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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

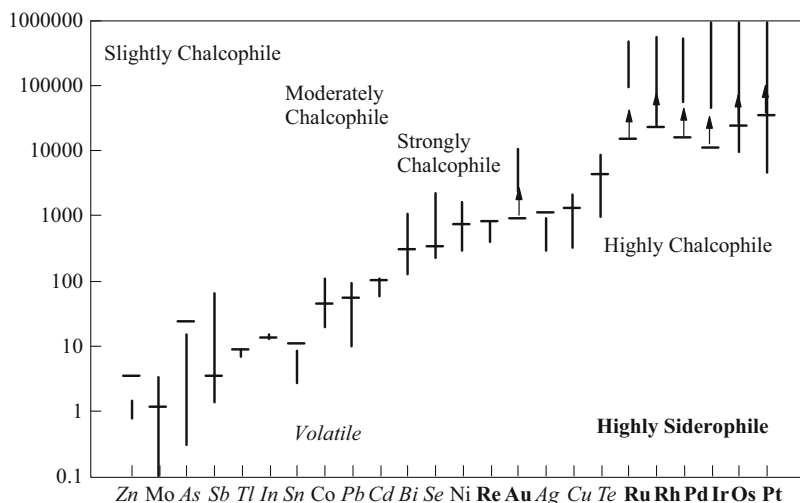
Whereas the concepts outlined by Goldschmidt are useful, as is evidenced by the fact the terms, siderophile, chalcophile, and lithophile are in daily use by geochemists, the behavior of an element depends on the composition of the system, oxygen fugacity (fO_2), temperature, and pressure (Li and Audétat, 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).

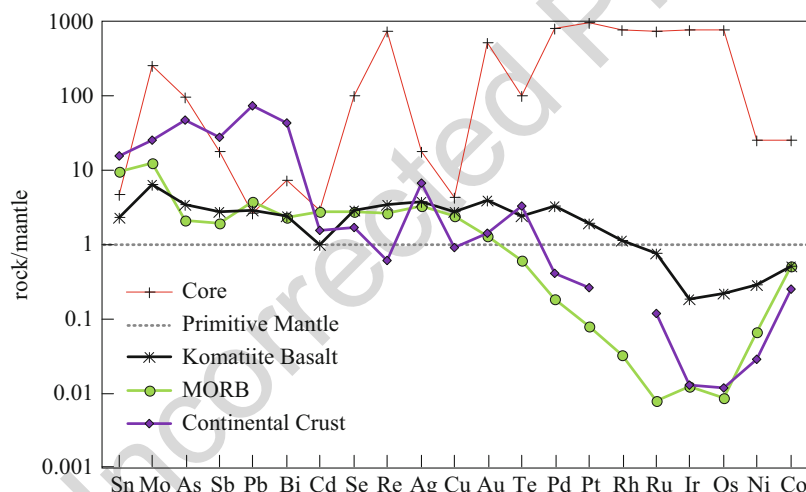
Among the group that behave as highly chalcophile elements under crustal conditions are the PGE which together with Au and Re are commonly referred to as highly siderophile elements because of their very high partition coefficients into Fe alloy (Harvey and Day, 2016 and references therein). The highly 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, the komatiitic basalt, the 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 (2014); continental crust from Rudnick and Gao (2003); komatiitic basalt from this work (median of 52 samples from the Cape Smith Fold Belt northern Quebec)).

Au2

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

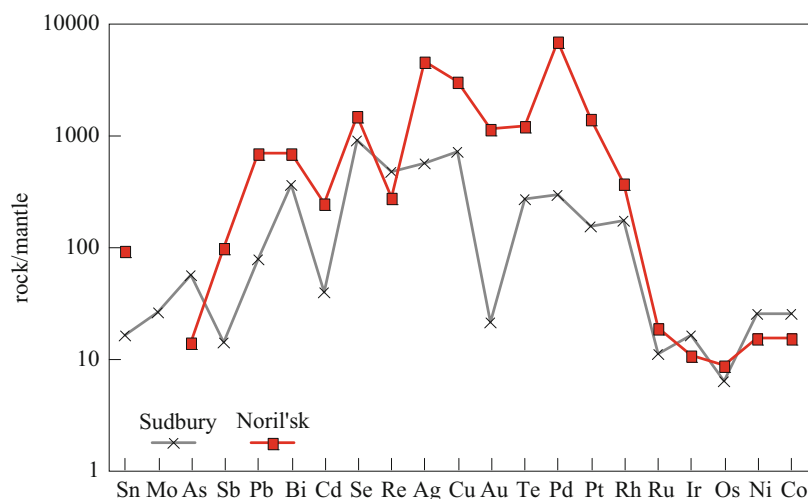
and Co are present at less than one times mantle and behave as
 compatible elements.

