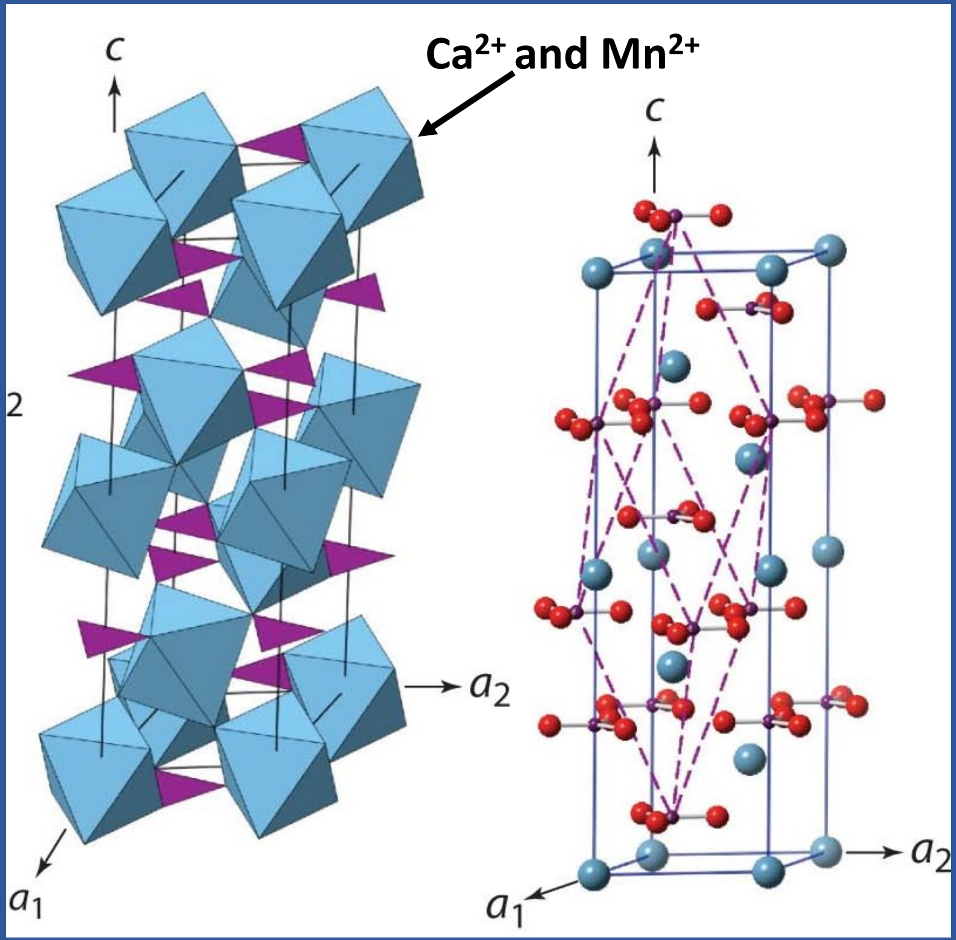


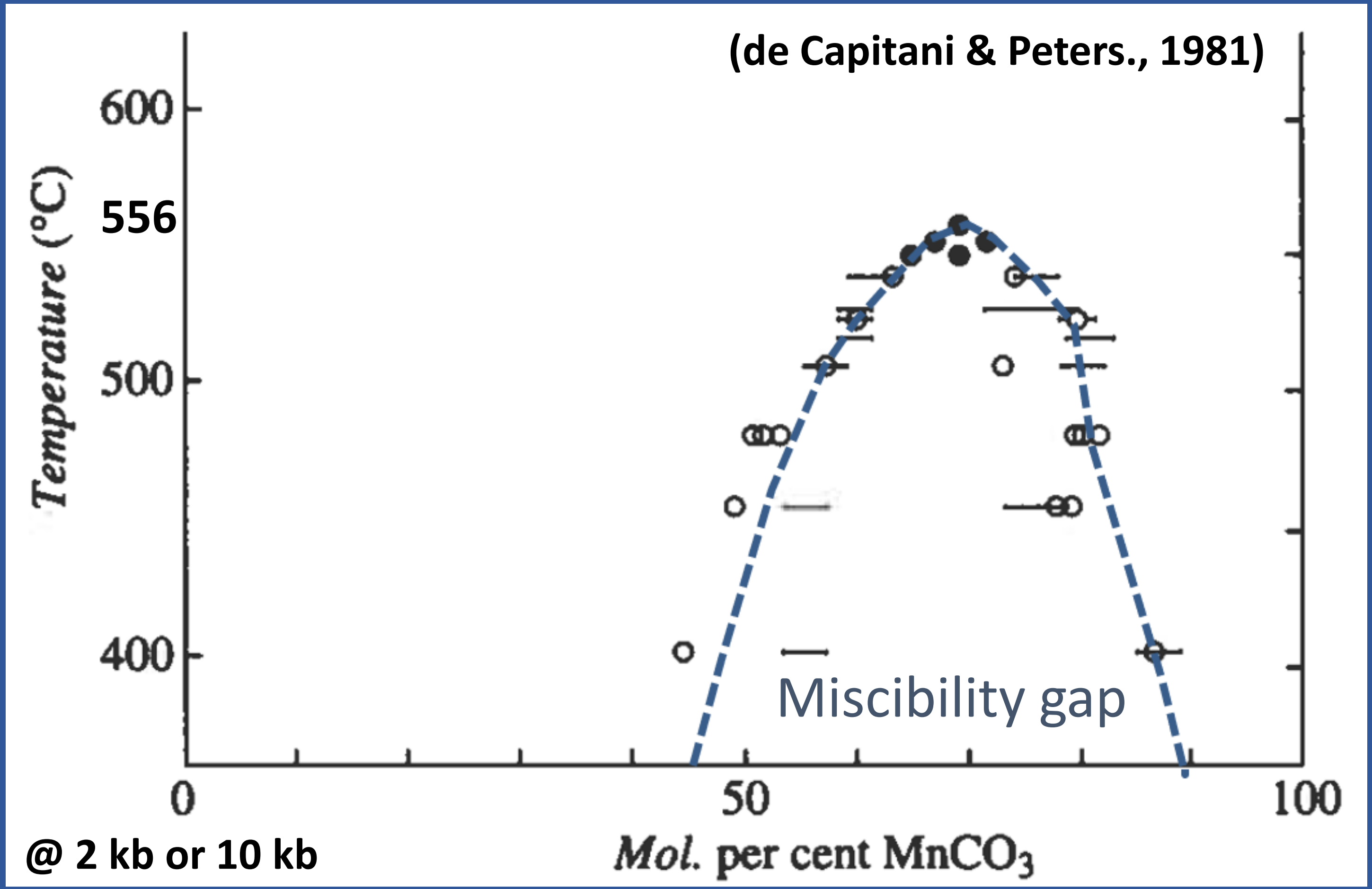


The rhombohedral Bravais lattice is derived from the hexagonal lattice – which is difficult to conceptualize.

