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COBALT

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Element Data

Atomic Symbol: **Co**

Atomic Number: **27**

Atomic Weight: 58.933195 g/mol

Isotopes and *Abundances*: ^{59}Co 100%

1 Atm Melting Point: 1495°C

1 Atm Boiling Point: 2927°C

Common Valences: 2+, 3+

Ionic Radii: 65 pm (2+, 6-fold coordination)

Pauling Electronegativity: 1.88

First Ionization Energy: 7.88 eV

Chondritic (CI) Abundance: 513 ppm^a

Silicate Earth Abundance: 102 ppm^a

Crustal Abundance: 26.6 ppm^b

Seawater Abundance: ~3-300 pmol/kg^c

Core Abundance: 0.25%^d

a. Palme et al. (2014)

b. Rudnick and Gao (2014)

c. Bruland et al. (2014)

d. McDonough (2014)

Properties

Cobalt (chemical symbol, Co) is a d-block transition metal, bluish-white. It appears in the first long period of the Periodic Table between iron and nickel. Cobalt shares many chemical and physical properties with these two elements. Naturally occurring Co consists of a single stable isotope: ^{59}Co , whereas ^{60}Co is an artificial isotope that is an important γ -ray source. Cobalt has two

main oxidation states (2+ and 3+). The common oxidation state for simple compounds is Co^{2+} . Depending upon geometry and environment, Co ionic radii vary between 56 pm and 90 pm. Cobalt is a transitional, compatible and siderophile (chalcophile and lithophile in the Earth's crust) element, has a high melting point of 1495°C and is ferromagnetic. Cobalt has an electronegativity of 1.88 on the Pauling scale and displays a first ionization potential of 7.88 eV. More details can be found in Blackman (2006), Raveau and Seihk (2012) and Haynes (2015).

History and Use

Cobalt has been utilized by the society since the Bronze Age, mainly to impart a rich blue color to glass and ceramics. Its name derives from the German word Kobald (goblin or evil spirit) and Greek word cobalos (mine), because Co minerals fooled miners with their bright colors. However, it was only

isolated as a pure metal by Swedish chemist Brandt in 1735. Demand for Co remained subdued until the turn of the 20th century and the development of cobalt-chromium alloys. Indeed, the demand for Co increased considerably after the Second World War, driven by the use of high-purity Co in jet engines and gas turbines. Cobalt demand has further accelerated in the past thirty years. Indeed, it reflects the increased use of Co as an essential constituent of materials used in high-technology industries including rechargeable batteries, superalloys and catalysts. Cobalt, like Fe, can be magnetized and so is used to make magnets. It is alloyed with Al and Ni to make particularly powerful magnets. Other alloys of Co are used in jet turbines and gas turbine generators, where high-temperature strength is important. Cobalt metal is sometimes used in electroplating because of its attractive appearance, hardness and resistance to oxidation and thus corrosion. Cobalt salts

have been used for centuries to produce brilliant blue colors in paint, porcelain, glass, and pottery. Cobalt is one of the elements defined as a critical metal to clean energy over the next 5-15 years, because of its use in lithium ion batteries: each electric-powered vehicle will demand 9.4 kg of Co (Crundwell et al. 2011). Although Co does not get a ton of press, it's a pretty important metal in this day and age. The artificial radionuclide ⁶⁰Co is widely used in cancer treatment, as a tracer, and for radiotherapy.

Geochemical Behavior

Cobalt is often associated with Ni, Ag, Pb, Cu and Fe-Mn ores, from which it is most frequently obtained as by-product (Gunn 2014). The main known ore deposits are found in Katanga (Democratic Republic of Congo) whereas some recent discoveries evidenced that central Pacific Ocean may have Co-rich deposits (i.e., manganese nodules and Co-rich ferromanganese crusts)

at relatively shallow depths. Almost 50% of the world's cobalt supply in 2014 was mined in the Democratic Republic of Congo. Mining and smelter activities in Katanga have contaminated soil, water and urban environments (Pourret et al. 2016).

Cobalt forms a number of minerals: cobaltite [CoAsS], skutterudite [CoAs_{3-x}], erythrite [Co₃(AsO₄)₂·8H₂O], spherocobaltite [CoCO₃] and heterogenite [CoO(OH)]. It is widely distributed in igneous and sedimentary rocks, and minerals. Cobalt is also present in meteorites (i.e., iron-nickel metal contains a few tenths of a percent cobalt). Its average content in the Earth's crust is approximately 25-30 ppm, though widely distributed, stands only 33th in order of abundance and is less common than all other transition metals except scandium. It is, however, more dispersed in the crust than either of those elements, and concentrated mineral deposits are consequently rare. The average Co contents of CI chondrites

estimated in a few studies are quite consistent, ranging from 500 ppm to 513 ppm. The bulk Earth has a Co content of 880 ppm, lower than that in the metallic core (0.25%). Cobalt contents in the bulk continental crust vary significantly from 15 ppm to 30 ppm. In particular, Co is most abundant in ultramafic rocks with an average concentration of 110 ppm. During differentiation of a basaltic magma most of Co enters the ferromagnesian minerals. Cobalt content of these minerals depends on the total number of Fe-Mg lattice sites and is independent of the Fe/Mg ratio. Cobalt is strongly coherent with Mg in granitic rocks and behaves like Mg in its partition relations between metamorphic minerals. The acceptance of both Co and Mg is more selective at lower grades of metamorphism. These aspects have been further reviewed by Gunn (2014), McDonough (2014), Palme et al. (2014) and Rudnick and Gao (2014).

