

## Article

# Geochemical Characterization of Rock Samples from Selected Fiji Mine Sites to Evaluate On-Site Environmental Vulnerabilities

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**Abstract:** Although mining contributes to about 1.4% of Fiji's gross domestic product (GDP), the excavated rocks from mining may have detrimental effects on the environment. In this study, rock samples from five Fiji mine sites were selected to assess their geochemical characteristics from an environmental point of view. The mineralogical and chemical constituents, release and retention mechanisms of hazardous elements, and acid/neutralization potential of the rock samples were investigated to understand their environmental impacts on-site. The results showed that sulfide minerals typically found in the rock samples, such as pyrite, chalcopyrite, and sphalerite were responsible for the release of hazardous elements such as Cu, Pb, and Zn via oxidation. Leachates of rock samples from Mt Kasi, Nukudamu, and Wainivesi exceeded the World Health Organization (WHO) regulatory limit for Cu (2 mg/L), Pb (0.01 mg/L), and Zn (3 mg/L) in drinking water. In contrast, no hazardous elements were leached from the Tuvatu and Vatukoula rock samples, which could be attributed to the dissolution of calcite and dolomite that buffered the pH and limited heavy metal mobility. The acid–base accounting (ABA) and accelerated weathering test by hydrogen peroxide indicated that most of the rock samples containing sulfide minerals were likely to generate acidity. Furthermore, the results highlighted that once carbonate minerals are depleted in the rock samples, acid mine drainage (AMD) generation is inevitable. These findings reaffirm the need for committed effort in environmental management of the mine sites to prevent environmental issues associated with AMD.

**Keywords:** geochemical characterization; sulfide and carbonate minerals; hazardous elements; leaching; acid mine drainage



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## 1. Introduction

### 1.1. Background

Mining is generally considered an accepted form of development contributing to global growth. Despite this, it remains inherently disruptive to the environment and affected communities wherever it is undertaken. Sub-standard mining practices, insufficient monitoring and control, and lack of prudent rehabilitation programs often lead to long-term environmental degradation. Due to its extractive nature of accessing and extracting target minerals, mining operations often require the removal of surface vegetation and soils, including alteration of habitats and landforms, which changes surface water hydrology, hydrogeology, and soil profiles, and finally affects human health [1]. Mining operations are also notorious for inducing erosion and land subsidence as well as generating blasting noise, vibration, dust, hazardous wastes, rocks and tailings, and polluted effluents such as acid mine drainage (AMD). The negative impacts of mining are often exacerbated

in developing countries because of the large knowledge gaps in leading practices and limited applications of advanced technologies for ore extraction, mineral processing, and mine waste management [2–5]. For instance, local communities' concerns only focus on physically observable changes such as river water discoloration, odor, taste, or feel rather than chemical quantification and understanding of underlying scientific processes unknown to them [2].

Sustainable mine waste management remains an ongoing challenge for the mining industry. Waste rocks and tailings, for example, pose special concerns because of their complex geochemical characteristics and the huge volume generated. In fact, for gold as well as copper (Cu) mining, about 99% of the extracted ores are deposited back into the environment as tailings [6,7]. When geochemical properties of mine wastes are not thoroughly understood, it leads to inappropriate treatments with limited functionalities that can worsen their long-term impacts. Waste rocks may contain sulfide minerals such as pyrite ( $\text{FeS}_2$ ), which not only generate AMD due to their oxidation in the presence of water and atmospheric oxygen but also release hazardous elements into the environment [7–9]. AMD is a notorious discharge from mining areas, and its generation is considered one of the most pressing and serious environmental problems facing the mining industry. Once generated, AMD's strongly acidic pH has the potential to mobilize other hazardous elements present in coexisting minerals that have detrimental effects on nearby ecosystems [9,10].

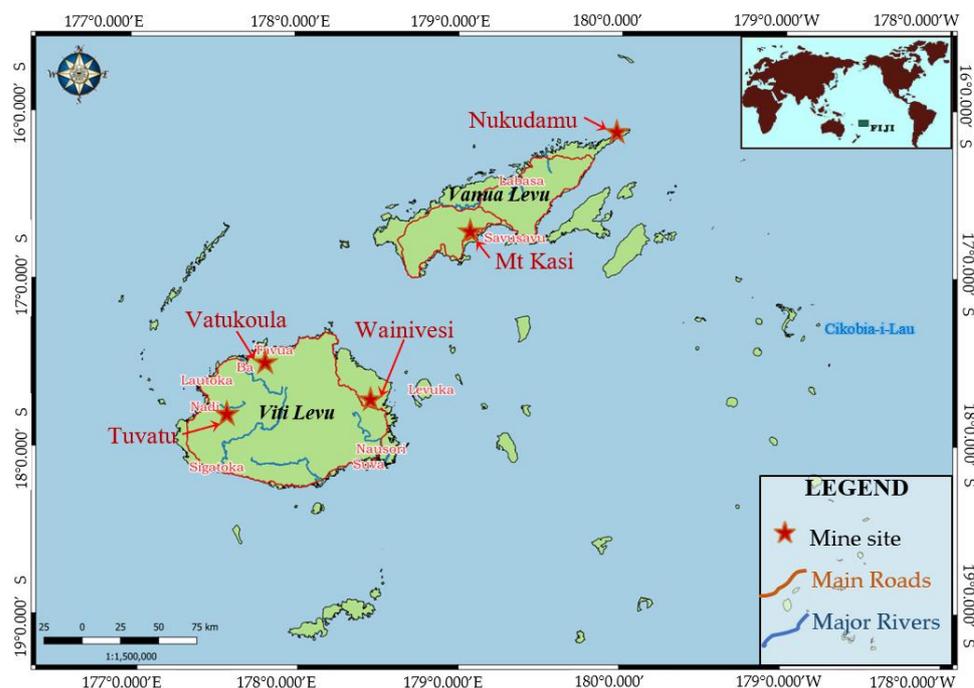
Despite Fiji's long mining history and growing interest in mineral development, there remain limited available narratives about mining, which concentrate mostly on the benefits of mineral extraction with little literature explaining the orebody's geochemical nature. The Vatukoula Gold Mine (VGML), because of its long existence, is the most studied mine in Fiji [11–17]. However, only a few studies have been conducted on the other mining areas of the country. Moreover, the majority of these previous works focused on the chemical properties of river water and its sediments, including heavy metals and metalloids in Fiji's mine sites. Kumar et al. (2021), for example, highlighted the influence of the discharge from the Toko tailings storage facility (TSF) of Vatukoula on the nearby river sediments [11]. These authors conducted a similar study on potentially toxic elements across the Wainivesi River, which also receives discharge from the Wainivesi mine [13]. In both studies, they assumed that mining discharges contributed to the contamination of the rivers since the mine sites are located within the study area but failed to directly relate the contamination with certainty to the respective mines.

This means that the properties of excavated rocks from mines and how they relate to their environmental impacts remains poorly understood in Fiji. This knowledge gap can be addressed by the present study by investigating the geochemical characteristics of Fiji mine sites. In this study, sixteen fresh orebodies' rock samples were evaluated from five representative mine sites. The study rationale focused on the general geochemical characterization of the rock types of the orebodies of each mine to provide an understanding of how such rock types influence the vulnerability of each site due to their geochemical properties and make-up when disturbed by mining activities. Therefore, the specific objectives of this work are to (1) characterize the mineralogy and geochemical compositions of the rock samples, (2) analyze the leachate characteristics, and (3) investigate the acid-generating potential of the rocks using acid–base accounting and pH tests with hydrogen peroxide. The current study is important for the sustainable development of Fiji's growing mining sector and is equally significant for better and more comprehensive evaluation of mining's environmental impacts.

## 1.2. Study Sites

Fiji is an archipelago of about 330 islands with a combined landmass of 18,376 km<sup>2</sup> and lies southwest of the Pacific Ocean as shown in Figure 1. As a developing nation, Fiji is largely isolated along the edge of the Pacific Ring of Fire and is richly endowed with minerals, which the country exploits to support its economy. Fiji's climate is mainly tropical,

characterized by a high rainfall season (2000–4000 mm) from November to April and dry season from May to October with temperatures of 20–30 °C throughout the year [18,19].



**Figure 1.** The map of Fiji and locations of Mt Kasi, Nukudamu, Tuvatu, Vatukoula, and Wainivesi mining sites where rock samples were collected.

The rocks collected for this study are fresh samples and are assumed to be representative of the orebodies of the studied mines. A summary of the geology of each mine site is presented herein based primarily on the work of Colley and Flint (1995). At Mt Kasi, the underlying rock was described as basaltic andesite flows, breccias, and tuffs, cut by an altered feldspar porphyry of dacitic composition. The primary ore-bearing minerals were native gold, pyrite, enargite (luzonite), tennantite, goldfieldite, chalcopyrite, tellurides, and cassiterite, whereas secondary minerals included covellite, chalcocite, and neodigenite [20,21]. The Nukudamu mine site sits on the rocks of the Udu volcanic group, which is composed of massive flows, breccias, tuffs, and associated sediments, mostly of submarine origin, generally of fine grained or glassy and containing phenocrysts of andesine, quartz, pyroxene, classified as rhyodacite due to the high content of silica. The Nukudamu deposit is described as Kuroko type, and the mineralization consists primarily of massive Cu, zinc (Zn), and iron (Fe) sulfides (pyrite) with coexisting minerals such as kaolinite, smectite, chalcedony, and quartz [20,22,23].

