

# O

## Oxygen

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### Element Data

Atomic Symbol: O  
Atomic Number: 8  
Atomic Weight: 15.999  
Isotopes and Abundances:  $^{16}\text{O}$ , 99.763%;  $^{17}\text{O}$ , 0.037%;  
 $^{18}\text{O}$ , 0.200%  
1 Atm Melting Point:  $-218.79\text{ }^{\circ}\text{C}$   
1 Atm Boiling Point:  $-182.96\text{ }^{\circ}\text{C}$   
Common Valences: 2, 1,  $-1$ ,  $-2$   
Ionic Radii: 136 pm (threefold coordination), 138 pm  
(fourfold coordination), 140 pm (sixfold  
coordination)  
Pauling Electronegativity: 3.44  
First Ionization Energy: 1313.9 kJ/mol  
Chondritic (CI) Abundance: 0.46 mass fraction  
Silicate Earth Abundance: 0.44 mass fraction  
Crustal Abundance: 0.47 mass fraction  
Seawater Abundance: 0.89 mass fraction  
Core Abundance: 0.005–0.05 mass fraction

### Properties

Oxygen is distinguished from virtually all other elements by its extraordinary electronegativity. It is surpassed in its affinity for electrons only by fluorine. For this reason, concentrations of oxygen play a critical role in many geochemical

cycles and in the basic structures of rocky planets. The multiple valence states of numerous geochemically relevant elements are linked to the availability of oxygen.

Oxygen is also distinctive in being a major component of not only rock, but also of volatile components in planetary bodies. The oxygen-bearing volatiles include  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ .

The electronic configuration  $1s^2 2s^2 2p^4$  lends itself to forming covalent bonds with other oxygen atoms. The dioxygen molecule,  $\text{O}_2$ , is a colorless and odorless gas comprising 21% of Earth's atmosphere. Oxygen is classified as a lithophile element and occurs mainly in the crust and mantle of rocky planets. Bonding between Si and O is approximately 50% covalent and 50% ionic (Pauling 1980). Silicon is coordinated by four oxygen atoms forming the  $[\text{SiO}_4]^{4-}$  group that polymerizes to varying degrees to form the basis for the crystal structures of silicates, the most common rock-forming minerals.

Because oxygen has ionic radii of several times those of the cations it bonds to (Shannon 1976), the crystal structures of rock-forming oxide and silicate minerals can be described as tightly packed oxygen atoms with cations occupying the interstices of the oxygen atoms. Oxygen therefore constitutes about 90% of the volume and about half the mass of typical rocks.

There are three stable isotopes of oxygen:  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ . These isotopes are especially useful as tracers in geochemical reactions because the mass differences are relatively large compared with the average atomic mass of oxygen, resulting in readily measurable partitioning of isotopes between phases, and because oxygen occurs in great abundance in rock, water, and air.

### History

Three people are variously credited with the discovery of dioxygen gas in the eighteenth century. Swedish apothecary

Karl Wilhelm Scheele in 1771 discovered the gas as a product of heating mercuric oxide, magnesium nitrate, potassium nitrate, and silver carbonate. He referred to this emitted gas as “fire air,” a reference to the fact that the gas ignited charcoal dust. He published the result in 1777 (Scheele 1777). His discovery predates those of Antoine Laurent de Lavoisier and Joseph Priestly, but his publication postdated these works.

Lavoisier, a French chemist, explored the properties of air as a reagent for combustion beginning in 1772 (Guerlac 1961). He gave oxygen its name in 1779 and recognized that reactions with oxygen were responsible for combustion. Prior to Lavoisier’s insight, combustion was thought to release the fictive, ethereal substance referred to as “phlogiston.” Lavoisier discovered that phosphorous and sulfur gained weight when combined with air rather than losing weight as predicted by the phlogiston theory. He also showed that air is ~20% oxygen (on a molecular basis).

During this same period, British clergyman and natural philosopher Joseph Priestley conducted experiments in 1771 and 1772 showing that plants emit a gaseous component found in air that is in turn consumed by animals, foreshadowing the discoveries of photosynthesis and respiration, processes that produce and consume oxygen in air, respectively. He further recognized the liberation of oxygen from heated mercuric oxide in 1774 (West 2014) and published his result in 1775 (Priestley 1775). Priestly mistakenly believed that the gas that would be named oxygen by Lavoisier was a “dephlogisticated air.” Because Priestly published first, his discovery of oxygen is often given priority.

