

Post-refinement data handling

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- Crystallographic Information Files (cif's)
 - High-pressure features
 - Response to cif-checker
 - Parametric data handling

- Post-refinement analysis tools
 - Mostly for inorganic structures

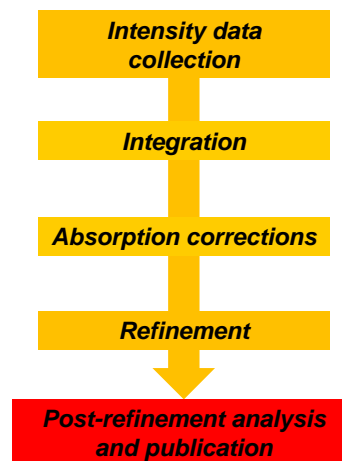
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Post-refinement analysis

- Structure validation
 - Getting past the cif-checker

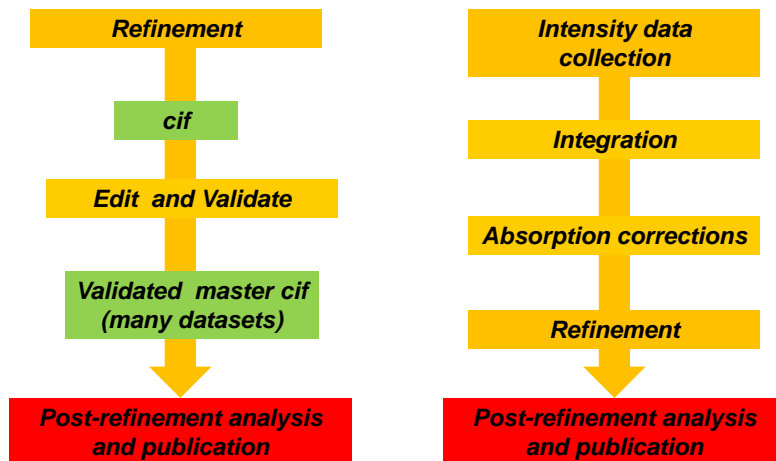
- Parametric data:
 - Challenges
 - Opportunities to exploit self-consistency



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Post-refinement analysis



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Parametric data, so report P,T

- In each data block:
- **_cell_measurement_pressure**
 - pressure in kilopascals at which unit cell parameters were measured
- **_diffrn_ambient_pressure**
 - mean hydrostatic pressure in kilopascals at which diffraction intensities were measured
- **UNITS!!!**
 - 1 GPa = 10 kbar = 1,000,000 kPa

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Parametric data, so report P,T

- Don't forget the temperatures:
- **`_cell_measurement_temperature`**
 - temperature in Kelvin at which unit cell parameters were measured
- **`_diffrn_ambient_temperature`**
 - mean temperature in Kelvin at which diffraction intensities were measured

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Some optional items

- **`_diffrn_ambient_pressure_gt`**
- **`_diffrn_ambient_pressure_lt`**
 - mean hydrostatic pressure in kilopascals above which (`*_gt`) or below which (`*_lt`) the intensities were measured
- **`_exptl_crystal_pressure_history`**
 - relevant details concerning the pressure history of a sample
- **`_pd_prep_pressure`**
 - preparation pressure of the sample in kilopascals
 - (from powder cif dictionary)
- **`_cell_wave_vectors_pressure_max`**
- **`_cell_wave_vectors_pressure_min`**
 - maximum and minimum values of the pressure in kilopascals between which the modulation wave vector(s) were measured

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From macromolecular cif dictionary

- [_cell_measurement.pressure](#)
- [_diffrn.ambient_pressure](#)
- [_diffrn.ambient_pressure_gt](#)
- [_diffrn.ambient_pressure_lt](#)

- [_cell_measurement.pressure_esd](#)
 - standard deviation of [_cell_measurement.pressure](#)
- [_diffrn.ambient_pressure_esd](#)
 - standard deviation of [diffrn.ambient_pressure](#)

- [_exptl_crystal_grow.pressure](#)
 - ambient pressure in kilopascals at which the crystal was grown
- [_exptl_crystal_grow.pressure_esd](#)
 - standard deviation of [exptl_crystal_grow.pressure](#)

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Alerts of level A

- These must be answered!