The Tuvatu mine site is surrounded by the Nadele breccia of the Wainimala Group and comprises massive, coarse, polymict, multicolored breccia, and sedimentary units of thin layered siltstone, sandstone, and mudstone [24]. The Nadele breccia is unconformably overlain by the Koroimavua volcanic group, which has shoshonitic affinities and includes andesitic and biotite-bearing dacitic lithic and crystal tuffs, grits, and agglomerates. Intrusive monzonite is locally brecciated with quartz–tourmaline replacement and veins infilled with potassium feldspar (K-feldspar) and biotite [20,25]. The Vatukoula mine site rocks are derived from a potassium-rich shoshonitic magma with olivine basalt (absarokite) parent magma to shoshonite, trachyandesite (banakite), and monzonite by-products [20]. Its mineralization is described as a low-grade, porphyry Cu type associated with steep caldera faults spatially related to epithermal gold mineralization [26–29].

As for Wainivesi, its host rocks are highly silicified andesites and dacites displaying brecciation with rare basic rocks, suggested to be originally calcareous [30], and contain other rock units including tuffs, shaly volcanoclastic beds, and breccias. The origin of

the Wainivesi deposit is still ambiguous, but its mineralization is described as massive sulfide occurring within the hydrothermal breccia, banded, and brecciated with a variety of mineral assemblages [20].

## 2. Materials and Methods

### 2.1. Sample Collection, Preparation, and Characterization

The rock samples (0.5–1 kg) were collected from five selected mine sites (Mt Kasi, Nukudamu, Tuvatu, Vatukoula, and Wainivesi) as shown in Figure 1, with the respective details provided in Table S1. The Tuvatu and Vatukoula mines are located on the western side of Viti Levu island, with active mining leases, and Wainivesi on the east with a special exploration license. Mt Kasi and Nukudamu mines are both located on Vanua Levu island. Mt Kasi is currently under special prospecting license to further explore its mineral potential after abandonment of more than 30 years while Nukudamu was abandoned since it ceased operation in 1968.

The bulk rock samples were crushed to <2 mm sizes and stored in air-tight containers. The samples were further crushed to <50 µm, powder pressed into two separate pellets, and then analyzed by XRD (MultiFlex, Rigaku Corporation, Tokyo, Japan) and X-ray fluorescence (XRF) (SpectroXepos, Rigaku Corporation, Tokyo, Japan) for their mineralogical and chemical compositions, respectively. All the X-ray diffraction (XRD) patterns were identified using Match!® software (Crystal Impact, version 3.3.8, Bonn, Germany) and quantified into relative percentage abundance. Furthermore, validation of mineralogy of selected samples (M2, N1, T3, V1, V4, and W1) was carried out using an optical microscope. The total carbon (TC) and inorganic carbon (IC) of the rock samples (<2 mm) were measured using the total carbon analyzer (TOC-VCSH, Shimadzu Corporation, Kyoto, Japan) with a solid sample combustion unit (SSM-5000A, Shimadzu Corporation, Kyoto, Japan). Finally, loss on ignition (LOI) test was conducted to assess analytical accuracy of total volatile measurements, mainly added to other oxides totaling  $100 \pm 1.0\%$ . Loss on ignition (LOI) was determined through gravimetry by heating the sample (<2 mm) inside a furnace at 750 °C for 1 h after drying in an oven at 110 °C for 24 h [31,32].

### 2.2. Batch Leaching Tests

The leaching experiment was based on the Environmental Agency of Japan Notification No. 46 [33], which was applied to evaluate the leaching concentrations of Al, Cu, Ca, Fe, K, Mg, Na,  $\text{SO}_4^{2-}$ , Si, Pb, and Zn from the rock samples [34]. This method was considered relevant as it closely simulates the effects of rainfall on mined rocks considering that Fiji has a predominantly tropical climate and still does not have a national standard leaching test protocol. For the experiment, 15 g of crushed rock sample (<2 mm) was added to 150 mL of deionized (DI) water in a 250 mL Erlenmeyer flask and placed in the shaker for 24 h at 120 rpm. This method is widely used in excavated and hydrothermally altered rocks that simulate on-site environmental vulnerabilities via leaching [35–37]. The pH (Laqua pH meter F-71, SS112, Horiba Ltd., Kyoto, Japan), electrical conductivity (EC) (CM-31P, CM-31P-W, DKK-TOA Corporation, Tokyo, Japan), oxidation–reduction potential (ORP) (RM 30P, DKK-TOA Corporation, Tokyo, Japan) and temperatures were measured after the leaching tests. The leachates were then filtered through 0.45 µm Millex® membrane filters. All filtrates were acidified with 1% nitric acid ( $\text{HNO}_3$ ) before chemical analysis. Alkalinity was measured in leachates with pH > 4.8 by titrating a known volume of the sample's leachate to pH 4.8 with 0.01 M of sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Hazardous elements and major ions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES ICPE 9800, Shimadzu Corporation, Kyoto, Japan).

### 2.3. Quality Assurance and Quality Control

The analysis was conducted in triplicate together with certified reference materials (Table S2) traceable to NIST SRM® (Merck KGaA, Darmstadt, Germany) for accurate leachate concentrations. All the chemicals used were reagent grade. Blank solutions

(Millipore Milli-Rx 12 $\alpha$  system, Merck Millipore, California, CA, USA) were analyzed 3 times for each analytical session and calibrations were conducted on concentrations ranging from 0.1 to 20 mg/L to obtain the mean and relative standard deviation for each element using ICP-AES (margin of error  $\pm$  2%–3%, detection limit 0.01–0.001 mg/L) [38].

#### 2.4. Statistical Analysis and Thermodynamic Modeling

Principal component analysis (PCA) was performed using Origin Pro<sup>®</sup> software (Version 9.8, OriginLab Corporation, Northampton, MA, USA) on the batch leaching results. This multivariate statistical method is especially useful in finding correlations in complex systems with high-dimensional data where several components must be considered at the same time. The PCA was applied to understand the correlations between the different variables and identify dominant factors of the batch leaching results. The thermodynamic calculations of the leachates were determined using Visual MINTEQ 3.1 (USEPA, Stockholm, Sweden) [39]. The input parameters include the pH, temperature,  $p_e$ , alkalinity as  $\text{HCO}_3^-$ , and components of the leachates (Al, Cu, Ca, Fe, K, Mg, Na,  $\text{SO}_4^{2-}$ , Si, Pb, and Zn).

#### 2.5. Acid–Base Accounting and pH Test with Hydrogen Peroxide

The acid generation potential of the rock samples was investigated to determine their likelihood of producing acidity using acid–base accounting (ABA) and a pH test with hydrogen peroxide (pH ( $\text{H}_2\text{O}_2$ )). The ABA test was used to evaluate the acid-neutralizing potential (NP) and acid-generating potential (AP) of rock samples [40,41]. In this experiment, NP was determined by weighing 2 g of crushed rock samples (<2 mm) into a 250 mL Erlenmeyer flask with 90 mL of deionized (DI) water, which was then thoroughly mixed. The mixture was then treated with 1 mL of 1M hydrochloric acid (HCl), which was added again after 2 h. The suspension was allowed to react at room temperature for 24 h and then titrated to pH 8.3 with 1M sodium hydroxide (NaOH). The NP (kg  $\text{CaCO}_3$ /t) was calculated using Equation (1). Meanwhile, the AP was determined using 1 g of crushed rock sample (<2 mm) mixed with 100 mL of 15%  $\text{H}_2\text{O}_2$  (pH = 7), which was kept at room temperature for 48 h before being heated to remove residual  $\text{H}_2\text{O}_2$ . After cooling, its acidity was determined by titration with 1 M NaOH to pH 8.3. The AP (kg  $\text{CaCO}_3$ /t) was calculated using Equation (2) from the content of sulfide sulfur ( $S_{\text{sulfide}}$  %), which was determined by leaching with  $\text{H}_2\text{O}_2$  and calculated according to Equation (3). The difference between the values of NP and AP is the net acid-neutralizing potential ( $\text{NNP} = \text{NP} - \text{AP}$ ):

$$\text{NP} = (50 \times (Xa - Yb))/c \quad (1)$$

where X is volume of HCl (mL), Y is volume of NaOH (mL), a: normality of HCl (mol/L), b refers to normality of NaOH (mol/L), and c represents the mass of sample (g):

$$\text{AP} = 31.25 \times S_{\text{sulfide}} \quad (2)$$

$$S_{\text{sulfide}} = 1.6 \times V \quad (3)$$

where, V is the volume of NaOH (mL).

If the NNP value is below  $-20$  kg  $\text{CaCO}_3$ /t, acid generation is likely to occur; if the NNP value is between  $-20$  and  $20$  kg  $\text{CaCO}_3$ /t, the acid generation is uncertain; and if the NNP value is above  $20$  kg  $\text{CaCO}_3$ /t, the rock sample is unlikely to generate any acidity.

