Tetragonal structure of $CaSiO_3$ perovskite above 20 GPa

Shim, Jeanloz, & Duffy

GRL (2002)

Crystallography Review

Images removed due to copyright considerations.

Miller Index

Xray Diffraction

Octahedra = CN: 6

6 Oxygens
1 Silicon

Perovskite Structure

Cubic a=b=c

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Orthorhombic a>b>c

Previous Studies

- Determined EOS to CMB with Energy dispersive X-ray diffraction
- CaSi Perovskite has a cubic structure (Pm3m)
- Theoretical study proposed a tetragonal to cubic phase transformation in the lower mantle.

Raw Xray Pattern

Integrated Diffraction Pattern

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Expected Peak Positions

Integrated Diffraction Pattern

Results

- Pressure measurements from 19.7 – 45.8 GPa
- Peak splitting observed for 200 and 211
- 0.4% shorter c-axis than a-axis
- This amount of distortion is smaller than resolution for energy dispersive diffraction
- Intensity of splitting is a function of geometry 200>211>110

- More intense peak of the doublet occurs at lower angle
- Intense line should originate from atomic planes normal to the two identical a-axes of the tetragonal unit cell (200)
- Less intense line should originate from planes normal to the c-axis (002)

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Unit Cell Parameters

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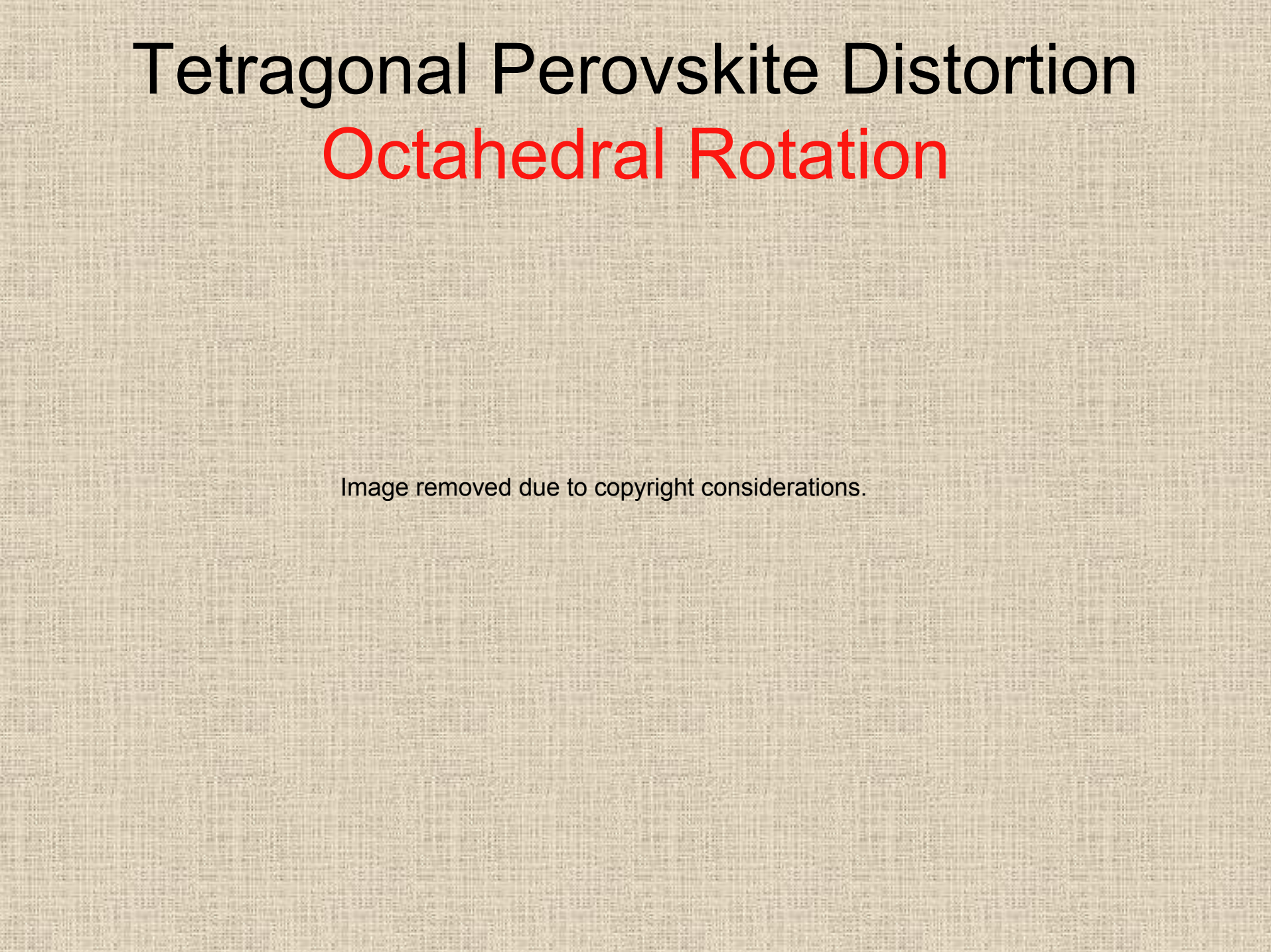
- Isothermal bulk modulus = 255 +/- 5 GPa