Commonly ionic radii are not shown at their correct scale.

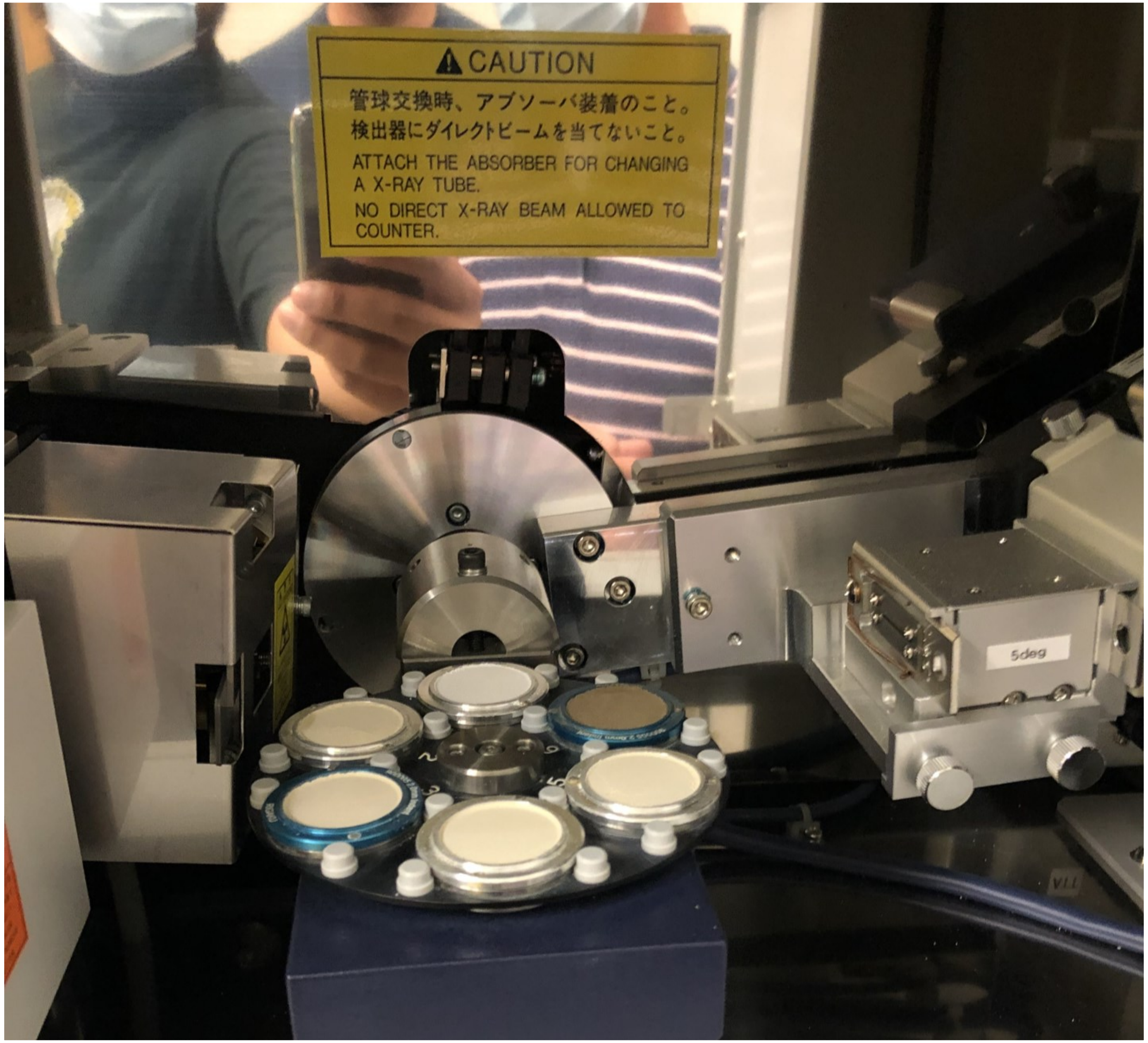
Anionic groups are over simplified and therefore not displayed correctly.



