



# The chlorine abundance of Earth: Implications for a habitable planet



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## ABSTRACT

The Cl, Br and I contents of Earth are depleted by a factor of 10 relative to predicted values from chondritic and solar abundances. Possible explanations for the apparent discrepancy include (1) unrecognized sequestration of Cl in the core, (2) a much higher nebular volatility than normally presumed or (3) a preferential loss of the heavy halogens during planetary accretion. We tested the first assumption by conducting high pressure–temperature equilibration experiments between silicate and metal. At 15 GPa and 1900 °C, the  $D_{\text{Cl(metal-silicate)}}$  value for Cl is less than 0.007, indicating that the core is not a significant reservoir for Cl. The concentration of Cl in all chondritic classes follows a depletion trend very similar to that of Na and Mn, arguing against a low condensation temperature for Cl. Instead, we propose that the depletion of the heavy halogens is due to their unique hydrophilic behavior. Almost half of Earth's Cl and Br inventory resides in the ocean and evaporites, demonstrating the unique affinity for aqueous solutions for these elements. During planetary accretion, there would have been a strong sequestration of halogens into the crustal reservoir. 'Collisional erosion' during planetary accretion provides a mechanism that would uniquely strip the heavy halogens out of an accreting Earth. Had such loss not occurred, the salinity of the oceans would be  $10 \times$  the present value, and complex life would probably never have evolved.

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## 1. Introduction

With the exception of some nuclides that are processed in the Sun (e.g., deuterium and Li), the solar abundances of elements are essentially the same as those of the total solar system. The least processed and most primitive meteorites from a chemical standpoint are the CI chondrites. Although they have undergone low temperature alteration, it appears that this alteration occurred in a closed system (Lodders, 2003) and the overall relative abundances of most elements are preserved and the same as the Sun. The compositions of all other rocky bodies from the inner solar system have some degree of elemental depletion in proportion to each element's volatility. There is a regular progression in the depletion, with more volatile elements (those with a lower condensation temperature) having a greater depletion relative to CI chondrites. On Earth, the heavy halogens Cl, Br, and I are depleted by an order of magnitude more than would be predicted on the basis of their assumed volatility. Several proposals for the anomalous depletions have been made, including sequestration into the core (McDonough, 2003) or extremely low condensation temperatures (Zolotov and Mironenko, 2007). In order to better understand the

halogen budget of Earth, we have conducted high  $P$ – $T$  partitioning experiments between molten metal and silicate to estimate the contribution from the core and evaluate different hypotheses for Earth's halogen depletion.

Following collapse of the solar nebula, temperatures would have exceeded 1500 K within 2.5 astronomical units (AU) (Boss, 1988), decreasing away from the Sun. In this early, high temperature period, all but the most refractory elements were stable in the vapor phase. During cooling, elements became incorporated into growing solids when the condensation temperature for the element – or phase that hosts the element – was reached. Preceding and during condensation, gases would be continuously lost either to the deeper parts of the solar system or drawn into the Sun, so that the more volatile elements should be more depleted in the inner planetary bodies, a scenario recognized by Urey (1951). This putative process forms the basis for most accretion models for planetary bodies. In the region of Earth formation, the most refractory elements (those that condense above 1400 K), such as Al, Ca, Zr and the rare earth elements (REE) may have never been volatilized, or condensed only shortly after the collapse of the nebula. The ratios of refractory elements in bulk Earth are roughly the same as those in CI chondrites, supporting the idea that the CI chondrites represent the average nebula composition. More volatile elements are depleted relative to CI chondrites; a manifestation of partial loss before the

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condensation temperature for that element was reached. The concentration ratio of an element relative to CI chondrites follows a smooth depletion trend as a function of volatility (Sun, 1982). Using thermodynamically or experimentally constrained condensation temperatures, the composition of Earth (and other inner planetary bodies) can be modeled and compared with estimates from terrestrial materials (e.g., Cassen, 1996; Grossman, 1972; Grossman and Larimer, 1974). The relationship between volatility and concentration has been used to estimate the composition of the core (McDonough, 2003) and terrestrial concentrations for elements that are difficult to otherwise constrain.

The anomalous depletion of Cl (and the other heavy halogens Br and I) on Earth is apparent from the relationship between concentration normalized to CI chondrites vs. condensation temperature (Fig. 1). No other moderately volatile lithophile elements show such extreme depletion. There are three possible explanations for the data: (1) there is a missing Cl reservoir on Earth,

(2) the assumed condensation temperatures for the halogens are too high, or (3) a late-stage process occurred that preferentially removed Cl from Earth. Each of these scenarios is considered in the following sections.

