

Chalcophile Elements

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Definition

The term chalcophile (derived from the Greek for copper-loving) was originally introduced by Goldschmidt (1923) to describe the group of elements that are concentrated in sulfide minerals in meteorites. Traditionally this group is defined as the elements Ag, As, Bi, Cd, Cu, Hg, In, Pb, S, Sb, Se, Te, Tl, and Zn. Goldschmidt classified the other elements in meteorites into two groups: those associated with Fe alloy as siderophile (iron loving) and those concentrated in silicates minerals as lithophile (rock loving). Subsequently Goldschmidt applied his classification to the whole Earth and modified it to include two new groups of elements: atmophile, those concentrated in the atmosphere and biophile elements, those concentrated by organic processes (Goldschmidt, 1930).

Distribution in Terrestrial Rocks

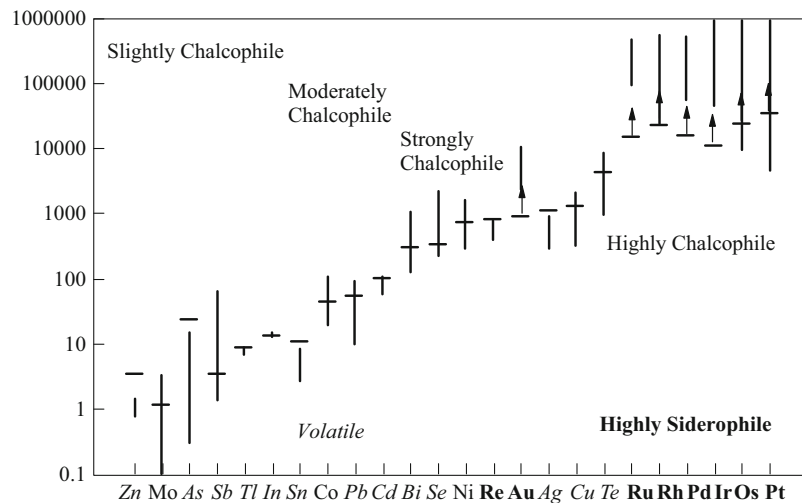
Whereas the concepts outlined by Goldschmidt are useful, as is evidenced by the fact the terms, siderophile, chalcophile, and lithophile are in daily use by geochemists, the behavior of an element depends on the composition of the system, oxygen fugacity (fO_2), temperature, and pressure (Li and Audétat, 2015); thus, its behavior may vary depending on the context. Lodders (2003) outlined the behavior of the elements during condensation of the elements to form the solar system, and under these low fO_2 conditions, the chalcophile group is restricted to Ag, Cd, Hg, In, Pb, S, Se, Te, and Zn. Low fO_2 conditions would also have prevailed during the segregation

of the earth's core and consequently many elements behaved in a siderophile manner. Current estimates of the core composition show enrichment of up to 1000 times primitive mantle (Figure 2) for elements such as the platinum-group elements (PGE; Ru, Rh, Pd, Os, Ir, Pt). In contrast at the oxygen fugacities found in the Earth's mantle and crust, Fe alloy is very rarely present and many elements that are siderophiles in meteorites and during core segregation partition into sulfide minerals rather than Fe alloy and thus behave as chalcophile elements.

The partition coefficients between sulfide droplets and mid-ocean ridge basalts (MORB) give an indication of how chalcophile each element is under crustal conditions (Figure 1). Elements with partition coefficients between 1 and 10 may be described as slightly chalcophile (Zn, Mo, As, Sb, Tl, In, and Sn.), those with partition coefficients in the range 20–100 as moderately chalcophile (Pb, Co, Cd), those with a partition coefficient in the 100–1000 range as strongly chalcophile (Bi, Se, Ni, Re), and those with partition coefficients above 1000 as highly chalcophile (Au, Cu, Te, Ru, Rh, Pd, Os, Ir, Pt).