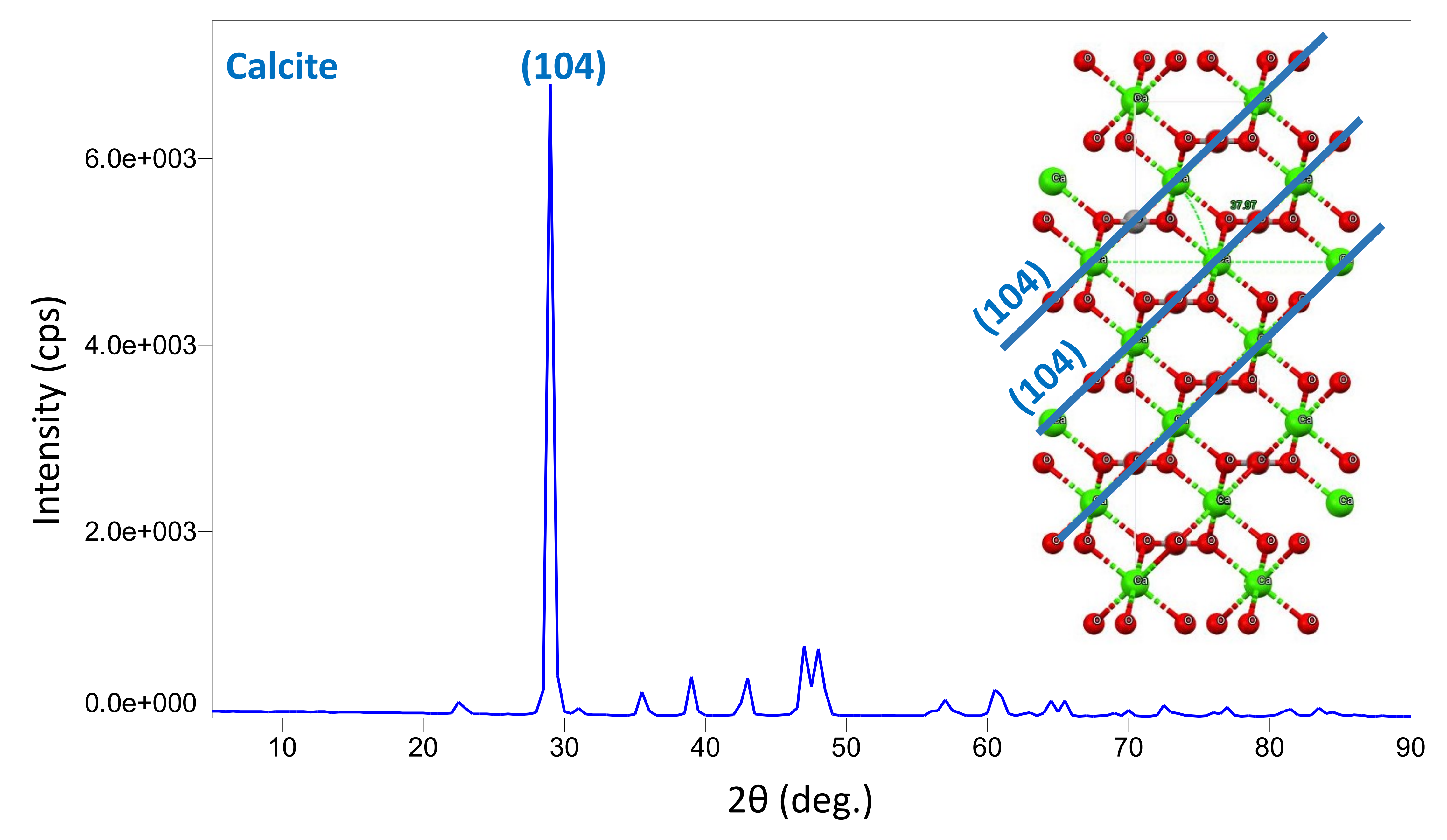


Solid solutions change depending on the size and valency of the cations. This is complex! Complete solid solution, limited solid solution, paired solid solutions!

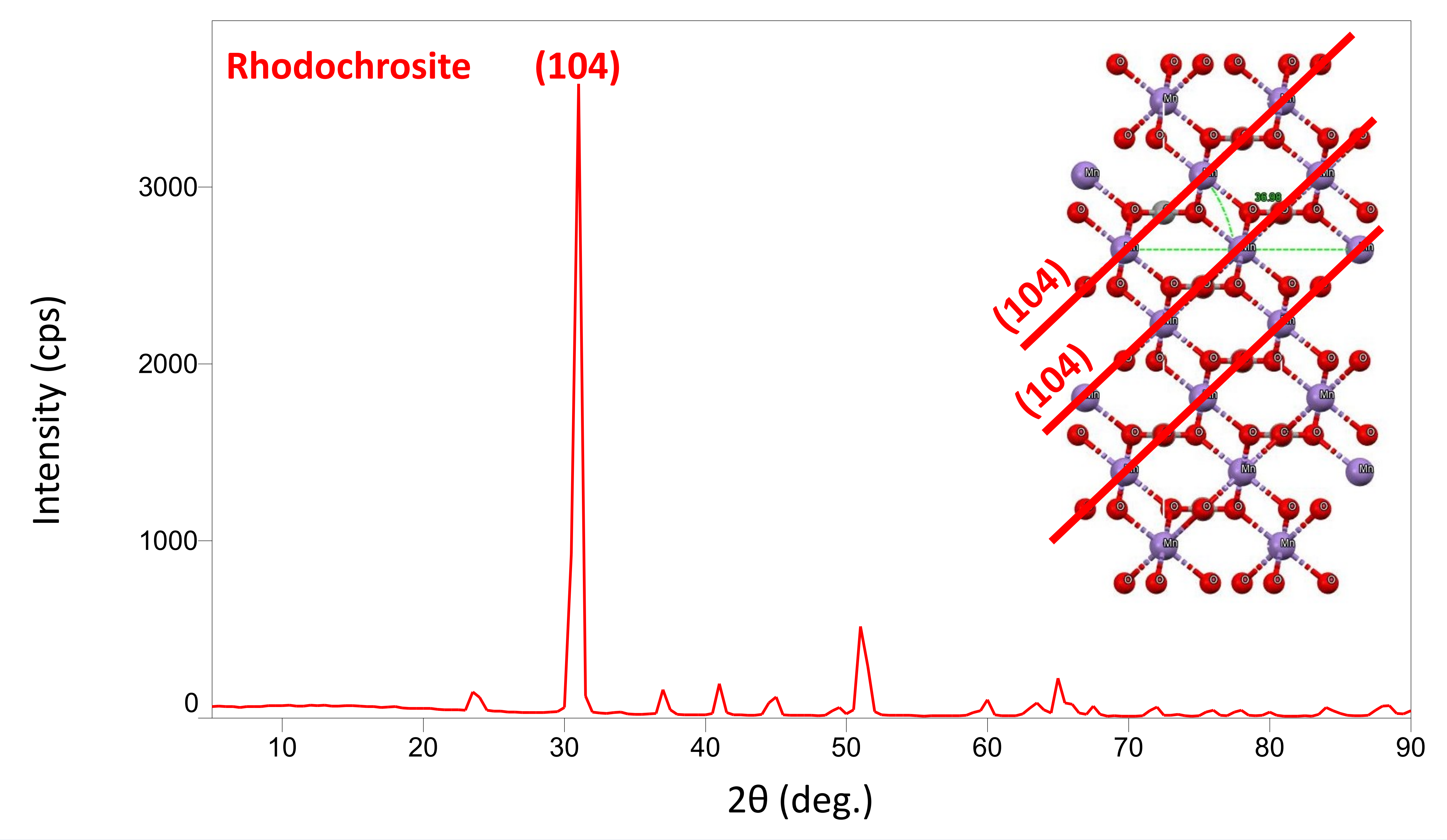
Below 556° C calcite and rhodochrosite have a limited solid solution, due to Ca^{2+} being about 23% larger than Mn^{2+} in carbonate minerals.