Cobalt is also a naturally occurring element in air, soil, plants and water. The mean concentration of Co in the open ocean is very low (~40 pmol/kg) which in part reflects its short residence time. Co^{2+} is the principal aquatic species in seawater (Bruland et al. 2014). There has been considerable speculation on its mode of uptake in deep-sea manganese nodules and crusts. Cobalt tends to be associated with either Mn or Fe oxyhydroxides (Brown and Calas 2012). Cobalt may substitute as exchangeable Co^{2+} in marine manganates and then be oxidized to Co^{3+} by Mn^{4+} , whereas Co^{3+} may substitute for Fe^{3+} in Fe oxyhydroxide minerals. Cobalt may also be incorporated in birnessite as Co(II) at pH 7 and Co(III) above pH 8. The aqueous speciation and chemistry of Co in terrestrial environments is now an important focus of research, as the solution speciation of Co has a critical influence on its biological activity in the environment. Although there is a lack

of comprehensive data on aqueous Co concentrations in soil porewaters, groundwater and surface waters, natural Co concentrations vary mostly from 0.006 $\mu\text{g/L}$ to 0.43 $\mu\text{g/L}$ (Gaillardet et al. 2014). Cobalt is considered as moderately mobile with a mobility 10 times less than that of Na. Cobalt chemistry is dominated by the Co(II) oxidation state in the aqueous phase of terrestrial environments primarily due to the extremely low solubility of Co(III). There is no universal agreement on the importance of Co(II) complexation in the solution phase of terrestrial environments and, furthermore, on the nature of the major binding inorganic and organic ligands. The kinetics of Co(II) complexation to, and dissociation from, natural organic complexing ligands are such that the speciation of Co is likely to significantly diverge from estimates based on thermodynamic equilibrium calculations. As a result, an accurate understanding of Co bioavailability, toxicity and transport in

terrestrial aquatic environments will only be achieved when thermodynamics can be reconciled with reaction kinetics.

Biological Utilization and Toxicity

Cobalt is an essential trace element in life and plays an important role in biochemical reactions essential for life, notably in the coenzyme cobalamin (Co chelated to four N atoms at the center of a porphyrin-like structure; Chivers 2014). Cobalamin has a complex biochemistry, and there is a number of cobalamin-dependent enzymes. Cobalamin-dependent enzymes influence nodulation and N₂ fixation in legume plants that can be used to supply nitrogen in crops (Underwood 1977). Cobalt deficiency affects nodule development, function and nitrogen fixation. Cobalamin, also called Vitamin B-12, is essential for human and animal health, nutrition and growth. The amount needed is very small. Dietary Co intake is estimated to range 5–40 µg/day in

the general human population (Simonsen et al. 2012).

Understanding the factors which affect Co uptake by plants across a range of soil types is essential for food quality as well as for possible remediation of contaminated sites. The relevant pedogenic processes contributing to Co uptake from soils by plants includes total, extractable and exchangeable soil Co concentrations, pH and other soil chemical parameters, microbial variations as well as anthropogenic inputs. In soils, Co is fixed by Mn-oxides in a non-extractable form and its bioavailability is inversely proportional to the Mn content of the soil (Collins and Kinsela 2012).

High and frequent Co exposures can affect nervous system and cause an *axonopathy* (Flora 2014). Chronic inhalational intake of cobalt dust can lead to diffuse-inflammatory reactions of the bronchial mucosa and chronic respiratory tract disorders (Banza et

al. 2009; Cheyns et al. 2014). In large doses, some Co forms are carcinogenic. Some plant species, also called metallophytes, have adapted to natural and contaminated Co-rich soils (Faucon et al. 2007). Among these metallophytes, some are able to hyperaccumulate Co in plant shoots (>300 ppm, without toxicity symptoms and growth inhibition).

Summary

Cobalt production hugely increases in the last decade as the global demand for Co increases. However, its exploitation becomes a new urgent environmental issue, especially in region such as Democratic Republic of Congo. Cobalt has been suggested to be a potentially dangerous pollutant and the United States Environmental Protection Agency classifies Co in the priority list of environmental risk elements. A better understanding of Co biogeochemical behavior may support to assess the risk to the environment and to

human health, and to assist in developing new remediation tools.

Cross-References

Copper;

Siderophile Elements;

Trace Elements;

Transition Elements;

Fe-Mn Crusts and Nodules;

Manganese;

Ore deposits;

Complexation.

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