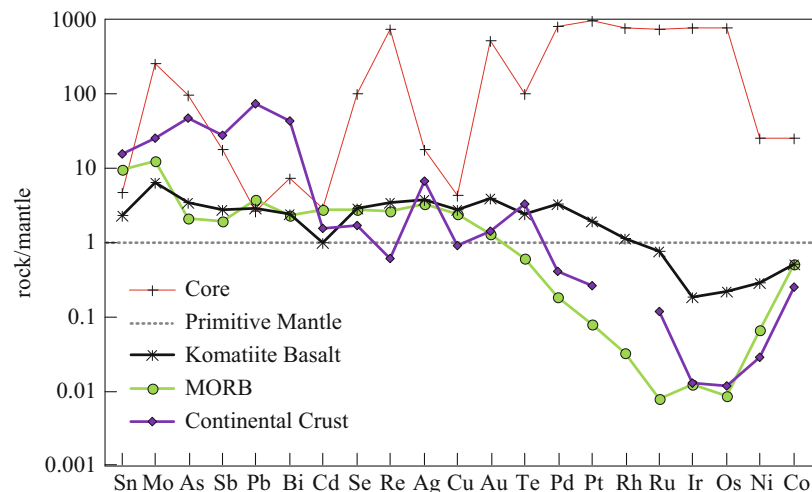
Among the group that behave as highly chalcophile elements under crustal conditions are the PGE which together with Au and Re are commonly referred to as highly siderophile elements because of their very high partition coefficients into Fe alloy (Harvey and Day, 2016 and references therein). The highly siderophile elements attract a great deal of interest because of their potential to investigate the early history of planetary formation. In particular the relatively high concentrations of the highly siderophile elements in the Earth's mantle suggest that it is not in equilibrium with the core and that, during late meteorite bombardment, highly siderophile elements were added to the mantle (Dale et al., 2012).

The behavior of the chalcophile elements during mantle melting can be considered by inspection of a mantle-normalized plot of average MORB and komatiitic basalts (Figure 2). The elements are plotted in approximately



Chalcophile Elements, Figure 1 Partition coefficients between mafic magma and sulfide liquid. — indicates partition coefficients between MORB and sulfide droplet; I indicates range of values from experiments conducted at fO_2 between -2 FMQ $+2$; \uparrow indicates minimum partition

coefficients; italics indicates the element is volatile; bold indicates that the element is highly siderophile (Data from Barnes and Ripley (2016) and references therein, plus Li and Audétat (2015)).



Chalcophile Elements, Figure 2 Concentrations of chalcophile elements in the core, komatiitic basalt, MORB, and the continental crust normalized to primitive mantle and plotted in order of incompatibility with komatiitic basalt (Data for the core from McDonough and Sun

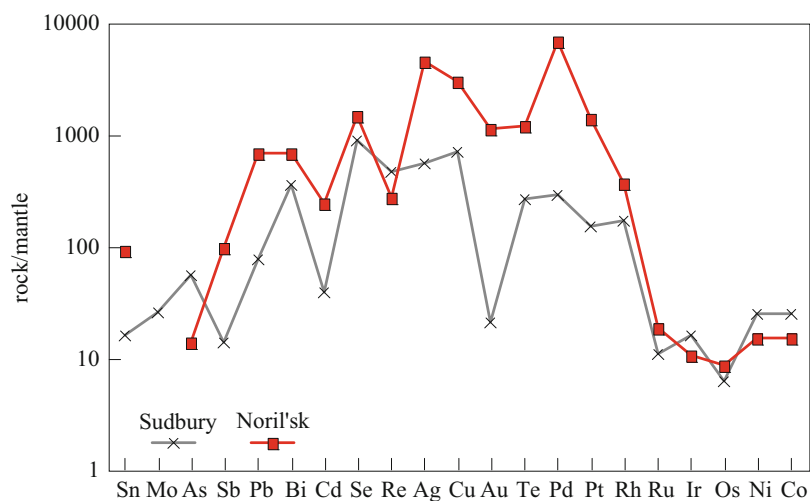
(1995); mantle from Lyubetskaya and Korenaga (2007); MORB from Arevalo and McDonough (2010); continental crust from Rudnick and Gao (2003); komatiitic basalt from this work (median of 52 samples from the Cape Smith Fold Belt northern Quebec)).