## Stellar Origins

Oxygen is the third most abundant element in the Galaxy, superseded only by H and He (Lodders 2003). The lightest and most abundant isotope of oxygen,  $^{16}\text{O}$ , is produced by helium fusion (He burning) mainly in large stars that are at least ten times the mass of the Sun. It is the most abundant nuclide synthesized in stars (Clayton 2003).  $^{16}\text{O}$  created in stars is ejected into the interstellar medium by the explosion of Type II supernovae where it is then available for incorporation into the next generation of stars. Because it is a product of He burning, the synthesis of  $^{16}\text{O}$  is not dependent on the existence of other “metals” (metals is the term used for elements heavier than H and He in astronomy). It is therefore a primary nuclide.

The stellar nucleosynthesis of the two heavier isotopes of oxygen,  $^{17}\text{O}$  and  $^{18}\text{O}$ , relies on the prior existence of  $^{16}\text{O}$ ,  $^{12}\text{C}$ , and  $^{14}\text{N}$ ; stars with no “metals” cannot produce these isotopes of oxygen.  $^{17}\text{O}$  and  $^{18}\text{O}$  are therefore secondary nuclides and are rare compared with  $^{16}\text{O}$ .  $^{17}\text{O}$  is produced in lower mass stars in their red giant phase or from novae (Clayton 2003). It

is made from H and  $^{16}\text{O}$  during hydrogen fusion (H burning) in the CNO cycle.  $^{18}\text{O}$  is synthesized during He burning in massive stars using  $^{14}\text{N}$  as a reactant (Clayton 2003). Novae and ejecta from red giant stars disperse  $^{17}\text{O}$  to the interstellar medium while  $^{18}\text{O}$  is scattered by Type II supernovae.

As stars produce more “metals,” the secondary  $^{17}\text{O}$  and  $^{18}\text{O}$  nuclides grow in abundance with the square of time while the amount of  $^{16}\text{O}$  grows linearly with time. The overall  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  isotopic ratios are therefore expected to have grown approximately linearly with time in the Milky Way Galaxy in a process known as Galactic chemical evolution (Tinsley and Cameron 1974; Young et al. 2011).

## Cosmochemical Significance

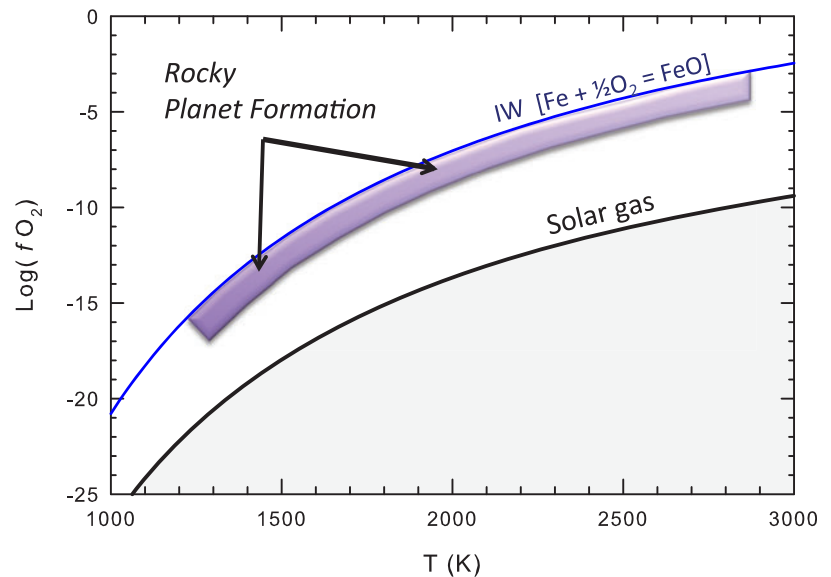
The nonideal partial pressure of oxygen, oxygen fugacity, is a thermodynamic quantity that characterizes the level of oxidation for a system. The fugacity,  $f_{\text{O}_2}$ , is meant to correct the pressure of  $\text{O}_2$  in a system from a standard state of one bar and from a mole fraction in the gas of unity. The  $f_{\text{O}_2}$  symbol is therefore usually an abbreviated way of writing  $f_{\text{O}_2}/P_{\text{O}_2}$  where the denominator pressure  $P_{\text{O}_2}$  is understood to be unity (pure  $\text{O}_2$  at one bar); oxygen fugacity is a measure of the activity, or nonideal concentration, of  $\text{O}_2$ . It can always be defined thermodynamically to measure the degree of oxidation even in circumstances where the quantity of free dioxygen is for all practical purposes indistinguishable from zero. The parameter  $\Delta\text{IW} = \log(f_{\text{O}_2}) - \log(f_{\text{O}_2})_{\text{IW}}$ , quantifies the difference in oxygen fugacity at a given temperature from that defined by the equilibrium reaction  $\text{Fe}$  (Iron) +  $\frac{1}{2}\text{O}_2 = \text{FeO}$  (Wüstite), the IW reaction. The oxygen fugacity of a planet or planetesimal can be calculated relative to the IW reference using corrections for the concentrations of FeO in the bulk silicate portion and Fe in the metal core:

$$\Delta\text{IW} = 2\log\left(\frac{x_{\text{FeO}}^{\text{silicate}}}{x_{\text{Fe}}^{\text{metal}}}\right) + 2\log\left(\frac{\gamma_{\text{FeO}}^{\text{silicate}}}{\gamma_{\text{Fe}}^{\text{metal}}}\right),$$

where  $x$  are mole fractions of the species indicated and  $\gamma$  are activity coefficients that correct for nonideal mixing. The intrinsic oxygen fugacity of the Earth is constrained by the 8 weight percent FeO in the mantle and its Fe-rich core to a  $\Delta\text{IW}$  value of  $-1$  using nonideal mixing or  $-2$  based on the assumption of ideal mixing. Estimates of the amount of oxygen in Earth’s core vary from approximately 0.5% by mass to as much as 5% by mass (Huang et al. 2011; Badro et al. 2015; Rubie et al. 2015).

Studies of meteorites reveal that, like the Earth, most rocky bodies in the solar system formed with oxygen fugacities approximately five orders of magnitude higher than that defined by a hydrogen-rich gas of solar composition

**Oxygen, Figure 1** Plot of the logarithm of oxygen fugacity versus temperature (K) for a gas of solar composition and for the equilibrium Fe (Iron) +  $\frac{1}{2}\text{O}_2 = \text{FeO}$  (Wüstite) (IW). The conditions corresponding to rock formation in the early solar system are indicated.



(Figure 1). The presence of significant amounts of iron bonded to oxygen in silicates in chondrite meteorites testifies to this relatively high oxygen fugacity during rock formation in the early solar system (Grossman et al. 2012).

The fugacity of oxygen in the protoplanetary gas was controlled by the reaction  $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$  (Krot et al. 2000). In order to form rocks like those comprising the Earth, the ratio of  $\text{H}_2\text{O}/\text{H}_2$  must have increased by a factor of nearly 400 relative to the solar value. The relative abundances of water ice and  $\text{H}_2$  gas were, therefore, the first-order controls on the fugacity of oxygen and the oxidation state of the elements comprising rocky planets.

The distribution of the three isotopes of oxygen among planets and asteroids constitutes one of the most distinctive and mysterious chemical features of the solar system (Clayton et al. 1973). In general, for the great majority of physico-chemical processes, kinetic and equilibrium variations in  $^{18}\text{O}/^{16}\text{O}$  ratios should be approximately twice those for  $^{17}\text{O}/^{16}\text{O}$  ratios because of the 2:1 ratio in the mass differences involved ( $18 - 16 = 2$  vs.  $17 - 16 = 1$ ). In other words, the fractionations are mass dependent. However, the dominant trend exhibited by minerals in meteorites that come from a variety of asteroid types is one in which  $^{18}\text{O}/^{16}\text{O}$  ratios vary by about the same magnitude as  $^{17}\text{O}/^{16}\text{O}$  ratios. This mass-independent ~1:1 relationship between oxygen isotope ratios includes the terrestrial planets and the Sun (McKeegan et al. 2011). The  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor ends of the array of solar system oxygen isotope ratios are evidently anchored by the Sun and pristine waters, respectively (Young 2007) (Figure 2).