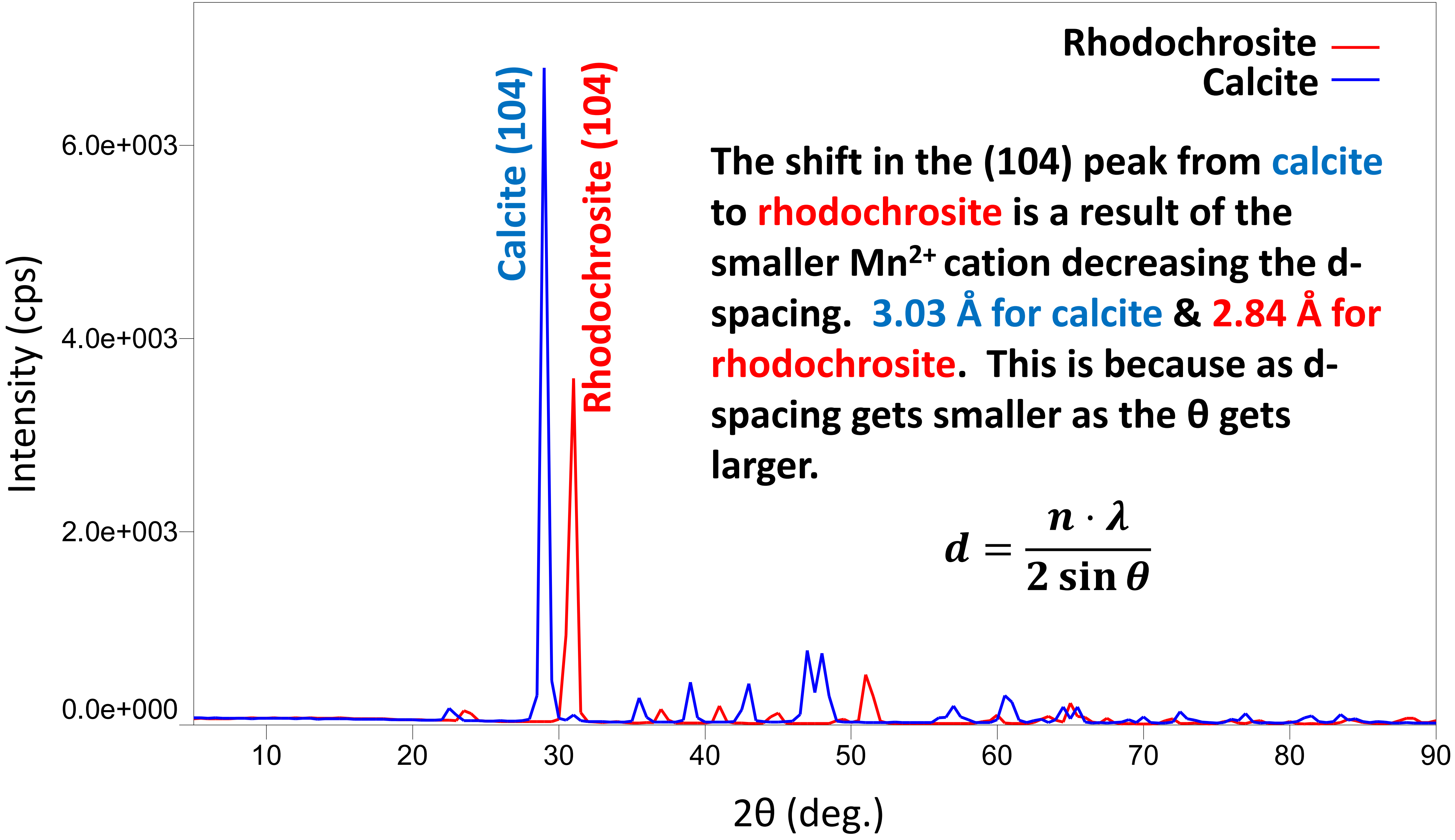
Students utilized a powdered X-ray diffraction (PXRD) to analyze calcite and rhodochrosite.



Calcite PXRD pattern measured by the students. Note the position of the (104) plane.

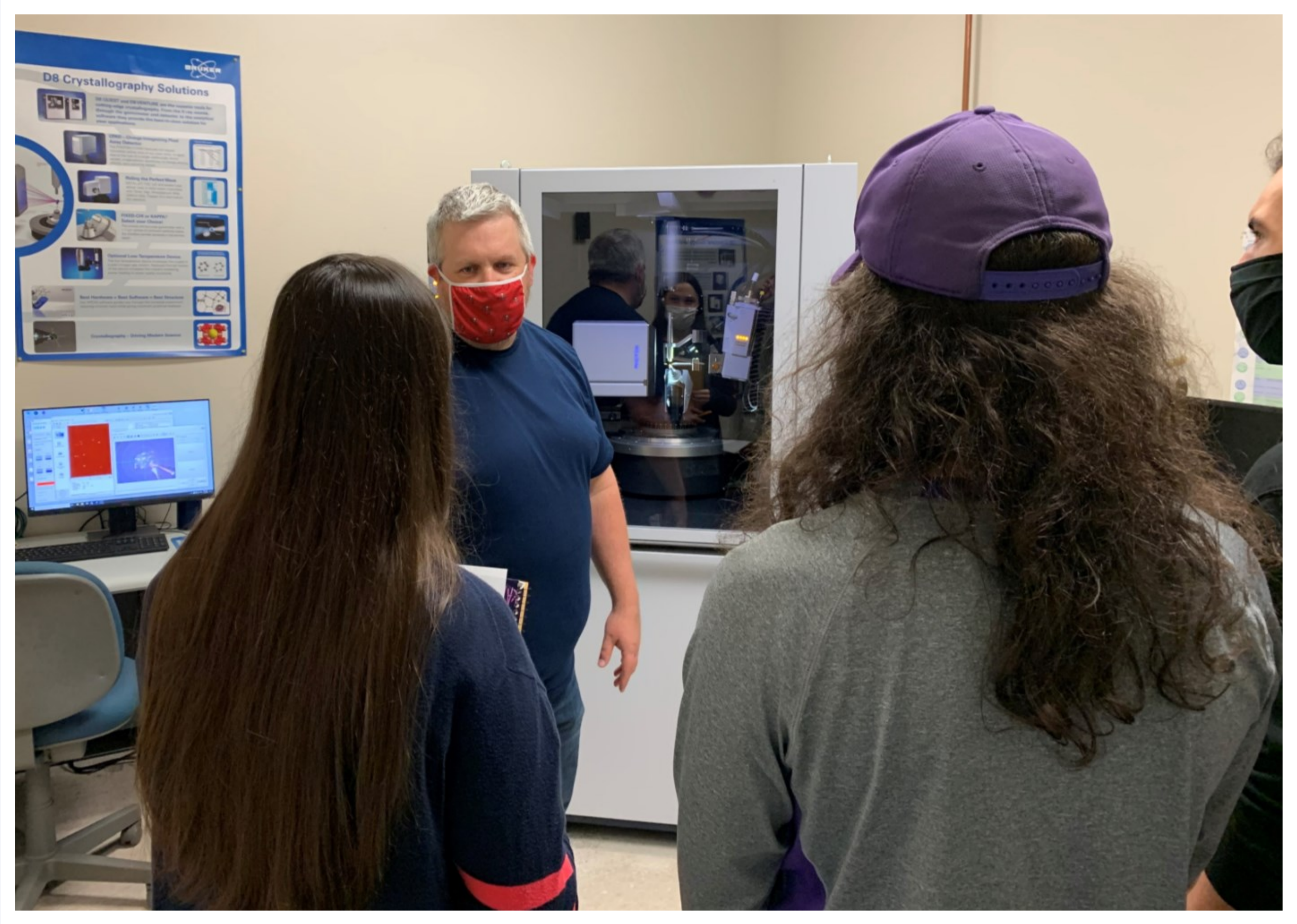


Rhodochrosite PXRD pattern measured by the students. Note the position of the (104) plane.



