Unifying Geochemical Scenario for the Origin of a High Cellular Potassium to Sodium Ratio in Living Cells

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Potassium ion is the most common compound in all living organisms, with intercellular $[K^+]:[Na^+]$ ratios greater than 1 across all domains of life. While most natural aquifers are rich in sodium, it is believed that localized potassium-rich environments were crucial for initiating prebiotic reaction networks leading to the origin of life. Several current hypotheses, based on modern geochemical observations, suggest that hydrothermal fields and their associated clays could have provided such environments. My work expands on current prebiotic theories regarding the origins of high potassium concentrations by providing a geochemical basis for the empirical observations proposed by other authors. Here, I show how abiotic enrichment in potassium can occur during the acidic alteration of a wide range of aluminum silicate rocks through the formation of alum salts $(KAl(SO_4)_2 \cdot 12H_2O)$. I further propose how simple and well-known alum chemistry can lead to the accumulation of important biological molecules, such as phosphates, ammonia, and carboxylic acids. I provide a general thermodynamic model, proof-of-concept experiments, and a chemical rationale for the plausibility and importance of potassium-rich environments in the origin of life. This work suggests that potassium enrichment could have been one of the earliest steps in the origins of life, defining the reaction conditions where most prebiotic reactions took place. Since potassium is both the most common and simplest component in all living organisms on Earth, understanding the geochemical conditions that lead to potassium enrichment is valuable for comprehending the origins of life on Earth and the search for life elsewhere in the universe, including on our closest neighbor, Mars.

origins of life | geochemistry| sodium-potassium gradient | membrane potential| astrobiology

Introduction

Biochemistry of Sodium and Potassium

Most of the origin of life research has been focused on prebiotic synthesis of precursors of peptides and nucleic acids, metal sulfides and the rise of reaction networks formed by small molecules. Less widely appreciated is the surprising similarity of the internal composition and smaller components that are common to all living cells, indicating common chemical origins of life, and likely pointing to the environments where life begun. Some of these similarities, named "Chemical Fossils" by George Whitesides are high Potassium to Sodium ratio in all living cells, thiol and thioester chemistry, metal sulfides, isoprenoids and condensed phosphates (Whitesides, 2016).

Potassium is the most abundant cation in the cytoplasm across all domains of life; as a general rule, intermolecular potassium concentration is one or two orders of magnitude larger in living cells compared to non-living environments, where, generally, the predominant cation is sodium. The ratio of potassium to sodium inside the cells is usually much larger than 1, and approximately the inverse of the ratio observed in non-living environments (Table 1). Some organisms, predominantly animals, spend up to 40% of all their energy maintaining this ratio.

Despite very limited chemical activity of potassium, it has numerous functions in living cells: it maintains osmotic pressure of cell interior, it is a necessary cofactor for several oldest highly conserved enzymes, including ribozymes, GTPases and peptidyl transfer units (Danchin, 2019). Potassium channels, responsible for extraction of Potassium from the environment, have been found in all types of living organisms and include $[K^+]/[Na^+]$ ATPases in animals, where

they are the basis of cognition, and conserved families of transporter channels in bacteria, fungi

and plants known as Trk/Ktr/HKT(Corratgé-Faillie et al. 2010).

Table 1. Examples of K^+/Na^+ distribution in living and non-living systems.

	[Na⁺], mM	[K⁺], mM	[K⁺]/[Na⁺]
Living systems			
Animals			
Humans (*Homo Sapiens Sapiens*)	10	135	13.5
Snail (*Planorbis corneus*)	2.4	49.2	20.5
American Cocroach (*P.Americana*)	20	30-98*	1.5-4.9
Bluefish (*Pomatomus saltatrix*)	26.0	95.0	3.65
Plants			
White beans (*Phaseolus vulgaris*)	7**	460**	60
Bamboo	2.1**	136**	65
Kelp (*Saccharina japonica*)	22.8**	101**	3.65
Rice	0.15**	1.69**	11.26
Fungi			
Yeast (*Saccharomyces cerevisiae*)	22**	245**	11.13
Shitake mushroom (*Lentinula edodes*)	4**	78**	19.2
Slime mold (*Physarum polycephalum*)	8.6	32	3.72
Bacteria			
Staphilococus Aureus **(Gram positive)**	64	708	11.06
E. coli **(Gram Negative)**	o.49•[Na+]ext	150-465***	>1
Salinabacter ruber **(Halophilic)**	0.38	0.60	1.58
Spirulina (*Arthrospira platensis)***(Cyanobacteria)**	42**	32**	0.78
Archea			
Halococcus morrhuae	3170	2030	0.64
Halobacterium Salinarium	1370	4570	3.35
Non-living systems			
Sea water (mean value)	464	12	0.026
Dead Sea	1410	155	0.11
Thermal vents	10-1000	1-60	0.04-0.1
Crater lakes (pH<1.5)	1-40	1-45	0.1-2
River Water (estimation)	0.26	0.07	0.3

*Varies during development stages
** in mmol/kg dry weight
*** Increased with increase of osmolarity of the medium

In 2012 Mulkijanian *et al.* provided strong arguments, based on analysis of evolution of oldest enzymes, in favor of life starting in potassium rich environments rather than evolving to use potassium later on (Mulkidjanian et al. 2012). These and several follow up papers pointed out that modern hydrothermal fields sometimes produce vapor enriched in potassium that potentially, and condensation of the vapor could lead to potassium rich environments where life started. An alternative approach to the potassium-rich environments have been suggested by H. Hansma, who pointed out that biotite micas are usually rich in potassium and magnesium, and small, nanosized compartments between the mica sheets could have been assembly points of early Earth polymers (Hansma, 2022). Since biotite mica formation is associated with volcanic fields and rock weathering in general, this hypothesis can be seen as co-existing with Mulkijanian ideas.

Sodium and Potassium are small alkaline cations; they do not have any strong catalytic activity in aqueous reactions, and have been usually considered as counter ions, equilibrating negative charges of "more interesting" molecules. Because of their remarkable different role in living cells, Bracher's group have studied their role in prebiotic chemistry, to find chemical basis of this difference. His group have shown that sodium and potassium salts have distinct activity in peptide condensation reactions, with potassium favoring linear peptide formation, vs. cyclic peptides favored by sodium (Campbell T.D., 2019).

Instead of trying to find out the set of primordial reactions responsible for the selection of potassium, I would like to point out to the simple thermodynamic differences based on the solubilities of their salts. While the inorganic salts, such as chloride, sulfate and nitrate have very similar solubility for both cations, potassium salts of biologically relevant anions, such as

phosphates, oligophosphates and carboxylic acids are almost an order of magnitude more soluble than sodium salts (Table 2). Given that some of the early prebiotic reactions could have happened in very concentrated solutions, created either by wet-dry cycles or molecular crowding in the presence of early prebiotic polymers, an order of magnitude higher concentration of the reagent can lead to 10x increase in observed reaction rate, which would make a big difference in early selection processes. However, concentrations of organic acids as phosphates are presumed to have been very low on early Earth and a mechanism of enrichment for these compounds has to be proposed first. Since potassium is much more abundant geochemically, finding potassium rich environments seems to be a more straightforward starting point.

Table 2. Chemical solubility of salts of sodium and potassium in g/100mL water at 25°C. Last row in bold shows solubility of alum salts, used for cation separation in this study.

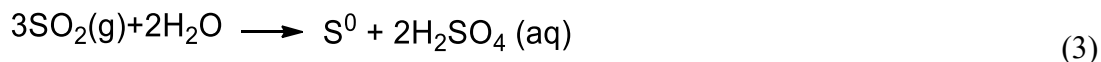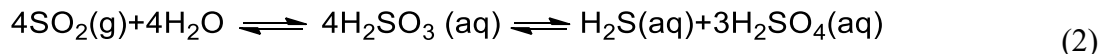| Anion	$[K^+]$, g/100mL	$[Na^+]$, g/100mL
$H_2PO_4^-$	86.9	22.6
HPO_4^{2-}	150	7.7
PO_4^{3-}	92.3	12.1
$P_2O_7^{6-}$	187	6.7
Acetate	256	46.4
Oxalate	36.4	3.41
Formate	337	81.2
Succinate	46	3.2
HCO_3^-	33.7	9.6
CO_3^{2-}	111	21.5
Cl^-	34.2	35.9
NO_3^-	33	87.6
SO_4^{2-}	120	28.1
$Al(SO_4)_2 \cdot 12H_2O^-$	**14**	**250**

The best way to do it is by first understanding the sources of alkaline cations in natural waters. Both sodium and potassium in natural waters come from the chemical weathering of common crustal rocks, igneous and sedimentary, such as granites, basalts and shales(Kastner

1974). Feldspars are common mineral components of most crustal rocks; sodium rich feldspars (enriched in albite, $NaAlSi_3O_8$, ΔG^0 = -884.0 kcal/mol)(Huang 1974) are formed at higher temperatures than potassium feldspars (K-spare, $KAlSi_3O_8$, ΔG^0 = -892.6 kcal/mol)(Huang 1974) and weather out faster, eventually producing ground water with $[Na^+]>[K^+]$. Feldspar weathering occurs as a reaction with ground waters saturated with respect to the atmospheric CO_2 with resulting low concentrations of sodium and potassium in aqueous solution (< 1 mM at environment temperature).

$$2Na(K)AlSi_3O_8 + 2CO_2 + 11\ H_2O \rightleftharpoons$$

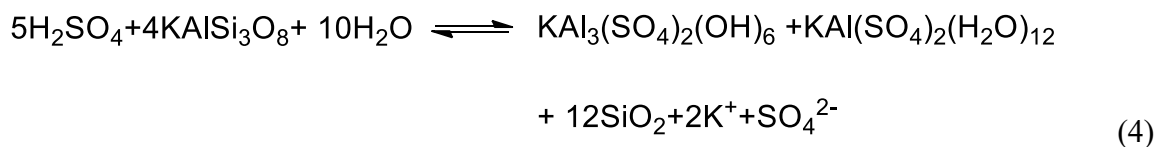$$Al_2Si_2O_5(OH)_4 + 2Na^+(K^+) + 2HCO_3^- + 4\ H_4SiO_4 \qquad (1)$$
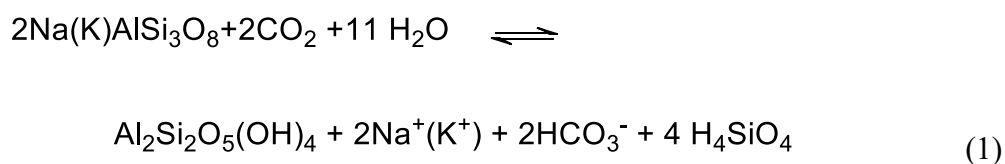
In case of potassium-rich volcanic lakes proposed by Mulkijanina et al, the weathering of rocks follows different mechanism and is the result of leaching K-enriched volcanic rocks by ultra-acid volcanic waters (Varekamp 2015).

Rocks at volcano-hydrothermal fields undergo acidic alteration (White 2013). Alteration means interaction of an aqueous solution with rock when a set of igneous minerals, formed at high temperature and unstable at the Earth's surface, dissolves and a new set of stable low-temperature-pressure minerals is formed. When aqueous solutions are acidic, the set of stable minerals are rich in aluminum and includes aluminum sulfates, aluminum hydroxides and a number of clay minerals enriched in aluminum and silica, including mica and biotite. Common sources of acidity are magmatic HCl and sulfuric acids. The latter is formed in condensed magmatic vapors by aqueous redox-disproportionation of the absorbed magmatic SO_2 according to the reactions (2) and (3):(Kusakabe et al. 2000)

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$$4SO_2(g)+4H_2O \rightleftharpoons 4H_2SO_3 \text{ (aq)} \rightleftharpoons H_2S(aq)+3H_2SO_4(aq) \tag{2}$$

$$3SO_2(g)+2H_2O \longrightarrow S^0 + 2H_2SO_4 \text{ (aq)} \tag{3}$$

Sulfuric acid can react with aluminosilicate matrix of rocks, and form aluminum sulfate salts alum and alunite, for example:

$$5H_2SO_4+4KAlSi_3O_8+ 10H_2O \rightleftharpoons KAl_3(SO_4)_2(OH)_6 +KAl(SO_4)_2(H_2O)_{12}$$
$$+ 12SiO_2+2K^++SO_4^{2-} \tag{4}$$

There is a set of Al-sulfate minerals with different solubility in water, and thus can undergo precipitation-based separation proposed in the previous step. The most recent estimations of their thermodynamic properties (Stoffregen et al. 2000) have confirmed that Na-alunite ($NaAl_3(SO_4)_2(OH)_6$) is about two orders of magnitude more soluble than alunite ($KAl_3(SO_4)_2(OH)_6$), and alum ($KAl(SO_4)_2 \cdot 12H_2O$) (Table 2).

A two-stage mechanism based on alum formation can be proposed for the K^+-enrichment of an aqueous solution: (1) aluminum oxide and sodium and potassium cations are extracted from aluminosilicate rocks in the presence of sulfuric acid; (2) formed solution is slowly evaporated allowing formation of sodium and potassium alum salts; (3) soluble sodium salts are removed by stepwise washing of the solution with neutral water; (3) the remaining less soluble potassium alum salts are re-dissolved with fresh rain or ground water of low ionic strength, forming potassium rich lakes or pools (Figure 1).

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Figure 1. Mechanism of potassium enrichment proposed in the paper. Acidic alteration of wide range of aluminosilicate rocks results in formation of aluminum sulfate salts of sodium and potassium (alums), which remarkably different solubility creates neutral potassium rich pools surrounded by acidic sodium rich environment.

Results

First part of this work shows potassium enrichment possibility via thermodynamic calculations with volcanic rocks of different composition: basalts and rhyolites. Second part demonstrates viability of proposed approach by achieving cation separation using pure ß-Al$_2$O$_3$ oxide as well as igneous and metamorphic rocks with different degree of alteration. Both theoretical and experimental approaches suggest that potassium alum can achieve potassium over sodium enrichment comparable to those found in modern intercellular environments.

Formation of Potassium- Rich Environments: Thermodynamic Calculations

To find the optimal conditions for separation of sodium and potassium we used water rock titration method (Hedenquist & Taran 2013). Specifically, in this calculation, to 1kg

aqueous solution of 0.1M sulfuric acid at 25°C were added isothermally small portions of rhyolite or basalt rocks and allowed to reach equilibrium after each step (Table 3). We excluded Mg^{2+} from the calculations for the sake of simplicity, since Mg^{2+} sulfates are highly soluble and will remain in aqueous phase. Here we present results for basalt. Results for rhyolite were very similar and are included in SI.

Table 3. Chemical composition of the simplified rhyolitic and basaltic rock used in modeling (wt.%, without Mg)

	Rhyolite	Basalt
SiO_2	76.0	52.4
Al_2O_3	12.5	18.2
FeO	2.5	8.0
Fe_2O_3	1.0	4.6
CaO	3.1	10.7
Na_2O	4.1	5.0
K_2O	1.2	2.1

The rock to water weight ratio varied from 1/1000 to 1/10, and the source of all chemical species except sulfate, including $[Na^+]$ and $[K^+]$, was the rock itself. The equilibrium set of minerals and the associated aqueous solutions as a function of rock-water ratio at 25°C is shown in Figure 2.   In a region at rock/water ratio ~ 20 g/kg supernatant has a high Al^{3+}, Na^+ and K^+ concentrations. We selected a composition of the solution with maximum Al^{3+} and K^+ concentration at r/w = 16 g/kg and modeled it's evaporation by stepwise loss of vapor and increase in concentration of all components that resulted in precipitation of new minerals. Precipitation started after ~50% of the vapor loss with silica, alum and anhydrite phases. In the region corresponding to 50-90% evaporation, alum is a predominant K-bearing salt. Sodium-rich minerals, such as highly soluble Na_2SO_4 occur only at the end of the evaporation, when the solution has lost more than 92% of water vapor (Figure 2).

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To form a potassium rich environment, we equilibrated 60 g of the precipitated mineral mixture from the previous step, consisting of ~70 wt% of alum, 20 wt% of amorphous silica and 7.5% of anhydrite and less than 0.1 wt% of Na^+ salts, with 1 kg of pure water. The resulting solutions are practically Na-free with a final K^+/Na^+ ratio >300 for the rhyolite mixture and K^+/Na^+ ratio > 30 for the basalt mixture.
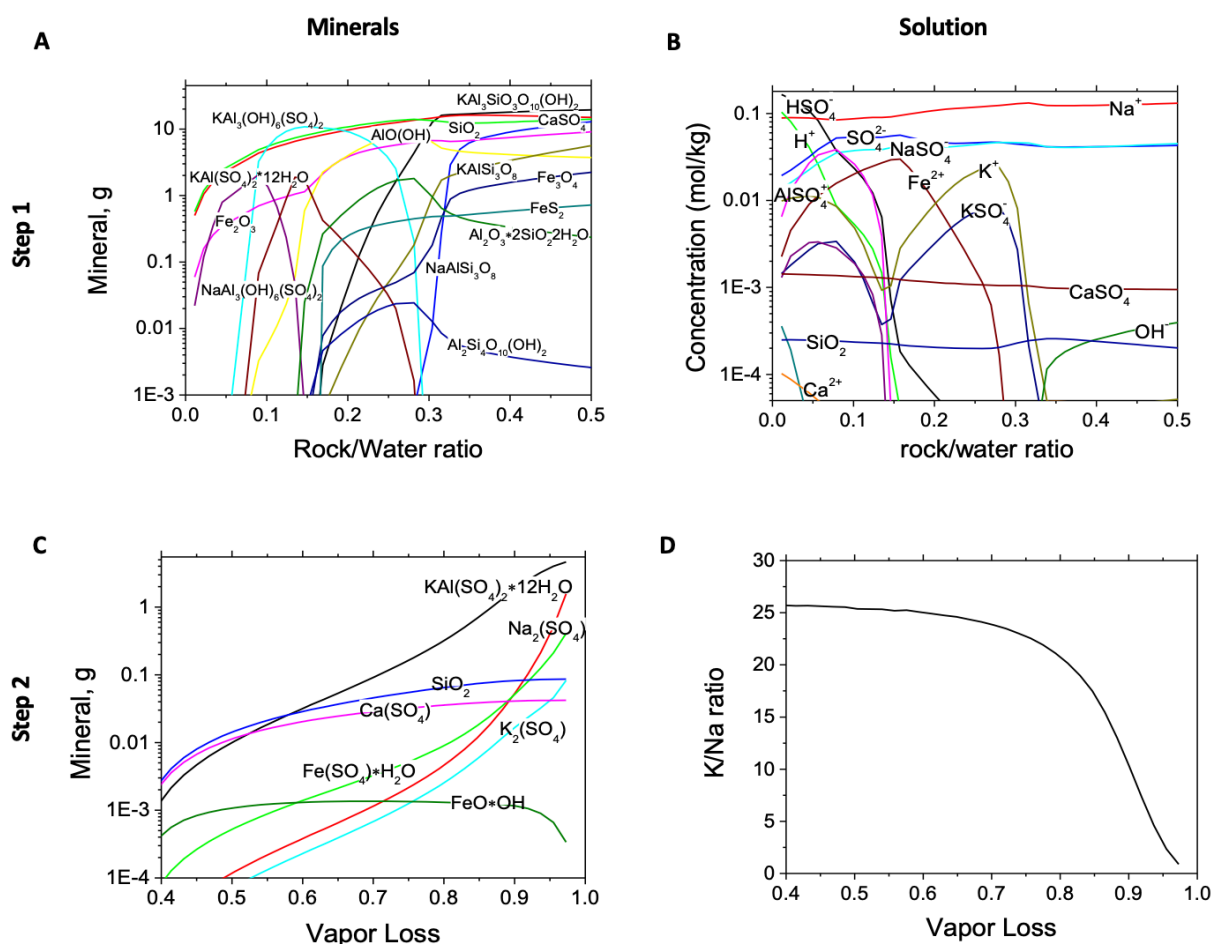

Figure 2. Thermodynamic analysis of two-step potassium enrichment mechanism. **Top row:** granite rock reacts with sulfuric acid, resulting information of secondary minerals (left) and supernatant rich in sulfates, aluminum and alkaline and alkaline-earth cations (right). **Bottom row:** supernatant resulted from initial basalt-acid interactions precipitates, forming set of

secondary minerals (left). Equilibration of these minerals with pure water results in potassium-rich solution over wide range of water concentrations (right).

Experimental Formation of Potassium-Rich Solutions via Rock Leaching and Evaporation cycles.

To simulate water rock interactions on Early Earth we conducted leaching of several igneous and metamorphic rocks of variable aluminum content. We added acidic sulfate solutions with pH 1and $[K^+]/[Na^+]$ ratio 1:5, which is close to the upper limit of natural potassium rich waters, to finely crushed rocks with the initial water to rock weight ratio 10:1 and left the mixture to evaporate at controlled relative humidity under nitrogen atmosphere. We observed that most consistent results were obtained at relative humidity 20 to 30%. At lower humidity sodium sulfate tended to "creep" (Van Enckevort & Los 2013) out of solution and precipitate outside the wells where evaporation took place.

We equilibrated the solution with the rocks for one month, followed by 3 days of evaporation. Large transparent orthogonal crystals up to 1 cm in diameter usually appeared when 90% of the solution had evaporated (Figure 2A). Rates of formation of alum crystals were the fastest for zeolites, and the slowest for basalt and layered clays. Crystals were collected, weighted to calculate yield and analyzed by XRD analysis with subsequent database search that confirmed the formula $KAl(SO_4)_2 \cdot 12H_2O$, corresponding to alum (Table 3, Figure 5 and SI). To demonstrate the formation of potassium-rich environments, we decanted supernatant, briefly washed remained solids with distilled water, re-dissolved the solid in fresh portion of distilled water, and took aliquot of solution for the subsequent ICP analysis (Table 5). Potassium content of resulting solutions was broadly correlated with aluminum content of the minerals.
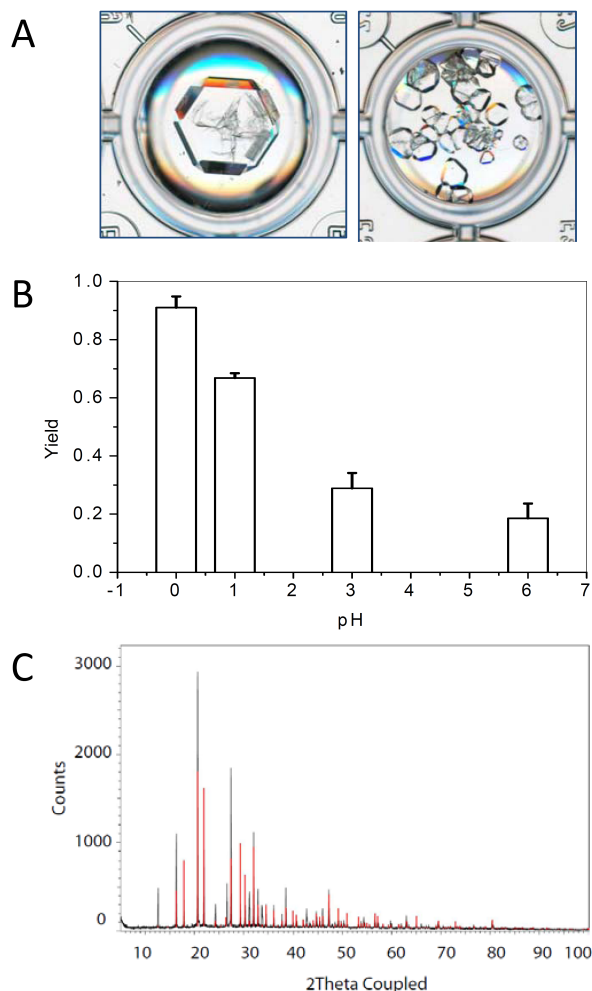
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Figure 3. (A) Formation of potassium aluminum sulfate (alum) crystals from solution of K_2SO_4/Na_2SO_4 1/5 in presence of $Al_2(SO_4)_3$ at the bottom of the plastic well in the 96-well plate, 5 mm wide; (B) Yield as a function of pH of K-alum obtained from 1:1 K^+:Na^+ solution and β-Al_2O_3 solid. (C) Alum formation on palygorskite clay confirmed by XRD of the crystal (thin lines) and synthetic alum spectra from the database (thick lines).

Further study using β-Al_2O_3 as a solid reactant showed that formation of alum crystals depends on pH of the solution. Yield of the alum crystals precipitated from the 1:1 K^+:Na^+ aqueous solution decreased with increase in pH (Figure 3B).

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Table 4. ICP analysis of K^+:Na^+ ratio of the crystals collected from the surface of different minerals after complete evaporation of the solvent with initial 1:5 K^+/Na^+ ratio

Mineral Chemical formula (when known)	Type of mineral	Al:Si ratio in mineral	Yield, % of $KAl(SO_4)_2 \cdot 12H_2O$	K+/Na+ final ratio *
Aluminum Oxide Al_2O_3	Synthetic	1:0	**74±3**	1:0
Molecular Sieve 3A $2/3K_2O*1/3Na_2O*Al_2O_3*2SiO_2*9/2H_2O$	Zeolite	1:1	**35±6**	34:1
Stilbite $(Na, Ca, K)_6(Al_8Si_{28}O_{72})*nH_2O$	Zeolite	1:4	75±3	1:0
Bentonite Mixture of $Al_2(Si_2O_5)(OH)_4$ (Kaolinite) and $(NaCa)_{0.33}(AlMg)_2(Si_4O_{10})(OH)_2nH2O$ (Montmorillonite)	Mixture of clays	1:1 to 1:2	5±1	10:1
Palygorskite $(Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$	Layered clay	1:2	7±1	7:5
Basalt Rock composed of minerals and glass with approximate composition of 45–55 wt% SiO_2, 2–6 wt% total alkalis, 0.5–2.0 wt% TiO_2, 5–14 wt% FeO and 14 wt% or more Al_2O_3	Igneous rock	1:3	11±5	8:1

* Determined by ICP analysis as described in the text. Practical detection limit based on calibration curves was at 1/50 K^+/Na^+ ratio.

To link this work with current visionof high potassium environment I obtained alum from reaction of basalt powder and sulfuric acid. Experimental basalt weathering led to the formation of biotite mica (Figure 4) as one of the major decomposition products. These results link proposed model with broader observations made by Hansma and Dibrova;
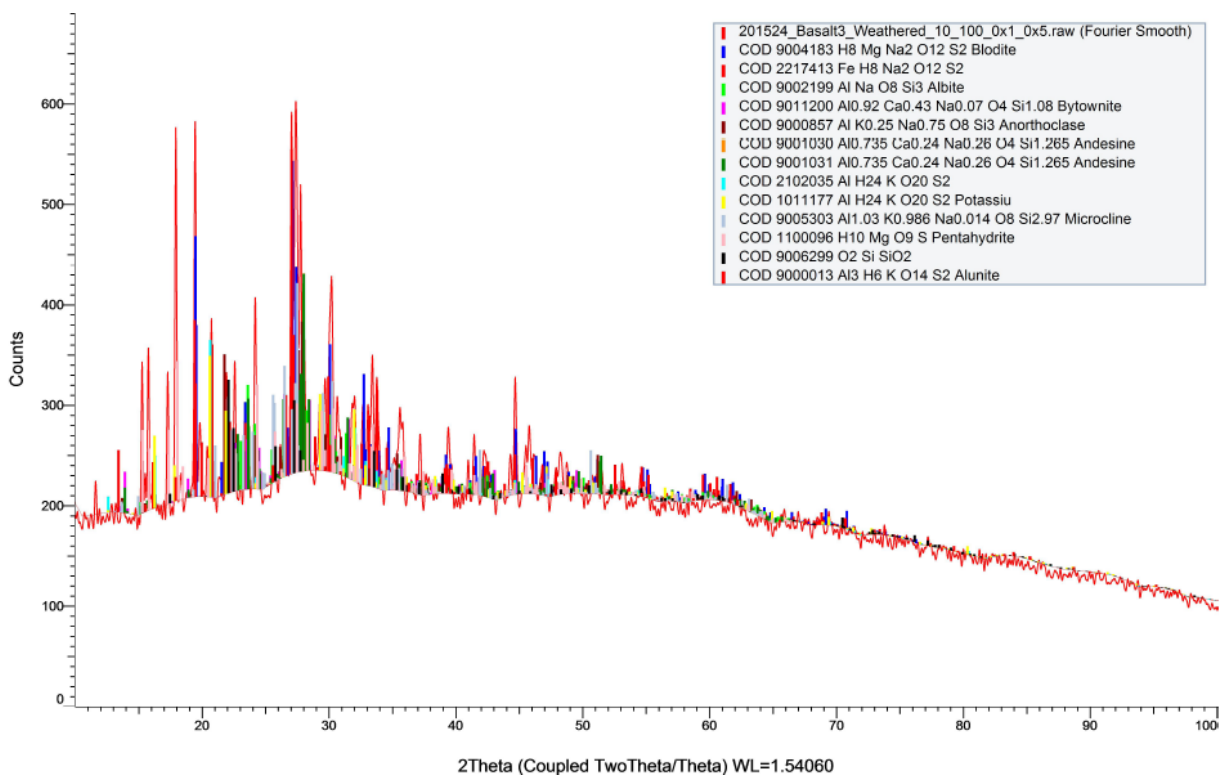
Mineral	Formula	Composition
Biotite (Mica)	$H_8MgNa(SO_4)_2 \cdot 4H_2O$	13.79
Andesine	$FeNa_2(SO_4)_2 \cdot 4H_2O$	10.2
Bytownite	$Al_{0.92}Ca_{0.43}Na_{0.07}O_4Si_{1.265}$	9.79
Microcline	$Al_{1.03}K_{0.986}Na_{0.014}O_8Si_{2.97}$	9.38
Pentahydrite	$MgSO_4 \cdot 5H_2O$	8.17
Albite	$NaAlO_8Si_3$	8.07
Anorthoclase	$K_{0.25}Na_{0.75}AlSi_3O_8$	4.08
Potassium Alum	$KAl(SO_4)_2*12H_2O$	3.96
SiO2	SiO_2	2.58
Alunite	$KAl_3(SO_4)_2(OH)_6$	1.60

Figure 4. Residual minerals formed after weathering of basalt (after removal of alum and complete water evaporation)

We observed that crystallization took place at low temperatures. To examine the influence of temperature on potassium enrichment, we performed the reaction in boiling water,

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simulating hydrothermal environments. At this temperature aluminum sulfate salts decomposed producing a mixture of sulfates of both cations with no enrichment in potassium.

Conditions used in these experiments are mild temperature, temperatures (20-70 $^{\circ}$C), dry atmosphere (humidity below 30%, to allow evaporation), volcanic activity with SO_2 rich fumaroles as a source of sulfuric acid, and periodic rain and draught seasons. This fits well with the field observations on oldest zircons, which were formed at mild temperatures and were found incrusted in bed of strongly weathered clays(Wilde et al. 2001).

Discussion

Spontaneous formation of potassium rich solutions fits within the other processes and reactions already explored in different origin of life scenarios. Evaporation and re-dissolution processes described here have been used extensively in the origins of life research, including the formation of vesicles made of fatty acids,(Deamer et al. 2006) phosphorylation of sugars(Powner et al. 2009), polycondensation of RNA,(Da Silva et al. 2015) amino acids(Hosni et al. 2015) and carboxylic acids.(Forsythe et al. 2015). We also observe biotite formation that has been highlighted as a potential potassium-rich assembly hub for prebiotic macromolecules by Hansma (Hansma, 2022), thus consolidating different views on origin of potassium.

Aluminum oxide is the key component in proposed mechanism of potassium enrichment. Despite the ubiquity of aluminum and sulfates, there is no known organism that actively uses them: the most common anions used by living organisms are phosphates and carboxylic acids. Since none of those are abundant on a geological scale[26] a mechanism for concentration of these salts had to exist. Potassium alum has been used historically to concentrate and precipitate diluted solutions of organic molecules by neutralizing negative charge and allowing big portions of organic molecules to coagulate. Several plausible routes to prebiotic organic molecules over

the years have been proposed: mainly, the delivery of organic carbon by carbonaceous chondrite meteorites and CO_2 condensation in reductive environments. In both cases carboxylic acids and sometimes alcohols and sugars are common products are observed in low concentrations. Precipitation with alum salts would be a plausible concentration mechanism for the organics produces vie either pathway.

In addition to the enrichment in potassium and ammonium, acid leaching and subsequent evaporation of brines could have facilitated the concentration of phosphates. The main source of phosphates is apatite ($Ca_{10}(PO_4)_6(OH,F,Cl)_2$, present in igneous rocks at 0.1-1 wt%[0]. During rock's leaching with sulfuric acid, apatite is dissolved, calcium is trapped as anhydride ($CaSO_4$) and phosphoric acid is liberated. The same leaching mechanisms that led to potassium accumulation could facilitate phosphate extraction from apatite bearing rocks. Phosphate can react with aluminum sulfate and form insoluble precipitate with aluminum oxide[30] which ca be re-dissolved in solutions of di and tricarboxilic acids[31].

Apart from anion concentration, potassium cations are close in size to ammonia cations and can be partially substituted by the later in alum and alunite crystalline structures[29]. Ammonia is less abundant in rocks than potassium and probably its minerals could be found as trace minerals in larger potassium alum deposits. Ammonia salts are often found around volcanic lakes: ammonium alunite has been reported in volcanic gas sublimates at Vulcano volcano.

Another key players in prebiotic reaction are metal sulfides. Metal- sulfur clusters are among oldest coenzymes found in all living organisms and there is a general agreement that they origins were mineral, probably beginning from biomineralization of iron sulfides, such as pyrites.[35] Pyrite is common in volcanic environment, and it was observed in all modeling experiments where it is formed during rock weathering with high rock/water ratios (Figure 2A).

In practical terms it means that if potassium rich pond is formed from discharge of acidic spring, the shores, where water to rock ratio is the lowest, would be enriched in pyrite.

Components that we suspect to be building blocks for the first cells could have been found in abundance in potassium alum rich environments, resolving a *concentration problem*, pointed out by de Duve and Miller[36][37] that inevitably arises in other prebiotic chemistry scenarios. We suggest that the possibility of formation of such environments could be an indicator of habitability of the planet.

Alum has been observed at southern highlands of Terra Sirenum on Mars, and has been suggested an indicator for previous life on Mars.[38] It would be interesting to establish K^+/Na^+ ratio of these mineral deposits (for example, from degree of efflorescence during changes in temperature). Potassium rich deposits could indicate if Mars ever had rains and periodic changes in the levels of liquid water necessary to accumulate important prebiotic molecules for further steps in the origins of life.

Conclusions

Potassium is a major constituent of all living organisms and it has been previously suggested that life started in potassium rich environments, which are uncommon due to higher abundance of chemically similar sodium ion. We have shown that during the multistep acidic alteration of basalt and rhyolite – two of the most common components of the Earth's crust - the resulting eluent is enriched in potassium via formation of poorly soluble alum mineral. Evaporation and equilibration processes, necessary for the enrichment of potassium are often used in origin of life studies for synthesis of a range of biomolecules and well-known alum chemistry could have led to accumulation of other prebiotic molecules, such as phosphates,

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carboxylic acids, iron sulfides and ammonium. Both chemical and geochemical reactions might well have converged early, in which case environments with high potassium concentrations or high K^+/Na^+ ratios would be the signatures of life or processes related to its origins.

Experimental

Thermodynamic Simulations:

We modeled water-rock interaction using the HCS-7 thermochemical computer code (HSC Chemistry(Roine 2007), www.outotec.com). Thermodynamic data for most aqueous species and minerals in the HSC database were taken mainly from SUPCRT92(Johnson et al. 1992) updated to SUPCRT95. Data for some aqueous species and minerals was compiled from other sources, up to 2005(Sverjensky et al. 1997). We simulated weathering of two types of common igneous rocks with the composition of each rock provided in Table 1: generalized rhyolite (volcanic rocks rich in SiO_2, poor in iron and magnesium oxides) and generalized basalt (volcanic rocks rich in iron and magnesium oxides). Magnesium was excluded from the set of main components for the reason of simplicity and because at low temperature and under acidic conditions its minerals are unstable and all magnesium transferred into the aqueous phase.(Giggenbach 1988)

The prebiotic chemistry experiments are conducted across a wide range of temperatures, from -20 to 100 ^{o}C, however the results of the analysis of the isotopic composition of Acasta Gneiss zircons suggest that early Earth had temperate surface temperatures (20 ^{o}C) during the times of life's origins.(Wilde et al. 2001) After taking into account this information we chose to perform the simulations at 25 ^{o}C.

Evaporation Studies:

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Molecular Sieve 3A 8-12 mesh beads were obtained from EM Science; Al_2O_3, K_2SO_4, Na_2SO_4 GR ACS from EMD; Kaolin USP from Sigma; Montmorillonite K10 from Aldrich; other minerals were obtained from WARD's Natural science Geology Study pack.

In typical experiment acidic sulfate brine, pH 1, 1:5 to 1:10 [K+]/[Na+] ratio, was added to finely-ground solids, with 10:1 initial water to rock ratio. Solutions were equilibrated up to one month (monitored by change in pH), sometimes addition of distilled water to maintain the same water level was necessary. After equilibration, 90% of water was evaporated, thereby causing potassium aluminum sulfate salts to crystallize out of solution.

Formed crystals were collected, weighted (yield reported as an average of 3 independent experiments) and characterized by XRD (D2 Phaser); remaining liquid was decanted, solid washed with distilled water, decanted, fresh solid added and 200 µL of supernatant placed into 15 mL Falcon tubes, dissolved in 10 mL with 2% HNO_3 and [K+]/[Na+] ratio was analyzed by ICP-AES in radial mode (ICP AES Leeman Labs PS-1000). Concentrations were calculated from calibration curves.

Acknowledgement

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