Reassessing Pauling's Rules

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Introduction

Pauling's rules have been used in solid-state chemistry for 9 decades [1,2]. Surprisingly, there is no statistically sound analysis on their performance yet. We attempt to close this gap and start from the statistical analysis of the coordination environments of ca. 5000 experimentally-known oxides from the Materials Project database [3,4].

Methods

Stable Oxides from the *Materials Project* [3]

↓

Coordination environments from the *ChemEnv* [4] package in *pymatgen* [5]

↓

New *Python* code to analyze the Pauling rules

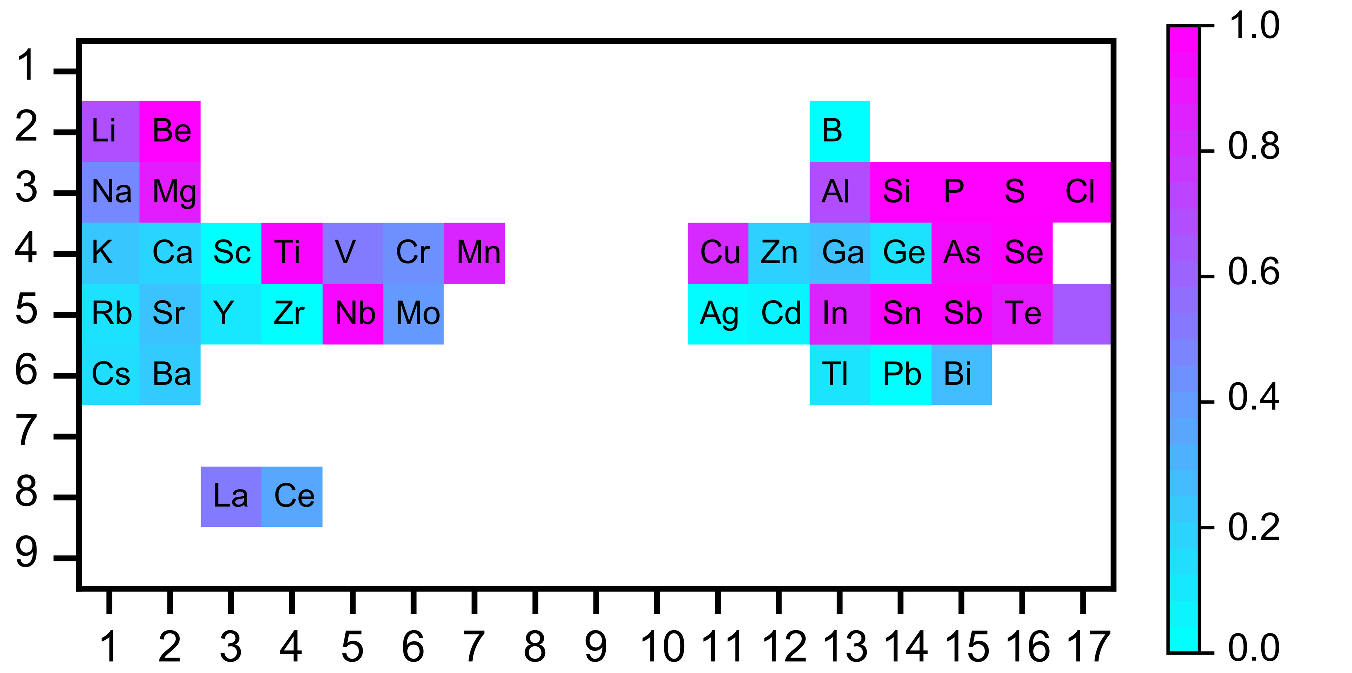
1. Radius Ratio Rule

"*[...] The coordination number of the cation [is determined] by the radius ratio [of cation and anion].*" [1]

a. Use of Pauling's univalent radii [2]

b. Only coordination environments from Pauling's book [2]