The pH ( $\text{H}_2\text{O}_2$ ) test was considered alongside the ABA technique to accurately predict the likelihood of acid generation of the rock samples. The method follows the Japanese Geotechnical Standard—JGS 0271-2016, [42] a streamlined technique that simulates the long-term natural process of mineral breakdown through weathering in cases of mineral extraction caused by mining. The pH ( $\text{H}_2\text{O}_2$ ) acidification test uses the oxidation principle, in which  $\text{H}_2\text{O}_2$ , a strong oxidant, oxidizes sulfide minerals exposed during the test. In the experiment,  $\text{H}_2\text{O}_2$  solution was first prepared by neutralizing a pre-determined volume of 30%  $\text{H}_2\text{O}_2$  to pH 6 using 10 mmol/L of NaOH. Rock samples weighing 2 g (<2 mm)

each were transferred into 100 mL beakers ( $mt = wt.$  of beaker +  $wt.$  of sample), and then 20 mL of  $H_2O_2$  was carefully added. The beakers were covered in plastic wrap with holes to release pressure during oxidation. The solution was then placed in a sand bath heated to  $60\text{ }^\circ\text{C}$  in a fume hood. Any violent reaction was controlled by stirring the solution or temporarily removing it from the sand bath to cool. The reaction was completed when fizzing or bubble formation became negligible. The solution was then allowed to cool down to room temperature. The beaker and the remaining solution were reweighed, and DI water was added until the new weight of  $mt + 20\text{ g}$  was reached. The resultant solution was thoroughly mixed and the pH was measured. The pH threshold acidification potential is 3.5, and samples with  $pH < 3.5$  have AMD-generating potential [43,44].

### 3. Results and Discussion

#### 3.1. Mineralogical and Chemical Properties of the Rock Samples

The chemical and mineralogical composition of Mt Kasi (M1–M3), Nukudamu (N1–N4), Tuvatu (T1–T4), Vatukoula (V1–V4), and Wainivesi (W1), including their TC and IC contents, are summarized in Table 1 and Figure 2. The Mt Kasi samples (M1, M2, and M3) are mainly composed of  $SiO_2$  (79.3 to 90.4 wt%),  $Al_2O_3$  (2.0 to 17.0 wt%), and sulfur (S; 6.28 to 6.76 wt%), with nacrite ( $Al_2Si_2O_5(OH)_4$ ), pyrite ( $Fe_2S$ ), and arsenopyrite ( $FeAsS$ ) as identified minerals (Figure 2a). Pyritic minerals (Figure S1) could not be confirmed in M2 with XRD; however, an optical microscope confirmed the presence of both quartz and pyritic minerals (Figure S1a). In the Nukudamu samples, N1 and N3 had high contents of  $SiO_2$  at 79.1 wt% and 68.5 wt%, respectively, while N4 and N2 contain 40.0 to 96.5 wt%  $Fe_2O_3$ . These results are consistent with the mineralogical compositions of the samples that identified cristobalite ( $SiO_2$ ), albite ( $Na(AlSi_3O_8)$ ), goethite ( $FeOOH$ ), and hematite ( $Fe_2O_3$ ) as major mineral constituents (Table S3). Sulfide-bearing minerals such as arsenopyrite, enargite ( $Cu_3AsS_4$ ), and pyrite (Figure 2b) were also detected in N2 and N3 with substantial amounts of Pb, Zn, Cu, and As ranging from 208 to 986 mg/kg. The presence of pyritic minerals, plagioclase, and magnetite ( $Fe_3O_4$ ) was also confirmed with an optical microscope in N1 (Figure S1b).

At Tuvatu, anorthite ( $CaAl_2Si_2O_8$ ), augite ( $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$ ), and orthoclase ( $KAlSi_3O_8$ ) were the major minerals, and minor minerals included quartz, calcite ( $CaCO_3$ ), diopside ( $MgCaSi_2O_6$ ), and dolomite ( $CaMg(CO_3)_2$ ) (Table S3). Surprisingly, pyritic minerals were detected with an optical microscope in T3 (Figure S1c), but were not detected by XRD (Table S3). The Tuvatu samples were predominantly of silicate origin but unlike the Mt Kasi and Nukudamu samples, carbonate minerals such as calcite and dolomite were detected in minor quantities (Figure 2c), which is consistent with (Clark et al., 2022, 2023), who found plagioclase and pyroxene as major minerals and rare disseminated pyritic minerals with minor carbonates [45,46]. The average chemical composition of the samples indicates relatively high contents of  $SiO_2$  (59.1 wt%), with  $MgO$  (6.2 wt%) and  $CaO$  (5.8 wt%), which correlated with the silicate and carbonate minerals detected by XRD. The TC and IC were generally low, with contents ranging from  $<0.01$  to 0.76 wt%. The XRD results of the Vatukoula rock samples (V1, V2, V3, and V4) revealed augite, orthoclase, and diopside as their major mineral constituents, while calcite, quartz, and augite are present as minor minerals (Figure 2d). Trace amounts of dolomite (Table S3) including pyritic minerals (V1 and V4) were detected (Figure S1d,e). These identified minerals are well supported by the XRF average chemical composition of  $SiO_2$  (51.7 wt%),  $MgO$  (8.2 wt%),  $CaO$  (9.5 wt%), TC (up to 1.26 wt%), and IC contents (up to 1.69 wt%). Meanwhile, the Wainivesi (W1) (Figure 2e) sample is mainly composed of sphalerite ( $ZnS$ ) and quartz with nacrite, and chalcopyrite as a minor mineral component. This is consistent with the high chemical contents of Zn (358,000 mg/kg), Cu (28,700 mg/kg), and S (70.7 wt%) in the sample. The oxidation of sulfide minerals from rock samples could pose a threat to the surrounding soil and surface water, as highlighted by Kumar et al. (2021) [13], which linked the presence of toxic elements in the sediments and surface water of the Wainivesi River to the weathering of exposed rocks around the mine.

**Table 1.** Chemical compositions of the rock samples from the XRF analysis and the TC/IC test.

Sample	SiO <sub>2</sub> (wt%)	TiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na <sub>2</sub> O (wt%)	K <sub>2</sub> O (wt%)	P <sub>2</sub> O <sub>5</sub> (wt%)	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	S (wt%)	TC (wt%)	IC (wt%)	LOI %
M1	79.3	0.64	17.0	4.90	<0.01	<0.01	0.04	0.02	0.02	0.11	92	2	61	15	10	6.28	0.10	<0.01	7.06
M2	90.4	0.34	2.00	2.76	<0.01	<0.01	0.03	0.14	0.13	0.08	137	1	29	28	3	6.31	0.01	<0.01	1.62
M3	84.1	0.39	12.9	3.79	<0.01	0.03	0.05	0.00	0.03	0.17	38	<2	67	11	4	6.76	<0.01	<0.01	5.46
N1	79.1	0.47	13.8	2.35	<0.01	0.31	1.93	6.51	0.50	<0.01	50	1	50	5	140	0.37	0.02	<0.01	0.99
N2	2.88	0.36	1.47	96.5	0.03	<0.01	0.11	<0.01	0.03	<0.01	619	<2	986	208	535	1.30	0.13	<0.01	7.01
N3	68.5	0.01	0.54	26.4	0.09	<0.01	0.05	<0.01	0.05	0.36	590	<1	327	519	460	0.81	0.01	<0.01	5.91
N4	1.84	0.11	6.50	40.0	0.01	<0.01	0.08	0.63	0.02	0.06	7	<1	83	21	59	52.3	0.67	<0.01	7.60
T1	62.7	0.52	21.2	3.89	0.06	8.27	3.35	5.25	0.12	0.27	<1	<1	6	<1	59	0.05	0.76	0.61	1.68
T2	53.7	0.73	16.3	11.4	0.22	8.21	10.6	2.71	2.93	0.67	6	<1	152	3	87	0.19	0.01	<0.01	0.52
T3	58.0	0.57	18.6	8.05	0.23	5.49	7.03	3.06	4.64	0.47	4	<1	190	8	112	0.83	0.04	0.06	1.17
T4	62.4	0.45	20.2	2.69	0.07	3.18	2.40	3.92	7.63	0.35	66	1	30	21	180	0.76	0.01	0.46	1.11
V1	43.2	0.44	11.9	9.93	0.24	9.16	13.7	1.81	2.59	0.33	4	<1	144	4	76	2.30	1.26	1.69	4.87
V2	57.9	0.46	20.3	6.47	0.15	4.89	5.04	3.28	4.64	0.64	1	1	82	9	78	0.05	0.65	0.56	3.51
V3	46.5	0.49	12.4	10.2	0.20	14.0	13.0	1.23	0.83	0.30	3	<1	126	5	81	0.51	0.98	0.72	3.97
V4	59.1	0.50	19.5	6.82	0.16	4.93	6.24	4.52	4.26	0.67	2	<1	161	9	82	0.21	0.31	0.37	1.36
W1	23.6	0.04	3.51	10.7	<0.01	0.02	<0.01	<0.01	0.42	0.03	80	1600	28,700	507	358,000	70.7	<0.01	<0.01	4.41

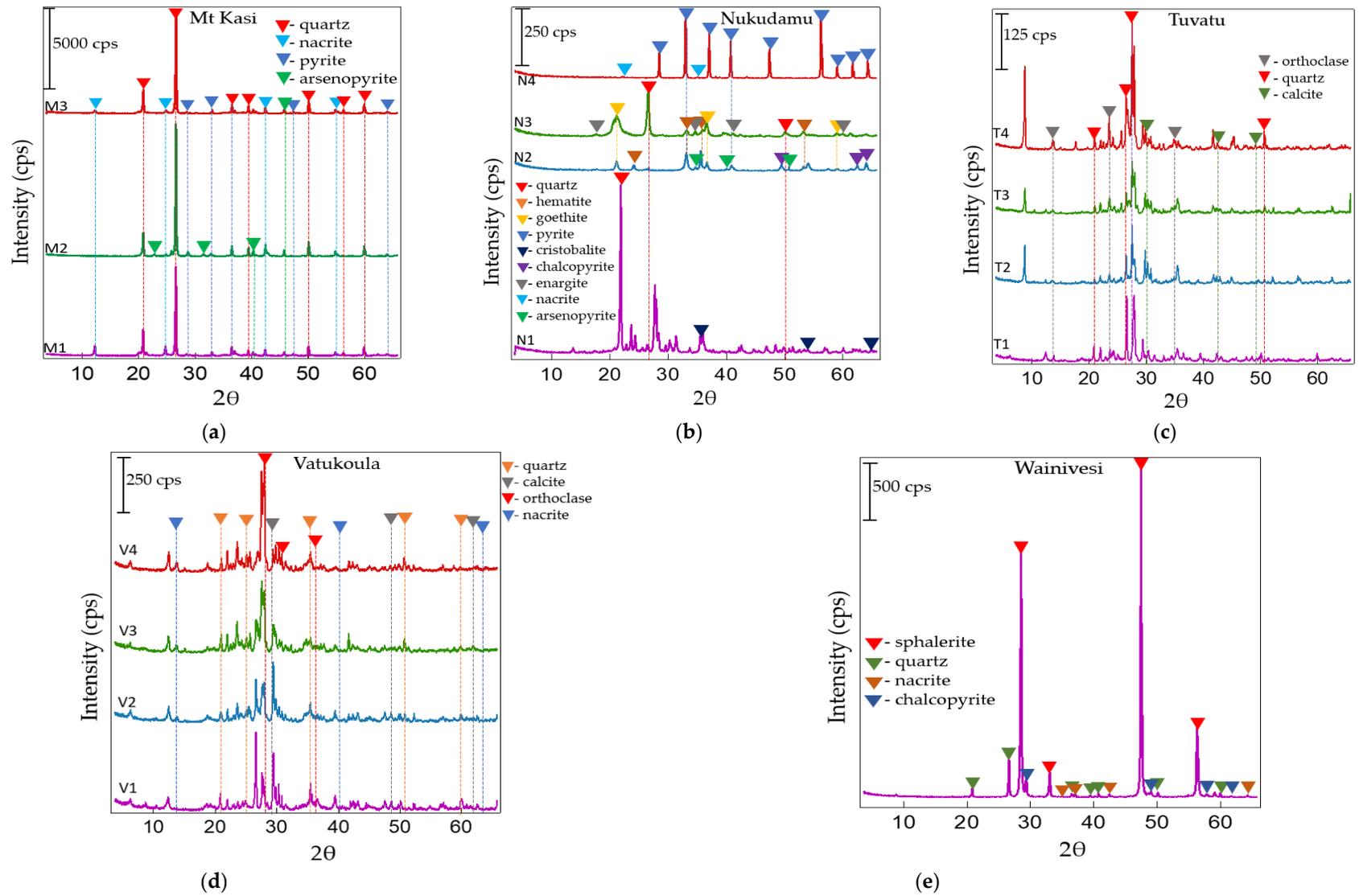
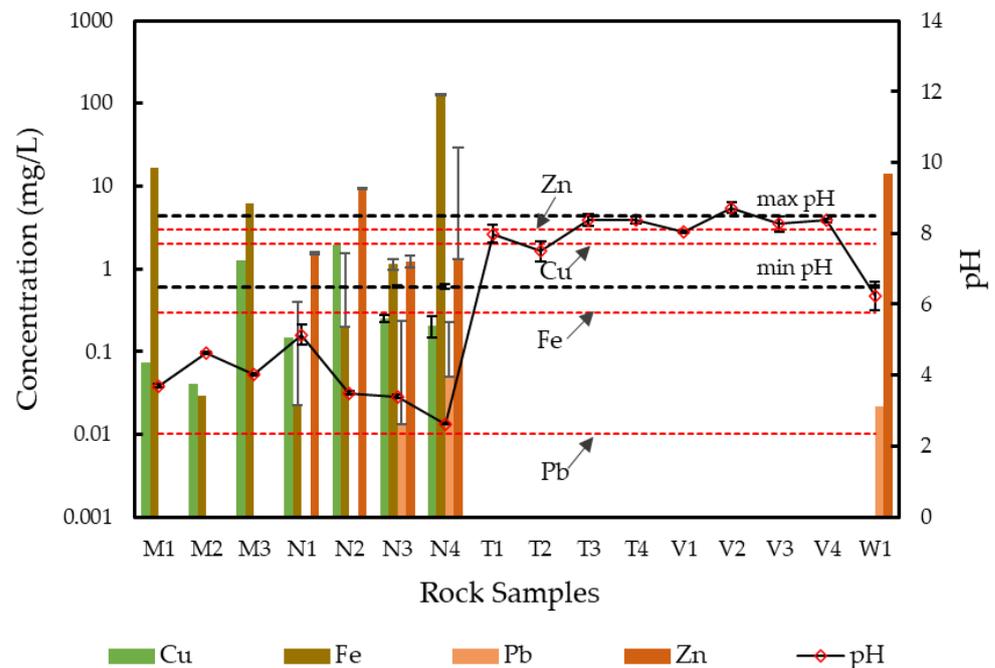


Figure 2. XRD patterns for the mineralogical composition of (a) Mt Kasi, (b) Nukudamu, (c) Tuvatu, (d) Vatukoula, and (e) Wainivesi.

### 3.2. Leachate Characteristics of the Rock Samples—Release and Retention Mechanisms

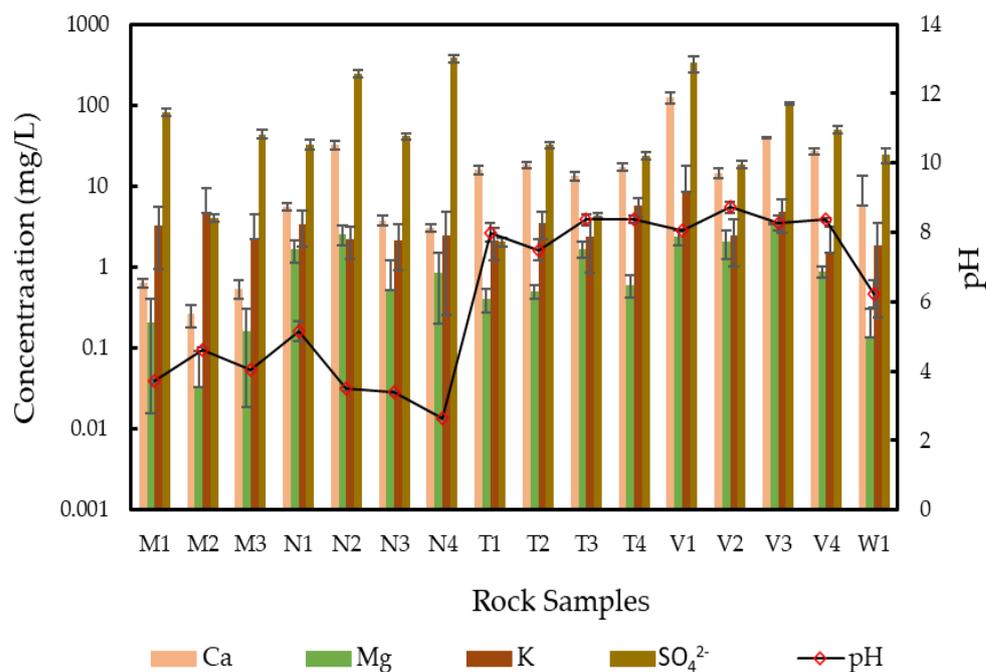
Figures 3 and 4 illustrate the pH and concentrations of Cu, Fe, Pb, Zn and coexisting ions (Ca, K, Mg, and  $\text{SO}_4^{2-}$ ) after batch leaching tests, which were compared with the WHO guideline values for drinking water [47] and is the same standard adopted for drinking water quality in Fiji. Lower pH values were obtained for Nukudamu (2.6 to 5.1) and Mt Kasi (3.7 to 4.6). The Wainivesi rock sample indicated a weakly acidic pH of 6.2. Based on the WHO drinking water guidelines for pH, Mt Kasi, Nukudamu, and Wainivesi leachates were all below the regulatory range (pH 6.5 to 8.5). The low pH might be attributed to the oxidation of sulfide minerals, i.e., pyrite, chalcopyrite, arsenopyrite, and sphalerite found in the rocks [48,49]. Pyrite is typically ubiquitous, associated with most of the base metals, and usually problematic due to AMD generation when exposed to oxidizing conditions. Oxidation products, such as Fe(III) hydroxysulfate [50] (pH < 3), sulfate ( $\text{SO}_4^{2-}$ ), ferrous iron ( $\text{Fe}^{2+}$ ), and hydrogen ( $\text{H}^+$ ) ions are released into the solution, and the ferrous iron is further oxidized to ferric iron ( $\text{Fe}^{3+}$ ) generating more acidity [49].  $\text{Fe}^{3+}$  in the acidic solution also tends to oxidize other metal sulfide minerals in the rock samples, consequently releasing more metal,  $\text{H}^+$ , and  $\text{SO}_4^{2-}$ . The mobility of the dissolved metal ions in the rocks, soils, or sediments is governed by the balance between the release and retention mechanisms under a given geochemical condition [37]. Sulfide oxidation is likely the most dominant release mechanism of Cu, Pb, Zn, and  $\text{SO}_4^{2-}$  (Figure 4) in the Mt Kasi, Nukudamu, and Wainivesi rock samples. This is also reflected in the higher Eh values of leachates from these three rock samples (Table S4). Kelderman and Osman (2006) and Popenda (2013) highlighted that the increase in solubilization of ions including hazardous metals such as Cu, Pb, and Zn due to higher redox potential could be attributed to the oxidation of heavy metal sulfide bindings [51,52].



