Cl/H_2O of mantle-derived magmas: Relation to seawater salinity

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We compare Cl/H_2O ratios of major magmatic contributors to Earth's exosphere with seawater (Cl/H_2O = 0.02), and calculate the Cl/H_2O of the bulk magmatic contribution. In mid-ocean ridge basalt (MORB) and ocean island basalt (OIB) sources, Cl is more incompatible than H_2O [1, 2]. The mantle output of Cl in MORB is often obscured by Cl from shallow assimilation [3]. Earlier limits (mantle Cl/K<0.07; [3]) are too high for most MORB. We propose that mantle Cl/K is ≈0.005 for NMORB and ≈0.035 for most E-MORB. These are based on the lowest ratios of MORB, especially from ultraslow ridges where assimilation is least [3]. NMORB values are consistent with depleted MORB melt inclusions [4]. EMORB Cl/K is similar to OIB, which ranges from 0.02 for EM-type to 0.08 for HIMU basalts [5]. K_2O/H_2O is 0.25 in NMORB to >1.25 in EMORB and OIB. Mantle Cl/H_2O≈0.004 in NMORB. In EMORB and OIB that have not degassed, Cl/H_2O≈0.03-0.06.

Estimation of the contribution of subduction magmas is complicated by degassing of H_2O. Undegassed back-arc basin glasses from Lau and Mariana have Cl/H_2O that is *slightly* higher or lower than seawater. Published Cl/H_2O contents in other arc magmas based on melt inclusions range from <0.02 to 0.14. We suggest that higher values reflect preferential degassing of H_2O (despite CO_2 inclusion 'filters') and that primary H_2O contents, based on the most reliable inclusions, were higher and Cl/H_2O lower. Notably, Cl/H_2O in subduction magmas globally is less variable than LIL/H_2O, suggesting that Cl and H_2O are coupled throughout magmagenesis, and Cl/H_2O may be mineralogically or slab determined. REE and LIL on the other hand are scavenged later by the H_2O-Cl fluid. Based on magma fluxes e.g. (NMORB>EMORB+OIB) and Cl and H_2O concentrations (OIB>EMORB>NMORB), the integrated magmatic output has Cl/H_2O nearly equal to seawater. It is thus not possible for magmatism to change seawater salinity over time. It is more likely that seawater salinity controls magmatic Cl/H_2O, through subduction recycling in arcs and the deeper mantle.

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Isotope effects generated during in the NO_x cycle

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The NO_x cycle is the fundemental driver of tropopheric chemistry and results in the prodcution of nitric acid and nitrate aerosols in the atmosphere. Atmospheric nitrate is known to have large ^{17}O isotopic anomalies, which has been hypothesized to be due to interactions with ozone that occurs during NO_x cycling. We have tested this hypothesis by conducting expermeints of isotope effects that occur during NO_x cycling. Using a range of conditions, photolysis cycling produced $\Delta^{17}O$ values that spanned 0-45‰. The range of values could be explained by a competition between NO_x exchange with O atoms and NO_x oxidation by ozone, which is a strong function of NO_x/O_2 ratio in the reaction chamber. Isotopic equilibrium occurs on short times scales and is a function of the light intensity emmitted by the xenon lamp. The data can be quantitatively reproduced using a kinetic model that accounts for exchange and vaious oxidation mechanism. Pressure and tempertaure dependce of NO_x $\Delta^{17}O$ values has also been investigated and is tightly coupled to the temperature/pressure dependence of $\Delta^{17}O$ that arisies during ozone formation. We discuss the implications of the data in the context of understanding chemical kinetics and interpreting nitrate $\Delta^{17}O$ values observed atmospheric aerosols and precipitation.