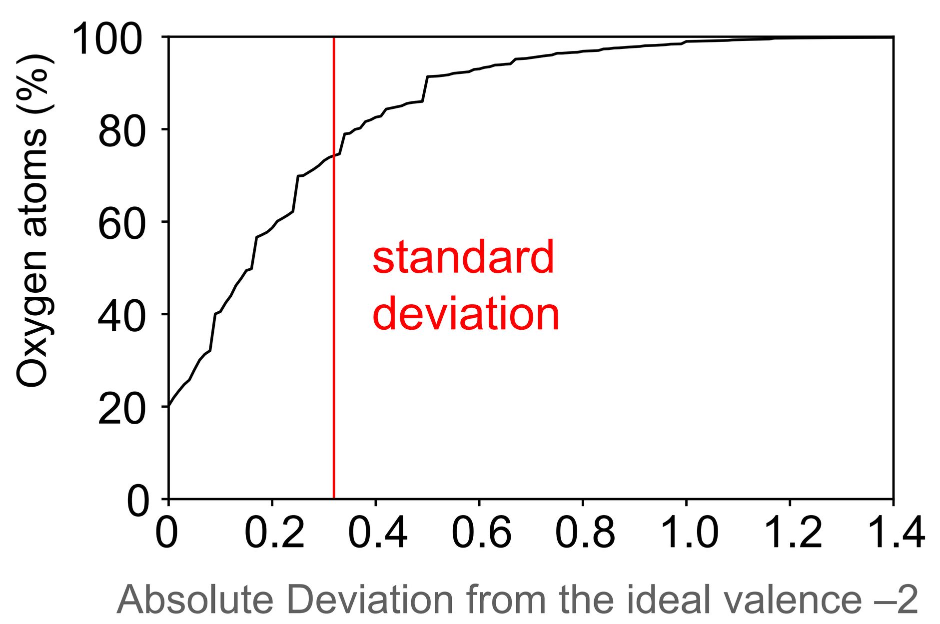
Rule fulfilled for 66% of all tested environments.



2. Electrostatic Valence Principle

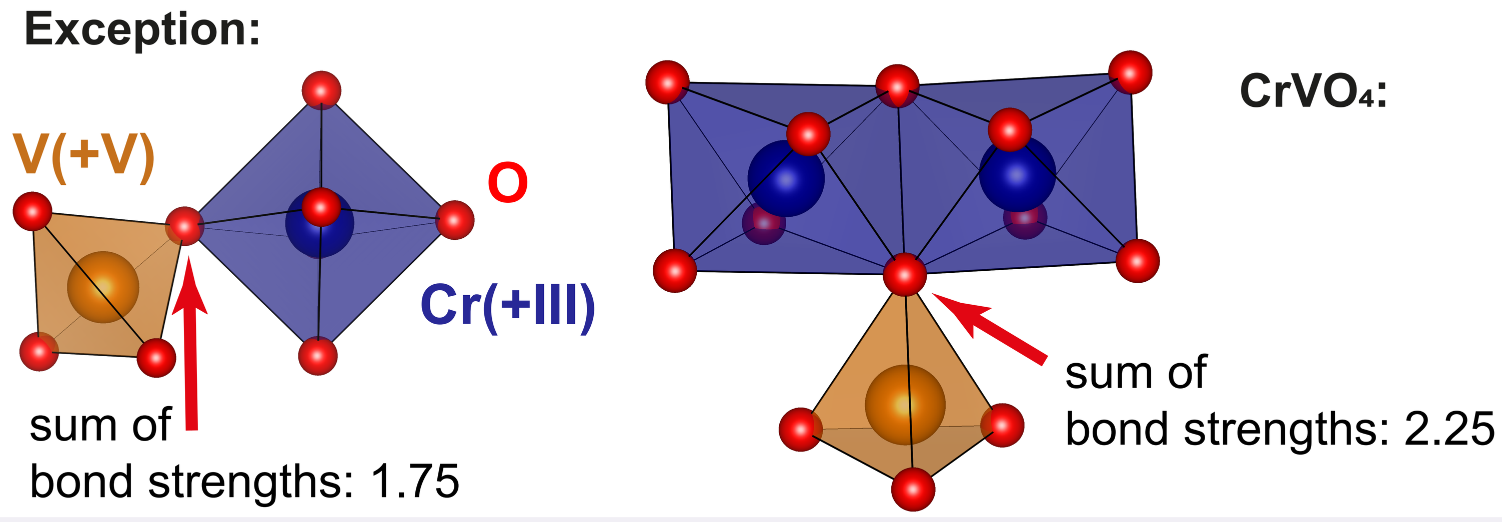
"*In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner [...] .*" [1]

Is the electrostatic valence rule fulfilled for each oxygen?



The rule is exactly fulfilled for around 20% of the oxygen atoms.

