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Copper

Xingcheng Liu and Xiaolin Xiong Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

Element Data

Atomic Symbol: Cu Atomic Number: 29 Atomic Weight: 63.546 u

Isotopes and Abundances: ⁶³Cu 69.15%, ⁶⁵Cu 30.85%

1 Atm Melting Point: 1084.6 °C 1 Atm Boiling Point: 2562 °C Common Valences: 2+, 1+

Ionic Radii: 1+: fourfold: 60 pm, sixfold: 77 pm; 2+:

Fourfold: 57 pm, sixfold: 73 pm Pauling Electronegativity: 1.9

First Ionization Energy: 745.5 kJ mol⁻¹ Chondritic (CI) Abundance: 131 ppm Silicate Earth Abundance: 20–30 ppm

Crustal Abundance: 27 ppm

Seawater Abundance: 0.4-5 nmol/kg

Core Abundance: 125 ppm

Properties

Copper (Cu) is a reddish metal with an atomic number 29, standard atomic weight of 63.546, and melting point of 1357.8 K at 1 atm. It was moderately volatile during the Earth formation by accretion of solid material condensed from the solar nebula. As a siderophile element, it partitioned into the core during the separation of metallic core from molten silicate mantle. In the silicate Earth, it behaves as a chalcophile element and usually forms stable sulfides; chalcopyrite (CuFeS₂) is the most common copper-bearing sulfide. In nature, copper is the 26th most abundant element in the Earth's crust, with concentrations ranging from 26 ppm in the lower continental crust to 28 ppm in the upper continental crust; the concentration in the oceanic crust is lower at 44 ppm. Concentrations in MORB range from 60 to 80 ppm, in arc basalts from 50 to 100 ppm, and in oceanic island basalts from 80 to 120 ppm (White 2013).

History and Use

Cu was the first metal people learned to smelt and this discovery ended the Stone Age in many parts of the world. The

discovery that alloying it with tin produced bronze, a stronger metal, led to the Bronze Age.

Due to its high electrical conductivity, tensile strength, ductility, creep resistance, corrosion resistance, low thermal expansion, and high thermal conductivity, copper is extensively used in building construction, power generation and transmission, electronic product manufacturing, and the production of industrial machinery and transportation vehicles nowadays (Doebrich 2009). Besides the pure metal, copper is often alloyed with zinc, tin, gold, and nickel in industrial applications.

The US Geological Survey estimates the global mine production and consumption of Cu is over 18 and 20 million metric tons in 2015, respectively. Major producing countries include Chile, China, and Peru.

Geochemical Behavior: Magmatic Processes

Copper dissolves in silicate melts (natural magmas) dominantly as Cu¹⁺ and perhaps in very minor amounts as Cu²⁺. Copper is believed to dissolve in silicate melts mainly as CuO_{0.5}. The solubility of Cu in sulfur-free silicate melts increases with increasing temperature and increasing oxygen fugacity (Liu et al. 2015 and references therein). Zajacz et al. (2012, 2013) also suggest that Cu dissolves in silicate melts dominantly as Cu–O complex, while Cu–S and Cu–Cl complexes are not significant; thus, its solubility is enhanced only slightly by the presence of chlorine (Cl) and sulfur (S) in the melts.

In magmatic evolution, the geochemical behavior of Cu is controlled by the partition coefficients between silicate minerals, Fe–Ti oxides, sulfides, and magmas. The partition coefficients (given in Table 1) suggest that Cu is highly incompatible in silicate minerals (generally <0.2), incompatible to moderately compatible in Fe–Ti oxides, and highly compatible in sulfides. It should be noted that the partition coefficients are generally controlled by compositions of silicate melts, temperature, pressure, and oxidation state. Thus it's important to know the chemical and physical environmental conditions while applying the partition coefficients to predict the geochemical behavior of Cu.

Geochemical Behavior: Hydrothermal Processes

In contrast, the behavior of Cu in fluids (volatile phases) is a different story. The presences of S and Cl significantly enhance the solubility of Cu in the geological fluids. According to direct Cu K-edge X-ray absorption near-edge structure (XANES) spectra, Berry et al. (2006) suggest that Cu⁺ is stable in high-temperature brines in synthetic