- **PROBLEM:** `_diffrn_reflns_theta_full` (too) Low
12.64 Deg.
RESPONSE: Due to limited opening angle of the diamond anvil cell.

- **PROBLEM:** `_diffrn_measured_fraction_theta_full` Low
0.43
RESPONSE: Due to limited opening angle of the diamond anvil cell.

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Cif-checker warnings

- **The value of R(int) is greater than 0.12**
 - R(int) given **0.131**
 - **RESPONSE:** Data quality lower than normal because data collected from crystal in diamond-anvil pressure cell

- **Expected hkl max differ from CIF values**
 - From the CIF: `_diffrn_reflns_theta_max` **28.29**
 - From the CIF: `_reflns_number_total` **461**
 - From the CIF: `_diffrn_reflns_limit_max hkl` **6. 9. 9.**
 - From the CIF: `_diffrn_reflns_limit_min hkl` **-7. -9. -9.**
 - TEST1: Expected hkl limits for theta max
 - Calculated maximum hkl **9. 11. 9.**
 - Calculated minimum hkl **-9. -11. -9.**

- **RESPONSE:** Data restricted because data collected from crystal in diamond-anvil pressure cell

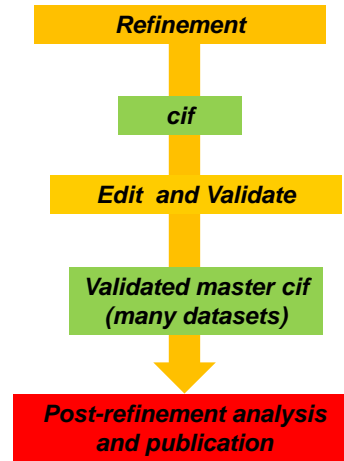
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Validate cifs separately

```

VTXHP_CaSnO3.cif - Notepad
File Edit Format View Help
data CaSnO3_P00
_chemical_name 'CaSnO3'
_chemical_formula_sum 'Ca Sn O3'
_symmetry_space_group_name_H-M 'P b n n'
loop_
_symmetry_equiv_pos_as_xyz
  'x,y,z'
  '-x,-y,1/2+z'
  '1/2+x,1/2-y,1/2+z'
  '1/2-x,1/2-y,1/2-z'
  '1/2-x,1/2+y,z'
  '1/2+x,1/2-y,-z'
  '-x,-y,-z'
_diffn_ambient_pressure 100
_cell_length_a 5.5142(2)
_cell_length_b 5.6634(2)
_cell_length_c 7.88162(17)
_cell_angle_alpha 90.0000
_cell_angle_beta 90.0000
_cell_angle_gamma 90.0000
_cell_formula_units_Z 4
loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Ca -0.01265(16) 0.0505(3) 0.2500
Sn 0.5000 0.0000 0.5000
O1 0.0993(8) 0.4646(6) 0.2500
O2 0.6987(4) 0.2988(4) 0.0528(3)
    
```



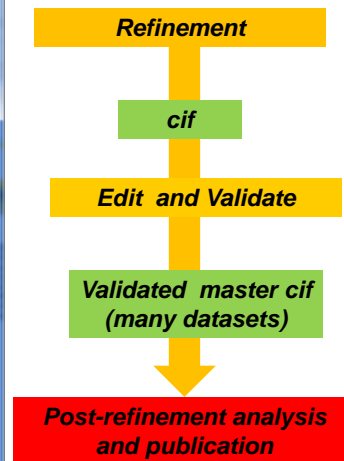
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Build a master cif

```

VTXHP_CaSnO3.cif - Notepad
File Edit Format View Help
data_global
loop_
_publ_author_name
  'Zhao J'
  'Ross M L'
  'Angel R J'
_journal_name_full 'Physics and Chemistry of Minerals'
_journal_volume 31
_journal_year 2004
_journal_page_first 299
_journal_page_last 305
_publ_section_title
  'Tilting and distortion of CaSnO3 perovskite to 7 GPa determined fr
  single-crystal X-ray diffraction'
data CaSnO3_P00
_chemical_name 'CaSnO3'
_chemical_formula_sum 'Ca Sn O3'
_symmetry_space_group_name_H-M 'P b n n'
loop_
_symmetry_equiv_pos_as_xyz
  'x,y,z'
  '-x,-y,1/2+z'
  '1/2+x,1/2-y,1/2+z'
  '1/2-x,1/2-y,1/2-z'
  '1/2-x,1/2+y,z'
  '1/2+x,1/2-y,-z'
  '-x,-y,-z'
_diffn_ambient_pressure 100
_cell_length_a 5.5142(2)
_cell_length_b 5.6634(2)
    
```