**Figure 3.** Leachate concentrations of Cu, Fe, Pb, and Zn and the pH of Mt Kasi (M1–M3), Nukudamu (N1–N4), Tuvatu (T1–T4), Vatukoula (V1–V4), and Wainivesi (W1). The dotted lines indicate the WHO drinking water guideline for Cu, Fe, Pb, Zn, and pH (minimum and maximum values; 6.5–8.5).

Although Cu, Fe, Pb, and Zn were detected in the leachates, they were not consistently leached from all the rock samples (Figure 3; Table S4). Higher concentrations of Fe at  $16.8 \pm 3.72$  mg/L,  $6.08 \pm 1.45$  mg/L,  $1.15 \pm 0.20$  mg/L, and  $129 \pm 0.20$  mg/L were observed at Mt Kasi (M1, M3) and Nukudamu (N3, N4), respectively, which exceeded the limit for Fe (<0.3 mg/L) in drinking water. Copper leached only from the Mt Kasi and Nukudamu

samples at lower concentrations of up to  $1.94 \pm 0.41$  mg/L (N2) and was around the WHO drinking water standard at 2 mg/L. High Zn concentration was observed in the leachates of samples from Wainivesi ( $14.2 \pm 3.22$  mg/L) and Nukudamu (N2;  $9.54 \pm 1.32$  mg/L). Meanwhile, Pb leached only from two of the four Nukudamu rock samples (N3 and N4) with concentrations of  $0.02 \pm 0.02$  and  $0.05 \pm 0.06$  mg/L, respectively, and concentrations of  $0.02 \pm 0.04$  mg/L for the Wainivesi sample. Compared with the WHO guidelines for dissolved Pb and Zn in drinking water, the Nukudamu (N3 and N4) and Wainivesi rock samples exceeded the threshold limit of 0.01 mg/L for Pb, while N2 exceeded the limit for Zn 3 mg/L. The high Pb leaching concentration from the Wainivesi rock samples could be the possible reason for the elevated levels of Pb found in the Wainivesi River [13].



**Figure 4.** Leachate concentrations of Ca, Mg, K, and  $\text{SO}_4^{2-}$  and the pH of Mt kasi (M1–M3), Nukudamu (N1–N4), Tuvatu (T1–T4), Vatukoula (V1–V4), and Wainivesi (W1) samples.

In contrast, the Tuvatu and Vatukoula rock samples showed higher pH ranging from 7.5 to 8.7. The alkaline pH could be attributed to the dissolution of carbonate minerals (i.e., calcite and dolomite) in the rock samples (Figure 2c,d and Table S3), which releases divalent cations (Ca, Mg, Fe) and  $\text{HCO}_3^-$  that raise the leachate pH to near neutral. This is supported by the higher Ca concentrations in T1–T4 and V1–V4 samples (Figure 4), and no hazardous elements were released from these rock samples. To gain more insights into the retention mechanism of the hazardous elements, thermodynamic calculations using Visual MINTEQ were conducted. The results indicate that calcite and dolomite were undersaturated (Table S5), suggesting the dissolution of these minerals. Equilibrium dissolution of calcite and dolomite consumes  $\text{H}^+$  and generates aqueous carbonate species, e.g., hydrozincite, smithsonite, hydrocerussite, and cerussite [53,54], which are later reflected in Nukudamu (N1) and Wainivesi (W1) leachates. Although the saturation indices (SIs) for N1 and W1 indicated the dissolution of calcite and dolomite, Pb and Zn were released probably due to the lack of carbonate minerals to consume  $\text{H}^+$ . This is supported by the undersaturation of hydrozincite, smithsonite, hydrocerussite, and cerussite (Table S5). The SIs showed that the mobility of Pb and Zn in the two samples could be controlled by the dissolution of calcite and dolomite in the system because it promotes Pb/Zn carbonate surface precipitations. The gradual co-precipitations of Pb, Zn, and Cu with carbonates could enhance the stability of the hazardous elements in the system [48].

However, no such speciation (Pb/Zn-carbonates) was observed in the Tuvatu and Vatukoula rock samples. The high buffering effect of Tuvatu and Vatukoula samples may have been enhanced to a lesser extent by clay minerals such as kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) [55] as indicated by positive *SIs* for this mineral. Although the pH buffering reaction of Al-bearing phases between pH 4 to 4.5 [56] could occur through gibbsite dissolution (*SIs* < 0) in Mt Kasi and Nukudamu and may lead to the sequestering of hazardous elements, this contribution is not as pronounced as those observed with carbonate minerals in the Tuvatu and Vatukoula rock samples. Once the carbonate minerals are depleted, however, environmental vulnerability might be inevitable via the release of hazardous elements from the rock samples. It is also relevant to note that arsenic (As), even though identified by the chemical analysis in rock samples of Mt Kasi and Nukudamu, was outside the focus of the leaching analysis and should be considered for future investigations.

### 3.3. Relationship between the Rock Samples and Their Vulnerability in Generating Acid Mine Drainage

To identify the factors controlling the leachate chemistry when the rock samples are in contact with water, PCA was used to extract important and inter-correlated dependent variables of the samples from the leachates using 15 variables (pH, EC, ORP, Al, Cu, Fe, Mg, Mn, Pb, Zn, Ca, K, Na,  $\text{SO}_4^{2-}$ , and Si) (Table 2, Figure S2). The results showed that the 4 principal components accounted for 77.5% of leachate concentration with eigenvalues > 1. The PC1 (31.6%) had positive loadings of Pb, Fe, ORP, and EC, and to some extent also Cu and  $\text{SO}_4^{2-}$ , though with lower loadings, which could be related to chalcopyrite and pyrite. The loadings of these variables were related to the high loadings of negative pH. This component indicates that the release of Pb, Cu, and  $\text{SO}_4^{2-}$  were associated with the higher ORP and more acidic pH of the rock samples, which was attributed to the enhanced oxidation of sulfide minerals [48]. The PC2 (21.1%) indicated high loadings of EC, Mg, Ca, K, and  $\text{SO}_4^{2-}$ . The highest contribution of Ca and  $\text{SO}_4^{2-}$  was related to the minerals controlling the EC of the leachate pH such as calcite, gypsum, and dolomite. This means that these minerals influenced the buffering mechanism of the rock samples. Meanwhile, the PC3 and PC4 accounted for only 16.6 and 8.6%, respectively. Contributions of Al and Si could infer the effects of phyllosilicate and clay minerals on the leachate chemistry (e.g., kaolinite, orthoclase, and anorthite); however, the contributions of Al and Si on the leachate chemistry from PC3 and PC4 were not very pronounced.

The *ABA* test results in Figure 5 show that rock samples from Mt Kasi, Nukudamu, Wainivesi, Tuvatu (T1), and V4 from Vatukoula had negative *NNP* values (<−20 kg  $\text{CaCO}_3/\text{t}$ ). This means that rock samples from these sites were likely to generate acidity when exposed to oxidizing conditions. The negative *NNP* supports the presence of sulfide minerals in these samples. Although T1 contained some carbonate minerals, the *ABA* test suggests that once its carbonate neutralization capacity is depleted, acid generation might occur. Meanwhile, sample V1 from Vatukoula had *NNP* (20.5) (>20 kg  $\text{CaCO}_3/\text{t}$ ), indicating that it is a non-acid-producing rock and unlikely to generate AMD. The remaining samples, T3, T4, V2, and V3, had *NNP* values between −20 to 20 kg  $\text{CaCO}_3/\text{t}$ , suggesting uncertainty to generate acidity.

The pH ( $\text{H}_2\text{O}_2$ ) acidification test results are illustrated in Figure 6. The rock samples M1, M3, N2, N3, N4, T3, and W1 had pH < 3.5, which means that they are likely to generate acidity. Although the Tuvatu (T3) rock sample was characterized as having an alkaline leachate pH with a mineralogy dominated by silicates and carbonates, the *ABA* test, indicated uncertainty while the pH ( $\text{H}_2\text{O}_2$ ) test showed a pH of 3.2. This means that the sample remains likely to generate acidity if the neutralization capacity of the carbonate minerals in the sample are exhausted. These results could be extended to the other rock samples that were in the *ABA* uncertainty range. On the other hand, the Mt Kasi sample (M2) and Nukudamu (N1), which initially recorded acidic leaching pH, had pH > 3.5, indicating non-acid forming rocks based on the pH ( $\text{H}_2\text{O}_2$ ) test. This implies that a single acid test could not completely provide the certainty of acid production of rock from these mine sites. In comparing the acid-forming potentials of the samples using the two

techniques, the *ABA* method showed that 68.7% of the samples were acid forming while pH ( $H_2O_2$ ) captured 43.8%. This discrepancy could be attributed to the disparity in approaches applied in these techniques. On the one hand, *ABA* is based on *AP* and *NP* by measurement of sulfur and carbonate, respectively, for the *NNP* calculation [57,58]. However, *ABA* is a widely applied technique that is found to be more appropriate for short- to long-term acid generation evaluation, but its testing procedure can be exhaustive and give three overlapping outcomes. The pH ( $H_2O_2$ ) tests, on the other hand, use oxidation via a strong oxidant to completely oxidize sulfides exposed during the experiment but occasionally tend to overestimate the acid-producing potential of samples. In terms of its ease of use, this test is a more streamlined approach to determine acid-forming potential made popular in Japan with an immediate and definite outcome [43,44]. The significant differences in the tests could be attributed to the reaction rate and the nature of the reactant used (i.e., 1M HCl and 15%  $H_2O_2$  for the *ABA* test and 30%  $H_2O_2$  for the pH( $H_2O_2$ ) test) with the availability of the minerals (i.e., sulfide and carbonates) to react also influencing the different outcomes of the 2 methods. The pH( $H_2O_2$ ) method uses strong  $H_2O_2$  which might accelerate and react intensely with sulfides and, in the process, cause the dissolution of carbonates neutralizing its effect compared with *ABA*, which reacts individually with sulfide and carbonate minerals with less intensity. In addition, the contrast may be attributed to *ABA* potential to assess the capacity of rocks to neutralize acid, which is essential for effective mine waste management and rehabilitation as well as regulatory compliance. In contrast, the pH( $H_2O_2$ ) test, which originated in Japan, is a simpler method that provides immediate results based on the oxidation of sulfide minerals.

