

## The importance of oxygen

Oxygen is the most abundant element in Earth's crust. By weight, it's 46.3% of the crust, on a molar basis it's 60.2% of the crust, and by volume it's an amazing 94.2%. Most of our minerals contain oxygen, either as oxides or as oxysalts like the silicates, carbonates, sulfates, etc., where the "ate" ending indicates inclusion of an  $O^{2-}$ -bearing radical group. However, that only begins to reveal the importance of oxygen, and specifically  $O^{2-}$ , to geochemistry.

In a sense, oxygen shapes the periodic table (or at least the Earth Scientist's Periodic Table of the Elements and Their Ions). Examination of the periodic table shows that, of the 92 elements that occur in nature, 80 occur as positively charged entities (as cations), whereas only 18 occur as negatively charged entities (or anions). That's a considerable imbalance in favor of elements robbed of some electrons (hence their positive charge) as opposed to elements that have swiped electrons (to have negative charge). The imbalance goes further, in that cations commonly have positive charge as great as 6+ (like the nominal  $S^{6+}$  of sulfate), and they can have a positive charge of 7+ (as with  $Cl^{7+}$  in perchlorate). By contrast, the most negative charge commonly found is only 2-, as in  $O^{2-}$  and  $S^{2-}$ , and the greatest negative charge is only 4-, as in  $C^{4-}$  of carbides. Thus not only do elements robbed of electrons outnumber those doing the stealing, but some of the robbed elements have been robbed extensively.

So who has swiped all these electrons and thereby had such an impact on the periodic table? It's oxygen, of course. Oxygen's extreme abundance (more than half of all the atoms in Earth's exosystem) and its readiness to accept two electrons make it the very disproportionate sink of electrons across the entire expanse of geochemistry.

Oxygen's influence is also revealed by what we commonly fail to say in our everyday geochemical language. When we say that a particular cation usually enters into six-fold coordination, we almost always mean "six-fold coordination with  $O^{2-}$ ". When geochemists say that a cation makes weak bonds or strong bonds,

we usually mean "weak (or strong) bonds to  $O^{2-}$ ", because we're thinking of the formation of silicates, or other oxysalts, or oxides. When geochemists talk about solubility, we almost invariably mean "solubility in  $H_2O$ ", the oxygen-dominated fluid of the Earth, rather than solubility in the other solvents of which a chemist might think. When geochemists distinguish between harder cations that tend to bond to  $O^{2-}$  and softer cations that tend to bond to softer anions like  $S^{2-}$  or  $Br^-$ , we have to remember that we work in a natural world so rich in water that  $O^{2-}$  almost always dominates as the readily available negative ligand atom or potential negative bond.

Finally, it's worthwhile to remember that  $O^{2-}$  is not only abundant but also somewhat unique. If we move down through the anions of Group VIIA, and thus from  $F^-$  to  $Cl^-$  to  $Br^-$  to  $I^-$ , we find they make halides with properties falling in gradients from  $F^-$  to  $I^-$ . The same seems to be true of Group VA anions, from  $N^{3-}$  to  $P^{3-}$  to  $As^{3-}$  to  $Sb^{3-}$ . However, when one considers the anions of Group VIA, and thus from  $O^{2-}$  to  $S^{2-}$  to  $Se^{2-}$  to  $Te^{2-}$ , one finds that substances formed by the latter three fall in gradients, but that oxides are a world of their own. See, for example, this book's page on "Density of minerals IV: Simple anions", where densities of sulfides, selenides, and tellurides make linear trends, but oxides fall off those trends because of their exceptionally large densities. The difference between  $O^{2-}$  and the anions below it can be seen linguistically in our use of the word "halides" to encompass substances made by all the Group VIIA anions, but our lack of any parallel word to encompass substances made by all the group VIA anions.

To summarize, (i) oxygen is remarkably abundant, (ii) it exerts a huge influence on redox chemistry (even giving that chemistry part of its name), (iii) it's so abundant that it's almost always the assumed ligand atom or bond when we consider coordination chemistry, and (iv) it's unique relative to its companion Group VIA anions. Oxygen may form the background of geochemistry that we Earth scientists never notice, but it clandestinely plays a huge role in mineralogy and geochemistry.