

Experimental Simulation of Chemical Weathering in the Hadean Eon by Anhydrous and Hydrus HCl Vapor

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Hydrochloric and hydrofluoric acids are the primordial acids. Their presence is virtually guaranteed during cooling of a stellar gas cloud due to the extremely strong covalent bonds of HCl and HF gases. Hydrochloric was the only strong acid ($pK_a >$) present during planetary accretion since the overwhelming presence of hydrogen gas prevented the formation of strong oxyacids such as HNO_3 and H_2SO_4 . Thus, gaseous HCl (anhydrous or hydrus) was the first chemical-weathering agent on the Earth's surface. The immature crust of the Hadean Earth consisted predominantly of olivine, calcic plagioclase, and pyroxene – all of which are unstable in aqueous acid solutions. But what would be their weathering behaviour if subjected to *gaseous* HCl? In very simple experiments we attempted to simulate chemical weathering conditions that existed before the condensation of liquid water onto Earth's newly solidified crust.

To test the efficacy of gaseous HCl as a chemical-weathering agent, two minerals common to the early-formed crust were exposed to HCl vapour at room temperature. The minerals chosen for reaction were an olivine (FO_{84}) and a plagioclase (AN_{72}). Precisely weighed aliquots of these powdered minerals ($<106\mu m$) were exposed separately to anhydrous HCl vapour and hydrus HCl vapour in a vacuum desiccator. In the first experiment, anhydrous HCl vapour was introduced into the desiccator from a liquid-nitrogen cold trap. In the second experiment, hydrus HCl vapour was generated in the desiccator by drawing a vacuum on ^{12}N HCl. The durations of the hydrus and anhydrous experiments were 5 and 12 days, respectively. At the end of each experiment, the samples were removed for evacuation in a separate desiccator and then weighed to the nearest 0.01mg. A weighed aliquot of each reacted mineral powder was slurried with a weighed amount of demonised water to determine the quantity of chloride salts formed.

Table 1 presents the results of both experiments. Much more mass was gained in the hydrus experiment than in the anhydrous experiment. This larger increase in mass was due to formation of hydrated chloride salts. About 25 times more olivine was altered in the HCl/ H_2O experiment as compared with the anhydrous HCl experiment. This is ample testimony to water (even as a vapour) acting as a chemical-weathering facilitator. Between the hydrus and anhydrous experiments, the increase in fayalite moles weathered was an order-of-magnitude more than the increase in forsterite moles weathered. Moreover, both minerals reacted incongruently in both experiments. Plagioclase was less reactive than the olivine in both experiments. We did not analyse the plagioclase leachates for soluble aluminium; hence, we cannot comment whether Al was solubilized to yield aluminium chlorides or whether it formed a clay

by-product. But the plagioclase leachate was dominated by acidity in the form of iron-chloride complexes. After slurrying the weathering product, we noticed that the plagioclase must have had inclusions of magnetite as evidenced by small grains of this mineral clinging to the teflon-coated magnetic stirring bar. It was minor amounts of magnetite, not the plagioclase, which were preferentially altered. This analytical result re-emphasised what was learned from the olivine results – namely, that iron was the most leachable of all the major elements acting as cations in silicate and oxide minerals that were likely to be present in the Earth's earliest formed crust.

The fact that HCl can alter minerals in a waterless vacuum indicates that accreting minerals in the solar nebula were also subject to attack by HCl gas. Thus, all the chloride on Earth did not necessarily arrive in the form of gaseous HCl; anhydrous chlorides of Fe, Na, Ca, Mg, and K were probably coating silicate and oxide minerals in the accreting planetesimals. And unless Earth's first-formed micas and amphiboles had orders-of-magnitude higher concentrations of Cl than their post-Hadean counterparts, then melting of chloride salts on the molten Earth should have partitioned the chloride-bearing cations into silicates and oxides with the attendant release of HCl gas. This HCl vapour, as demonstrated in our experiments, would proceed to chemically alter the minerals in the newly established crust. This event would then be followed by the greatest chemical-weathering assault in Earth's history, once the atmosphere's temperature cooled sufficiently to form hydrus HCl vapour and, ultimately, aqueous HCl.

Reactant	Anhydrous		Hydrus	
	μ moles Altered Per Gram Reactant	Salt Formed Upon Alteration	μ moles Altered Per Gram Reactant	Salt Formed Upon Alteration
Olivine (FO_{84})				
Forsterite	170	$MgCl_2$	3700	$MgCl_2 \cdot 6H_2O$
Fayalite	3	$FeCl_2$	810	$FeCl_2 \cdot 4H_2O$
Plagioclase (AN_{72})				
Anorthite	38	$CaCl_2$	19	$CaCl_2 \cdot 2H_2O$
Albite	6	$NaCl$	24	$NaCl$
Magnetite	22	$FeCl_2/FeCl_3$	210	$FeCl_2/FeCl_3 \cdot nH_2O$

Initial masses of reactants (weighed to the nearest 0.01 mg) were 2.0±0.1 grams.

Table 1. Results of the Anhydrous and Hydrus HCl Weathering Experiments