Minerals	Liu et al.	F & C	Lee et al.	A & P	Recommended
Olivine	0.04-0.20	0.06-0.21	0.03-0.16	0.02-0.07	0.1
Orthopyroxene	0.04-0.24	0.15-0.82	0.03		0.1
Clinopyroxene	0.04-0.45		0.04	0.01-0.07	0.2
Garnet	0.01-0.06		0.004		0.04
Amphibole	0.04-0.20		0.05		0.1
Plagioclase	0.02-0.12				0.08
Spinel	0.18-1.3		0.22		0.5
Fe-Ti oxides	0.2-1.8			0.17-0.63	1
Sulfides	L & A	K & W	Zajacz et al.	M & B	
MSS (pyrrhotite)	280-42,000		50-9400		
Sulfide liquid	800-4600	38–675		1060-2130	

Copper, Table 1 Partition coefficients of Cu between mineral and silicate melts

Data are from Liu et al. (2014, 2015); F & C, Fellows and Canil (2012); Lee et al. (2012); A & P, Audétat and Pettke (2006); L & A, Li and Audétat (2012, 2015); K & W, Kiseeva and Wood (2013); Zajacz et al. (2013); M & B, Mungall and Brenan (2014).

MSS monosulfide solid solution.

fluid inclusions. In addition, Cu typically occurs as $CuCl_2^-$ ($\pm Cu(HS)_2^-$) in natural hydrothermal systems, in which the partition coefficients of Cu between volatile phases and silicate melts range from dozens to several hundreds (Simon and Ripley 2011; Pokrovski et al. 2013). This means that Cu will be transported into brines or vapors from ascending magma in magmatic–hydrothermal processes if the magmatic aqueous fluids are present. The mass transfer of Cu from magmas to volatile phase(s) is the most important process in the development of a porphyry Cu deposit (Audétat and Simon 2012, and references therein).

Ore Deposits

Most copper is extracted from ore deposits as copper sulfides. Porphyry Cu deposits and sediment-hosted Cu deposits contain most portions of the world's Cu resources. Porphyry ore deposits supply over 70% of the world's copper. They dominantly formed above subduction zones and most of them are genetically related to intermediate to felsic calc-alkaline magmas, which provide metals and fluids (e.g., H₂O, CO₂, Cl, and S) for the ore formation. However, the most important controlling factor(s) is still debated.

Individual copper deposits may contain millions of tons of copper and generally are developed by using open-pit mining methods (Doebrich 2009).

Natural Waters

Copper exists in natural waters mainly as Cu²⁺ and is readily complexed by hydroxyl and carbonate. Surface water concentrations of dissolved Cu are 63.55 ppt in the open ocean

and 1.48 ppb in the rivers (global average) (Bruland et al. 2014; Gaillardet et al. 2014). The Cu^{2+} in surface waters is buffered by a strong Cu-binding class of organic ligands, called L_1 , which chelates nearly 99.8% Cu^{2+} and reduces the Cu^{2+} concentration to a nontoxic condition for phytoplankton. Without organic complexation, the dominant species of Cu would be $Cu(CO_3)^0$ and approximately a factor of 20 lower than the total dissolved concentration (Bruland et al. 2014 and references therein).

Biological Utilization and Toxicity

Cu²⁺and Cu⁺ can participate in a wide spectrum of interactions with proteins to drive diverse structures and biochemical reactions. As life evolved, more complex roles for Cu arose, concurrent with the elaboration of mechanisms to tightly regulate acquisition and distribution of Cu and provide protection against Cu toxicity (Festa and Thiele 2011). It is an essential and required trace element in plants and animals but can be toxic to some microorganisms at relatively low concentrations. Defects in Cu homeostasis lead to human disease. On the other hand, excess Cu intake induces toxicity for human.

Summary

Humans have been using copper for several thousands of years. As an industrial material, it is significant and widely used in modern society. As a trace element in Earth, it also provides insight into the crust—mantle differentiation, the formation of ore deposits, and the redox history of magmas.