## 2. Estimation of the Cl content of Earth

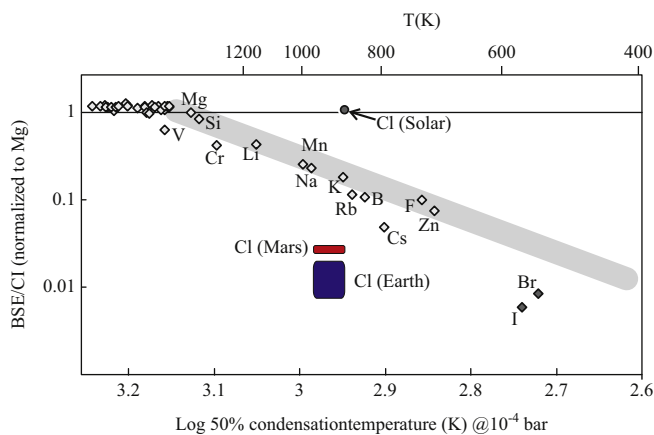
### 2.1. Earth Cl abundance estimates from chondritic abundances

The Cl concentration of Earth can be estimated from the Cl concentration of chondrites and an assumed condensation temperature from the solar nebula. The Cl contents of CI chondrites (Ivuna and Orgueil) are  $704 \pm 10$  ppm (Lodders, 2003). Solar abundances are only slightly higher using element ratio data (e.g., Cl/Si) (Asplund et al., 2006; Lodders, 2003). Assuming CI chondrites as an Earth source, and a planetary volatility loss of 80% for Earth due to its closer proximity to the Sun relative to chondrites (Humayun and Cassen, 2000) ( $X_{\text{remaining}} \approx 0.2$ , defined as the point on volatility trend for a condensation temperature of  $\sim 900$ – $950$  K, Fig. 1), the total Cl on Earth should be  $8.2 \times 10^{23}$  g. This value ( $C_{\text{BSE}}/C_{\text{Cl}} = 0.18$ ) would plot on the Planetary Volatility Trend in Fig. 1.

Alternatively, an Earth model based on a mix of chondrites in appropriate proportions to give the correct Earth oxygen isotope ratios can be used for estimating predicted Cl concentrations. Using an oxygen isotope mixing model for Earth (Lodders, 2000) and Cl abundance data from Lodders and Fegley (1998) based on 70% EH (Cl abundance—570 ppm), 21% H (Cl—140 ppm), 5% CV (Cl—250 ppm), 4% CI (Cl—700 ppm) yields a precursor Cl abundance of 470 ppm. If this precursor composition ultimately delivered only 20% of Cl to Earth (based on the volatility trend of Fig. 1), then Earth should contain  $5.5 \times 10^{23}$  g Cl.

### 2.2. Crust and mantle

The total Cl content of Earth is the sum of the core, mantle and crustal contributions (Table 1). Cl in the crust is a sum of the ocean, evaporite, brine and crustal rock abundances. Our estimate of  $5.8 \times 10^{22}$  g is slightly higher than a previous estimate of



**Fig. 1.** Volatilization trend for lithophile elements. The ratios of the concentration of elements in the bulk silicate Earth (BSE) to CI chondrites is plotted as a function of presumed condensation temperature in the solar nebula. Cl, Br and I all fall well below the predicted value for Earth. Possible explanations include a missing sink (the core), a much lower volatilization temperature or a preferential loss of the heavy halogens during planetary formation. Solar values are from Asplund et al. (2006), Mars data from Dreibus and Wänke (1987), condensation temperatures from Fegley and Lewis (1980), Lodders (2003). Modified from McDonough (2003).

**Table 1**  
Cl abundances for crust and mantle.

	Amount	Ref.	Comments
<b>Crust</b>			
Ocean	$2.7 \times 10^{22}$ g		From mass of ocean and a chlorinity of 19.4/mil
Evaporites	$1.4 \times 10^{22}$ g	Eggenkamp (1994)	
Brines	$1.5 \times 10^{22}$ g	Land (1995)	Half of original estimate which is a maximum value
Crustal rocks	$2.27 \times 10^{21}$ g	Schilling et al. (1978)	
Total	$5.8 \times 10^{22}$ g		Sum of above
	$4.55 \times 10^{22}$ g	Schilling et al. (1978)	
	$3.8 \times 10^{22}$ g	Jambon et al. (1995)	Evaporites+ocean
<b>Mantle</b>			
	$1.07 \times 10^{22}$ g (2.7 ppm)	McDonough (2003)	Calculated by subtracting crustal component from bulk silicate earth value
	$9 \times 10^{22}$ g (22 ppm)	Schilling et al. (1978)	Total Earth less crustal total
	$14 \times 10^{22}$ g (35 ppm)	Jambon et al. (1995)	
	$8.4 \times 10^{22}$ g (21 ppm)	Dreibus and Wänke (1987)	Calculated assuming 680 ppm Cl in CI chondrites
	$1.6 \times 10^{22}$ g (4 ppm)	Bonifacie et al. (2008)	Assuming $10 \times$ enrichment in MORB over mantle
	$0.36 \times 10^{22}$ g (0.9 ppm)	Saal et al. (2002)	Calculated from MORB melt inclusion chemistry
	$1.2 \times 10^{22}$ g (3 ppm)	Burgess et al. (2002)	Halogens in Siberian and African diamonds
	$7.8 \times 10^{22}$ g (19 ppm)	Michael and Cornell (1998)	Calculated from Cl/K ratio of 0.08 in mantle
Average	$4.6 \times 10^{22}$ g* (11 ppm)		
Bulk Silicate Earth—total	$10.4 \times 10^{22}$ g		

\* Excluding anomalously high value from average.

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