decreasing normalized abundance in komatiitic basalt. For komatiitic basalt most of the chalcophile elements from Sn to Pt are present at the two to three times mantle concentrations. Moderately incompatible lithophile elements such as Sm are present in these rocks at similar to slightly higher levels (three to four times mantle); thus most of the chalcophile elements behave as incompatible elements and sulfide phases do not appear to control the behavior of the chalcophile elements at the high degrees of partial melting required to produce komatiitic basalts. In contrast the Ir-platinum-group elements (IPGE, Os, Ir, Ru, and Rh), Ni,

and Co are present at less than one times mantle and behave as compatible elements.

The concentrations of the chalcophile elements in MORB show a wider range of values. Tin and Mo are present at close to ten times mantle, most of the chalcophile elements (As to Cu) show a lower degree of enrichment in the range of twice to three times mantle. Tellurium, Au, Ni, and Co are present at 0.1–1 times mantle exhibiting compatible behavior, and the PGE are extremely depleted at 0.01–0.1 times mantle. The variations in the behavior of the chalcophile elements in MORB are generally attributed to the presence of residual

Chalcophile Elements, Figure 3 Mantle-normalized concentrations of chalcophile elements from the two largest magmatic Ni-sulfide deposits, Sudbury and Noril'sk (Data from Dare et al. (2011) and Zientek et al. (1994)).



sulfides in the MORB source. The PGE exhibit extreme depletion because of their very high partition coefficients into sulfides, whereas the moderately chalcophile elements exhibit a much smaller degree of depletion because the sulfide phases will affect their bulk partition coefficients less (Patten et al., 2013). Tin and Mo at ten times mantle show an enrichment similar to incompatible lithophile elements, suggesting that the presence of sulfide phases has a negligible influence on these elements.

The average continental crust is depleted in most moderately to strongly chalcophile elements and like MORB is particularly depleted in PGE (Figure 2). However it is enriched at 10–100 times mantle in the slightly to moderately chalcophile elements Sn to Pb and in the strongly chalcophile elements Bi and Ag (Figure 2).

Naturally all of the chalcophile elements are concentrated into magmatic sulfide liquids when they segregated from mafic magmas, and the Ni and PGE ore deposits that form from the liquids are enriched in all of these elements (Barnes and Ripley, 2016). Most of the chalcophile elements are enriched by a factor of 100–1000 relative to mafic magma (Figure 3). The slightly chalcophile elements are less enriched with enrichment factors of approximately 10 reflecting their lower partition coefficients (Figures 1 and 3).

During crystallization of magma, the silicate liquid may become saturated in a magmatic-hydrothermal fluid. Some chalcophile elements and S partition into these fluids. For example, fluid inclusions from Cu-Mo porphyries are enriched in Cu, Mo, Zn, Ag, Tl, Au, Pb, and Bi (John et al., 2010). The fluids then react with country rocks and the chalcophile elements are deposited along with sulfides as a result of the reactions (Keith et al., 1997; John et al., 2010; Richards, 2011).

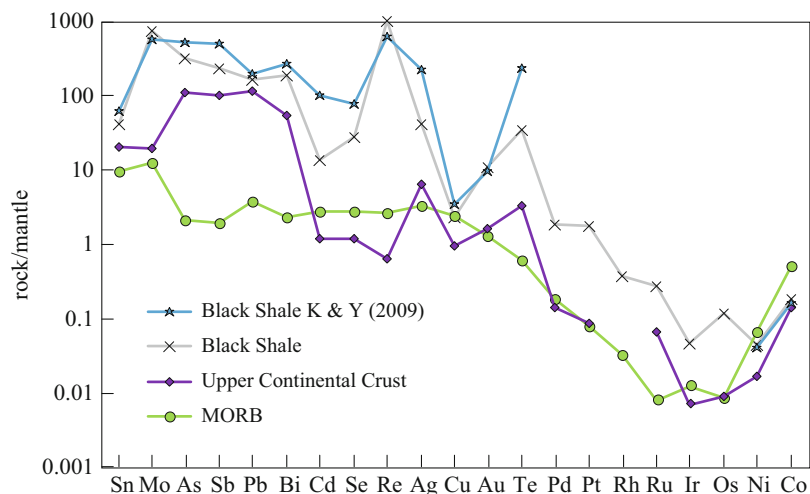
At low pressures the silicate magma or a magmatic-hydrothermal fluid may become saturated with a vapor. Some chalcophile elements preferentially partition into the