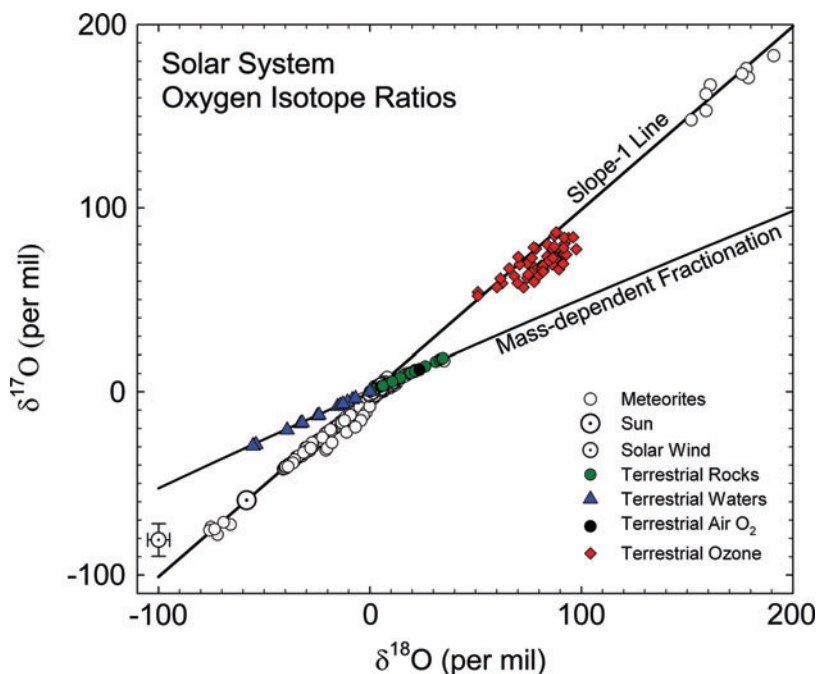
Explanations for this enigmatic trend include the residual effects of Galactic chemical evolution, intramolecular disequilibrium during oxidation reactions, and CO photochemistry (Young et al. 2008). In the case of CO photochemistry,

the 1:1 relationship between the two oxygen isotope ratios arises because of the effect of CO self shielding whereby abundant  $\text{C}^{16}\text{O}$  shields ultraviolet (UV) light that would otherwise liberate oxygen by the reaction  $\text{C}^{16}\text{O} + \text{UV} \rightarrow \text{C} + ^{16}\text{O}$ , depriving the ensuing reservoir of liberated oxygen of  $^{16}\text{O}$ . Atomic oxygen reacts with hydrogen to produce water, thus a paucity of atomic  $^{16}\text{O}$  causes a paucity of  $^{16}\text{O}$  in water, simultaneously increasing  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  in the water (Yurimoto and Kuramoto 2004; Lyons and Young 2005). Any explanation for the oxygen isotope distributions in the solar system must account for the fact that all evidence points toward water having high  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  compared with rocks in the early solar system.

The apparent excess of  $^{17}\text{O}/^{16}\text{O}$  relative to  $^{18}\text{O}/^{16}\text{O}$  compared with expectations from normal “mass-dependent” isotope partitioning is expressed as the  $\Delta^{17}\text{O}$  value (usually in per mil). This iconic parameter appears to be a fingerprint-like characteristic for each body formed in the solar system. Two important exceptions are the Earth and Moon, which stand out in having identical  $\Delta^{17}\text{O}$  values that signify extensive intermingling of the proto-Earth and proto-lunar reservoirs (Wiechert et al. 2001; Young et al. 2016). The intermingling is most often attributed to the giant impact that evidently formed the Moon.

## Applications of Oxygen Isotopes in Geochemistry

Shifts in the oxygen isotopic compositions of waters and rocks are used as records of water-rock interactions. Under hydrothermal conditions, exchange of oxygen between water and rock at temperatures greater than  $\sim 300^\circ\text{C}$  decreases  $^{18}\text{O}/^{16}\text{O}$  in the rock. These signatures can be used for



**Oxygen, Figure 2** Plot of oxygen isotope ratios for solar system materials. The ratios  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  are represented as per mil deviations from Vienna Standard Mean Ocean Water (VSMOW) such that for reservoir  $i$   $\delta^{17}\text{O} = 1000[(^{17}\text{O}/^{16}\text{O})_i / (^{17}\text{O}/^{16}\text{O})_{\text{VSMOW}} - 1]$  (and

similar for  $\delta^{18}\text{O}$ ). The slope-1 line that characterizes the solar system is shown for reference. The mass-dependent fractionation line represents fractionation of oxygen relative to Earth's mantle.

identifying regions that are likely to host mineralization (Taylor 1974).

Differences in oxygen isotope ratios between minerals formed at thermodynamic equilibrium can be used as geothermometers, providing estimates of equilibration temperatures in igneous and metamorphic rocks. Minerals with different structures, and therefore different bond strengths involving oxygen, make the best thermometers (e.g., quartz formed in equilibrium with magnetite).

Isotopes of oxygen are also used to trace reactions between water and rock on a global scale. An important example is the oxygen isotopic composition of ocean water over geological timescales. New oceanic crust formed at midocean ridges experiences ingress of seawater that reacts with rock at high temperatures near 300 °C. Far from the ridges, older ocean crust is infiltrated by cool water resulting in submarine weathering. At high temperatures, reactions with basalt increase the  $^{18}\text{O}/^{16}\text{O}$  of the water. At low temperatures, reactions with basalt decrease the  $^{18}\text{O}/^{16}\text{O}$  of the water. The relative rates of these two opposing reactions serves as a buffer for the oxygen isotopic composition of Earth's oceans (Muehlenbachs and Clayton 1976).

Harold Urey first pointed out that the temperature-dependent  $^{18}\text{O}/^{16}\text{O}$  partitioning between calcite and water in the oceans could be used to reconstruct the temperatures of the oceans with time (Urey 1948). Since that original suggestion, the calcite-water oxygen isotopic paleothermometer has

been a mainstay of paleoclimate reconstruction. The pattern of glacial-interglacial cycles over the last 600,000 years was enabled by this method, for example. Subsequent refinements dealt with the effect of sequestration of light oxygen isotopes in ices on ocean water  $^{18}\text{O}/^{16}\text{O}$  (Shackleton and Opdyke 1973), confounding the temperature isotopic signals in the carbonate grown in the water. More recently, the uncertainties associated with the convolution of the isotopic effects of temperature and ice volume have been circumvented by the use of the relative abundances of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate. The concentrations of these heavy isotope bond pairs provide an intramineral isotope thermometer that is independent of the isotopic composition of the water and thus of ice volume (Gosh et al. 2004).

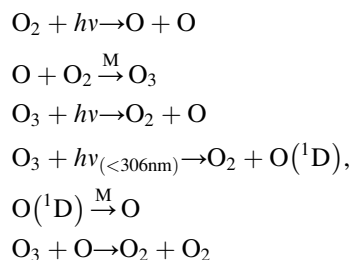
## Oxygen in the Atmosphere

Twenty one percent of the molecules in Earth's air are  $\text{O}_2$  (more precisely, the molecular mixing ratio of  $\text{O}_2$  in air is 21%). The concentration of dioxygen in air is the result of two cycles operating on disparate timescales. On shorter timescales of about a 1,000 years (Bender et al. 1994), the concentration of  $\text{O}_2$  in air is a balance between the global rate of  $\text{O}_2$  production by photosynthesis and the global rate of  $\text{O}_2$  uptake by aerobic respiration. Oxygen generated by photosynthesis comes ultimately from the oxygen comprising

water. On longer geological timescales, O<sub>2</sub> uptake by weathering and the effective oxygen production by carbon burial (or rather, the absence of a long-term sink in the form of carbon oxidation) control the amount of O<sub>2</sub> in air over hundreds of thousands to millions of years (Lasaga and Ohmoto 2002). Short-term variations in O<sub>2</sub> abundance in air arise from variations in the rates of photosynthesis and respiration, while the long-term cycle of weathering and carbon burial governs the permissible amount of oxygen in Earth's atmosphere over geological time. The first appearance of significant levels of atmospheric dioxygen appeared during the Great Oxygenation Event (GOE) about 2.4 billion years before present in the Paleoproterozoic Era (Holland 2006). The possibility that there were multiple "whiffs" of O<sub>2</sub> prior to the GOE and marked decreases in O<sub>2</sub> after the GOE is debated (Lyons and Reinhard 2009). Regardless, atmospheric O<sub>2</sub> levels rose from maximal values of just 1–3% after the GOE to nearer to present-day levels of more than 5–18% in the Neoproterozoic. Widespread carbon deposition in the Carboniferous Period led to still higher concentrations of atmospheric O<sub>2</sub> (Catling and Claire 2005).

Molecular oxygen in Earth's atmosphere is not in oxygen isotopic equilibrium with the oceans. The <sup>18</sup>O/<sup>16</sup>O ratio of atmospheric O<sub>2</sub> is greater than that of ocean water by about 2.3–2.4%, a value that is several times greater than that dictated by thermodynamic equilibrium. The high <sup>18</sup>O/<sup>16</sup>O in air is referred to as the Dole effect (Dole 1935) and reflects the kinetic isotope effect of respiration and the lack of a significant isotope effect associated with photosynthesis.

