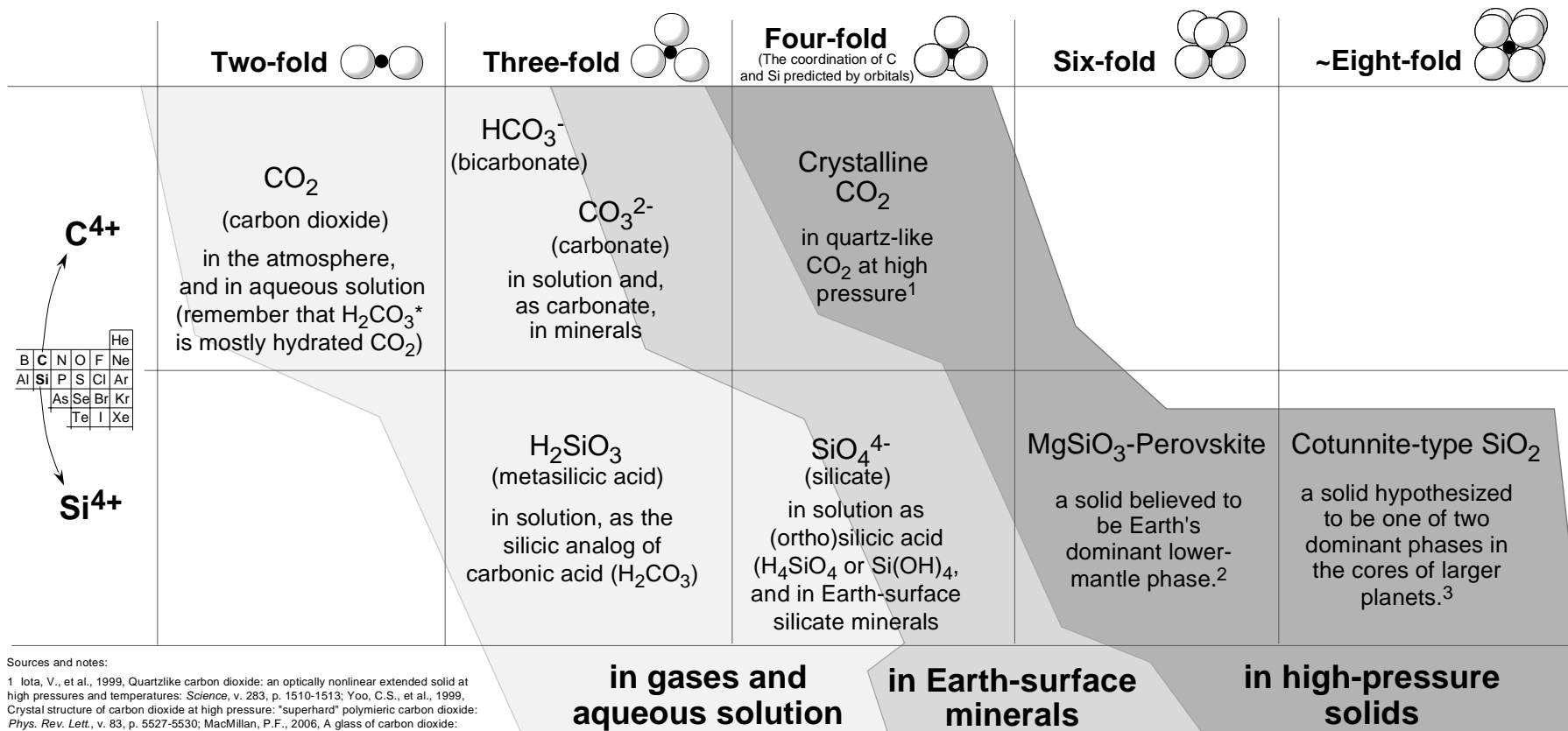


## Variation in C-O and Si-O coordination

Beginning geology students are taught that  $\text{Si}^{4+}$  coordinates with four  $\text{O}^{2-}$ s, in the silica tetrahedron found in all silicate minerals that occur at Earth's surface. Mineralogy students go on to learn that coordination is dictated by the ratio of cation radius to anion radius, so that radius ratios predict coordination. However,  $\text{Si}^{4+}$  actually enters into three-fold, four-fold, six-fold and perhaps eight-fold coordination. This diagram lays out that variation in coordination, and does the same for  $\text{C}^{4+}$  too.

The point of this diagram is that coordination of cations varies with environmental context. Coordination can be low in solution, where repulsion between cations is irrelevant. It is greater in Earth-surface minerals, where cation-cation repulsion necessitates shielding between cations and thus requires greater coordination with anions. Coordination is even greater in minerals expected deep within the Earth or inside larger planets, where pressure allows compression of the "fluffy" anions and thus allows higher coordination of anions around cations.



Sources and notes:

1 Iota, V., et al., 1999, Quartzlike carbon dioxide: an optically nonlinear extended solid at high pressures and temperatures; *Science*, v. 283, p. 1510-1513; Yoo, C.S., et al., 1999, Crystal structure of carbon dioxide at high pressure: "superhard" polymeric carbon dioxide; *Phys. Rev. Lett.*, v. 83, p. 5527-5530; MacMillan, P.F., 2006, A glass of carbon dioxide; *Nature*, v. 441, p. 823.

2 Williams, Q., et al., 1989, Geophysical and crystal chemical significance of  $(\text{Mg,Fe})\text{SiO}_3$  perovskite, in Navrotsky, A., and Weidner, D.J., eds., *Perovskite: A Structure of Great Interest to Geophysics and Materials Science*; AGU Geophysical Monograph 45, p. 1-12.

3 Umemoto, K., et al., 2006, Dissociation of  $\text{MgSiO}_3$  in the cores of gas giants and terrestrial exoplanets; *Science*, v. 311, p. 983-986. Umemoto et al. hypothesize that  $\text{MgSiO}_3$ -perovskite dissociates at unearthly pressures into  $\text{MgO}$  and a "cotunnite-type  $\text{SiO}_2$ " phase. They show their "cotunnite-type  $\text{SiO}_2$ " phase in 9-fold coordination, whereas Strunz and Nickel (2001) indicate coordination in cotunnite ( $\text{PbCl}_2$ ) is 7-fold.

4 Prewitt, C.T., and Downs, R.T., High-pressure crystal chemistry, in Hemley, R.J., ed., *Ultra-high Pressure Mineralogy: Reviews in Mineralogy* v. 37, p. 283-317. "The oxygen atom is more compressible than the cations. Total electron density calculations for coesite and stishovite show that the bonded radius of the oxygen atom decreases by 0.20Å while the radius of the Si atoms decreases by 0.02Å with the change in coordination . . . . The electron density of oxygen falls off rather rapidly compared to the electron densities around cations . . . ."

Independent  $\text{C}^{4+}$  and  $\text{Si}^{4+}$  ions coordinate free of constraints imposed by crystalline structures.

$\text{C}^{4+}$  and  $\text{Si}^{4+}$  ions in crystalline structures must have their positive charge shielded from that of other cations and so must have closest packing of  $\text{O}^{2-}$  anions possible at Earth-surface pressures.

High pressure reduces the volume of the electron clouds of  $\text{O}^{2-}$  anions, allowing them to enter into higher coordination with cations.<sup>4</sup>