And lock it against editing!

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Use your master cif for everything!

Validated master cif
(many datasets)

- Generate tables for publication:
 - Cell parameters
 - Positional parameters
 - Bond lengths and angles

- Geometrical parameters
 - Polyhedral distortions
 - Polyhedral tilts

cifReader

IVTON

Isodisplace

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cifReader

- Reads 1 cif at a time
 - Containing multiple datablocks
 - Research tool and badly written
 - But available at www.rossangel.net
 - And produces tables (e.g. bond lengths etc) and basic calculations, without any cutting and pasting!

- Command line driven
 - But undocumented

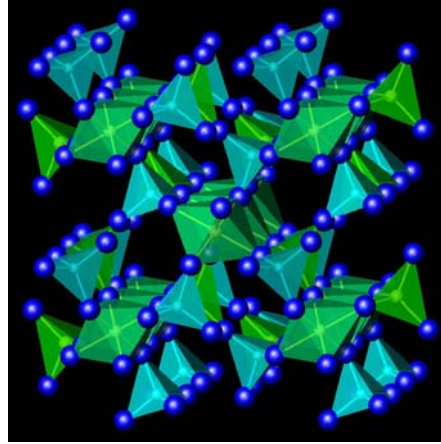


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The concept of polyhedra

- In inorganic structures it is usual to group all chemical bonds reaching an atom and to define its coordination polyhedron
- Structures are considered as built from these strongly-bonded polyhedra
- Structural evolution:
 - Polyhedral internal changes
 - Tilts of the polyhedra



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cifReader and polyhedra

```

DoS_cif.exe - Shortcut
19-JUL-12:14:40:Dataplotter>list bonds
Enter central atom name (or ALL):Sn

      BONDS FROM CENTRAL ATOM SN          BETWEEN 2.00 AND 2.50 ANGSTROM
Pressure Temperature O1      O2      O2      O2      N  AUERAGE  QE      AU      UOLUME
0.000  298.000  2.0549  2.0549  2.0572  2.0572  2.0559  2.0559  6  2.0560  1.0007  2.466  11.576
0.074  298.000  2.0537  2.0537  2.0488  2.0488  2.0571  2.0571  6  2.0532  1.0006  2.254  11.530
1.500  298.000  2.0511  2.0511  2.0487  2.0487  2.0538  2.0538  6  2.0512  1.0007  2.472  11.495
2.610  298.000  2.0460  2.0460  2.0430  2.0430  2.0519  2.0519  6  2.0469  1.0008  2.635  11.423
3.940  298.000  2.0412  2.0412  2.0405  2.0405  2.0462  2.0462  6  2.0426  1.0006  2.008  11.354
5.180  298.000  2.0358  2.0358  2.0392  2.0392  2.0431  2.0431  6  2.0393  1.0006  2.128  11.298
5.980  298.000  2.0351  2.0351  2.0315  2.0315  2.0452  2.0452  6  2.0373  1.0007  2.303  11.263
6.730  298.000  2.0320  2.0320  2.0268  2.0268  2.0411  2.0411  6  2.0333  1.0006  1.974  11.199

LIST BONDS> Enter central atom name:_
    
```

$$\text{Quadratic elongation: } \langle \lambda \rangle = \frac{1}{n} \sum_i (l/l_0)^2$$

$$\text{Bond angle variance: } = \frac{1}{n-1} \sum_i (\theta_i - \theta_0)^2$$

(Robinson et al., Science 172 (1971) 567-570)