The shift in the (104) peak from calcite to rhodochrosite is a result of the smaller Mn^{2+} cation decreasing the d-spacing. 3.03 Å for calcite & 2.84 Å for rhodochrosite. This is because as d-spacing gets smaller as the θ gets larger.

$$d = \frac{n \cdot \lambda}{2 \sin \theta}$$

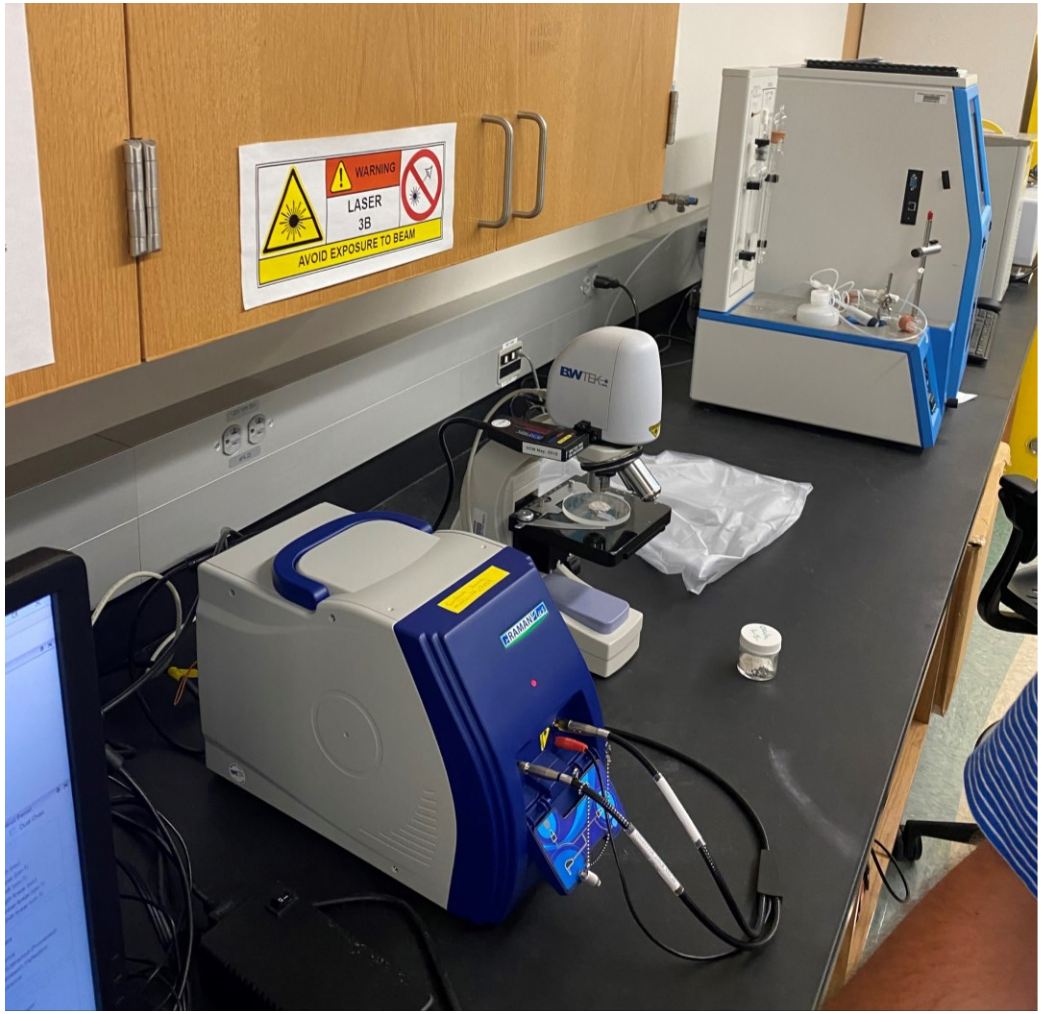


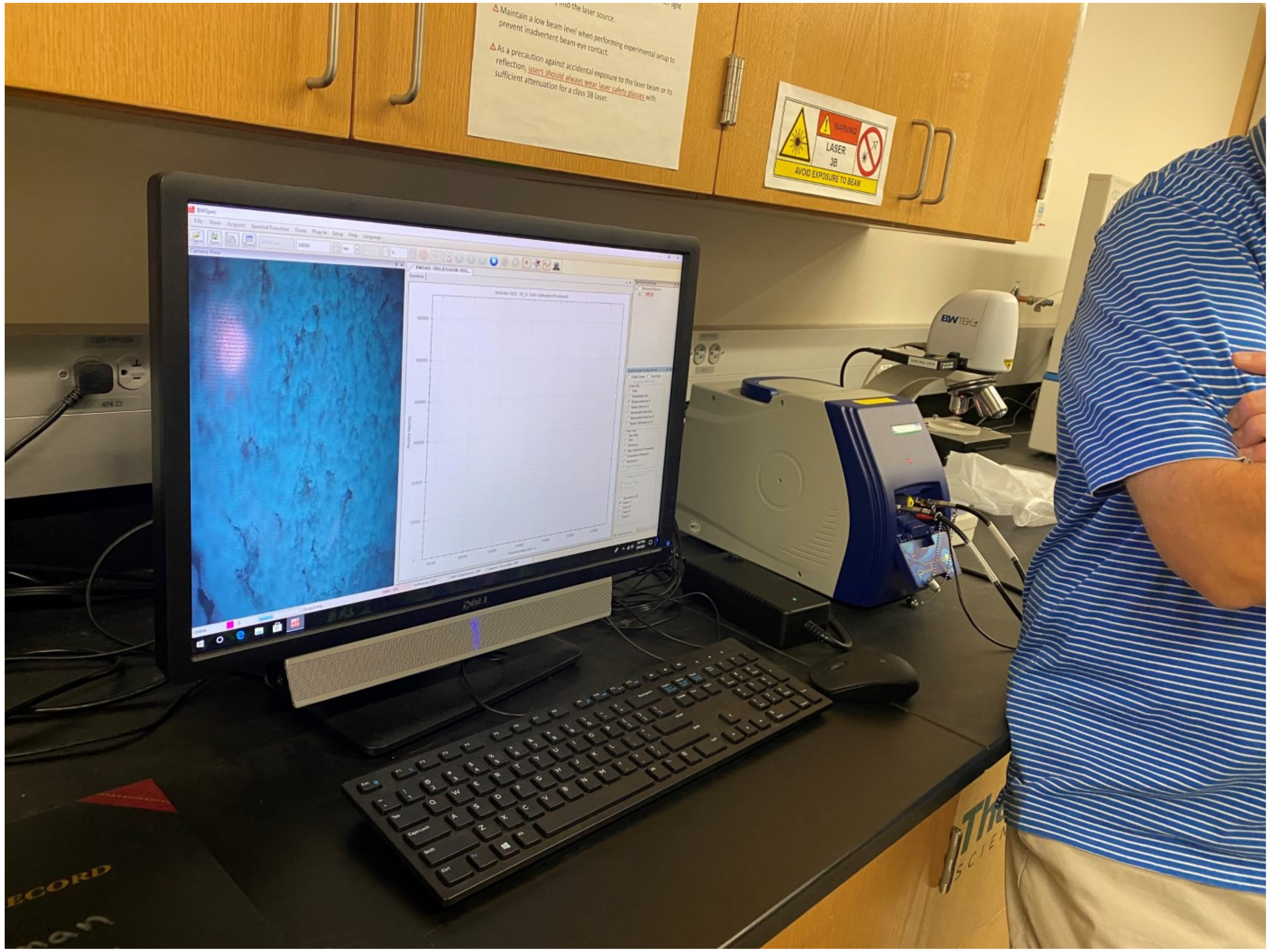
Students utilized a single crystal X-ray diffraction (SCXRD) to analyze calcite and rhodochrosite. This was the most impactful instrument that could clearly show the unit cell dimensions.