Tetragonal Perovskite Distortion

Octahedral Rotation

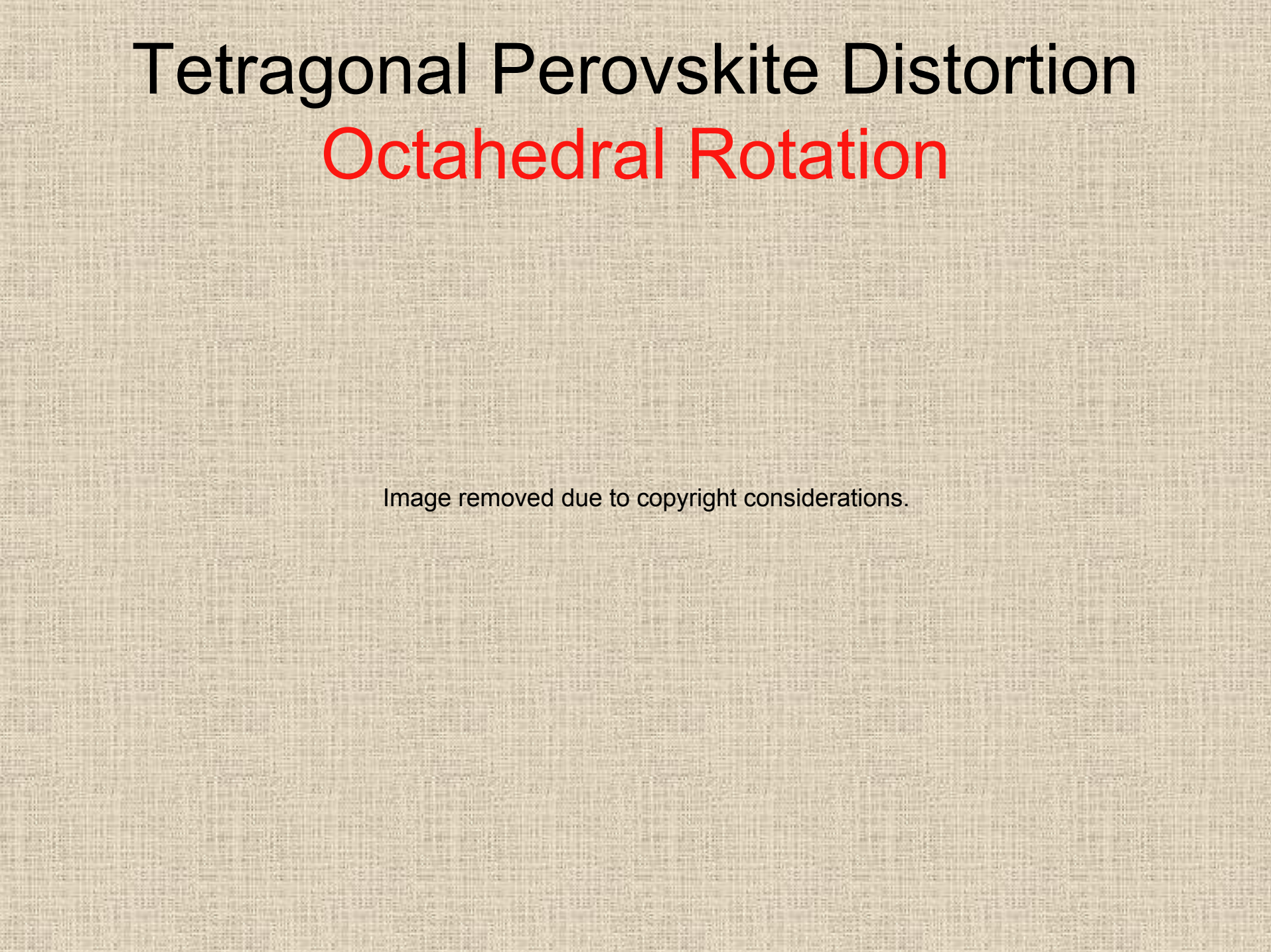


I4/*mmm*

- Octahedra around a-axis
- Octahedra rotate by 4.9 +/- 1.7o @ 45.8 GPa
- Si-O bond length along c-axis is shorter by 0.6 +/- 0.3%
- Three crystallographically distinct Ca sites