For some alternative approaches see Porai-Koshits & Aslanov, J.Struct.Chem. 13 (1972) 244; Muettterties & Guggenberger, J.Am.Chem.Soc. 96 (1974) 1748-1756; Dollase, Acta Cryst. A30 (1974) 513-517; Drew, Coord.Chem.Rev. 24 (1977) 179-275

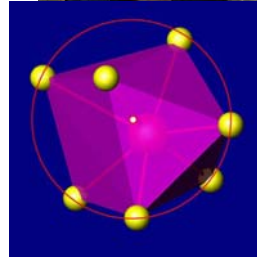
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IVTON

- **Developed by Tonci Balic-Zunic**
 - Balic-Zunic & Vickovic, *J.Appl.Cryst.* (1996) 29, 305
 - Available from TonciB@snm.ku.dk

- **Calculates new polyhedral parameters**
 - Based on centroid
 - The centre of the best sphere fitted to the vertices of the polyhedron.
 - Can describe displacement of atom from centre
 - Can describe distortion of coordination atoms independent of central atom position.

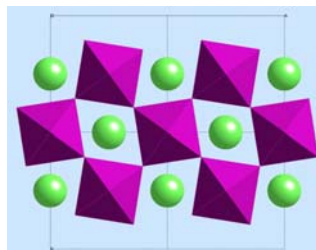


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Isodisplace

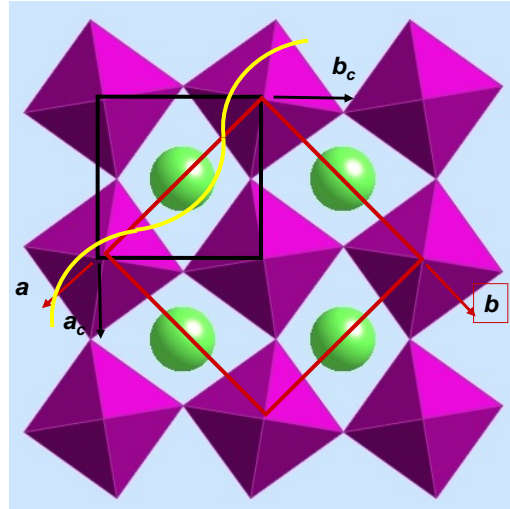
- **Analyses structural evolution in terms of symmetry-adapted modes**
 - 'Frozen phonons'
 - Use when structure approximates a higher symmetry
 - For perovskites and octahedral frameworks can obtain tilt angles (*Acta Cryst. B67: 302 (2011)*)
 - Unambiguous separation of tilts and distortions



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One tilt as a stationary plane wave

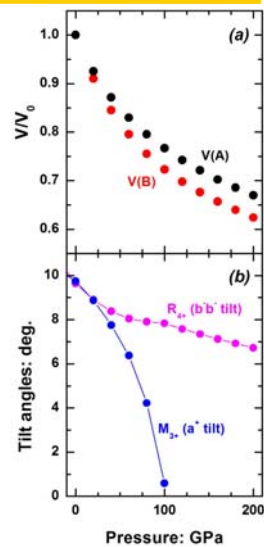


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Isodisplace

- <http://stokes.byu.edu/iso/isodistort.html>
- Work on one refined structure at a time
- Decomposes the distortions from higher symmetry
 - Need a model of the high-symmetry structure
 - Load both to Isodisplace (Mode 4)
 - Obtain 'mode amplitudes'
 - Convert to tilt angles (Acta Cryst. B67: 302 (2011))



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Summary

- **Validate each structure**
- **Create Master cif**
 - Lock it
 - Validate it
 - Avoid cut and paste errors!
- **Generate tables for publication from it**
- **Do all post-refinement analysis from it!**
- **Avoid cut and paste errors!**