Sample	a axis (Å)	c axis (Å)	c/a ratio	α (°)	β (°)	γ (°)	Volume of unit cell ($Å^3$)	Space Group
Calcite	4.999	17.013	3.403	90	90	120	368.22	$R\bar{3}c$
Rhodochrosite	4.771	15.629	3.276	90	90	120	308.25	$R\bar{3}c$

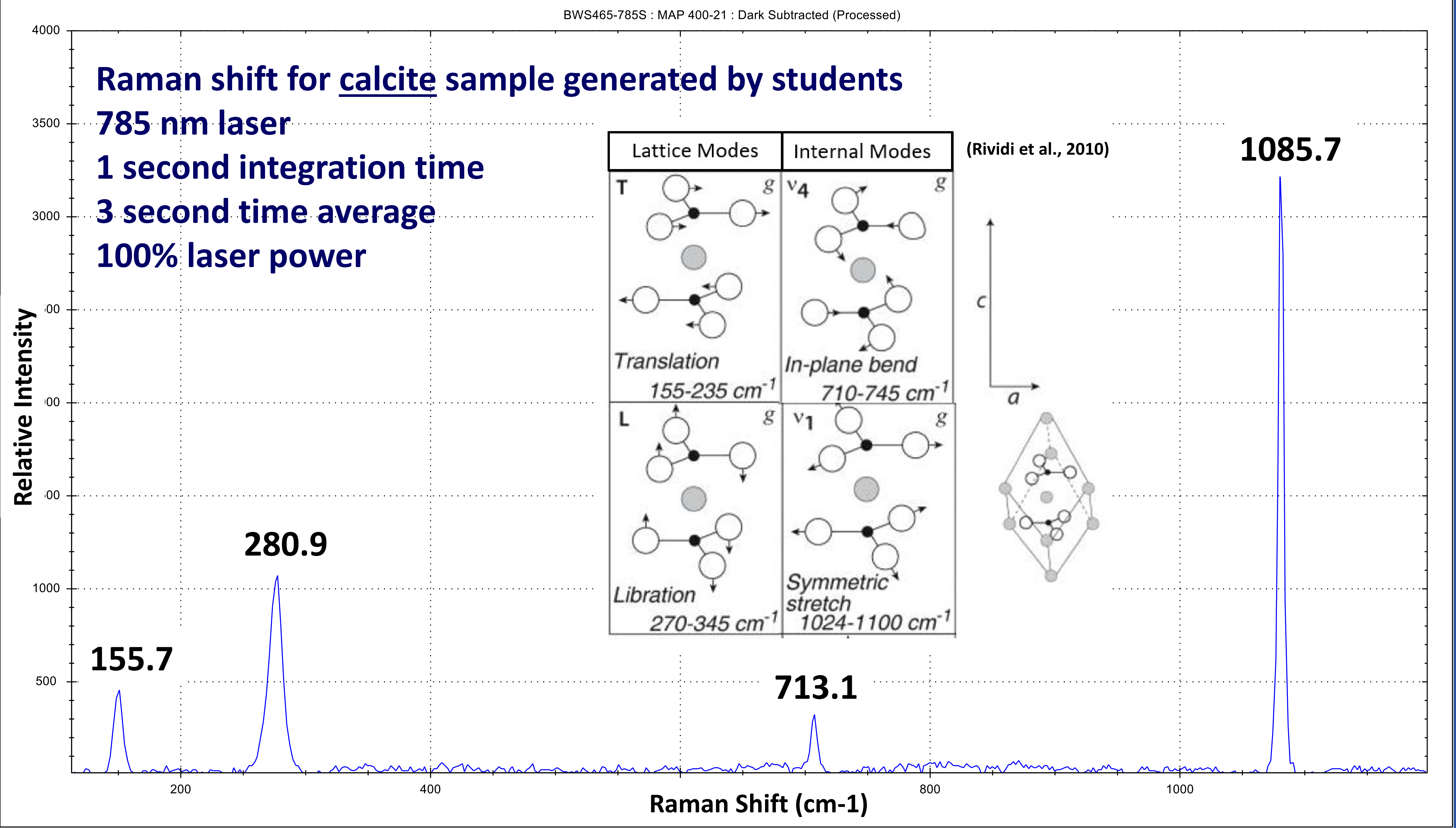
SCXRD data collected by GEOPATH students during the summer of 2021.

Note the decrease in the a axis, c axis, c/a ratio, and unit cell volume between calcite and rhodochrosite. This is the result of the size decrease of Mn^{2+} compared to the larger Ca^{2+}.