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

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



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

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

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

117 During crystallization of magma, the silicate liquid may
 118 become saturated in a magmatic-hydrothermal fluid. Some
 119 chalcophile elements and S partition into these fluids. For
 120 example, fluid inclusions from Cu-Mo porphyries are
 121 enriched in Cu, Mo, Zn, Ag, Tl Au, Pb, and Bi (John et al.,
 122 2010). The fluids then react with country rocks and the
 123 chalcophile elements are deposited along with sulfides as a
 124 result of the reactions (Keith et al., 1997; John et al., 2010;
 125 Richards, 2011).

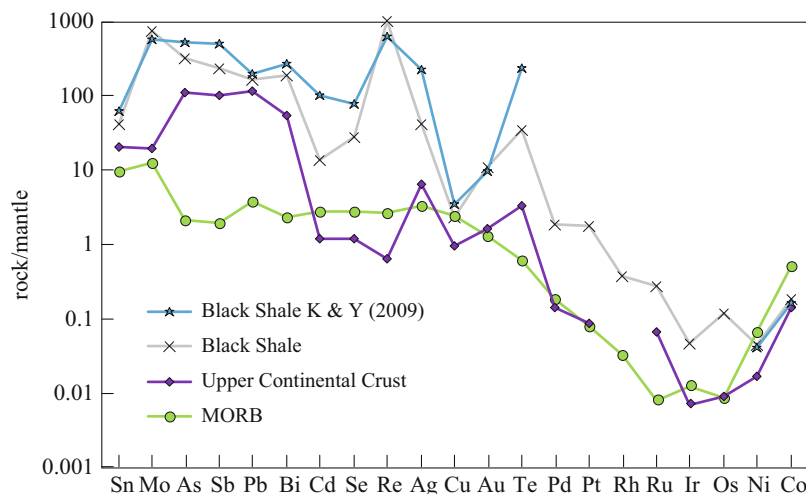
126 At low pressures the silicate magma or a magmatic-
 127 hydrothermal fluid may become saturated with a vapor.
 128 Some chalcophile elements preferentially partition into the

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

137 Black shales are also enriched in many chalcophile ele-
 138 ments (Figure 4). [Some black shales, such as those in south-
 139 ern China, show much greater degree of enrichment than the
 140 median (Xu et al., 2013).] Relative to the upper crust
 141 (a potential source of the clastic component of the shales),
 142 the median black shale is enriched by a factor of 2 to 10 for
 143 most of the elements (Ketris and Yudovich, 2009). Molybde-
 144 num, Cd, Se, Ag, and Te show larger enrichments in the range
 145 of 30–100, and Re shows the most extreme degree of enrich-
 146 ment at 1000. Ketris and Yudovich (2009) did not provide
 147 estimates for the PGE. But based on a survey of the literature,
 148 the PGE are also enriched in black shales at approximately ten
 149 times crustal values (Figure 4). The origin of the enrichment
 150 of the metals in black shales has been much debated with one
 151 school of thought favoring the precipitation of the metals
 152 from seawater in anoxic basins (Xu et al., 2013) and the
 153 other school suggesting that the metals are derived from
 154 hydrothermal fluids (Orberger et al., 2003). Recently models
 155 involving both processes have become popular (Slack et al.,
 156 2015).

157 Over the past few years, the concentrations of chalcophile
 158 elements in pyrites from black shales have become the focus
 159 of intense study as a means of exploration for Au deposits
 160 (Large et al., 2011). In this model the chalcophile elements are
 161 precipitated by organic matter and pyrite and incorporated
 162 into the pyrite during diagenesis. During greenschist facies
 163 metamorphism, the pyrite recrystallizes and releases many of
 164

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)).



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

168 **Summary**

169 The chalcophile elements can be divided into slightly, mod-
 170 erately, strongly, and highly chalcophile based on their parti-
 171 tion coefficients between silicate and sulfide melts. Some of
 172 the highly and strongly chalcophile elements (PGE, Au, Re)
 173 are also highly siderophile, and thus most of the budget of
 174 these elements is found in the Earth's core. The slightly
 175 chalcophile elements Sn, Mo, As, Sb, and Pb together with
 176 Bi are enriched in the continental crust. Black shales are an
 177 important reservoir of most chalcophile elements in the
 178 Earth's crust. MORB is slightly enriched in most chalcophile
 179 elements except the highly chalcophile elements. In the
 180 Earth's crust highly chalcophile elements are only found in
 181 significant quantities in magmatic sulfide deposits.

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