**Table 2.** Principal component analysis (PCA) including total variance, eigenvalue, and cumulative frequency for the leachates of rock samples.

Variables	PC1	PC2	PC3	PC4
pH	<b>−0.381</b>	0.141	−0.078	−0.276
EC	<b>0.308</b>	<b>0.393</b>	−0.082	0.103
ORP	<b>0.362</b>	−0.171	0.181	<b>0.310</b>
Al	0.253	−0.049	<b>0.471</b>	−0.081
Cu	0.238	−0.097	<b>0.469</b>	−0.077
Fe	<b>0.317</b>	0.220	−0.299	0.166
Mg	−0.076	<b>0.325</b>	<b>0.345</b>	−0.062
Mn	0.121	−0.186	0.049	<b>0.316</b>
Pb	<b>0.331</b>	0.129	−0.358	−0.058
Zn	0.178	−0.111	0.139	−0.618
Ca	−0.123	<b>0.452</b>	0.209	−0.125
K	−0.163	<b>0.395</b>	0.072	0.143
Na	−0.297	0.052	0.047	0.290
SO <sub>4</sub> <sup>2−</sup>	0.262	<b>0.451</b>	0.097	0.021
Si	−0.216	−0.008	<b>0.306</b>	<b>0.410</b>
Eigenvalue	5.00	3.03	2.42	1.30
Variance%	31.6	21.1	16.6	8.6
Cumulative%	31.6	52.7	69.2	77.5

Note: Bold text indicates variables that accounted significantly under each PC.

Incorporating the two methods coupled with geochemical characterization and thermodynamic calculation provided insights into the acid production and neutralization potentials of rock samples. Thus, it is still safe to assume that the samples (M2, N1, and T3) have the potential to generate acidity as confirmed by their mineralogy and leaching behavior. The tests have established that Mt Kasi, Nukudamu, and Wainivesi mine sites are the most vulnerable because of sulfide minerals that have the potential to generate AMD. Furthermore, the various geochemical characterization suggests the susceptibility of those samples in uncertainty range, which discloses important information about their vulnerability once the carbonate minerals are depleted. The results demonstrate that the degree and scope of environmental vulnerability are often dictated by the geochemical

properties of extracted ores. The vulnerability worsens if mining and waste management best practices are lacking; therefore, AMD generation would likely persist for a long time even after mining has ceased [9,59–61]. Thus, close attention should be paid to the abandoned sites and proper environmental management practices should be seriously applied to currently operating mine sites. The above knowledge adds valuable contributions to a more prudent mining permitting process and strengthens mining policies and frameworks to ensure improved post-mining rehabilitation programs.

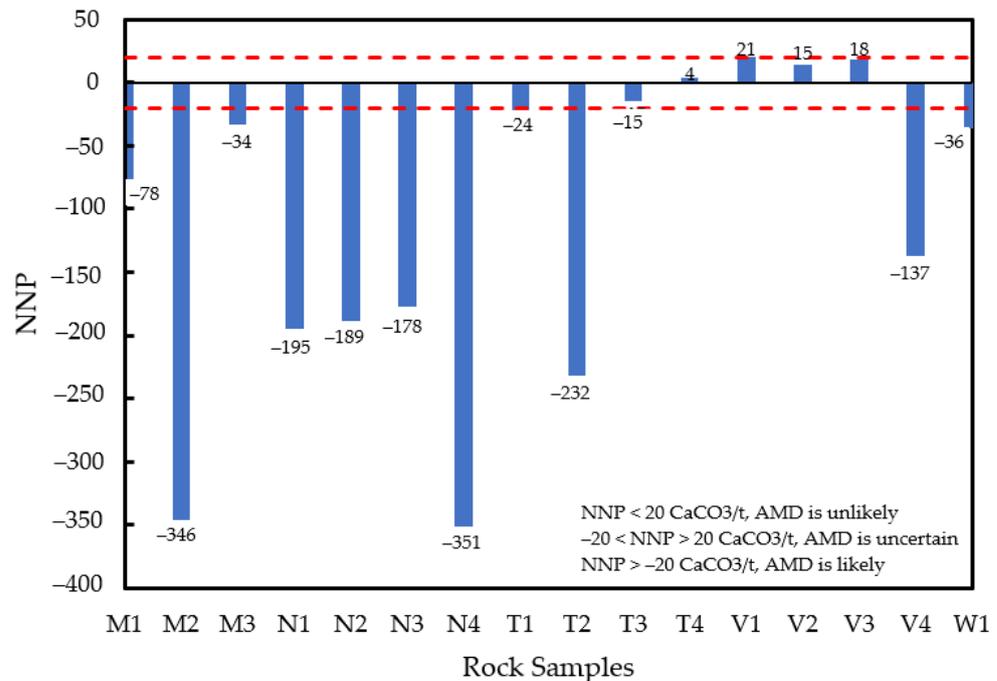


Figure 5. Acid–base accounting (ABA) for Mt Kasi (M1–M3), Nukudamu (N1–N4), Tuvatu (T1–T4), Vatukoula (V1–V4), and Wainivesi (W1) rock samples.

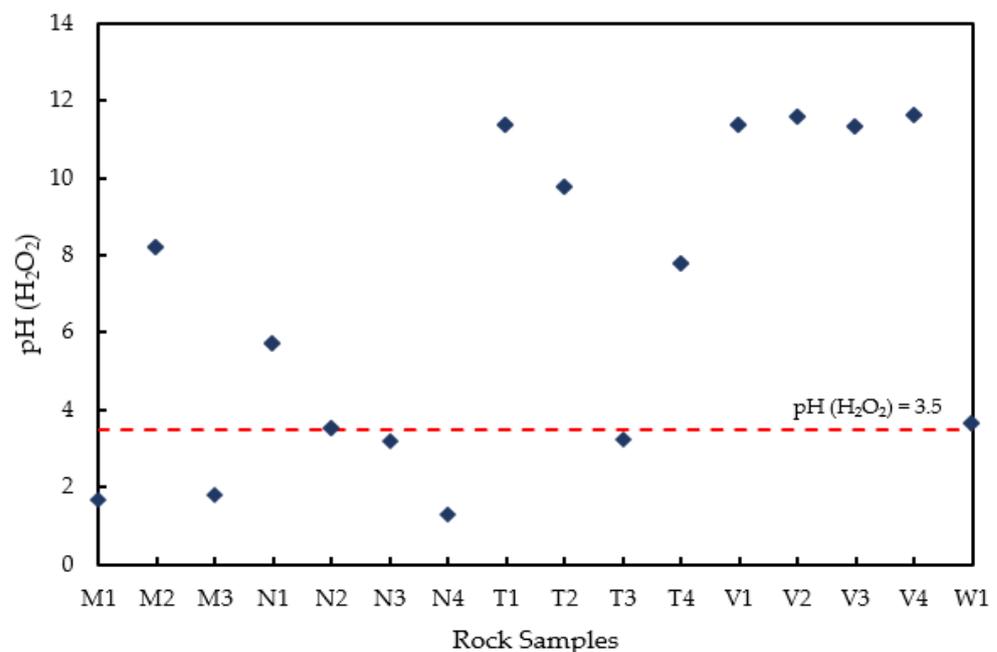


Figure 6. Hydrogen peroxide pH test (pH (H<sub>2</sub>O<sub>2</sub>)). The dotted line indicates the threshold for acidification potential (pH = 3.5).