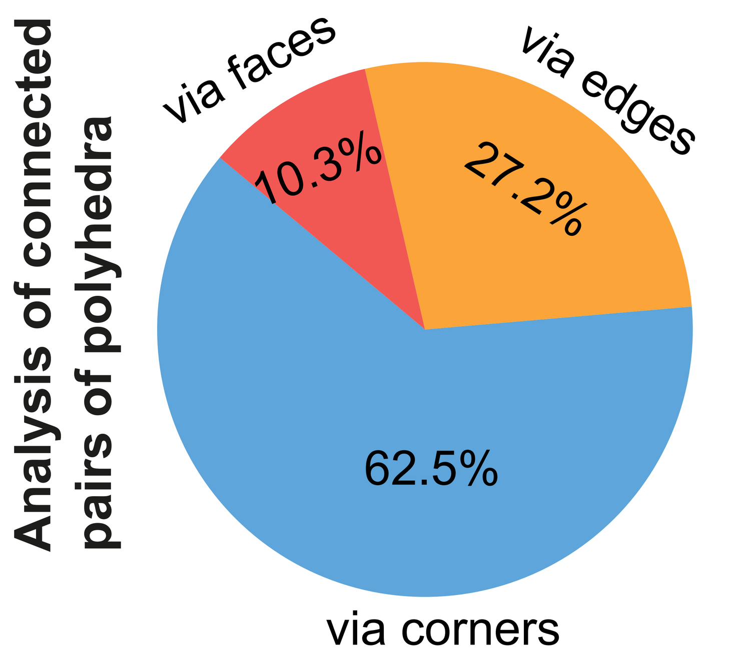
Exception:



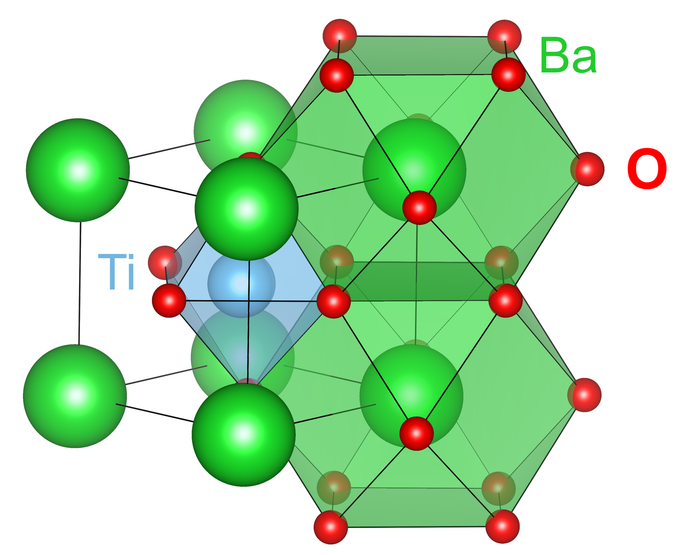
3. The Sharing of Edges and Faces

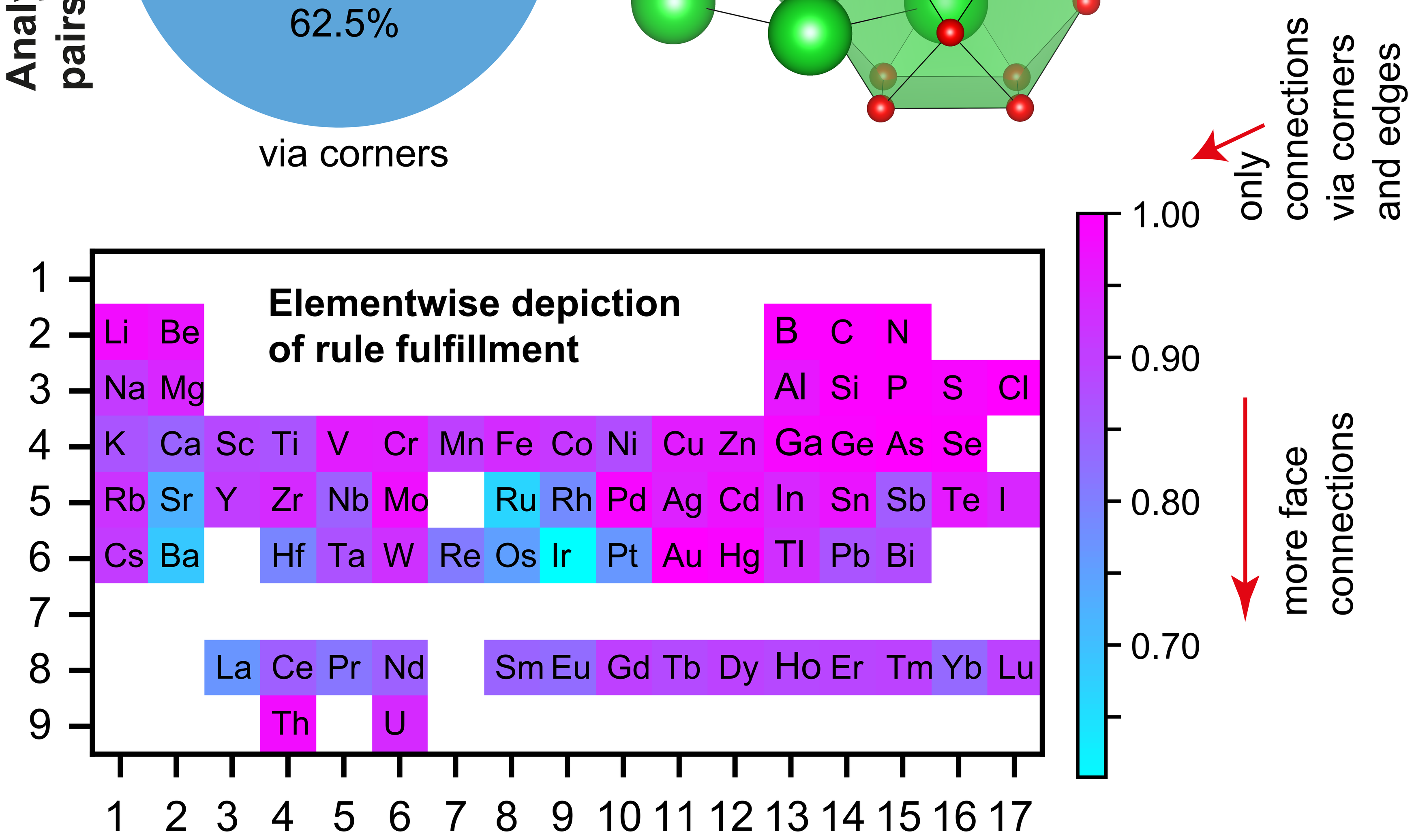
"*The presence of shared edges, and particularly of shared faces, in a coordinated structure decreases its stability; [...].*"

Test for connected pairs of polyhedra in stable oxides:



Exception to Rule:



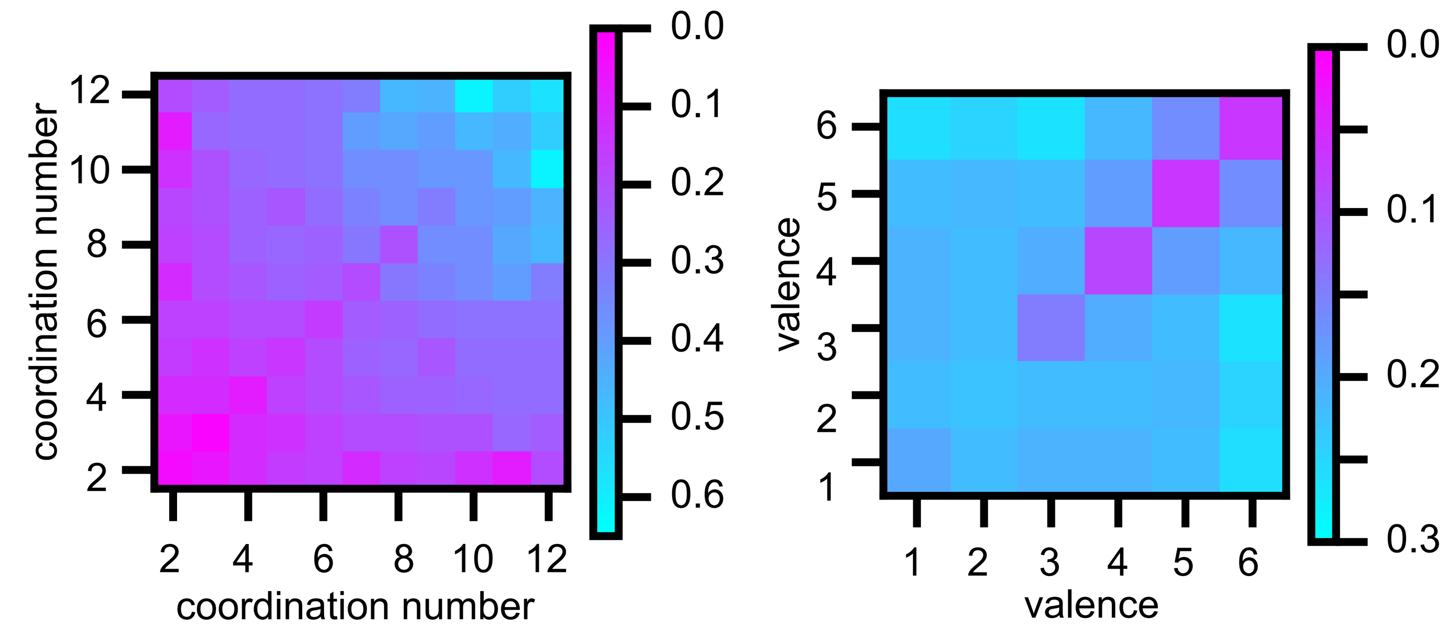


4. The Nature of Contiguous Polyhedra

"*In a crystal containing different cations those with large valence and small coordination number tend not to share polyhedron elements with each other.*"

Test for pairs of polyhedra with a distance smaller 8 Å in stable oxides that contain different cations (i.e., they differ in their valence and coordination number):

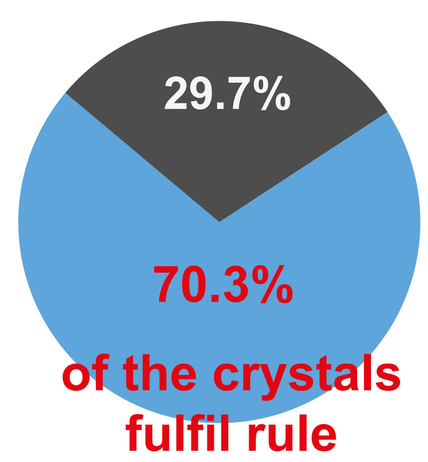
Share of connected pairs of polyhedra as a function of coordination numbers and valences



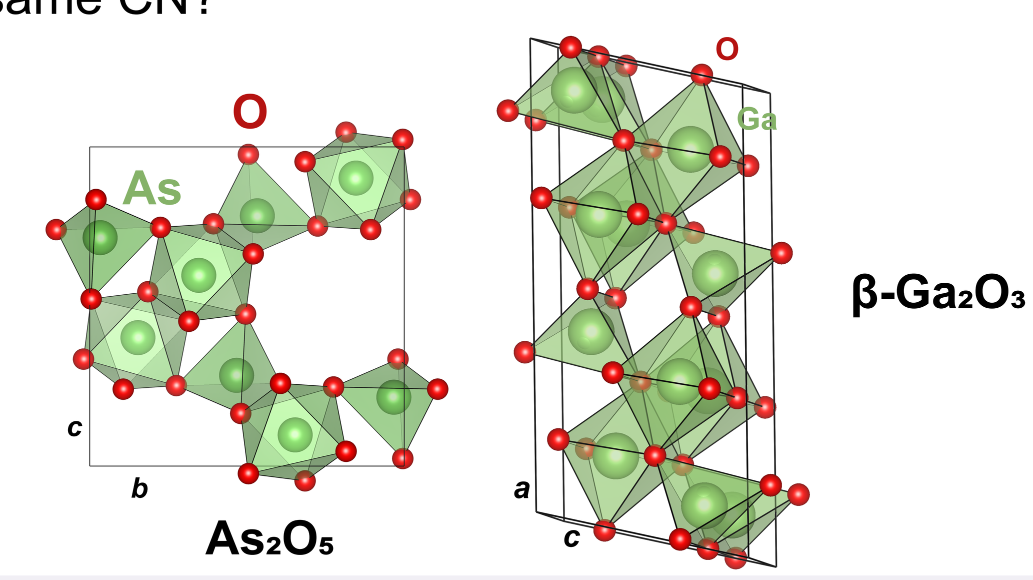
5. The Rule of Parsimony

"*The number of essentially different kinds of constituents in a crystal tends to be small.*"

In how many crystals do all cations of the same element and valence have the same CN?



Exceptions:



References

[1] L. Pauling, *J. Am. Chem. Soc.* **1929**, *51*, 1010. [2] L. Pauling, The Nature of The Chemical Bond and the Structure of Molecules and Crystals, Cornell University Press, Ithaca, New York, **1960**. [3] A. Jain, et al. *APL Materials* **2013**, *1*, 011002. [4] D. Waroquiers, et al. *Chem. Mater.* **2017**, *29*, 8346. [5] S. P. Ong, et al. *Comp. Mater. Sci.* **2013**, *68*, 314. Published in J. George et al. *Angew. Chem. In. Ed.*, DOI: 10.1002/anie.202000829.