Tetragonal Perovskite Distortion

Octahedral Rotation

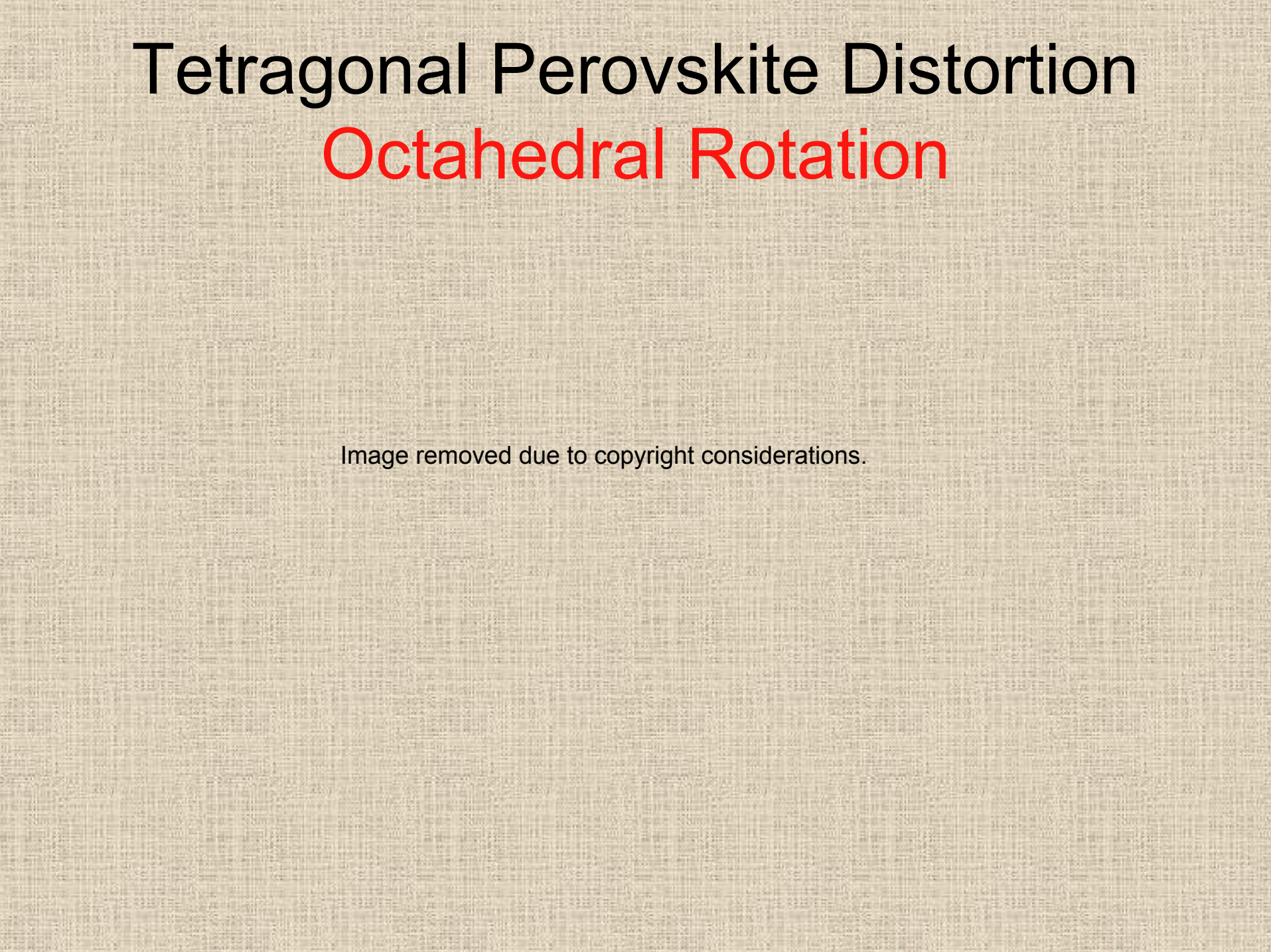


P4/*mbm* & I4/*mcm*

- Octahedra rotation about the c-axis
- Contraction of the a-axis
- Contrary to diffraction pattern

Tetragonal Perovskite Distortion

Octahedral Rotation



MgPv & CaPv
Si-O Bond Length vs. Pressure

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“There appears to be an intrinsic anisotropy in these two materials”

Discussion

- More pronounced peak splitting with more pressure medium indicates distortion is not due to differential stress
- Recent 1st principle calculations suggest an orthorhombic structure
- Resolution of current x-ray diffraction study can not resolve orthorhombic distortion (0.13%)
- Is tetragonal distortion stable at High T and High P?

Conclusions

- If tetragonal distortion is real at ambient conditions in the mantle – elastic properties and their directional dependence can be very different from cubic perovskite

- Since the dodecahedral site of perovskites is the main repository of large cations in the mantle (U, Th, Sr, etc.) – distortion of this site may have important consequences for the partitioning of these elements in the lower mantle