



Article

Potassium and Metal Release Related to Glaucony Dissolution in Soils

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Abstract: Plant nutrients such as potassium (K) may be limited in soil systems and additions (i.e., fertilizer) are commonly required. Glaucony is a widely distributed and abundant marine-derived clay mineral present in soils worldwide which may serve as a source of potassium. The South Island of New Zealand contains numerous deposits of glaucony-rich rocks and related soils providing an opportunity to explore how glaucony might be a beneficial source of potassium. Here, the geochemistry of glaucony and its suitability as a mineral source of soil K from four deposits in New Zealand was examined using spatially resolved chemical analyses and dissolution experiments. Geochemical and morphological analyses revealed that glaucony from all deposits were K-enriched and were of the evolved (6%–8% K₂O) to highly evolved type (>8% K₂O). Glaucony derived from growth inside pellets contain elevated K and Fe concentrations compared to bioclast-hosted glaucony. Solubility analysis showed that K was released from glaucony at rates higher than any other metal present in the mineral. Additionally, decreasing the pH and introducing an oxidizing agent (i.e., birnessite which is ubiquitous in soil environments) appeared to accelerate K release. Trace metals including Cr, Zn, Cu, and Ni were present in the solid phase analysis; however, further investigation with a focus on Cr revealed that these elements were released into solution at low concentrations and may present a source of soil micronutrients. These results suggest that glaucony may offer a source of slow releasing K into soils, and so could be used as a locally sourced environmentally sustainable K resource for agriculture, whether in New Zealand or worldwide.

Keywords: glaucony; potassium; fertilizer; geochemistry; chromium

1. Introduction

Potassium (K) is an essential macronutrient for plant growth and is involved in essential biochemical processes in plants [1–3]. In soils, a majority of K is present in unavailable/nonexchangeable mineral forms such as feldspars and micas. Potassium that is bioavailable may be present as exchangeable K adsorbed onto soil colloids or in soil solutions. Soil solutions contain the most readily available source of K for plant uptake; however, K may be leached from the system and is dependent on a dynamic equilibrium with exchangeable/adsorbed potassium. Vegetation is largely dependent on the supply of exchangeable K which is directly related to the rate of transformation of K-containing minerals (i.e., feldspars and micas) [4–7]. In undisturbed soils, K availability and supply is generally not a concern, especially when the soils contain abundant mineral sources of potassium. When soils are utilized for agriculture, the relationships between nonexchangeable, exchangeable, soil solution K, plant uptake, and harvesting may result in an imbalance where K is being removed faster than it can

be supplied. This means that crop yields may not be adequately supplied with K resulting in soils that are K deficient.

In soil systems, the addition of fertilizers becomes necessary to avoid K deficiency in plants. Demand for K fertilizer is currently satisfied by mineral salts bearing high elemental concentrations of K [8]; however, the global requirement for K is expected to increase in the short-term future. Between 2012 and 2018 demand for K was expected to increase by 2.8% per year to 34 Mt, faster than demand increases for both P (1.9% p.a to 46 Mt) and N (1.5% p.a to 120 Mt) fertilizers [9]. Investigations into K-rich minerals may provide alternative fertilizer resources to benefit the agricultural industry.

Glaucy is an abundant, K- and Fe-rich clay mineral present in many marine-derived rocks. Deposits of glauconitic minerals are found in many countries including North America [10], India [11], Australia [12], and New Zealand [13,14]. Glaucy forms during periods of low sedimentation to the seafloor, and common environments for precipitation are on the inner-shelf to shelf-break in water depths between 50–500 m [15,16]. The precipitation of glaucony involves crystallites infilling host grains which are often faecal pellets or bioclast tests, but may also include clays, micas and quartz [11,16]. Over time, glaucony matures both chemically and structurally as K increases in concentration as the interlayer cation [15,17], and rocks containing glaucony may be terrestrially emplaced. The high K content of the clay mineral makes glaucony a beneficial source of K in soils and appealing as a soil conditioner for agricultural systems. Additionally, glaucony has been used in other applications including the removal of heavy metals from aqueous solutions, dating minerals and rocks, and to obtain lightweight aggregate [18–20].

Glaconitic minerals have been used as a K fertilizer in the past, and agricultural land containing indigenous glaucony is usually very fertile [17]. Historical accounts of using ‘greensands’ (rocks containing >50% glaucony) to enhance crop productivity date back to the 1760’s, when agricultural land in the northeast of North America showed long-term improvements following additions of glauconitic marls [21]. Glaucy is not commonly used in modern agriculture; however, it has been considered as an alternative form of potash (K_2O -derived from minerals) in many areas. In India, 3000 Mt of indigenous glauconitic sandstone has been identified which could offer an affordable, locally-derived source of slow releasing potash fertilizer [22]. The agricultural industry in Brazil is currently trying to decrease its reliance on imported potash and is using verdete, a metamorphosed greensand with 8%–10% K_2O which provides a slow release of K and other nutrients, while removing the issue of chlorinization associated with potassium chloride (KCl) [23]. In the Perth Basin of Western Australia, Potash West is developing a large (2119 km²) shallow deposit of greensand and phosphate rock with the intention of producing potash and superphosphate as commercial fertilizer products [12].

The South Island of New Zealand contains significant deposits of glauconitic minerals which potentially offers a source of K to the soils derived from glaucony-rich rocks and related sediments and as a natural additive for the agricultural industry. Glaucy deposits from the South Island have been the focus of chemical [13,14] and stratigraphic research [24]; however, no investigation into how glaucony may be beneficial to soils including its application to soils has been conducted. The key aims of this research are to assess the chemical variations between different deposits of glaucony and to determine the solubility of glaucony, both in terms of whether different deposits release K in different ways and whether there are concerns or benefits related to other elements released from glaucony into solution and soil systems. Additionally, birnessite, a common soil oxidizer, was used in dissolution experiments in order to discern if it may have any effect on element release, specifically focusing on the trace element Cr which is commonly enriched in glaucony.

2. Mineralogy of Glaucy

The general formula for glaucony is $K_{(x=y)}(Si_{4-x}Al_x)_{-4}(Fe^{3+}, Al, Mg, Fe^{2+})_{-2}O_{10}(OH)_2$ (where x is 0.2–0.6 and y is 0.4–0.6) [25]. Precipitation occurs as crystallites infill the pore spaces within sedimentary host grains or in porous structures on hard ground surfaces [15,25]. Parent grains can be composed of a range of materials including faecal pellets, bioclasts, silicate minerals, and clay minerals [17].

Pore spaces within granular particles provide a semi-connected micro-environment which creates passageways for the exchange of ions between ambient sea water, the interstitial fluids of the underlying sediments and the local chemical environment within the parent material itself [15]. As glauconitization proceeds inside the grain, so does dissolution of the parent material, eventually breaking the parent grain through cracking, fissuring, or displacement of pre-existing planes of weakness [25].

The terms maturation and evolution are often used to describe the mineralogical nature of glaucony. Potassium is regarded as the key indicator for the maturity or evolutionary state of glaucony, where K enrichment represents more mature minerals than K depleted grains. Chemical maturation involves the progressive enrichment in K and Fe with depletion in Al. Structurally, immature glaucony occurs as Fe-rich smectite clays which are pale green in color. As grains mature and incorporate K as the interlayer cation they evolve into minerals with illite to micaceous structures and appear as dark green to black colors. The maturity of glaucony is classified as nascent (<4% K₂O), slightly evolved (4%–6% K₂O), evolved (6%–8% K₂O) and highly evolved (>8% K₂O) [15,16]. Variations in mineral chemistry and structure have resulted in the terms ‘glaucony’ and ‘glauconitic minerals’ being used to describe the mineral as a facies, with the term ‘glauconite’ being reserved for grains with >6 weight % K₂O and micaceous structures [15–17,26].

3. Materials and Methods

3.1. Field Work and Sample Collection

Field work was undertaken in March 2014 at Oamaru, the mid-Waipara River, and the Oparara Quarry in Karamea. Samples were collected from all units containing visible glaucony. In weakly indurated rocks, fresh samples were collected by removing the outside 10–20 cm of weathered rock. The subscripts WP, OP, EQ, RF, CB, and GB represent Waipara, Oparara, Earthquakes, Ross Farm, Campbell’s Beach, and Gee’s Beach, respectively. GPS measurements were recorded where samples were collected (Table 1).

Table 1. Summary of outcrops and units sampled for geochemical analysis with glaucony % of bulk sediment by volume and dominant host material interpretations.

Outcrop	Samples	Units Sampled	Glaucony %	Dominant Host Grain
Earthquakes (44.87510° S, 170.62227° E)	EQ	Kokoamu Greensand; Otekaike Limestone	25–40; 10	Pellet + Trace Vermicular
Ross Farm (44.88038° S, 170.73837° E)	RF	Kokoamu Greensand	20–80	Pellet + Trace Vermicular + Bioclast
Gee’s Beach (45.16936° S, 170.90735° E)	GB	Gee Greensand	40–50	Bioclast + Pellets + Trace Vermicular
Campbell’s Beach (45.16938° S, 170.90730° E)	CB	Gee Greensand	50–60	Bioclast + Pellets + Trace Vermicular
Waipara (43.065121° S, 172.650291° E)	WP	Waipara Greensand	40–65	Pellets + Amorphous Grains
Oparara Quarry (41.215781° S, 172.145864° E)	OP	Stoney Creek Limestone	10	Bioclasts + Amorphous Grains

3.2. Sample Preparation

Weakly indurated samples were disaggregated by hand in warm water. Loose sediments were then wet sieved into 1000–500 µm, 500–212 µm, and 212–63 µm grain size fractions before being dried at 45 °C for 24 h. Glauconitic minerals were then separated from the bulk sample using a Frantz isodynamic magnetic separator. The separator operated at 1 A voltage, 14° sideways tilt and 20° longitudinal tilt, followed by a run using the same orientation of the unit and 0.5 A. Separated samples were then rinsed in dilute HCl (10%) to remove any traces of carbonate components aggregated to the surface of the glaucony grains, followed by rinsing 5 times with distilled water. A short ultrasonic bath (3 s) was the final stage of purification before the sediment was again oven dried at 45 °C for 24 h.

Grains were hand-picked using a fine paint brush under the binocular microscope. One hundred hand-picked grains were mounted on epoxy resin stubs. From the non-indurated rocks 11 samples were chosen to pick grains from. Three were from the Waipara River section and 8 were from various outcrops around the Oamaru region. Where possible, 3 grains were picked from each grain size for each sample, resulting in 9 grains representing a sample. Grain mounts were polished using gradually finer polishing agents, beginning with 120 fixed grit silicon carbide paper, followed by 3 μm , 1 μm , and eventually 0.5 μm diamond paste on 450 Lampan cloth. These grain mounts were used for analysis using laser ablation induction coupled plasma mass spectroscopy (LA-ICP-MS) and scanning electron microscope with energy dispersive X-ray spectroscopy (SEM + EDS).

Only well indurated samples were present at the Oparara Quarry. These grains could not be disaggregated by hand and mechanical crushing of the rock would have pulverized the glaucony making further analysis impossible. Instead the rock was cut into thin sections which were polished using the same method as described for the epoxy mounts above. These sections were used for LA-ICP-MS and SEM + EDS.

3.3. LA-ICP-MS

Sixty grains from the polished mounts were chosen to be analyzed for trace and rare-earth elements (REEs) using LA-ICP-MS facilities in the Otago Community Trust Centre for Trace Element Analysis at the University of Otago. Laser ablation was conducted with a Resonetics RESolution M-50-LR laser ablation system incorporating a Coherent CompexPro 102 193 nm ArF excimer laser and Laurin Technic two-volume sample cell. The laser was operated at a constant energy of 100 mJ and 12.5% transmission for an on-sample fluence of 4 J/cm². Ablated material was carried by He gas (650–750 mL/min) from a two-volume sample cell, mixed with Ar (650–750 mL/min) and N₂ (2–6 mL/min), and input into an Agilent 7500cs ICP-MS. Data for 52 mass peaks were collected in time resolved mode with one point per peak. Integration times were 10 ms for ³Li, ⁴Be, ²³Na, ²⁴Mg, ²⁷Al, ²⁹Si, ³¹P, ³⁹K, ⁴³Ca, ⁴⁵Sc, ⁴⁹Ti, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ⁶⁶Zn, ⁷¹Ga, ⁷²Ge, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵⁸Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁷Hf, ¹⁸¹Ta, ²⁰²Hg, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, and ²³⁸U.

Background (laser off) data were acquired for 20 s followed by 40 s with the laser using spot diameters of 75 μm , a 5 Hz repetition rate, a 200 μm long track at 5 $\mu\text{m/s}$, and approximately 20 μm deep giving about 100 mass scans. Each set of 9–12 samples was bracketed by analysis of standard glasses NIST 610 and 612 [27].

Raw mass peak count rates were background subtracted, corrected for mass bias drift and converted to concentrations using an offline spreadsheet. After triggering, several seconds are required for a steady signal to be reached, and these initial data were excluded from the calculations. Trace element concentrations were obtained by normalizing count rates for each element to those for Si in the sample and standard using known SiO₂ and trace element concentrations in National Institute of Standards and Technology (NIST) 610 [27] and the SiO₂ in the sample estimated by summing the major element oxides to 100 wt%.

3.4. SEM with EDS

Major element concentrations were measured using a JEOL JSM 6100 SEM with an Oxford Aztec EDS analysis system at the University of Canterbury. Polished epoxy grain mounts and a polished thin section were carbon coated prior to analysis. Measurements were made at 800x magnification with a 4 s acquisition time. Two squares were drawn on each grain to select the area to be scanned, these were about 100 μm^2 and were drawn in the most homogenous looking part of the grain. Images were taken of each grain prior to chemical analysis. Chemical data for 87 grains (77 from stubs and 10 from the thin section) were collected. Total Fe was calculated as Fe₂O₃ and mineral formulas were calculated as being anhydrous as no loss on ignition data was obtained.

3.5. Solubility Analysis

Two separate experiments were conducted to assess elemental release from glaucony into solution over time.

Experiment 1

Glaucony solubility was measured in H₂O (acidified to pH 3.7 with dilute HCl) over a 16 day period. ~0.37 g of glaucony from the 212–500 µm grain size fraction of WP were left in 40 mL of ultrapure water. Tubes were lying horizontally on a table shaker (IKA model KS260) operating at 50 revolutions per minute. Extractions of solution were made at 25, 73, 190, and 382 h. Ten mL of solution was extracted from 3 tubes resulting in a triplicate analysis for each time period. The extractions were filtered using 2 µm filters to remove solid particulates. Samples were kept in a room at 22 °C throughout the experiment. Two samples of ultrapure water were taken for analyses, one at 25 h and one at 382 h. Following each extraction, pH was measured using a Mettler Toledo Seven GoDuo Pro SG78 pH/conductivity probe.

Elemental proportions were measured using induction coupled plasma mass spectroscopy (ICP-MS) in the Chemistry Department at the University of Canterbury. Solutions were acidified using trace metal grade nitric acid to pH 2 before measurements of Na, Mg, Al, P, K, Ca, V, Cr, Mn, Co, Fe, Ni, Cu, Zn, As, Sr, Zr, Ru, Cd, Sn, Sb, Cs, Ce, Ti, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, Th, and U were made using an Agilent 7500cx ICP-MS with 2–260 atomic mass units quadrupole mass analyzer. Only K, Na, Mg, Fe, Ca, and Al measurements are presented here, but the complete dataset is available upon request.

Experiment 2

The second series of solubility experiments tested the influence of pH and the presence of birnessite (a high valent Mn oxide known to be a strong oxidizing agent in soil environments) on elemental release from glaucony. These experiments are similar to those conducted by Oze et al. [28] where birnessite was synthesized following the same methods. Please note that the synthetic birnessite was cleaned multiple times in ultrapure water and diluted HCl in order to ensure the removal of any easily releasable elements such as potassium. The experimental parameters are shown in Table 2. This experiment was run over 103 h at 25 °C using 0.25 g of magnetically separated glaucony from WP04 and EQ01. Samples were left in 10 mL of solution on a table shaker operating at 80 rotations per minute. The solutions were a pH 4.6 acetate buffered solution and a pH 8 NaOH buffered solution. All solution pHs were monitored and maintained throughout the duration of the experiments. Birnessite (0.015 g) was added to one of two samples at both acidic and basic pH, resulting in the analysis of glaucony solubility with and without birnessite at both high and low pH. All experiments were completed in triplicate. Elemental concentrations were measured using ICP-MS using a Thermo ICP-MS X Series II spectrometer at the Environmental Measurements Facility at Stanford University. The elements selected for analysis were Mg, Al, K, Ca, Cr, Mn, and Fe.

Table 2. Experimental parameters for glaucony solubility analysis with and without birnessite at pHs 4.6 and 8.

Sample	pH	Solution (mL)	Glaucony (g)	Birnessite (g)	Time (hours)
EQ	4.6	10	0.25	0.015	103.25
EQ	4.6	10	0.25	0	103.25
EQ	8	10	0.25	0.015	103.25
EQ	8	10	0.25	0	103.25
WP	4.6	10	0.25	0.015	103.25
WP	4.6	10	0.25	0	103.25
WP	8	10	0.25	0.015	103.25
WP	8	10	0.25	0	103.25

4. Results

Figures 1 and 2 display examples of the variation in the grain morphology of glaucony using binocular microscopy and scanning electron imaging. Table 1 summarizes the proportions of glaucony and the dominant host grains for sampled outcrops.

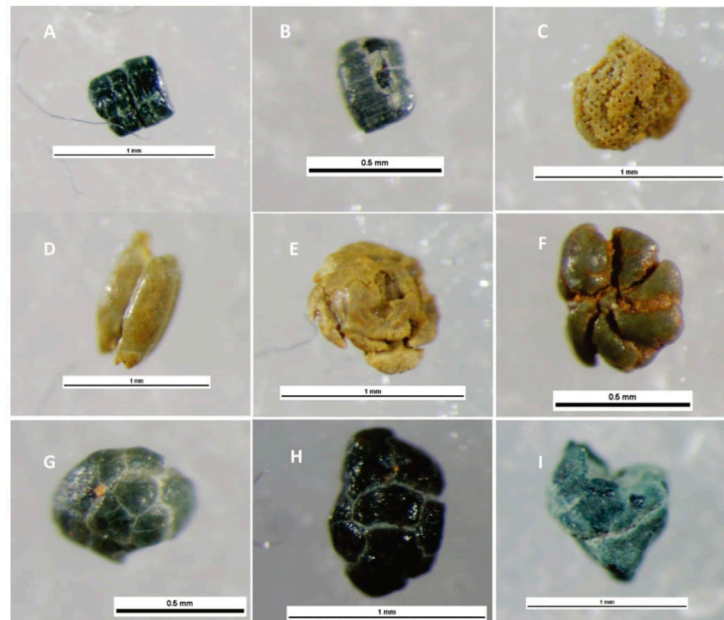


Figure 1. Binocular microscope images of grains of glaucony including: (A) Medium-dark green vermicular glaucony from Campbell's Beach (Gee greensand), (B) dark green vermicular glaucony from Earthquakes (Kokoamu greensand), (C) well preserved pale green glaucony derived from echinoderm host grain—Gee's Beach (Gee greensand), (D–F) pale green growth inside benthic foraminifera (Gee's Beach), (G) glaucony from Earthquakes (Kokoamu greensand), (H) glaucony and the Waipara (Waipara greensand), and (I) amorphous grain, possibly derived from lithic material (Waipara).

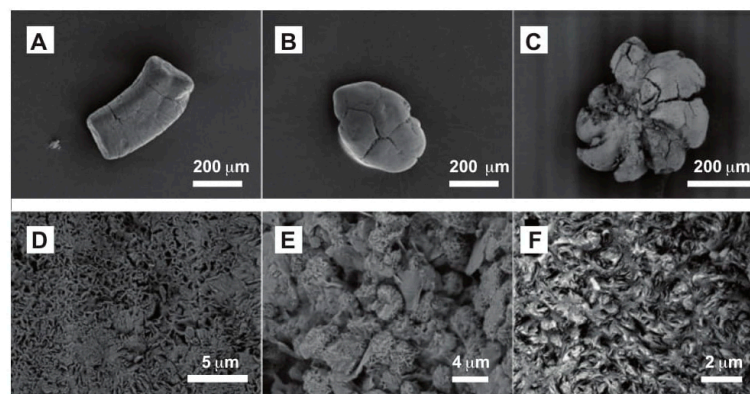


Figure 2. SEM images of glaucony grain surfaces and nanostructures of glaucony crystallites: (A) Vermicular grain with near parallel surface cracks—Ross Farm, (B) rounded pellet with surface cracks—Campbell's Beach, (C) benthic foraminifera—Gee's Beach, (D) ill-defined globules and caterpillar like structures showing aggregate nature of glaucony growth—Waipara greensand, (E) well developed plates and rosette structures of mature glaucony with co-precipitation of less mature crystals—dark green pellet from Campbell's Beach, (F) lamellar structures in highly evolved glaucony.

4.1. Major Elements

The average stoichiometric formula for all 88 grains of glaucony analyzed by SEM-EDS is $K_{0.74}(Fe_{1.27}Al_{0.30}Mg_{0.39})_{1.96}(Si_{3.77}Al_{0.23})_4(O_{10})(OH)_2$. Table 3 shows concentration averages, minima, maxima, and standard deviations for K_2O , SiO_2 , MgO , and Fe_2O_3 for all grains analyzed using SEM-EDS. Overall, K concentrations range from 6.75 to 9.84 wt%, with an average of 8.58 wt% and standard deviation of 0.81 (N = 88). The average K concentration is highest in grains from Campbell's Beach (9.40 wt%), and decreases in the following order: Ross Farm, Earthquakes, Waipara, Gee's Beach and Oparara with values of 8.95, 8.72, 8.66, 7.95, and 7.66 wt%, respectively. Standard deviations for K range from 0.87 at Gee's Beach (N = 12) to 0.32 at Campbell's Beach (N = 11).

Table 3. Average, standard deviation, maximum, and minimum concentrations for all grains measured by EDS.

	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	Fe ₂ O ₃
Oparara Quarry					
Average	3.74	12.34	54.11	7.66	22.15
Standard Deviation (N * = 9)	0.29	1.78	1.3	0.57	2.22
Minimum	3.03	10.07	52.29	6.77	19.47
Maximum	4.09	15.55	55.94	8.51	25.55
Earthquakes					
Average	4.06	6.73	56.72	8.72	23.77
Standard Deviation (N = 19)	0.41	1.26	0.97	0.66	1.21
Minimum	3.27	4.19	54.66	7.48	21.64
Maximum	4.9	8.97	58.5	9.65	26.08
Ross Farm					
Average	4.2	6.29	56.57	8.95	23.99
Standard Deviation (N = 14)	0.46	1.48	1.45	0.82	2.35
Minimum	3.51	4.41	55.14	6.97	18.45
Maximum	5.38	9.59	59.83	9.84	27.17
Campbell's Beach					
Average	4.35	5.84	56	9.4	24.41
Standard Deviation (N = 11)	0.17	0.73	0.33	0.32	0.98
Minimum	4.1	4.88	55.47	8.91	22.62
Maximum	4.54	7.04	56.35	9.81	25.48
Gee's Beach					
Average	3.53	5.72	53.23	7.95	29.57
Standard Deviation (N = 12)	0.52	0.96	2.14	0.87	3.36
Minimum	3	4.37	49.35	6.75	23.85
Maximum	4.41	7.18	57.02	9.73	34.15
Waipara Greensand					
Average	3.71	5.7	56.55	8.66	25.38
Standard Deviation (N = 27)	0.34	1.99	1.7	0.59	2.58
Minimum	2.72	3.45	51.35	7.34	19.16
Maximum	4.33	13.76	59.58	9.64	31.73

* N represents the number of grains analyzed.

The average concentrations for SiO_2 , Fe_2O_3 , Al_2O_3 , and MgO are 55.84, 24.97, 6.71 and 3.89 wt%, respectively. Correlations between these elements and K_2O are displayed in Figure 3. Iron correlates poorly with K when all grains are taken into account; however, when analyzed on an individual outcrop basis positive correlations are found. Grains from Ross Farm and the Oparara Quarry show the strongest correlations with R^2 values equal to 0.91 and 0.70, respectively. Magnesium also shows positive correlations with K in all outcrops. Gee's Beach and Campbell's Beach contain the strongest correlations with R^2 of 0.82 and 0.76, respectively. Aluminum correlates negatively with K in all

outcrops. Samples from the Oparara Quarry and Ross Farm contain the strongest correlations with R^2 values of 0.93 and 0.86, respectively. Silica displays negative correlations with K in the Waipara greensand, at the Oparara Quarry and Ross Farm ($R^2 = 0.53, 0.84$ and 0.85 , respectively). Silica shows the opposite trend at Gee's Beach and Campbell's Beach, where positive correlations are present with K ($R^2 = 0.55$ and 0.14).

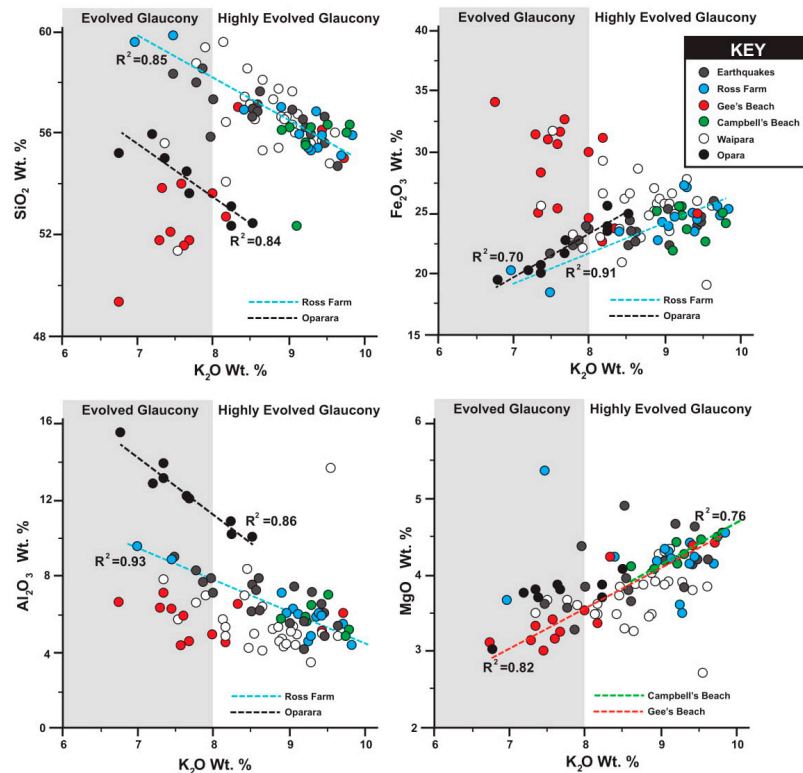


Figure 3. Major element plots showing EDS results for SiO_2 , Fe_2O_3 , Al_2O_3 , and MgO plotted against K_2O . Lines of best fit are plotted for R^2 values > 0.70 .

4.2. Trace Elements

Table 4 shows trace element concentrations and the standard deviations for grains analyzed using LA-ICP-MS. Titanium, V, Cr, Zn, and Rb are present in significantly higher concentrations than all other trace elements in all samples, with average values across all outcrops of 616, 212, 268, 172, and 335 mg kg^{-1} , respectively. Nickel is the next highest concentrated element with an average of 41 ppm across all outcrops. Titanium shows significant variation with 272 ppm at Campbell's Beach and 915 ppm at Waipara. Average V concentration ranges from 74 ppm (Campbell's Beach) to 418 ppm (Oparara). Chromium is present in relatively consistent concentrations in all outcrops, ranging from 174 ppm at Gee's Beach to 334 at Waipara. Zinc concentration shows only minor variation with Earthquakes and Campbell's Beach both measuring 130 ppm and Gee's Beach containing the maximum at 200 ppm. Rubidium is enriched at Oparara with 580 ppm. In outcrops from Oamaru, Rb ranges from 250 to 280 ppm and the Waipara greensand contains 335 ppm on average.

Table 4. Trace element averages and standard deviations for all grains measured by laser ablation induction coupled plasma mass spectroscopy (LA-ICP-MS).

Outcrop		Sc	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	Pb	Th	U
		Concentration (ppm)																			
Oparara	Average STDEV (N = 10)	8	502	418	263	58	22	79	53	197	29	580	48	3.6	41	1	40	43	12	0.6	0.6
		2.4	103	61	36	27	2.8	11	18	19	4.2	47	26	6.9	3.9	0.2	10	10	5.4	0.5	0.4
Earthquakes	Average STDEV (N = 11)	8.4	397	121	201	29	2.5	29	20	130	21	250	11	3.2	14	1	3.8	6.6	3.4	0.2	0.6
		2	177	63	56	19	1.1	5.7	14	48	3.6	20	2.5	2.4	5.4	0.2	1.7	5.6	1.5	0.1	0.2
Ross Farm	Average STDEV (N = 7)	9.2	448	102	282	16	3	29	27	145	20	280	10	4.3	19	2	3.5	7	5	0.3	0.6
		5.3	238	28	69	15	1.2	3.5	11	31	3.8	33	7	4.6	3.5	0.4	1.6	7	2.9	0.3	0.1
Campbell's Beach	Average STDEV (N = 3)	6.6	272	74	305	6.7	3.2	32	18	130	17	273	8.2	6.6	21	1.6	2.2	3.6	2.7	0.3	0.6
		0.2	96	3.4	69	0.7	0.3	1.9	5.5	20	0.3	7.2	1.1	3	1.4	0.1	1	0.4	1.8	0.3	0.1
Gee's Beach	Average STDEV (N = 8)	6.2	570	153	174	45	11	61	31	200	12	253	11	5.4	24	2.2	6.2	15	12	0.4	0.4
		1.6	470	124	111	31	4.8	31	12	60	3.3	13	3.6	5.2	7.3	1.5	3.4	14	11	0.4	0.2
Waipara	Average STDEV (N = 20)	18	915	251	334	56	4.1	19	21	189	25	335	7	1.2	26	4.6	5.8	24	5	1.2	0.8
		8.4	463	73	102	36	1.9	21	11	26	7.8	48	2	0.9	9.3	2.4	2.2	27	2.3	1.2	0.6
Total for all grains	Average STDEV (N = 59)	12	616	212	268	42	7.2	38	28	172	22	336	15	3.2	25	2.6	10	19	6.6	0.7	0.7
		7.4	405	130	100	32	7.1	28	17	46	7.4	117	18	4.1	11	2.2	13	21	5.8	0.8	0.4

N: number of grains analyzed.

4.3. Solubility of Glaucony

4.3.1. Experiment 1—No Birnessite at pH 3.7

The potassium concentration released from Waipara (WP) glaucony during lexiviation testing is shown in Figure 4. The first measured time interval at 25 h contained 700 ppb K. After 73 h the concentration of K increased to 800 ppb and after 190 h K concentration reached 1400 ppb. Over the total 400 h that grains were left to dissolve in acidified H₂O, 1640 ppb K was released into solution. The release of K was almost linear over the 400 h with a release rate of 2.7 ppb K h⁻¹. Figure 4 shows the concentrations and rates of Na, Mg, Fe, Ca, and Al release measured by ICP-MS. Sodium had the second highest release rate of 0.4 ppb Na h⁻¹. Chromium from these experiments was undetectable in most analyses and had a maximum concentration of 0.1 ppb.

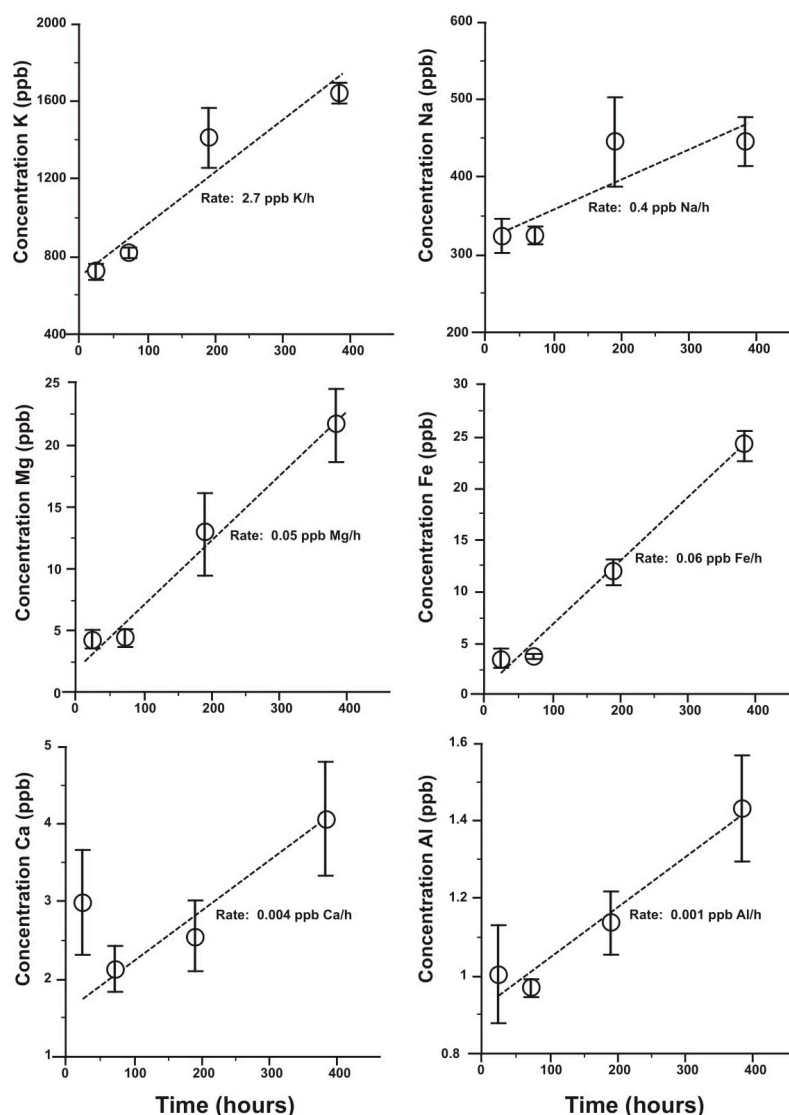


Figure 4. Concentration of K, Na, Mg, Fe, Ca, and Al dissolved from WP glaucony in acidified H₂O (pH 3.7) over ~400 h. Black lines are the line of best fit and rates of elemental release are provided.

4.3.2. Experiment 2—With and Without Birnessite at pHs 4.6 and 8

Figure 5 shows elemental concentrations dissolved from glaucony over 103 h in solutions of pH 4.6 and 8, both in the presence and absence of birnessite. The potassium concentration released from glaucony increased with decreasing pH and with the addition of birnessite. A value of 63,113 ppb

of K was released from a solution in one experiment containing birnessite at pH 4.6 over 103 h (i.e., $0.6 \mu\text{g h}^{-1}$). This was 9.3 times more K than the same sample at pH 4.6 without birnessite and 13 times more than the same sample dissolving at pH 8 with no birnessite. This relationship is true for both WP and EQ samples, which measure 8.66 and 8.72 wt% K_2O , respectively.

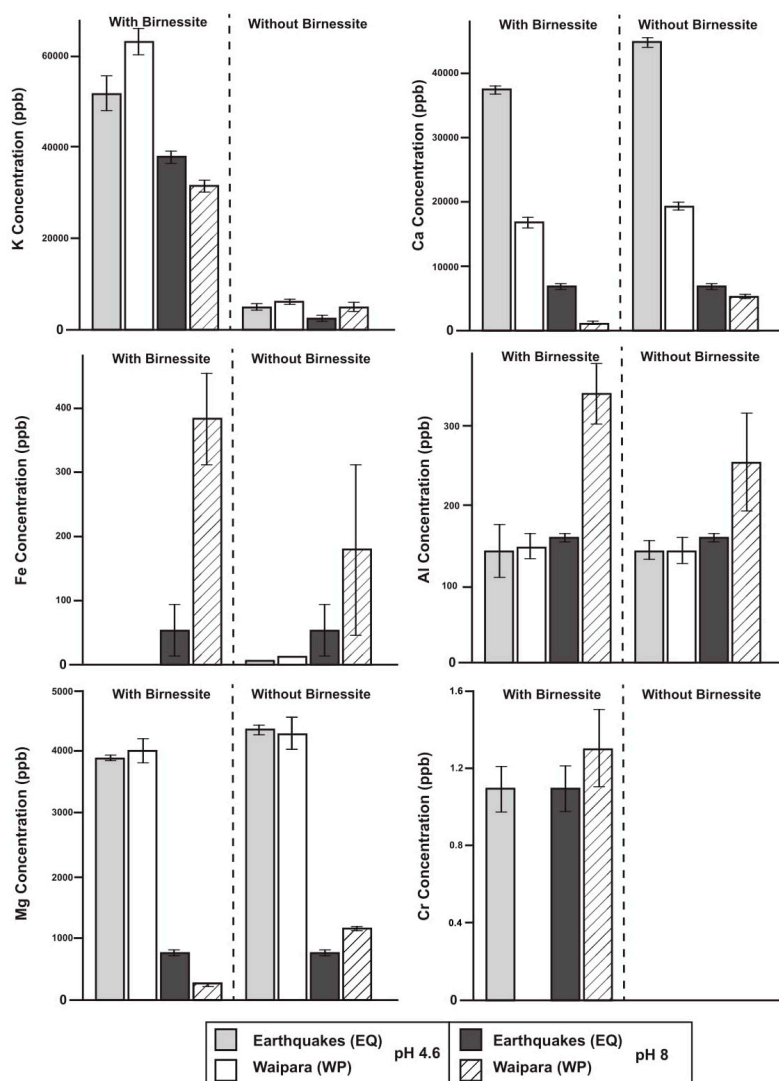


Figure 5. Elemental concentrations of K, Ca, Fe, Al, Mg, and Cr from solubility analysis with and without birnessite conducted at pH 4.6 and 8 on EQ and WP glaucony over a 103 h period.

Birnessite decelerates Ca release in both samples at either pH. Glaucony released an average of 1.14 times more Ca without birnessite in the system from EQ (either pH) and WP (pH 4.6) samples and 8.3 times more Ca from WP at pH 8. Birnessite also increased the rate of Cr released from glaucony. No Cr was present in samples that contained no birnessite and 1.1 to 1.3 ppm was released from samples containing birnessite. Manganese concentrations were also higher in samples containing birnessite. Birnessite does not appear to affect the release of Al into solution.

Acidic conditions accelerated the release of K, Mg and Ca. In solutions of pH 4.6 with and without birnessite, Ca concentrations averaged 29,589 ppm, whereas, in pH 8 solutions Ca averaged 4968 ppm. Potassium concentrations were 1.6 times higher in the acidic solution compared to the basic solution when birnessite was present, and 1.5 times higher in acidic conditions when birnessite was absent. Magnesium concentration increased eight-fold in the acidic solution compared with the basic solution in the presence of birnessite, and 4.7 times in the absence of birnessite.

Basic conditions accelerated Fe release. In the pH 4.6 solution, no Fe was detected, despite it being the second most abundant element in the solid phase (averaging 25.38 and 23.77 wt% in WP and EQ, respectively) (Table 3). In the basic solutions with and without birnessite, Fe concentration averaged 198 ppm. Neither basic nor acidic conditions had an effect on the release of Al into solution. Chromium release was only detected when birnessite was present.

5. Discussion

5.1. Glauconite Abundance and Geochemistry in Context to Paleoenvironment

All of the glaucony analyzed in this research falls into the evolved to highly evolved maturity parameters set by Odin and Matter [15]. Iron, Al, Mg, Si, and K are all present in concentrations comparable to published chemical data and the minerals analyzed in this research all fall into the true field of glaucony [15].

The concentrations of major elements generally show only minor variations between outcrops. The exceptions are the Stoney Creek limestone (Oparara Quarry) which is enriched in Al and depleted in Fe and K, and Gee's Beach which has a higher average Fe content. The sample from Oparara contained bioclastic-hosted glaucony. According to Banerjee et al. [11], the maturation of glaucony is hindered in bioclast-hosted grains as local alkaline conditions inhibit the dissolution of the calcite test, restricting the creation of new pore space and the percolation of seawater into the semi-confined micro-environment where maturation and further precipitation occurs [15]. These grains had less substitution of Fe for Al and the calcitic tests took longer to dissolve and lacked porosity and permeability, resulting in inhibited maturation and lower K content than pelletal-hosted glaucony which was prevalent in other outcrops.

The Gee Greensand, as sampled at Gee's Beach and Campbell's Beach, contains 30%–40% phosphorite in the bulk rock and was heavily bioturbated, indicating deposition in an organic-rich environment [29]. The high organic content would have created a relatively oxygen depleted seafloor sediment pile which increased the mobility of Fe, allowing diffusion through the seafloor sediments and creating increased Fe concentrations in the zone of glauconitization. The Waipara greensand and Campbell's Beach contain the next highest Fe concentrations and this is likely also due to the mobilization of Fe in sub-oxic conditions.

Trace elements, including heavy metals such as As and Cr, have been identified in glauconitic minerals and can contaminate soil. Elevated concentrations of As (7–31 ppm), Be (5–18 ppm), Cd (<0.2–1.2 ppm) and Cr (130–1000 ppm) were identified in greensands that were used as fertilizers on New Jersey pastoral land [10]. During the 1880's, 1 Mt of greensand was applied to New Jersey farmland per year, sometimes at rates up to 100 t per acre [30]. Arsenic concentrations up to $5.95 \mu\text{g L}^{-1}$ in New Jersey stream waters exceeded the state standard and were chemically fingerprinted to have derived from glauconitic sediments present in the groundwater environment [31]. For these reasons, the type and abundance of trace metals in glaucony needs to be addressed before using this mineral as a soil additive. Several trace elements of concern for soil contamination were present in the New Zealand glaucony including Cr, Zn, Ni, Cu, and U. From these elements, it was found that only Cr was present in elevated concentrations (averaging 268 ppm from all grains). For this reason, Cr was selected as an element for further assessment. As the oxidized form of Cr (i.e., hexavalent Cr or Cr (VI)) is toxic, birnessite, a known soil oxidizer, was combined with the dissolution experiments in order to determine if the New Zealand glaucony could potentially be a source of non-anthropogenic hexavalent chromium.

5.2. Glaucony as a Source of Soil K and Fertilizer Resource

Solubility analysis of glaucony from the Waipara Greensand in water (pH ~4) over 16 days showed that K was released into solution (Figure 4). Over one year 2.53 g of K will be released from one kg of glaucony, equating to ~6.94 mg of K per kg of glaucony per day. The results from this research are lower than concentrations measured by Karimi et al. [2], where 23 mg K per kg of glaucony per

day was measured from a crushed glauconitic sandstone containing 2.24 wt% K_2O dissolved in H_2O , and Rao and Rao [32] who measured 13 to 20 mg K per kg of glaucony. Plants require 50–100 kg of K per hectare per year [2]; therefore, ~20 t per ha of glaucony at 8.66 wt% K_2O (the concentration of K_2O in the Waipara greensand) would be required to satisfy the minimum plant requirement of K.

The specific gravity of glaucony ranges between 2.3–2.9 [17] and is most likely influenced by Fe content, where mature Fe-rich grains are denser than immature Fe depleted grains. Using the Waipara greensand as an example, the bulk rock contains 40%–65% glaucony which averages 25 wt% FeO. To produce 20 t of glaucony from an assay of 40% and a specific gravity of 2.70 g/cm^3 , 50 t or $\sim 18.50\text{ m}^3$ of bulk rock would need to be excavated to satisfy the requirements outlined above, assuming a bulk rock density of 2700 kg/m^3 (the composition is dominantly quartz and glaucony). Magnetic separation would be required to concentrate the glauconitic fraction.

The average representative stoichiometric mineral formula for glaucony from the Waipara greensand was $K_{0.75}(Fe_{1.29}Al_{0.27}Mg_{0.37})_{1.94}(Si_{3.82}Al_{0.18})_4$. From this it was calculated that K comprised 47.66 mg of the 0.37 g of glaucony in the sample which equates to 130 g of K per 1 kg of glaucony. Thus, in 24 h the proportion of K released into solution was 0.006% of the total K in the sample. If dissolution rates remain constant, then ~2% of the total K will dissolve from the mineral over one year. Rao and Rao [32] and Mazumder et al. [33] showed that the rate of K released into solution depends on the grain size and that finer grain sizes release more K than coarser grains. It would, therefore, be expected that over time the rate of K release would increase as the minerals undergo physical and chemical weathering and decrease in size and increase in surface area. Considering that the analysis conducted in this research used whole grains with no crushing, the K concentrations in solution reported above can be taken to represent minimum values. The release of K will be greater following crushing and subsequent increase of specific surface area where dissolution reactions occur.

When high valent Mn-oxides (birnessite) were present in the system, the mass of K released into solution increased. One explanation for this is that birnessite is aiding to oxidize a component of the glaucony structure, thereby, modifying the surface charge and fixing capacity of the clay structure. Another possibility is that birnessite may have contributed K, as $KMnO_4$ was involved its synthesis. Procedures were taken to ensure that the synthetic birnessite would not provide a source of K (i.e., electron microprobe, SEM-EDS, and XRD analyses for sample characterization and ensuring no detectable Mn release (detection limit at ~100 ppb) into solution at pH 5 over a period of 500 h). If birnessite was a major contributor of K, it would have provided similar K concentrations at each pH when the background (i.e., the no birnessite experiment) was taken into account. This was not the case. Overall, our analyses support that birnessite is accelerating the release of K from glaucony; however, there is the possibility that the synthetic birnessite may have been a K contributor. Additionally, our analyses suggest that birnessite may be adsorbing calcium. More investigation to how birnessite may be accelerating K release or potentially adsorbing Ca requires further study.

Assuming that this rate increase remains constant over time, the amount of glaucony required to satisfy plant demands would decrease from 20 t to 1.5 t ($\sim 1.4\text{ m}^3$ of bulk sediment) per ha per year if birnessite is present in the soil system. Furthermore, Tang et al. [34] showed that during the oxidation of Cr(III), Mn oxides were recycled in the presence of light and organic matter. In other words, after Mn(IV) has been reduced to Mn(III) it is regenerated by organic and/or oxygen radicals. The implication of this is that only a small amount of Mn oxides will facilitate enhanced K release from glaucony and this reaction pathway will be sustained as long as light and organic matter are present in the system. Therefore, given the ubiquitous presence of Mn oxides in soil environments it is likely that the release of K from glaucony will have a naturally occurring catalyst present before the product is even applied to the soil.

This is a simplified model of the K budget and adsorption onto soil colloids, and the excretion of plant enzymes for K release catalysis and additional sources/sinks of K will influence the total amount of K available. However, based on the solubility kinetics presented here, glaucony can provide a source of slow releasing K and one bulk application of mature glaucony may provide a base load which

satisfies the minimum end of the plant requirements of K for up to fifty years. Additional inputs of imported potash would be used as a supplement according to soil characteristics and crop demands for potassium. It is recommended that applications are restricted to naturally acidic soils and soils that contain Mn-oxides as these factors will increase K release.

One concern with regards glaucony dissolution was that Na was released into solution very quickly compared to all other elements. Over one year it is predicted that 384 mg of Na will be dissolved from one kg of glaucony. This represents 20% of the total Na content present in one kg of glaucony. Given that the analysis included uncrushed grains with a low surface area, 20% is a significant portion of the total mass of an element to be released in one year. The dissolution analysis was conducted using a magnetically separated bulk sediment of concentrated glaucony and it is likely that there were salts (NaCl) and other minor accessory phases which may have contributed to the high Na concentrations. If soil salinization is a concern, a pre-application wash with a dilute acid could remove Na in accessory phases. Additionally, if electrolytes in soil solution are a concern, then we would recommend additional dissolution experiments to reflect the electrolyte and dissolved organic matter levels of the soil that glaucony will be added to.

In addition to providing a source of K to soil, glauconitic minerals may affect the cation exchange capacity (CEC) of a soil. Tedrow [30] found that the CEC of a glauconitic sandstone was between 19 and 31 milli-equivalents/100 g soil and that the highest values were measured in the finest grain sizes. McRae [17] reported ranges between 5–39 milli-equivalents/100 g and suggested that the CEC varied inversely with the concentration of the interlayer cation. This is to be expected as the increase in interlayer cations will neutralize the net negative charge on the surface of glaucony. Therefore, the more mature and K-rich the glaucony in question is, the less it will initially contribute to the overall CEC of the soil to which it is added. Over time and with weathering, an application of glaucony will be expected to increase a soil's CEC, potentially above that created by naturally occurring clay colloids and humic matter.

The slow release of K avoids the possibility of upsetting the nutrient budget in downstream ecosystems. Leaching through soil profiles into groundwater systems and the interconnected surface water bodies can unintentionally transfer nutrients from the intended place of deposition (i.e., a farm) to sensitive ecosystems. When high concentrations of nutrients are suddenly introduced into environments the naturally established ecological diversity may become disrupted. In New Zealand, P is usually the limiting nutrient and additions of P will often trigger algal blooms [1,35], and therefore, increases in K content are not likely to disrupt the established ecology. However, in areas where it is determined that K is a limiting nutrient the slow release of K from glaucony could make it a desirable product to use in terms of avoiding ecosystem disruption while providing plants with a minimum long-term baseload of potassium.

5.3. Chromium in Glauconitic Minerals: Contaminant or Micronutrient?

Chromium exists in two stable oxidation states, trivalent chromium (i.e., Cr(III)) and hexavalent chromium (i.e., Cr(VI)). Of these, Cr(VI) is mobile and toxic, whereas, Cr(III) is less mobile and is a micronutrient [34,36–38]. Chromium (VI) is reduced to Cr(III) in the presence of organic matter, Fe (II) and reduced sulfur species [39]. Once reduced, Cr(III) is insoluble and precipitates as Cr-Fe oxyhydroxides, adsorbs to the surfaces of Fe/Al oxides or becomes complexed with organic material before settling to the seafloor [36]. The oxidation of Cr(III) to Cr(VI) is mediated by Mn oxides and these are considered major oxidants capable of oxidizing Cr in natural soil [28,34,36]. It should be noted that an additional naturally occurring oxidant of Cr(III) present in terrestrial systems, not assessed here, is hydrogen peroxide (H₂O₂) [40,41]. Chromium (VI) forms anionic species such as HCrO₄[−] and CrO₄^{2−} which are mobile in marine environments and soil systems.

The decomposition of labile organics in marine sediments remobilizes Cr resulting in bottom water enrichment. In the absence of MnO₂, Cr will be present as Cr(III) and will most likely be complexed with organic material or adsorbed onto Fe/Al oxides or hydroxyl groups of marine clays. In the presence

of MnO_2 or H_2O_2 , Cr may become oxidized and will be mobile in the marine environment. Given that glauconitic minerals precipitate in organic-rich marine environments in sub-oxic to near-neutral redox conditions, it is likely that Cr(III) is the prevalent valency in glaucony. Furthermore, due to the negative surface charge of the clay structure it is unlikely that the anionic species of Cr(VI) would be attracted to the surface of glaucony. Chromium concentrations are highest in grains from the Waipara greensand (334 ppm). This is likely due to high amounts of dissolved organic matter on the seafloor which complexed with Cr and increased its mobility, enhancing diffusion through the sediment pile and adsorption onto the surface of glaucony.

Despite measuring high concentrations in the solid phase analysis, Cr was negligible or undetectable in solution from the dissolution experiments, indicating that it is held tightly to the surface of glaucony. Over long time scales the total amount of Cr would eventually be released from glauconitic minerals into the soil, however, given that Cr(VI) is unfavorable in the presence of organic matter and Fe(II) species, it would be expected that the Cr that is eventually released will be present in the reduced form as Cr(III). This would then imply that Cr is present as a micronutrient and will be beneficial to soil and plants. The presence of Mn oxides did increase the Cr released into solution and this was probably in the Cr (VI) form (1.1 ppb over 103 h was not enough to determine the oxidation state of chromium). Overall, the rate of Cr release was so minimal and with the ubiquitous presence of Cr reducing agents (i.e., organic material and ferrous Fe) in soil that it appears Cr toxicity is not an issue relevant to the application of these glauconitic minerals to soil environments.

6. Conclusions

Glaucony from the South Island of New Zealand are geochemically similar and are of the evolved to highly evolved types. Subtle variations in major element concentrations reflect the host grain influencing the maturation process, resulting in K and Fe enrichment in faecal pellet-hosted glaucony compared to bioclast-hosted grains. In dissolution experiments, K was released from glaucony at faster rates than any other element (2.5 g K released from 1 kg of glaucony per year). Sodium was the next highest (0.38 g Na/kg glaucony/year) followed by Fe and Mg (both ~ 0.05 g/kg glaucony/year). The predicted mass of elements released over time suggests that large amounts of bulk rock would be required to meet plant requirements for K. However, the presence of naturally occurring oxidizing agents (birnessite) and increased acidity enhanced the release of K from glaucony, and this is considered a likely scenario to occur in natural soil environments. Additionally, the release of K could be accelerated by crushing grains to increase the surface area exposed to dissolution reactions. Given the abundance of glaucony, the ease at which it can be obtained and the benefits it may bring to soil systems, glauconitic minerals appear to be a beneficial source of soil K and micronutrients (such as Cr) and a feasible K fertilizer resource which can assist the agricultural industry, both in New Zealand and on the global stage.

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