In the stratosphere, O<sub>2</sub> photolysis by ultraviolet light (wavelengths ≤ 240 nm) liberates atomic oxygen that reacts to form ozone that in turn reacts with atomic oxygen or is photolyzed (λ < 340 nm) to form dioxygen. This Chapman cycle, named for its discoverer (Chapman 1930), can be described by the reactions



where *M* signifies a collision partner (mainly N<sub>2</sub>), O(<sup>1</sup>D) is the excited singlet state of oxygen, and *hν* refers to the energy of the UV light. The actinic flux of UV light (i.e., the integrated flux from the top of the atmosphere) and the number density of oxygen molecules conspire to produce a peak in the rate of ozone production at an altitude of approximately 25 km. The reaction that produces ozone (O<sub>3</sub>) causes a large mass-

independent oxygen isotope effect of several per cent (tens of per mil) (Thiemens and Heidenreich 1983).

Dioxygen in air is anomalously low in <sup>17</sup>O relative to Earth's rocks and waters by 0.4 per mil (Δ<sup>17</sup>O = 0.04%). Approximately 60% of this deficit is another manifestation of the Dole effect, 30% balances an excess in <sup>17</sup>O carried by O(<sup>1</sup>D) in the stratosphere caused by the mass independent fractionation associated with ozone formation, and 10% is due to evaporation and transpiration (evapotranspiration) of the water that provides the oxygen produced by photosynthesis (Young et al. 2014).

The <sup>17</sup>O deficit in dioxygen in air depends on the rate of O<sub>2</sub> turnover by photosynthesis, the concentration of O<sub>2</sub> determined by the balance between photosynthesis and respiration, and the concentration of CO<sub>2</sub>. Carbon dioxide enters the budget because O(<sup>1</sup>D) transfers excess <sup>17</sup>O imparted by ozone photolysis to CO<sub>2</sub>. Carbon dioxide mixes from the stratosphere to the troposphere where it exchanges oxygen isotopes with water at ground level. Water is in effect an infinite reservoir of oxygen so that exchange between CO<sub>2</sub> and H<sub>2</sub>O creates a sink for <sup>17</sup>O. The greater the concentration of CO<sub>2</sub>, the more <sup>17</sup>O is lost from the atmosphere.

Because biological processing of oxygen removes the stratospheric-induced <sup>17</sup>O deficit caused by the flux of CO<sub>2</sub> from the stratosphere to ground level, differences in Δ<sup>17</sup>O in atmospheric O<sub>2</sub> have been used as a monitor of gross primary productivity (Luz et al. 1999; Blunier et al. 2002). Disambiguating the effects of changing CO<sub>2</sub> concentration and biological productivity is a challenge (Young et al. 2014). Δ<sup>17</sup>O values in Neoproterozoic sulfates in the so-called cap carbonates have been used as evidence for high CO<sub>2</sub> concentrations in the waning stages of the Neoproterozoic global glaciation (snowball Earth) (Bao et al. 2008).

The concentration of the doubly substituted dioxygen isotopologue <sup>18</sup>O<sup>18</sup>O in the atmosphere can be used as another measure of biological productivity. This is because the abundance of <sup>18</sup>O<sup>18</sup>O is driven toward thermodynamic equilibrium by isotope exchange reactions with atomic oxygen in air, causing an excess of <sup>18</sup>O<sup>18</sup>O relative to the purely random distribution, but this isotopic species is depleted by photosynthesis (Yeung et al. 2015).

## Biological Utilization and Toxicity

Free dioxygen in Earth's atmosphere is a consequence of photosynthesis and thus is an important biosignature in the search for extraterrestrial life. Consumption of oxygen by aerobic respiration provides the energy for all higher organisms.

## Summary

Oxygen is the third most abundant element in the solar system and the most abundant element synthesized in stars. The electronegativity of oxygen influences the size of a planet's metallic core and is a key ingredient for the diversity of life. The three stable isotopes of oxygen are powerful tracers of cosmochemical, geochemical, and biogeochemical processes.

## Cross-References

- ▶ [Activity and Activity Coefficients](#)
- ▶ [Atmospheric Chemical Evolution](#)
- ▶ [Biogeochemistry](#)
- ▶ [Carbon Cycle](#)
- ▶ [Chondrites](#)
- ▶ [Earth's Atmosphere](#)
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- ▶ [Formation and Evolution of the Earth](#)
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- ▶ [Iron](#)
- ▶ [Meteorites](#)
- ▶ [Nucleosynthesis](#)
- ▶ [Oxygen Isotopes](#)
- ▶ [Thermodynamics](#)

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