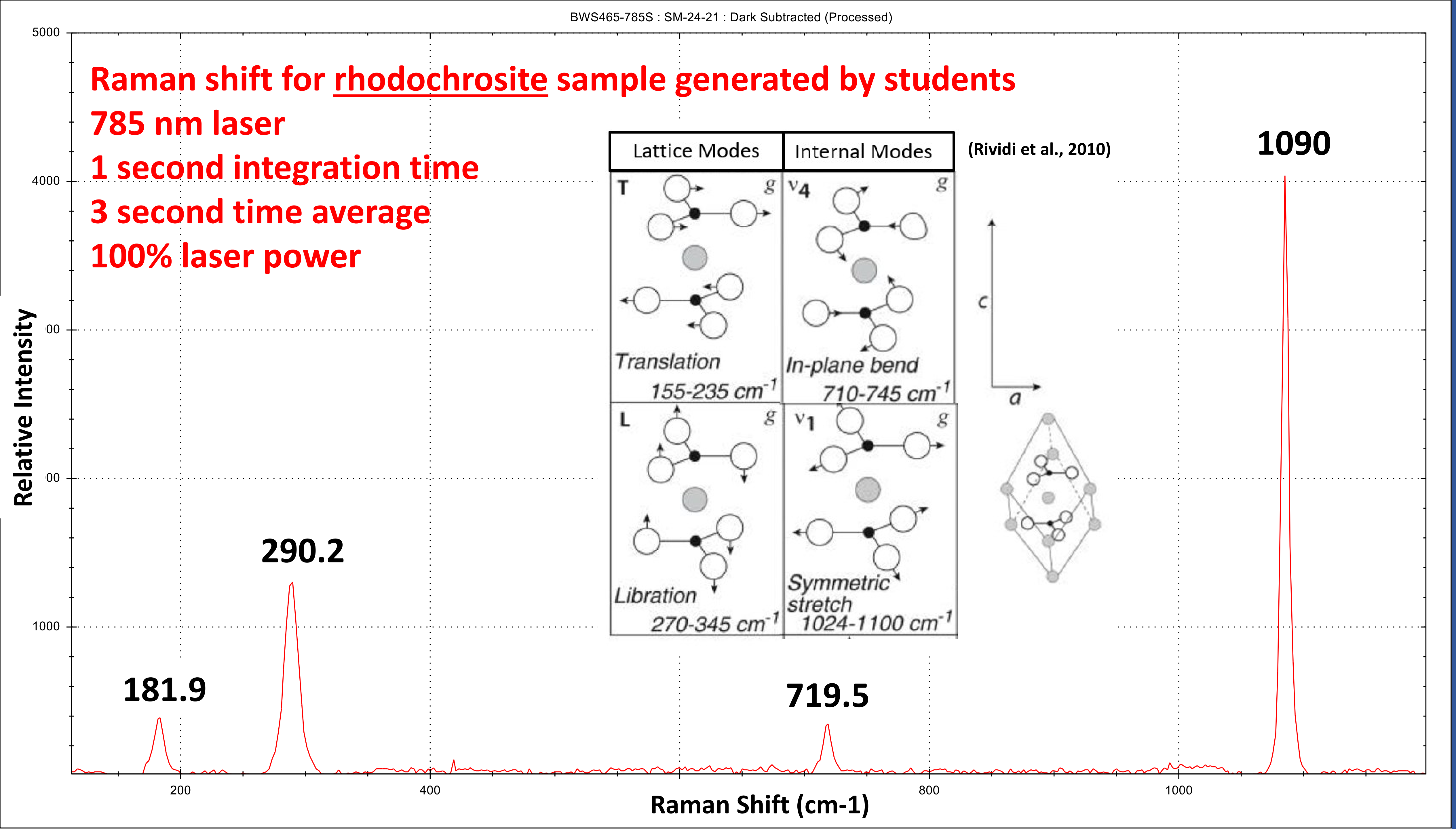


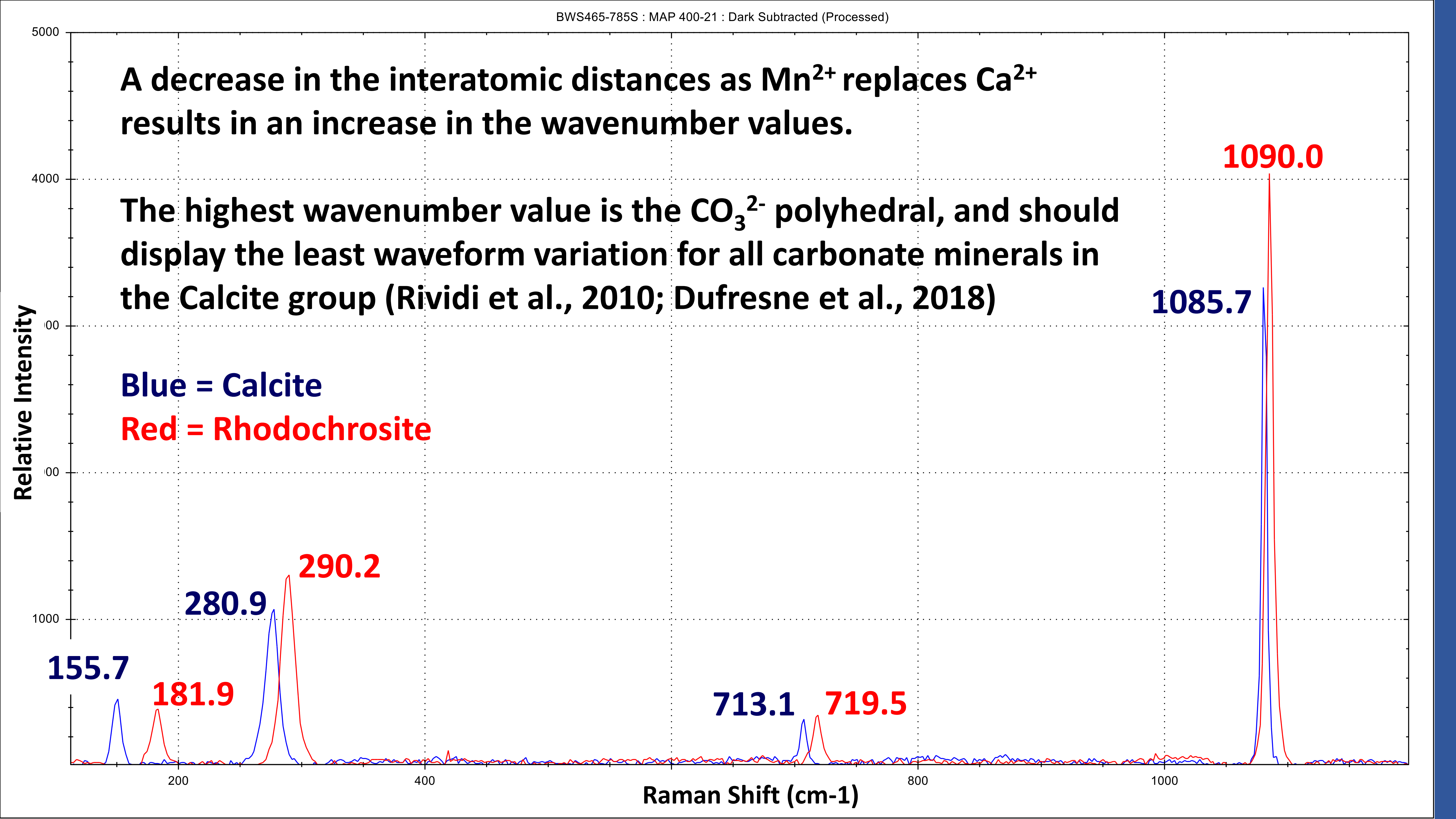


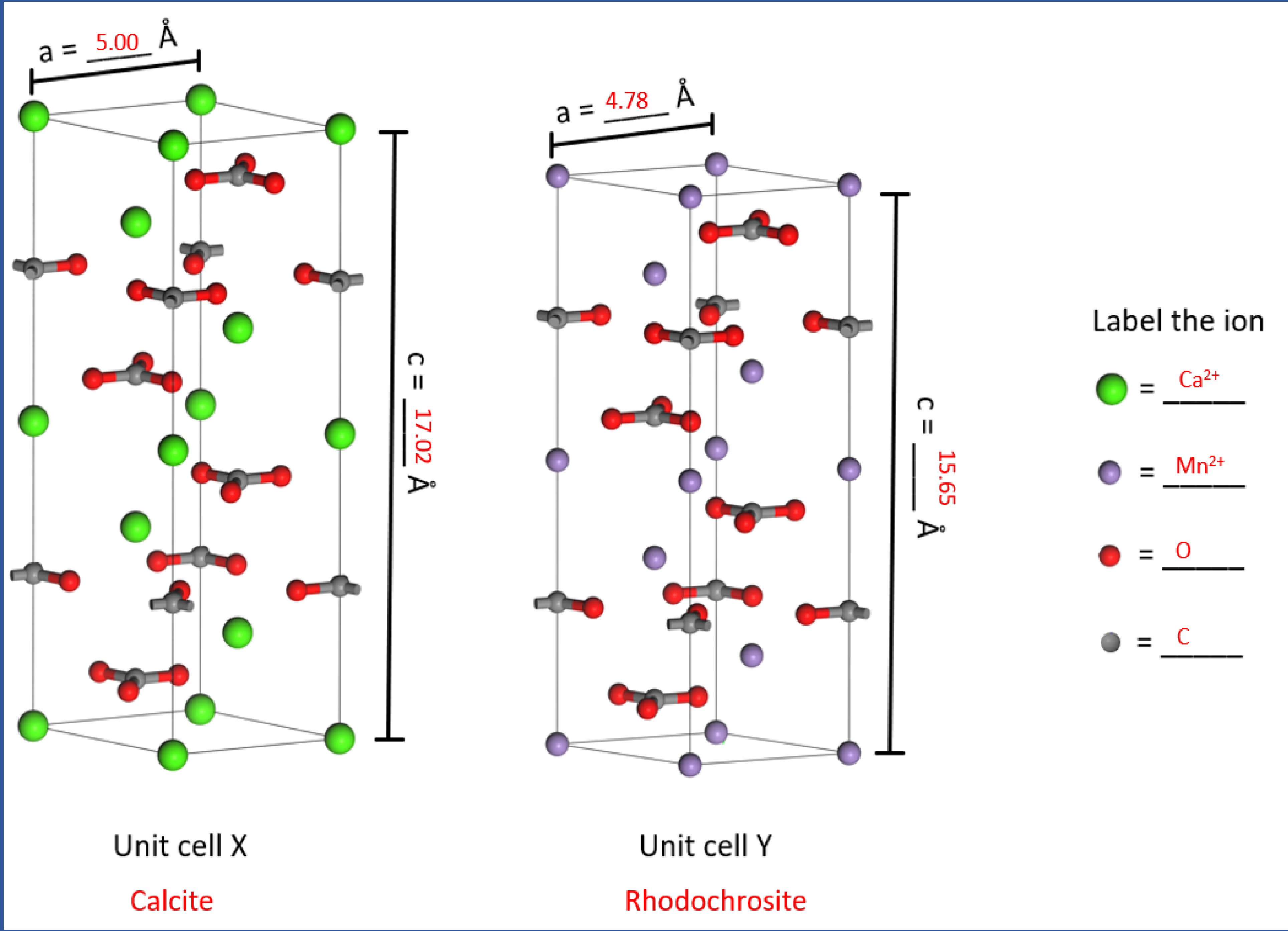
Students utilized a 785 nm Raman with a microscope setup to analyze calcite and rhodochrosite.



BWS465-785S : MAP 400-21 : Dark Subtracted (Processed)
Raman shift for calcite sample generated by students
785 nm laser
1 second integration time
3 second time average
100% laser power
Lattice Modes
Internal Modes
(Rividi et al., 2010)
T
Translation
155-235 cm-1
ν4
In-plane bend
710-745 cm-1
L
Libration
270-345 cm-1
ν1
Symmetric stretch
1024-1100 cm-1
c
a
1085.7
280.9
155.7
713.1
Relative Intensity
Raman Shift (cm-1)
4000
3500
3000
1000
500
200
400
800
1000


BWS465-785S : SM-24-21 : Dark Subtracted (Processed)
Raman shift for rhodochrosite sample generated by students
785 nm laser
1 second integration time
3 second time average
100% laser power
Lattice Modes
Internal Modes
(Rividi et al., 2010)
T
g
Translation
155-235 cm-1
ν4
In-plane bend
710-745 cm-1
L
Libration
270-345 cm-1
ν1
Symmetric stretch
1024-1100 cm-1
c
a
1090
290.2
181.9
719.5
5000
4000
1000
200
400
800
1000
Relative Intensity
Raman Shift (cm-1)


BWS465-785S : MAP 400-21 : Dark Subtracted (Processed)
A decrease in the interatomic distances as Mn^{2+} replaces Ca^{2+} results in an increase in the wavenumber values.
The highest wavenumber value is the CO_3^{2-} polyhedral, and should display the least waveform variation for all carbonate minerals in the Calcite group (Rividi et al., 2010; Dufresne et al., 2018)
Blue = Calcite