vapor phase. Based on their condensation temperatures during the formation of the solar system, Lodders (2003) defined Hg, Tl, In, Cd, Se, S, Sn, Te, Pb, Bi, Sb, Ag, Cu, As, and Au as volatile. Volcanic gasses and sublimates have been found to be enriched in these elements (Hinkley et al., 1994; Zelenski et al., 2013). Another effect of the vapor is that magmatic sulfide droplets in the magma may lose S during magma degassing. The loss of S destabilizes the sulfides and some of the chalcophile elements partition into the vapor.

Black shales are also enriched in many chalcophile elements (Figure 4). [Some black shales, such as those in southern China, show much greater degree of enrichment than the median (Xu et al., 2013).] Relative to the upper crust (a potential source of the clastic component of the shales), the median black shale is enriched by a factor of 2 to 10 for most of the elements (Ketriss and Yudovich, 2009). Molybdenum, Cd, Se, Ag, and Te show larger enrichments in the range of 30–100, and Re shows the most extreme degree of enrichment at 1000. Ketriss and Yudovich (2009) did not provide estimates for the PGE. But based on a survey of the literature, the PGE are also enriched in black shales at approximately ten times crustal values (Figure 4). The origin of the enrichment of the metals in black shales has been much debated with one school of thought favoring the precipitation of the metals from seawater in anoxic basins (Xu et al., 2013) and the other school suggesting that the metals are derived from hydrothermal fluids (Orberger et al., 2003). Recently models involving both processes have become popular (Slack et al., 2015).

Over the past few years, the concentrations of chalcophile elements in pyrites from black shales have become the focus of intense study as a means of exploration for Au deposits (Large et al., 2011). In this model the chalcophile elements are precipitated by organic matter and pyrite and incorporated into the pyrite during diagenesis. During greenschist facies metamorphism, the pyrite recrystallizes and releases many of

Chalcophile Elements, Figure 4 Comparison of mantle-normalized concentrations of chalcophile elements in black shales with the upper continental crust and MORB (Data from Ketris and Yudovich (2009), this work of literature survey, Hu and Gao (2008), and Arevalo and McDonough (2010)).



the chalcophile elements to metamorphic fluids which can migrate to low pressure zones where they precipitate Au and other chalcophile elements.

Summary

The chalcophile elements can be divided into slightly, moderately, strongly, and highly chalcophile based on their partition coefficients between silicate and sulfide melts. Some of the highly and strongly chalcophile elements (PGE, Au, Re) are also highly siderophile, and thus most of the budget of these elements is found in the Earth's core. The slightly chalcophile elements Sn, Mo, As, Sb, and Pb together with Bi are enriched in the continental crust. Black shales are an important reservoir of most chalcophile elements in the Earth's crust. MORB is slightly enriched in most chalcophile elements except the highly chalcophile elements. In the Earth's crust highly chalcophile elements are only found in significant quantities in magmatic sulfide deposits.

Cross-References

- ▶ Antimony
- ▶ Arsenic
- ▶ Bismuth
- ▶ Black Shales and Sapropels
- ▶ Cadmium
- ▶ Copper
- ▶ Earth's Core
- ▶ Geochemical Classification of the Elements
- ▶ Highlighted in Green Main Index Terms, Yellow Sub Index
- ▶ Indium
- ▶ Lead
- ▶ Mercury

- ▶ Meteorites
- ▶ Mid Ocean Ridge Basalts
- ▶ Ore Deposits
- ▶ Platinum-Group Elements
- ▶ Selenium
- ▶ Siderophile Elements
- ▶ Silver
- ▶ Sulfur
- ▶ Tellurium
- ▶ Thallium
- ▶ Zinc

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