#### 4. Conclusions

The geochemical characterization of rock samples from Fiji provides valuable insights into the potential environmental impacts of mining activities. The leachate concentrations of Cu, Pb, and Zn in the rock samples from Mt Kasi, Nukudamu, and Wainivesi exceeded the drinking water regulatory thresholds established by WHO. This is primarily attributed to the oxidation of sulfide minerals, which has been conclusively elucidated via a leaching experiment. In contrast, the retention of hazardous elements in the Tuvatu and Vatukoula rock samples was linked to the strong buffering effect of calcite and dolomite. Acidic pH and high redox potential of the rock samples were found to be key factors contributing to the release of hazardous elements. The ABA test, coupled with leaching tests and geochemical characterization, provides a comprehensive assessment of the acid potential of the rock samples from Fiji. The ABA test revealed that the rock samples from Mt Kasi, Nukudamu, and Wainivesi have a high potential to generate AMD, which was consistent with the results of the leaching test and are likely to persist compared with the Tuvatu and Vatukoula rock samples with minor carbonate minerals such as calcite and dolomite. Overall, the study highlights the importance of conducting thorough geochemical studies before approving mining activities to identify potential risks and mitigate environmental impacts. Characterization methods used in this study should be considered a mandatory requirement for mining approval to strengthen and improve mining development, waste management, and post-mining rehabilitation in developing countries such as Fiji.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13050661/s1>, Figure S1. Microscopic observation of rock samples M2, N1,T3, V1, V4, and W1. Figure S2. Graphical presentation of the PCA showing the first 3 components with significant inter-correlated dependent variables. Table S1. Rock sample details. Table S2. Quality assurance (QA) and quality control (QC). Table S3. XRD diffraction percentage mineralogical abundances (%) of the rock samples. Table S4. The EC, Eh, ORP, pe, and mean concentrations of co-existing elements, Al, Na, and Si, of the rock samples. Table S5. Saturation indices (SIs) of selected mineral phases in the leachates of the rock samples.

**Author Contributions:** Conceptualization, A.T.S. and T.I.; sample collection and methodology, A.T.S., T.A. and T.I.; validation, W.M., T.A., C.B.T. and T.I.; formal analysis, A.T.S., W.M., C.B.T. and T.A.; writing—original draft preparation, A.T.S.; writing—review and editing, W.M., T.A., C.B.T. and T.I.; visualization, A.T.S. and M.W; supervision, T.A. and T.I.; project administration, A.T.S.; funding acquisition, A.T.S., T.A. and T.I. All authors have read and agreed to the published version of the manuscript.

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#### References

1. Xu, Q.; Wang, G.; Liang, X.; Qu, S.; Shi, Z.; Wang, X. Determination of mining-induced changes in hydrogeological parameters of overburden aquifer in a coalfield, northwest China: Approaches using the water level responses to earth tides. *Geofluids* **2021**, *2021*, 5516997. [[CrossRef](#)]
2. McKinnon, E. The environmental effects of mining waste disposal at Lihir Gold Mine, Papua New Guinea. *Rural Remote Health* **2002**, *1*, 40–50.
3. Banks, G.; Paull, D.; Mockler, S. *The Social and Environmental Impact of Mining in Asia-Pacific: The Potential Contribution of a Remote-Sensing Approach*; Resource Management in Asia-Pacific Working paper No. 60; The Australian National University: Canberra, Australia, 2005.

4. Mudd, G.M.; Roche, C.; Northey, S.A.; Jowitt, S.M.; Gamato, G. Mining in Papua New Guinea: A complex story of trends, impacts and governance. *Sci. Total Environ.* **2020**, *741*, 140375. [[CrossRef](#)]
5. Worlanyo, A.S.; Jiangfeng, L. Evaluating the environmental and economic impact of mining for post-mined land restoration and land-use: A review. *J. Environ. Manag.* **2021**, *279*, 111623. [[CrossRef](#)] [[PubMed](#)]
6. Fashola, M.O.; Ngole-Jeme, V.M.; Babalola, O.O. Heavy metal pollution from gold mines: Environmental effects and bacterial strategies for resistance. *Int. J. Environ. Res. Public Health* **2016**, *13*, 1047. [[CrossRef](#)]
7. Park, I.; Tabelin, C.B.; Jeon, S.; Li, X.; Seno, K.; Ito, M.; Hiroyoshi, N. A review of recent strategies for acid mine drainage prevention and mine tailings recycling. *Chemosphere* **2019**, *219*, 588–606. [[CrossRef](#)] [[PubMed](#)]
8. Saharan, M.R.; Gupta, K.K.; Jamal, A.; Sheoran, A.S. Management of acidic effluents from tailing dams in metalliferous mines. *Mine Water Environ.* **1995**, *14*, 85–93. [[CrossRef](#)]
9. Akcil, A.; Soner, K. Acid Mine Drainage (AMD): Causes, treatment and case studies. *J. Clean. Prod.* **2006**, *14*, 1139–1145. [[CrossRef](#)]
10. Foli, G.; Apeah, O.B.; Amedjoe, C.G. Pre-mining water quality prediction from non-weathered sulphide ores along the Ashanti metallogenic belt in Ghana using Acid-Base accounting procedure. *Am. J. Sci. Ind. Res.* **2011**, *2*, 827–833. [[CrossRef](#)]
11. Kumar, S.; Islam, A.R.M.T.; Islam, H.T.; Hasanuzzaman, M.; Ongoma, V.; Khan, R.; Mallick, J. Water resources pollution associated with risks of heavy metals from Vatukoula Goldmine region, Fiji. *J. Environ. Manag.* **2021**, *293*, 112868. [[CrossRef](#)] [[PubMed](#)]
12. Singh, S.; Mosley, L. Trace metal levels in drinking water on Viti Levu, Fiji Islands. *South Pac. J. Nat. Sci.* **2003**, *21*, 31–34. [[CrossRef](#)]
13. Kumar, S.; Islam, A.R.M.T.; Hasanuzzaman, M.; Salam, R.; Islam, M.S.; Khan, R.; Rahman, M.S.; Pal, S.C.; Ali, M.M.; Idris, A.M.; et al. Potentially toxic elemental contamination in Wainivesi River, Fiji impacted by gold-mining activities using chemometric tools and SOM analysis. *Environ. Sci. Pollut. Res.* **2022**, *29*, 42742–42767. [[CrossRef](#)]
14. Ko, B.G.; Anderson, C.W.; Bolan, N.S.; Huh, K.Y.; Vogeler, I. Potential for the phytoremediation of arsenic-contaminated mine tailings in Fiji. *Soil Res.* **2008**, *46*, 493–501. [[CrossRef](#)]
15. Matanitobua, V.; Ng, J.; Chiswell, B.; Harris, H.; Aalbersberg, W.; Noller, B. Arsenic adsorption and desorption processes downstream of a Fijian gold mine. In *Arsenic in Geosphere and Human Diseases, Proceedings of the Arsenic 2010: Third International Congress on Arsenic in the Environment (As-2010), Tainan, Taiwan, 17–21 May 2010*; CRC Press: London, UK, 2010; pp. 176–178.
16. Matararawa, S. Gold Mining and Acute Respiratory Infection in Children: A Retrospective Cohort Study in Vatukoula, Fiji. Master's Thesis, University of Canterbury, Christchurch, New Zealand, 2018.
17. Rabuku, A.T.W.; Abdul, Q.M. Natural radioactivity measurement of gold mine tailings in Vatukoula, Fiji Islands. *Renew. Energy Environ. Sustain.* **2020**, *5*, 10. [[CrossRef](#)]
18. Matak, M.; Koshy, K.C.; Lal, M. Baseline Climatology of Viti Levu (Fiji) and Current Climatic Trends. *Pac. Sci.* **2006**, *60*, 49–68. [[CrossRef](#)]
19. Ongoma, V.; Rahman, M.A.; Ayugi, B.; Nisha, F.; Galvin, S.; Shilenje, Z.W.; Ogwang, B.A. Variability of diurnal temperature range over Pacific Island countries, a case study of Fiji. *Meteorol. Atmos. Phys.* **2021**, *133*, 85–95. [[CrossRef](#)]
20. Colley, H.; Flint, D.J. *Metallic Mineral Deposits of Fiji, No.4, Mineral Resources Department Memoir*; Government of Fiji: Suva, Fiji, 1995; 196p.
21. Turner, S.J. Fluid Inclusion, Alteration, and Ore Mineral Studies of an Epithermal, Mineralized Vein System: Mount Kasi, Vanua Levu, Fiji. Master's Thesis, University of Auckland, Auckland, New Zealand, 1986.
22. Colley, H.; Rice, C.M. A kuroko type ore deposit in Fiji. *Econ. Geol.* **1975**, *70*, 1373–1386. [[CrossRef](#)]
23. Colley, H.; Rice, C.M. Kuroko-type deposits in Vanua Levu, Fiji. *N. Z. J. Geol. Geophys.* **1978**, *21*, 277–285. [[CrossRef](#)]
24. Ashley, P.M.; Andrew, A.S. Petrographic, fluid inclusion and stable isotope investigation of a suite of samples from the Tuvatu prospect, Fiji. *Commonwealth Sci. Indust. Res. Org.* **1989**, *50*, 36.
25. Feudigmann, P.; Taylor, I.; Woodward, A.; Lee, A.F.; Morgan, D.M. *Lion One Metals Tuvalu Gold Project Preliminary Economic Assessment*; National Instrument 43-101 Technical Report; Lion One: Nadi, Fiji, 2015.
26. Ahmad, M.; Solomon, M.; Walsh, J.L. Mineralogical and geochemical studies of the Emperor gold telluride deposit, Fiji. *Econ. Geol.* **1987**, *82*, 345–370. [[CrossRef](#)]
27. Anderson, W.B.; Eaton, P.C. Gold mineralisation at the Emperor mine, Vatukoula, Fiji. *J. Geochem. Explor.* **1990**, *36*, 267–296. [[CrossRef](#)]
28. Eaton, P.C.; Setterfield, T.N. The relationship between epithermal and porphyry systems within the Tavua Caldera, Fiji. *Econ. Geol.* **1993**, *88*, 1053–1083. [[CrossRef](#)]
29. White, N.C.; Leake, M.J.; McCaughey, S.N.; Parris, B.W. Epithermal gold deposits of the southwest Pacific. *J. Geochem. Explor.* **1995**, *54*, 87–136. [[CrossRef](#)]
30. Houtz, R.E. *Geology of North Tailevu, Viti Levu*; Bulletin 1; Fiji Geological Survey: Viti Levu, Fiji, 1958; p. 19.
31. *JIS A 1226*; Test Method for Ignition Loss of Soils. Japanese Standards Association: Tokyo, Japan, 2020; pp. 1–10.
32. Marove, C.A.; Tangviroon, P.; Tabelin, C.B.; Igarashi, T. Leaching of hazardous elements from Mozambican coal and coal ash. *J. Afr. Earth Sci.* **2020**, *168*, 103861. [[CrossRef](#)]
33. *JLT-13*; Departmental Notification No. 13 on Leaching Test Method for Landfill Wastes. Japanese Environmental Agency: Tokyo, Japan, 1973.
34. Tabelin, C.B.; Hashimoto, A.; Igarashi, T.; Yoneda, T. Leaching of boron, arsenic, and selenium from sedimentary rocks: II. pH dependence, speciation, and mechanisms of release. *Sci. Total Environ.* **2014**, *473*, 244–253. [[CrossRef](#)] [[PubMed](#)]

35. Huyen, D.T.; Tabelin, C.B.; Thuan, H.M.; Dang, D.H.; Truong, P.T.; Vongphuthone, B.; Kobayashi, M.; Igarashi, T. The solid-phase partitioning of arsenic in unconsolidated sediments of the Mekong Delta, Vietnam and its modes of release under various conditions. *Chemosphere* **2019**, *233*, 512–523. [[CrossRef](#)]
36. Khoeur, K.; Sasaki, A.; Tomiyama, S.; Igarashi, T. Distribution of zinc, copper, and iron in the tailings dam of an abandoned mine in Shimokawa, Hokkaido, Japan. *Mine Water Environ.* **2019**, *30*, 119–129. [[CrossRef](#)]
37. Tabelin, C.B.; Silwamba, M.; Paglinawan, F.C.; Mondejar, A.J.S.; Duc, H.G.; Resabal, V.J.; Opiso, E.M.; Igarashi, T.; Tomiyama, S.; Ito, M.; et al. Solid-phase partitioning and release-retention mechanisms of copper, lead, zinc, and arsenic in soils impacted by artisanal and small-scale gold mining (ASGM) activities. *Chemosphere* **2020**, *260*, 127574. [[CrossRef](#)]
38. Mufalo, W.; Tangviroon, P.; Igarashi, T.; Ito, M.; Sato, T.; Chirwa, M.; Nyambe, I.; Nakata, H.; Nakayama, S.; Ishizuka, M. Solid-phase partitioning and leaching behavior of Pb and Zn from playground soils in Kabwe, Zambia. *Toxics* **2021**, *9*, 248. [[CrossRef](#)]
39. Gustafsson, J.P. *Visual Minteq 3.1 User Guide*; KTH, Department of land and Water Resources: Stockholm, Sweden, 2014; p. 550.
40. Lawrence, K.A.; Wang, Y. Determination of neutralization potential in the prediction of acid rock drainage. In Proceedings of the 4th International Conference of Acid Rock Drainage, Vancouver, BC, Canada, 31 May–6 June 1997; pp. 451–464.
41. Wang, L.; Li, Y.; Cui, X.; Wang, X.; Lu, A.; Wang, X.; Wang, C.; Gan, D. Weathering behavior and metal mobility of tailings under an extremely arid climate at Jinchuan Cu-Ni sulfide deposit, Western China. *J. Geochem. Explor.* **2017**, *173*, 1–12. [[CrossRef](#)]
42. *JGS 0271-2016; Test Method for Acidification Potential of Soils and Rock by Using Hydrogen Peroxide Solution*. Japanese Geotechnical Society: Tokyo, Japan, 2016.
43. Igarashi, T.; Oyama, T.; Saito, N. Experimental study on acidification potential of leachate from sedimentary rocks containing pyrite. *J. Jpn. Soc. Eng. Geol.* **2001**, *42*, 214–221. [[CrossRef](#)]
44. Inui, T.; Katayama, M.; Katsumi, T.; Takai, A.; Kamon, M. Evaluating the long-term leaching characteristics of heavy metals in excavated rocks. *J. Soc. Mater. Sci. Jpn.* **2014**, *63*, 73–78. [[CrossRef](#)]
45. Clarke, R.; Smith, D.; Naden, J. Source controls on: Regional geology and magmatic evolution of Fiji. *Lithos* **2022**, *432–433*, 106897. [[CrossRef](#)]
46. Clarke, R.; Smith, D.J.; Naden, J.; Holwell, D.; Mann, S. Mineralogical constraints on the genesis of an alkalic-type epithermal Au-Te deposit: Tuvatu, Fiji. *Ore Geol. Rev.* **2023**, *154*, 105279. [[CrossRef](#)]
47. World Health Organization. *Guidelines for Drinking-Water Quality*, 4th ed.; World Health Organization: Geneva, Switzerland, 2011.
48. Tabelin, C.B.; Igarashi, T.; Villacorte-Tabelin, M.; Park, I.; Opiso, E.M.; Ito, M.; Hiroyoshi, N. Arsenic, selenium, boron, lead, cadmium, copper, and zinc in naturally contaminated rocks: A review of their sources, modes of enrichment, mechanisms of release, and mitigation strategies. *Sci. Total Environ.* **2018**, *645*, 1522–1553. [[CrossRef](#)]
49. Igarashi, T.; Herrera, P.S.; Uchiyama, H.; Miyamae, H.; Iyatomi, N.; Hashimoto, K.; Tabelin, C.B. The two-step neutralization ferrite-formation process for sustainable acid mine drainage treatment: Removal of copper, zinc, and arsenic and the influence of coexisting ions on ferritization. *Sci. Total Environ.* **2020**, *715*, 136877. [[CrossRef](#)]
50. Bao, Y.; Guo, C.; Lu, G.; Yi, X.; Wang, H.; Dang, Z. Role of microbial activity in Fe (III) hydroxysulfate mineral transformations in an acid mine drainage-impacted site from the Dabaoshan Mine. *Sci. Total Environ.* **2018**, *616*, 647–657. [[CrossRef](#)]
51. Kelderman, P.; Osman, A.A. Effect of redox potential on heavy metal binding forms in polluted canal sediments in Delft (The Netherlands). *Water Res.* **2007**, *41*, 4251–4261. [[CrossRef](#)]
52. Popena, A. Effect of redox potential on heavy metals and As behavior in dredged sediments. *Desalination Water Treat.* **2014**, *52*, 3918–3927. [[CrossRef](#)]
53. Tangviroon, P.; Noto, K.; Igarashi, T.; Kawashima, T.; Ito, M.; Sato, T.; Mufalo, W.; Chirwa, M.; Nyambe, I.; Nakata, H.; et al. Immobilization of lead and zinc leached from mining residual materials in Kabwe, Zambia: Possibility of Chemical Immobilization by Dolomite, Calcined Dolomite, and Magnesium Oxide. *Minerals* **2020**, *10*, 763. [[CrossRef](#)]
54. Khoshraftar, Z.; Hadiseh, M.; Ahad, G. An insight into the potential of dolomite powder as a sorbent in the elimination of heavy metals: A review. *Case Stud. Chem. Environ. Eng.* **2022**, *7*, 100276. [[CrossRef](#)]
55. Mufalo, W.; Tangviroon, P.; Arima, T.; Igarashi, T.; Ito, M.; Noto, K.; Kawashima, T.; Nyambe, I.; Nakata, H.; Nakayama, S. Immobilization of Pb and Zn leached from mining residue materials in Kabwe, Zambia: Performance of calcined dolomite in column experiments. *J. Geochem. Explor.* **2023**, *249*, 107209. [[CrossRef](#)]
56. Gu, X.; Evans, L.J. Surface complexation modelling of Cd (II), Cu (II), Ni (II), Pb (II), and Zn (II) adsorption onto kaolinite. *Geochim. Cosmochim. Acta* **2008**, *72*, 267–276. [[CrossRef](#)]
57. Gunsinger, M.R.; Ptacek, C.J.; Blowes, D.W.; Jambor, J.L.; Moncur, M.C. Mechanisms controlling acid neutralization and metal mobility within a Ni-rich tailings impoundment. *J. Appl. Geochem.* **2006**, *21*, 1301–1321. [[CrossRef](#)]
58. Brady, K.B.; Cravotta, C.A. Acid base accounting: An improved method of interpreting overburden chemistry to predict quality of coal mine drainage. In Proceedings of the 13th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, USA, 8–9 April 1992.
59. Stewart, W.A.; Miller, S.D.; Smart, R. Advances in acid rock drainage (ARD) characterization of mine wastes. In Proceedings of the 7th International Conference on Acid Rock Drainage (ICARD), American Society of Mining and Reclamation (ASMR) 2006, St. Louis, MI, USA, 26–30 March 2006.

60. Simate, G.S.; Ndlovu, S. Acid mine drainage: Challenges and opportunities. *J. Environ. Chem. Eng.* **2014**, *2*, 1785–1803. [[CrossRef](#)]
61. Assawincharoenkij, T.; Hauzenberger, C.; Ettinger, K.; Sutthirat, C. Mineralogical and geochemical characterization of waste rocks from a gold mine in northeastern Thailand: Application for environmental impact protection. *Environ. Sci. Pollut. Res.* **2018**, *25*, 3488–3500. [[CrossRef](#)] [[PubMed](#)]

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