Red = Rhodochrosite
1090.0
1085.7
290.2
280.9
155.7
181.9
713.1
719.5
5000
4000
1000
Relative Intensity
200
400
800
1000
Raman Shift (cm-1)



Unit cells for calcite and rhodochrosite generated by student data from SCXRD.

Students take their data and apply it to these structures to better understand the relationship between cations, solid solutions, and unit cells.

Assessment utilizing Creative Exercises of Lewis et al. (2010)

- Before research experience the students never mention solid solutions or unit cells on the assessment

- They also never mentioned instrumentation as a means of studying minerals.

- The students can only describe the most basic physical properties of carbonates
  - Hardness
  - Luster
  - Reacts with acid

- Many confusing organic aragonite with mineral carbonates.

Assessment utilizing Creative Exercises of Lewis et al. (2010)

After experience with the XRD's and Raman, the students:

- Made correct statements about bond length between the M^{2+} cation and the closest neighbor differing for calcite and rhodochrosite due to the difference in unit cell sizes.

- Mentioned how this change in the unit cell is also effecting other physical attributes of the mineral (e.g., $MnCO_3$ does not react as easily as $CaCO_3$ with weak HCl; $MnCO_3$ is harder than $CaCO_3$)

- Mentioned utilizing instrumentation as a critical part of studying minerals.

- Could easily link unit cell size to the radius of the M^{2+} cation in carbonates.

More assessment to come at the end of the semester!