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Cross-References

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- ► Sulfide Minerals

References

- Audetat A, Pettke T (2006) Evolution of a porphyry-Cu mineralized magma system at Santa Rita, New Mexico (USA). J Petrol 47 (10):2021–2046
- Audétat A, Simon A (2012) Magmatic controls on porphyry copper deposits. Soc Econ Geol Spec Publ 16:573–618
- Berry AJ, Hack AC, Mavrogenes JA, Newville M, Sutton SR (2006) A XANES study of Cu speciation in high-temperature brines using synthetic fluid inclusions. Am Mineral 91(11–12):1773–1782
- Bruland KW, Middag R, Lohan MC (2014) 8.2 controls of trace metals in seawater. In: Turekian HDHK (ed) Treatise on geochemistry, 2nd edn. Elsevier, Oxford, pp 19–51
- Doebrich J (2009) Copper–A metal for the ages: U.S. Geological Survey fact sheet 2009–3031, 4 p. Available at http://pubs.usgs.gov/fs/2009/3031/
- Fellows SA, Canil D (2012) Experimental study of the partitioning of Cu during partial melting of Earth's mantle. Earth Planet Sci Lett 337:133–143
- Festa RA, Thiele DJ (2011) Copper: an essential metal in biology. Curr Biol 21(21):R877–R883
- Gaillardet J, Viers J, Dupré B. 7.7 trace elements in river waters. In: Turekian HDHK (ed) Treatise on geochemistry, 2nd edn. Elsevier, Oxford, pp 195–235
- Kiseeva ES, Wood BJ (2013) A simple model for chalcophile element partitioning between sulphide and silicate liquids with geochemical applications. Earth Planet Sci Lett 383:68–81
- Lee C-TA, Luffi P, Chin EJ, Bouchet R, Dasgupta R, Morton DM, Le Roux V, Yin Q-Z, Jin D (2012) Copper systematics in arc magmas and implications for crust-mantle differentiation. Science 336 (6077):64–68
- Li Y, Audétat A (2012) Partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide phases and hydrous basanite melt at upper mantle conditions. Earth Planet Sci Lett 355:327–340
- Li Y, Audétat A (2015) Effects of temperature, silicate melt composition, and oxygen fugacity on the partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide phases and silicate melt. Geochim Cosmochim Acta 162:25–45
- Liu X, Xiong X, Audétat A, Li Y, Song M, Li L, Sun W, Ding X (2014)
 Partitioning of copper between olivine, orthopyroxene, clinopyroxene, spinel, garnet and silicate melts at upper mantle conditions. Geochim Cosmochim Acta 125:1–22
- Liu X, Xiong X, Audetat A, Li Y (2015) Partitioning of Cu between mafic minerals, Fe-Ti oxides and intermediate to felsic melts. Geochim Cosmochim Acta 151:86–102
- Mungall J, Brenan J (2014) Partitioning of platinum-group elements and Au between sulfide liquid and basalt and the origins of mantle-crust fractionation of the chalcophile elements. Geochim Cosmochim Acta 125:265–289
- Pokrovski GS, Borisova AY, Bychkov AY (2013) Speciation and transport of metals and metalloids in geological vapors. Rev Mineral Geochem 76(1):165–218

- Simon AC, Ripley EM (2011) The role of magmatic sulfur in the formation of ore deposits. Rev Mineral Geochem 73(1):513–578 White WM (2013) Geochemistry. Wiley-Blackwell, Oxford, UK
- Zajacz Z, Candela PA, Piccoli PM, Wälle M, Sanchez-Valle C (2012) Gold and copper in volatile saturated mafic to intermediate magmas: Solubilities, partitioning, and implications for ore deposit formation. Geochim Cosmochim Acta 91:140–159
- Zajacz Z, Candela PA, Piccoli PM, Sanchez-Valle C, Wälle M (2013) Solubility and partitioning behavior of Au, Cu, Ag and reduced S in magmas. Geochim Cosmochim Acta 112:288–304

Copper Isotopes

Paul Savage

Department of Earth and Environmental Sciences, University of St Andrews, St Andrews, UK

Synonyms

Copper stable isotopes; Cu isotopes

Introduction

Copper has two stable isotopes, ⁶³Cu and ⁶⁵Cu, with relative abundances of 69.15% and 30.85%, respectively. A transition metal, Cu is moderately siderophile and strongly chalcophile (around 2/3 of Earth's Cu is thought to be stored in its core). Copper is redox-sensitive and is present in three oxidation states in terrestrial environments: native Cu⁰, Cu⁺ and Cu²⁺. Copper is both economically important and an essential micronutrient. For all these reasons, isotopic variations of Cu have the potential to inform us of processes, sources, and phenomena in all disciplines of the geosciences. A more detailed review of the myriad applications of Cu isotopes is given by Moynier et al. (in press).

Analysis

As with many other stable isotope systems, accurate, precise, and routine measurement of Cu isotope ratio was made possible with the advent of Multi-collector Inductively-Coupled-Plasma Mass Spectrometry (MC-ICPMS) and precisions of <50 ppm are now attainable. This is usually by solution analysis, whereby copper is isolated from a dissolved sample using ion exchange chromatography (Marechal et al. 1999); however, some in-situ laser ablation isotope analyses has been made (Ikehata and Hirata 2013). Variations in Cu isotopes are represented using the delta notation as δ^{65} Cu in permil (‰; Eq. 1), relative to the pure Cu standard NIST976: