Potential impacts of mining in Fiji on the surrounding environment: Toward sustainable mining management

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By

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ABSTRACT

Mineral mining is inherently highly impacting, but widely accepted in mining-dominated countries as a necessary development. Non mining countries are more eager to accept the need of essential raw materials supplied from mining critical for infrastructure development and technology advancement. Such demand has always placed mining in the most precarious position because of the environmental and social impacts generated often through sub-standard and unsafe mining practices to be label "necessary evil". Numerous approaches have been explored, trialled, and implemented to achieve safe and sustainable mining but a perfect outcome remains elusive.

The present study explores the chemical and mineralogical characterization of five mine sites in Fiji (Mt Kasi, Nukudamu, Tuvatu, Vatukoula and Wainivesi), and understands and evaluates such characteristics to determine the mine site's conditions. The influences of chemical and mineral properties on the site's environment vulnerability were also assessed and their potential to generate acid mine drainage (AMD). Furthermore, a similar but more detailed characterization study was conducted at two mine sites – Nukudamu and Vatukoula, specifically to assess how their chemical and mineralogical properties dictate the impacts of mining conducted onsite and AMD forming potentials to its surrounding environment.

The three commonly used laboratory test methodologies for rock, sediment, and tailings characterization include X-ray powder diffraction (XRD) analysis for mineral identification and X-ray fluorescence (XRF) analysis to quantify the chemical contents. The leaching experiment, which was the third method, were applied to replicate the release of soluble chemicals from its host through inducement by a known solvent. Occasionally, subject to the purpose of the study, additional tests such as sequential extraction (SE), acid base accounting (*ABA*), pH test with hydrogen peroxide (pH (H_2O_2)), total inorganic carbon (IC) and total organic (TC) analysis, and loss on ignition (LOI) tests with statistical analysis techniques are applied. Water quality analysis was also added to the Nukudamu and Vatukoula mine study, focusing on the transportation of hazardous elements on the surrounding mine site's environment.

Chemical and mineralogical characterization has the ability to provide accurate information about minerals and chemicals contained in an orebody to determine the mineral resources viability for the economic benefits of discovered ores. The method is equally useful in assessing the byproduct of mining and its potential consequences on the environment. Such abilities make it appropriate and necessary to become a requisite to mining applications as an additional screening tool for processing mining approvals to ensure that the critical information about an orebody is understood and that the best decision is reached pertaining to mine development. It is also a good knowledge to gain and understand when dealing with mining regulations and monitoring especially for officials in mining authorities who often lacks such technical specifics. Thus, it is an essential tool to assist not only miners but more importantly regulators. It further provides necessary baseline data for monitoring and managing the environmental impacts including the post-mining period.

The objective of this study is to apply chemical and mineralogical characterization methods to evaluate the environmental impacts of mineral extractions on surrounding environment of studied mine sites. The research also explores how the knowledge gained from this characterization study can improve mining approval systems and processes and further strengthen mining administration and management. It is expected that such improvement will lead to just, prudent and responsible decision making in the sustainable development of Fiji's mineral resources and in countries alike.

The chemical and mineral characteristics evaluation of the five mine sites noted that three mines (Mt Kasi, Nukudamu and Wainivesi) have real environmental threats since they have a potential to generate AMD due to their chemical properties and high sulfide mineral contents. This is also attributed to how the minerals have been exposed as the result of mining and ongoing weathering on site. The situation is worsened as all three sites lacks proper rehabilitation. In contrast, Tuvatu and Vatukoula mine, both active, has low sulfides but significant carbonate minerals with neutralization capacity to exhibit low environmental vulnerability.

The detailed study of Nukudamu mine site confirmed AMD by the pH (H_2O_2) acidification tests. The XRD analysis corroborated heavy presence of sulfide minerals

and accorded chemical compositions results by XRF tests from the altered and weathered rocks exposed on site to be responsible. High levels of hazardous element leachates were observed during leaching tests from the same rock type due to oxidation of sulfide minerals but none were observed for the hard, solid Kuroko type rock which exhibit low sulfides. The water sample analysis of the mine surface water runoffs agrees with the leaching results, exacerbated by ongoing weathering of exposed altered mineralized rocks on site. It is worth noting that further water sample analysis of Nataratara creek water receiving the discharge from mine site revealed acceptable water quality due to dilution and possible natural attenuation by oxide/hydroxide precipitates especially Fe as verified by SEM observation.

As for Vatukoula Gold Mine study, the rock samples were found to be basic in nature, however, altered, and mineralized rock veins mined for gold production showed abundance of sulfide minerals and metalloid composition. The heavy presence of carbonates, i.e., dolomites and calcite especially in host rocks, provided neutralization capacity through dissolution of carbonates to maintain the circumneutral pH of leachates in both rocks as well as tailings. Thus, such manifestation prevented AMD generation but pH (H_2O_2) acidification test proved altered and mineralized rocks do possess potential to form acid as they contain sufficient sulfide minerals. Interestingly, arsenic (As) mobilization was evident by the leaching and water quality study, to be more in altered, mineralized rocks and tailings. Gold mineralization at Vatukoula exist also in the form of arsenian pyrite (arsenopyrite) as possible source of As, which is part of the target mineral mined at VGML.

The discovered high sulfide mineral oxidations and carbonate minerals dissolution effects occurring in the studied sites are common mechanisms in such mining condition. However, the present study is the first to confirm such occurrence in Fiji and the connection to environment vulnerability of these mine sites. The generation of chemical and mineralogy characterization knowledge within mining jurisdictional authority brings confident to staff and add capacities to better evaluate mining applications that ensure responsible decisions pertaining to safer and sustainable mining development in Fiji and countries alike.

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Chapter 1 GENERAL INTRODUCTION

This chapter provides an overview of this research, its background, context, and the rationale behind the study. Much of the motivation emanates from mining in Fiji, its history, how it has advanced and contributed to nation building through benefits as well as drawbacks and how it can continue to develop progressively and sustainably. Despite mining's trouble past and often negative impacts on environment and social implications, it is nevertheless a necessary development. The statement remains true to Fiji, a country with an active mining industry with its accorded benefits but also faces associated ongoing challenges. Fiji is an archipelago of about 330 islands that lies approximately midway between the equator and the South Pole, south of the Pacific Ocean as shown in Figure 1.1. As a developing nation Fiji is largely isolated because of its geographical location from developed or big industrialized countries but lies along the edge of the Pacific Ring of Fire (Figure 1.1). A well-known volatile zone of frequent volcanic and seismic activities partially encircling the basin of the Pacific Ocean and is also a region rich with array of precious metal deposits (National Geographic Society, 2022). Fiji is recognized to have a small size economy with middle-income but one of the more developed of the Pacific Island countries and has some of the world's unique ecosystems and species, which international and local conservationist needs preserving (Ministry of Environment, Government of Fiji, 2020).

The study primarily uses chemical and mineral characterization as a process to assess rock, tailings and water samples collected from selected mine sites in Fiji and analyze using established laboratory techniques to provide information about the properties of these samples. The information was then analyzed to offer a better understanding about the samples collected from the sites and provide an overall chemical and mineralogical characteristic of the site. This chapter discusses why and how such characterization as a process is considered relevant to this study in addressing the research objectives. It also reflects on acid mine

drainage (AMD) as the most problematic challenges in mine waste management (Blowes et al., 2014) and how it relates to this study.

Figure 1.1 Map of Fiji with respect to its global location (latitude 12° S and 22° South and long 174° East and 178° West) and the Pacific ring of fire. (Map is source from maps of world with amendments by the author).

In order to fully comprehend mining, it is relevant to reflect on its history and purpose. An overview of mining in general and the situation in Fiji are also provided in this chapter. It discusses how mining is administered in Fiji reflecting on areas in which chemical and

mineral characterization can assist to improve mining administration systems and processes. It puts into context the relevancy of this study and its contribution to better understand the chemistry and the specific characteristics of the minerals extracted where mining was and is undertaken in Fiji. It explores the role of chemistry and mineralogy and its connections to mining related contamination in Fiji. Simultaneously, it assesses the suitability of the chemical and mineral characterization techniques used in this research best applicable to meet the Fiji's environmental condition. It is hoped that this study will address the knowledge gaps about chemical and mineral characterization information of mineral deposits and mined orebodies. Hence overall ambition is to apply the knowledge gained about chemical and mineral properties to strengthen mining administration especially mining approval processes in Fiji for safer mining and mine waste management.

1.1 Mining and its Global Trend

Mining in its simplest interpretation is the process of extracting useful minerals where they naturally occur on earth usually from an ore body, lode, vein, seam, reef, or placer deposit or deep on the ocean floor. Some examples of substances that are mined include coal, metals, oil and gas, gemstones, potash, also gravel and clay (National Geographic Society, 2022). Mining has been an element of society's growth ever since humans first found minerals in the prehistoric age. Other than agriculture, it has been a development activity that advances human habitation and is largely responsible for the global industrial revolution. Also, its advancement has created safer and better techniques for finding and exposing earth's minerals over time (National Geographic Society, 2022).

Mining has been a major economic driver in nations where it has been practiced, with contributions felt practically by all development sectors of society. Aside from supporting millions of works worldwide the mining industry supports everyday life by providing raw materials, minerals, and metals needed for daily existence throughout prehistoric times to modern living, innovation, and engineering achievements. It supports the health sector with

the provisions of minerals needed for medicines and metals for medical machineries like CT scans, pacemakers, defibrillator, lifesaving machines and surgical pins, bone plates, wires, rods, stent-electrodes, and screws. In addition, because of the ongoing infrastructure development and technological advancement, demand for mining products has never subsided and to satisfy global demands, there is a real expectation for more mining developments and its products (World Bank, 2020, Petrova 2021, Herrington, 2021). According to World Bank and International Energy Agency reports about green economy and minerals for transition to clean energy, mining is now more urgent to supply critical raw materials responsible for renewable energies, an important strategy to ensure the achievement of sustainable development goals (SDGs) (World Bank, 2020, International Energy Agency, 2021). The report highlights that Al, Co, Cu, Fe, Pb, Li, Ni, and Zn will be needed in much larger quantities to meet global renewable and carbon free energy targets. It stated that by 2050, the world's wind turbines will require 300% more metals, solar panels will require 200% more, and energy storage will require 1,000% more.

The fact is that the technologies for clean energy transition – wind, solar, hydrogen and electricity systems are actually significantly more intensive in their composition than current traditional fossil fuel-based energy supply systems (World Bank, 2020, International Energy Agency, 2021). According to the OECD Global Forecast, the green transition is expected to increase the global demand for non-ferrous metals faster than any other raw material demand, from 7 to 19 giga tons per year by 2060 (Bringezu et al., 2019, Petrova, 2020, Herrington, 2021). Electric vehicles, which are crucial to achieving CO_2 emissions reduction targets, will also need a lot of new materials that are otherwise not needed for conventional cars. A study commissioned by the International Copper Association, additional 978,000 tons of Cu are needed to meet demand for charging infrastructure in 2040, a dramatic increase from the 43,300 tons used for charging ports in 2021. Copper is used in portal charging cables, chargers, and wiring to electrical panels (Copper Alliance, 2022). Aluminium is also recognized for its potential in the transport of renewables because it is such a lightweight material. One of the most interesting aspects of Al is that it actually compensates for its initial energy consumption by providing significant energy savings during the use and recycling

phases. Hence, it is a recognized fact that the mining of minerals remains to have an essential role in future development; a role to ensure that SDG's are met and that maintaining and raising humans' standard of living worldwide will continue to be desired.

On the other hand, mining is an extractive process and by its nature involves destructive activities like the removal of vegetation, alteration of landforms like open cut mines or underground in order to access target minerals. Such activities when improperly controlled, compounded with sub-standard and unsafe mining practices causes destruction of habitats, changes of surface water hydrology and quality as well as hydrogeology and often disturb soil profiles (Xu et al., 2021, Bell and Donnelly, 2006, Gardner, 2001). The processing of target minerals in mining generates wastes in the form of waste rocks, slag heaps and tailings that form substrates is typically poor in nutrients, high in potentially toxic substances, and poorly retained water (Ledin and Pedersen, 1996). It also produces liquid waste discharges i.e., acid mine drainage (AMD) that have long lasting destructive impacts on the riverine ecosystem as well as human's health.

The impacts are multiplied if rehabilitation is neglected after the closure of mines. The severity and longevity of mining could potentially be reduced if more is understood about the orebodies chemical and mineral characters not only for its economic benefits but equally important the risks that it may generate when exploited. The same knowledge once gained can improve matching designs for proper rehabilitation of mine sites and be considered at the mine planning stage and reviewed and implemented progressively throughout mining to closure and post closure. These are the drawbacks that have troubled the history of mining and the reason for it opposition. Legacy issues from mining activities often because of poor practices in the past, have made it an unwelcome development and mine developers often denied access to land, especially where potential conflicts with nature conservation are foreseen (Gardner, 2001).

To limit the impact of mining, most countries have adopted the concept of sustainability to better manage mining and its impact towards the environment. A holistic approach to

minerals development, which attempts to satisfy economic, social, and environmental needs of the present generation without compromising the ability of the future generations to meet their needs (Brundtland, 1987, Down and Stocks, 1977). Sustainability in mining is nearly impossible because minerals are finite resources and are non-renewable, once exhausted it will take a very long time to replenish. Mining activity, therefore, is faced with the sustainability issue and if not properly addressed can lead to serious implications. However, it is possible to sustainably develop and manage the resources in a manner that avoids impacting the immediate surrounding environments and social capacity (Brundtland, 1987, Down and Stocks, 1977). The environmental impact of mining requires systematic assessments to be able to understand their detriments and benefits and application of chemical and mineral characterization becomes relevant.

There have been real attempts to seek alternative option to mineral mining due to the negativity surrounding mining. Recycling of mineable materials has been explored and industrialized countries, like Japan, have been using this approach for some time. However, according to relatable reports the ever-increasing demand for minerals cannot fully be satisfied by recycling alone in addition to the current rate of mineral extraction but more is needed to meet the ever-increasing demand for minerals extracted through more mining (OECD, 2019, World bank, 2020, Tabelin et al., 2021, MMSA, 2021).

This can be either compounded or addressed by mining authorities which in some occasions in the past have been criticized for lack of prudent due diligence of mining application. Such cases may result in inadvertent mine closure without proper post-mined rehabilitation, creating environmental consequences and so often social issues faced by local communities. On the other hand, competent mining jurisdictions with similar systems and processes have the necessary capability to identify improvement areas to be perfected before making decision to approve or refuse mining.

1.2 History of Mining in Fiji, its Administration, Impacts and Progression

Fiji has a long history of mining, mineral exploration started further back in 1868 following the discovery of alluvial gold by Charles Gurney in the gravels on the Navua River. Mount Kasi mine in Vanua Levu where commercial mining commenced in 1932 and operated until 1946 has produced an estimated 1,803 kg of Au (Mineral Resources Department, 1998). The mine re-opened in 1996 by Pacific Islands Gold and, produced a total of 1,691 kg of Au and 122 kg of Ag. Financial difficulties, exacerbated by falling gold prices, were cited as the main contributors to its early closure in 1996 (Mineral Resources Department, 1998).

At Vatukoula, subsequent discovery of Au in 1930's by William Borthwick along the Lololevu creek, paved the way in the setting up of a number of mining ventures eventually consolidated into the well-known Emperor Gold Mining Company Limited (Mineral Resources Department, 1998). Mining has continued unabated at Vatukoula since 1933 to become the premier mine in Fiji and has to date produced in excess of seven million ounces of Au and two million ounces of Ag (Vatukoula Gold Mine, 2010). In December 2006, Vatukoula Emperor Gold Mine was closed down due to a lack of profitable returns, and the mine was sold to Westech Mine, which ran it until River Diamond assumed management of the operation in 2008 through majority shareholder status (Soro, 2013). The mine is now under a new management team from China who acquired sole ownership in 2010 and currently operate as Vatukoula Gold Mine Limited – VGML (Vatukoula Gold Mine, 2010).

Tuvatu is another Au deposit previously explored and developed in 1997 by Emperor Gold Mine but was placed under care and maintenance in 2000 primarily because of financial challenges that the company was experiencing. Lion One company of Canada acquired the mine in 2011 and conducted extensive exploration to build its resource viability and was granted a mine development in lease in 2013. Although the COVID19 pandemic has slowed the development progress of the mine, the company is confident of Au production and exports it by end of 2023 (Mining Technology, 2019). The country also has base metal prospects that are currently extracted like the iron magnetite at the mouth of the Ba River, Viti Levu by

Amex Resources of Australia, and the bauxite at Naibulu east, in Vanua Levu by Arum Exploration Ltd, a local registered company of China.

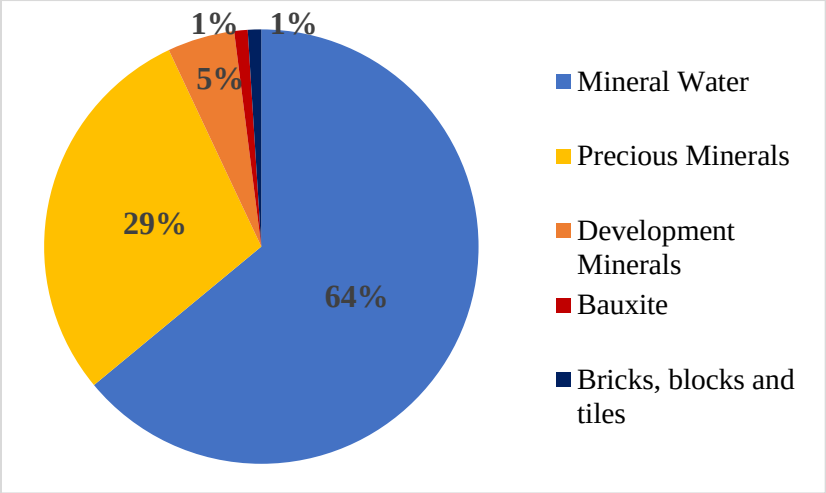

Figure 1.2 Contribution of mineral sector to Fiji's economy. Source: Fiji Bureau of Statistics, 2018.

Despite Fiji's small size, it has a number of significant mineral prospects that have also been explored and identified throughout the country including base metal sulfide deposits, disseminated porphyry Cu deposits, epithermal precious metal deposits, residual bauxite deposits and Mn and heavy minerals sand deposits, while prospecting has also continued for oil (Houtz and Phillips, 1963). Namosi in Viti Levu, for example, has been periodically explored over the past 50 years and is a highly prospective Cu-Au porphyry mineralised system where 930 million tons of Cu and Au reserves have been reported (Hosoi, 2008). Mineral exploration is ongoing at the Namosi prospect with joint venture of Newcrest (Australia), Mitsubishi and Nittetsu (Japan) companies.

The existence of several mining prospects such as Wainivesi (gold mine), Mount Kasi (gold mine), Korokayiu and Tikituru gold prospects, Cirianiu and Coqeloa gold prospects and smaller base metals deposits like Udu, the bauxite deposits at Wainunu, Vanua Levu and iron magnetite at the Kulukulu prospects enhances the country's mineral potentials. Metallic mineralization, as polymetallic base metal sulfide deposits, disseminated porphyry Cu

deposits, epithermal precious metal deposits, residual bauxite deposits, and Mn and heavy mineral sands deposits, is widespread in Fiji. The country also has potential for deep sea minerals that have previously been explored within its territorial water and economic exclusive zones.

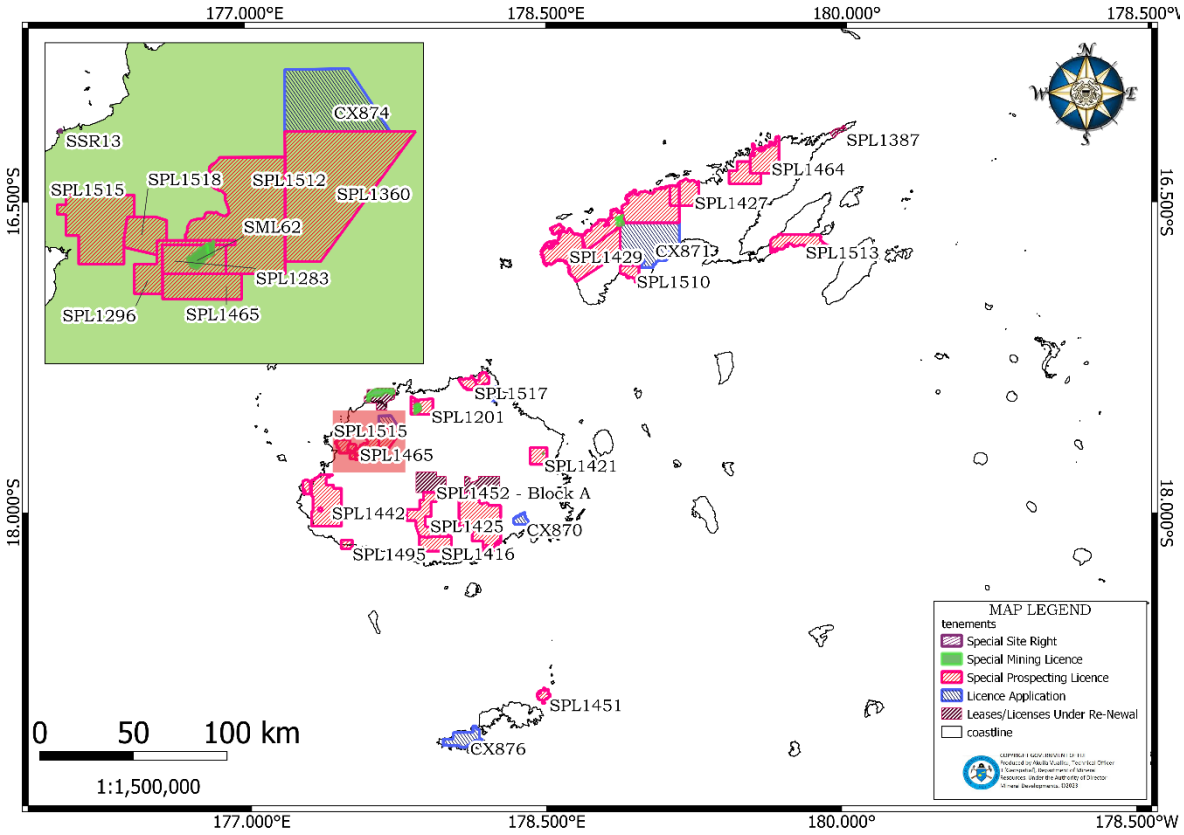

Figure 1.3 Tenement map of Fiji, showing the areas under mineral exploration and those under mining, and also illustrating the prospectivity of the country.

These prospects and mineral occurrences exemplify Fiji's considerable mineral potential and diverse geology with seven mining leases and thirty-five exploration licenses in which mining continuously contributes favorably to the country's economy (Figure 1.2). In fact, about one third of the country's land mass is under mineral exploration of some sort as presented in Figure 1.3, which continues to attract mineral developers. Table 1.1 lists the companies currently mining in Fiji and also mineral exploration ventures that are actively exploring for minerals with intention to mine in not-too-distant future.

Table 1.1 List of mining leases and intensive mineral explorations in Fiji as of September 2022 (Mineral Resources Department, Fiji, 2022).

Company Name	Exploration License / Mining Lease	Location	Target Minerals	Period
Vatukoula Gold Mine Limited (VGML)	Special Mining Lease (SML) 54, 55, 56.	Vatukoula, Tavua	Gold, Silver	Expires in 2025
Asia Pacific Resources	Special Mining Lease (SML) 58	Wainivesi, Tailevu	Gold, Silver	Expires in 2028
Amex Resources Limited	Special Mining Lease (SML) 60	Ba River delta, Ba	Iron magnetite	Expires in 2033
Aurum Exploration	Special Mining Lease SML) 61	Naibulu East, Bua	Bauxite	Expires in 2034
Lion One Metals Limited	Special Mining Lease (SML) 62	Tuvatu, Sabeto, Nadi	Gold, Silver	Expires in 2035
Namosi Joint Venture – Newcrest, Mitsubishi, Nittetsu	Special Prospecting License (SPL) 1420	Waisoi, Namosi	Copper, Gold	Expires in 2023
Aurum Exploration Limited	Special Prospecting License (SPL) 1423	Wainunu, Bua	Bauxite	Expires in 2023
Thunderstruck Resources Limited	Special Prospecting License (SPL) 1416/25	Nuku, Serua; Ruwailevu, Wainikoroiluva, Serua/Nadroga/Navosa/Namosi	Gold, Silver	Expires in 2025/24;
Kalo Exploration Limited	Special Prospecting License (SPL) 1464/1511	Dogotuki, Macuata / Saqani, Cakaudrova, / Coqeloa, Macuata	Gold, Silver	Expires in 2023 / 2024
Magma Mines Limited	Special Prospecting License (SPL) 1495	Kulukulu, Sigatoka, Nadroga	Iron magnetite	Expires in 2025

In order to better understand how mining is conducted in Fiji, one has to first understand the law that regulates mining, as well as the mineral industry (companies) that carries out mining. Although this is not the focus of this study, it is pertinent to put in perspective the systems and processes currently implemented for decision making to allow or refuse mining development to take place. It is also relevant to understand how this study can contribute to address or improve the process and performance of mining administration in Fiji.

Fiji's early mining law was introduced back in 1908 when the first Mining Ordinance was enacted to facilitate and regulate mineral sector developments. It granted prospectors and miners the security of tenure, exclusive exploration, and exploitation rights, while simultaneously protecting the proprietary rights of the landowners and the interests of the public. Between 1908 and 1965 it was updated and expanded in scope five times. The

changes made in 1965 enacted the reservation of minerals to state and transferred the administrative control over mineral resources from the statutory Mining Board to the Department of Mines now known as Mineral Resources Department under the administrative control of the Director of Mines. The current Mining Act was re-produced in 1978, with revisions to the regulations made in 1985 under the legal administration of the Mineral Resources Department (Soro, 2013).

Through the years, the Mineral Resources Department had implemented polices to improve and streamline the administration of mining in Fiji under the Fiji Mineral Policy (Tompkins, 1997). In 1999, the Department put together a draft Compensation Policy for the mineral sector to assist in addressing the growing concerns of the landowners and communities and is currently under review for possible implementation. Earlier in May 1998, the Department initiated a review of the current Mining Act, through a discussion paper on the issues confronting the government, industries, landowners, and the community, generally with respect to exploration and mining in Fiji. This resulted in the formulation of the Mineral Exploration and Exploitation Bill (MEEB) by reviewing Mining Act 1965. Its primary objective is to establish a transparent and progressive regime for the assessment, development, and utilization of Fiji's mineral resources. This is to accommodate the demands and safety of mining industry while also protecting the rights of landowners and achieving acceptable economic, social, and environmental outcomes that ensure Fiji's competitiveness both regionally and internationally. In addition, the review sought to incorporate modern concepts of occupational health and safety in the industry, a more transparent tenement approval process to be in line with newer environmental legislation. Since the formulation of MEEB in 1998, it has gone through a number of reviews and is now in its eleventh draft undergoing what is hoped to be its final revision for submission to parliament enactment process.

1.3 Environment Management and Mining in Fiji

In Fiji, environment management and social obligations remain a priority in the administration of mining and is relevant to reflect upon as it is part and partial of the rationale in this study. As favorable mining development in Fiji, it still warrants the necessary legal scrutiny given the likely impacts it poses to the environment as well as social implications. Application for mining can only be considered if an environment impact assessment has been conducted and approved, which is legally required by the Ministry of Environment under the EMA 2005 (Environment Management Act 2005) (Soro, 2013). Government places a strong emphasis on mining companies complying with agreed emission levels according to international standards as guidelines and also local standards, i.e., Fiji National Liquid Waste Standards (FNLWS) for activities listed under Schedule 3 of EMA 2005, then with the methods of abatement to achieve compliance. The FNLWS is the regulated discharge standard for liquid wastes from any premises listed under the Schedule 3 of the Environment Management Act 2005 of Fiji that includes mine liquid waste discharges. EMA 2005 sets environmental policies at two levels; the Ministry of the Environment coordinates the formulation and implementation of national policies, while MRD, as the main regulating agency for the mineral sector, sets complementary mineral sector policies with regards to environmental protection (Soro, 2013). This then provides investors with the flexibility to choose measures that reduce pollution levels in the most cost-effective manner, subject to government approvals. All Prospecting Licenses and Mining Leases are subject to established reporting requirements and regular on-site inspections undertaken by MRD's Mines Inspectorate officers together with the environment officers from its environment unit. This is to ensure all activities undertaken are in adherence to statutory requirements as specified in the relevant Act(s) and also to conditions of the prospecting licenses or mining lease.

The Fiji government promotes a self-regulatory approach to environmental monitoring. While it formulates socio-environmental standards, it works cordially with the mining industry to develop codes of practice that will enable the mining industry to meet or exceed

the best practice standards. It also recognizes the polluter-pays-principle that the developer is liable to pay compensation to any person or community whose lifestyle or income is adversely affected by the socio-environmental impacts of mining (Tompkins, 1997). In addition, the developer is responsible for all costs associated with mitigation and rehabilitation as required, from initial exploration to post-closure of mining. For instances where there is a significant risk of serious or irreversible damage, or an element of scientific or technical uncertainty exists regarding elements of mine development, Government then expects that every precautionary abatement and mitigation measures be taken and if so required they will be expected to address the worst case scenario (Tompkins, 1997). The existence of abandoned mine sites concludes that these requirements have not been implemented successfully in the past. Unfortunately, no single reason can be attributed for such failures (Soro, 2013).

Given the introduction of more recent and updated mining legislation in many countries worldwide, more change in Fiji is also anticipated to occur in the future for both exploration and mining activities. The growing concerns about the impact of mining locally against global demand for raw materials from mineral extraction are set to influence mining policies and set direction for mining legislation review. A report by Lum at al. (1991) highlights the importance of effectively dealing with social and cultural issues domestically and internationally to be amongst the most important legislative challenge for the feature of sustaining mineral development in Pacific Island countries. It adds that for over 65% of companies; social and cultural issues are a major priority and that the exploration and mining industry would prefer nations to adopt a modern and stable mining policy and legislative regime (Mineral Resources Department, 1998c).

1.4 Chemical and Mineral Characterization and its Relevancy to this Study

Geochemistry is the study of the chemistry of the earth, its rocks and minerals, including their chemical properties, distribution, behavior, and abundance of elements. To better

understand the chemistry and mineralogy of samples (rock, sediment, soil, or water), chemical and mineral characterization is the process often used to determine whether a given rock is rich in minerals, type of minerals and whether the minerals are significant. Chemical and mineral characterization is a systematic approach using a series of standard analytical techniques that focus on identifying minerals and quantifying chemical elements and compounds present in rock, soil, sediment, or water samples. There are three basic commonly used laboratory analysis methodology which includes X-ray powder diffraction (XRD) for mineral identification, X-ray fluorescence spectroscopy (XRF) to quantify chemical content and leaching experiments to replicate the release of soluble chemicals or minerals from its host through inducement of a known solvent. Occasionally, subject to the purpose of the study, additional tests such as sequential extraction (SE), total inorganic carbon test (TOC), loss on ignition (LOI), acid base accounting (*ABA*), and pH and hydrogen peroxide acidification test (pH (H_2O_2)) etc. may be applied.

Chemical and mineral characterization has been the standard analytical process used extensively in the mining sector because it has the ability to provide important information to identify and quantify contained target minerals or elements of an orebody system (Lapakko, 2002) hence determine the viability of the resources if mined. The above three laboratory analytical techniques have long been the basis for mineral identification and quantification by mineral exploration and mining companies (Shaffer, 2017; Yellepeddi, 2019) where mineral quantity and quality are paramount to ensuring that the economic benefits of discovered deposits are realized. The method is equally useful in determining the byproduct of mining and its potential consequences on the environment (Piatak et al., 2004; Simate and Ndlovu, 2014; Assawincharoenkij et al., 2018). This is due to the fact that chemical and mineral characterization of orebodies provide accurate information about minerals and chemical elements contained in an orebody to have potentials that affect the environment as well as the capacity to provide countermeasures. Hence, it presents a wider perspective on the benefits generated from mining such an orebody to also the potential environmental impacts that it poses, i.e., the pros and cons, as well as abilities to provide countermeasures prior, during and post mining. Such unique abilities make it necessary

requisites to mining applications as an additional screening tool for mining approval process to ensure that the critical information about an orebody is understood and that the best decision is reached pertaining to mine development. It is also a good knowledge to gain and understand when dealing with mining regulation and monitoring especially for officers of mining authorities. Thus, chemical and mineral characterization becomes an important tool to assist not only miners but more importantly regulators for the reasons aforementioned. It also provides necessary baseline data for monitoring and managing the environmental impacts including the post-mining period.

In Fiji there remains a genuine lack of study on the specific chemical and mineral characteristics of the country's mined and exploited orebodies. Similar lack of research interests on mineral extraction has been experienced. The limited available narrative focuses mostly on the benefits of mineral extraction with fewer explaining the orebody's chemical nature once minerals are exposed due to mining. Long-term environmental impacts on mine sites and its surrounding environment are imminent if the chemistry of the orebodies is less understood. Such knowledge is important in developing responsible policies that safeguard the industry, environment, and communities to ensure safer and sustainable mining practices as well as prudent rehabilitation and post-mined land use.

1.5 Acid Mine Drainage (AMD)

Mining and its processes can also harm the environment in other ways. Mining creates a type of water pollution known as acid mine drainage (AMD) and is the single most problematic issue of waste management in mining (Blowes et al., 2014). The United Nations has considered it to be the second biggest environmental problem to global warming (Tuffnell, 2017). Due to its significance in mining, it is relevant to briefly reflect upon without going into too much detail in this chapter and how it links to chemical and mineral characterization in this study. First, mining exposes sulfides in the soils and rocks. Sulfide is summarized as a naturally occurring mineral with any member or group of compounds of sulfur with one or

more metals (Zumdahl, 2018). When the streams or rainwater dissolves the sulfides, they form acids primarily AMD which are harmful to aquatic plants and animals (Oelofse, 2009, Rahman et al., 2022).

The processes leading to AMD are numerous and complex and involve chemical, biological, and electrochemical reactions and can follow a variety of chemical pathways involving surface interactions with dissolved O_2, ferric iron (Fe^{3+}), and microorganism (Blowes et al., 2014). Thus, AMD is produced when sulfide minerals (predominantly pyrite) come in contact with water and exposed to air, which allows them to oxidize and break down producing sulfuric acid. The reaction of pyrite (FeS_2) with oxygen and water is the main source of AMD and occurs under variety of conditions. Below is the AMD generation chemical reaction using the example of pyrite being oxidized and broken down from equations 1 to 6:

$$FeS_2 + O_2 + H_2O \rightarrow Fe_2^{+} + 2SO_4^{2-} + 2H^{+} \quad (1)$$

$$Fe^{2+} + O_2 + H^{+} \rightarrow Fe^{3+} + H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+} \quad (3)$$

$$FeS_2 + O_2 + H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^{+} \quad (4)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^{+} \quad (5)$$

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 4Fe^{3+} + 8SO_4^{2-} + 4H^{+} \quad (6)$$

Reactions (1) until (6) are general, and the main reaction of pyrite oxidation has been explained by Chen et al. (2015), Neculita et al. (2007), Pierre Louis et al., (2015), Kafeni et al., (2017). It occurs at neutral pH and shows the oxidation of pyrite with oxygen molecules in excess water. It explains that the Fe^{2+} (ferrous) ion is produced then reacts with O_2 to form Fe^{3+} (ferric) as facilitated by microbes (sulfur-oxidizing bacteria) e.g., *Thiobacillus thiooxidans and Thiobacillus ferooxidans*, where energy for their metabolism is from reaction (2) (RoyChowdhury et al., 2015). Reaction (4) represented the overall pyrite oxidation (reactions (1) – (3)). The pyrite oxidation reaction rate in (5) is faster than oxidation reaction (1) and shows that Fe^{3+} plays a role as the oxidizing agent in the complete oxidation of pyrite. Production of H^{+} ion makes the pH value drop dramatically and becomes high acid (RoyChowdhury et al., 2015). Precipitation of Fe^{3+} will form $Fe(OH)_3$ when the pH of the

system remains over 3.5 – 4.0 and turn into brown-yellow-orange colored substance known as “yellowboy”. Reaction (6) is the complete pyrite oxidation in presence of low water content. It should be noted that the above reactions for pyrite oxidation are simplified equations and do not fully describe the complex reactions required to reach the final reaction products (Nordstrom and Southham, 1997).

AMD can be generated in waste rock piles, tailings dams, pit wall rocks, heap leach pads, ore stockpiles and underground mine voids. Sulfuric acid due to low pH dissolves metals including Fe, Al, Mn, Cu, Pb, and Zn. The acid produced can also mobilize other metals such As, Cd, Cr, Co, and Ni (Savage et al., 2000; Nordstrom, 2002; Paktunc et al., 2006; Paktunc, 2008, Deditius et al., 2011). Sulfides are chemically stable when immersed in water, and generally only begin to oxidize once the host rock is excavated or exposed to the air. Sulfide oxidation and associated AMD generation proceed as long as there remains sulfide minerals in exposed geological materials. The duration of acid generation, and its associated liability, can last for hundreds of years after mining operations have ceased.

There have been numerous approaches discovered to remediate AMD and identifying the best remediation technologies is often another challenge. This is again where chemical and mineral characterization becomes practical because it makes known the necessary mineral and chemical information responsible for generating AMD, so matching countermeasures can be explored and implemented.

1.6 Statement of the Problem and Objective of the Study

History clearly shows that mineral sector developments offer unique benefits as well as pose special problems to surrounding environments and deleterious social impacts to nearby communities especially in developing countries (Bell and Donnelly, 2006). Fiji is not exempted from this reality, for over 80 years a number of mining ventures have reaped substantial benefits from the operations such as the Vatukoula gold mine and Nawailevu

bauxite mine. Most of these mines have sought to gradually comply with the evolving requirements that successive governments and legislation have set for mining and their environmental obligations. However, many other mining companies of the past (Nukudamu copper mine, Wainivesi gold mine, Mt Kasi gold mine) were far less diligent, having enjoyed the benefits of mineral exploitation. The lack of attention to safe mining and rehabilitation practices and abandonment of these sites has typically resulted in post-mined landscapes of limited value and ongoing residual environmental impacts arising from the mobilization of contaminants from these sites.

Despite this problematic history, however, there still remain significant potential for expansion of mining industries in Fiji, and the government seeks to develop this potential by increasingly looking towards more exploration and development from foreign investors (Soro, 2013). Such prospectivity and development potential has also created an urgent need to re-look at the administrative processes for mining within government and demand to explore opportunities for more research into mining and its unfavorable impacts to the local environment. This is due to poor examples from the past, which recognize the need to improve the processes and mechanisms of future mining approvals. The lack of scientific research into Fiji's mining sector, its impacts to the environment, social implications necessitate studies like this research to be conducted and encouraged to provide important information justifying prudent approach to safer and sustainable mining going forward.

This is where chemical and mineral characterization knowledge becomes pertinent to gain deeper understanding of the chemical and mineralogical nature and properties of mineral deposits and prospects i.e., mineral constituents and chemical contents and their potentials to generate wealth as well as impact on the environment. Part of the objective of this study is to justify that chemical and mineral characterization is an important requisite for mining approval process and knowledge to be understood by mining regulators. At present basic requirement for approval to mine focuses on mineral resource potential and feasibility, technical capacity and finance to be able carry-out safe mining according to approved mine plans. There remain less attention in the approval process diverted to chemical and mineral

properties to fully understand their potential impacts and consequences pertaining to environmental and possible countermeasures.

As mineral exploitation interests grow in Fiji, it is imperative that the industries and regulators have a good understanding of what chemical and mineral characterization is about and how it can have a positive influence in mining approval processes. This is because it provides pertinent information for sound understanding of the orebody's chemical properties. Such knowledge once gained, strengthens one's ability to scrutinize chemical and mineral information of an orebody to understand the basis of how minerals, elements, and compounds react, mobilize, or associate to either pose risk such as AMD or provide countermeasures. It will lead to consideration of better post-mined land rehabilitation to guarantee appropriate and sustainable post-mined land use. However, if it remains lacking, it raises concerns about the mining administration and casts doubt over the reliability of the systems and procedures for mining approvals and will continue to contribute to failures in mine rehabilitation resulting in abandoned mines.

1.7 Purpose of Study

The purposes of this study were:

1. To conduct chemical and mineral characterization of rock, tailings and water samples collected from studied mine sites in Fiji to understand their properties and evaluate their impacts to the environment
2. To explore and evaluate the hazardous elements mobilization and the potentials to generate AMD generation in these studied mine sites
3. To evaluate the mineral oxidation and dissolution mechanism occurring in these sites
4. To explore how chemical and mineralogy characterization can be applied to strengthen mining approval processes and assist decision making.

1.8 Outline of the Dissertation

The dissertation consists of five chapters. The content of each chapter is shown below:

In chapter 1, general introduction including the background, problem statement and contents of this study was described. A perspective on mining in general was described and associated issues focusing on Fiji.

Chapter 2 provides a preliminary chemical and mineral characterization study of rock samples collected from five selected mine sites in Fiji to deliver a general overview of the chemical and mineral properties of these mine sites. Further analysis was conducted to evaluate the level of vulnerabilities of each mine site on the surrounding environment.

In chapter 3, the detail chemical and mineral characterization of the rocks and water samples collected from Nukudamu abandoned mine site was studied. The acquired data were analyzed and discussed in relation to the mineral and chemical characteristics of the samples and potential impacts generated in such mining condition.

In Chapter 4, the detail chemical and mineral characterization of the rock, tailings and water samples directly collected from Vatukoula mine site was conducted to provide a perspective on the impact of active mining on site. The results were analyzed and discussed accordingly with respect to potential impacts on the surrounding environment.

In chapter 5, general conclusion based on the results obtained in this study was summarized. Also, a reflection on the impacts and contribution of this study was contextualized.

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Chapter 2 CHEMICAL AND MINERAL CHARACTERIZATION OF ROCK SAMPLES FROM SELECTED FIJI MINES SITES TO EVALUATE ON-SITE ENVIRONMENTAL VULNERABILITIES

2.1 Introduction

Mining is generally considered an accepted form of development contributing to global growth. Despite this, it remains inherently disruptive of 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 (Xu et al., 2021). 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 (McKinnon, 2002; Banks et al., 2005; Mudd et al., 2020; Worlanyo et al., 2021). 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 (McKinnon, 2002).

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 (Au) as well as copper (Cu) mining, about 99% of the extracted ores are deposited back into the environment as tailings (Fashole et al., 2016; Park et al., 2019). 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 (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 (Saharan et al., 1995; Akcil and Soner 2006; Park et al., 2019). 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 (Akcil and Soner, 2006; Foli et al., 2011).

Despite Fiji's long mining history and growing interest in mineral development, there remain limited available narratives about mining's environmental impacts, most studies concentrate more on the benefits of mineral extraction with little literature explaining the orebody's chemical nature. The Vatukoula Gold Mine (VGML), because of its long existence, is the most studied mine in Fiji (Sing and Mosley, 2003; Ko et al., 2008; Matanitobua et al., 2010; Matakarawa, 2018, Rabuku and Abdul, 2020; Kumar et al., 2021). 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 from mine sites near the studied area. 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 (Kumar et al., 2021). These authors conducted a similar study on potentially toxic elements across the Wainivesi River, which also receives discharge from the Wainivesi mine (Kumar et al., 2021).

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 remain poorly understood in Fiji. This knowledge gap can be addressed by the present study by

investigating the chemical and mineral 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 mineral and chemical 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 chemical and mineral properties and make-up when disturbed by mining activities. Therefore, the specific objectives of this work are to (1) characterize the mineralogy and chemical 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 and potential environmental impacts. 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.

2.2 Study Sites

Fiji is an archipelago of about 330 islands with a combined landmass of 18,376 km^2 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 (2,000–4,000 mm) from November to April and dry season from May to October with temperatures of 20–30 °C throughout the year (Mataki et al, 2006; Ongoma et al., 2021).

The rocks collected for this study are fresh samples and are assumed to be representative of the orebodies of the studied mines as shown in Figure 2.1. 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 is 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 (Turner, 1986; Colley and Flint, 1995). 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, and 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 (Colley and Flint, 1995; Colley and Rice, 1975; 1978).

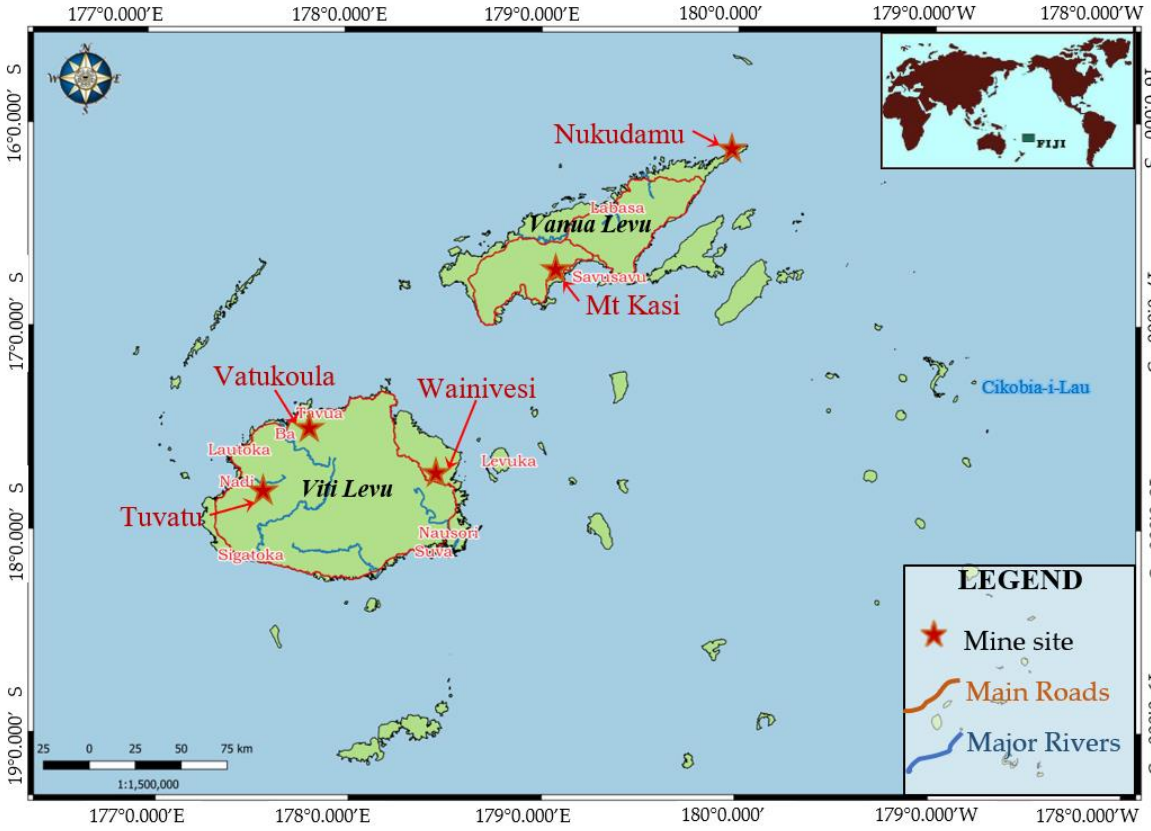


Figure 2.1 The map of Fiji and locations of Mt Kasi, Nukudamu, Tuvatu, Vatukoula, and Wainivesi mining sites where rock samples were collected.

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 (Ashley and Andrew, 1989). 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 (Colley and Flint, 1995; Feudigmann et al., 2015).

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 (Colley and Flint, 1995). It is a low-sulfidation epithermal gold vein deposit associated with alkaline type igneous rocks in volcanic setting, typical of other major gold mines in the southwest Pacific region including Grasberg mine in Indonesia, the Porgera and Lihir in Papua New Guinea. Its mineralization is described as a low-grade, porphyry Cu type associated with steep caldera faults spatially related to epithermal gold mineralization (Ahmad et al., 1987; Anderson and Eaton, 1990; Eaton and Setterfield, 1993; White at al., 1995).

As for Wainivesi, its host rocks are highly silicified andesites and dacites displaying brecciation with rare basic rocks, suggested to be originally calcareous (Hourtz, 1958), and contain other rock units including tuffs, shaly volcaniclastic 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 (Colley and Flint, 1995).

2.3 Materials and Methods

2.3.1 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 2.1, with the respective

details provided in Table 2.1. 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 X-ray diffraction (XRD) (MultiFlex, Rigaku Corporation, Tokyo, Japan) and X-ray fluorescence (XRF) (SpectroXepos, Rigaku Corpoation, Tokyo, Japan) for their mineralogical and chemical compositions, respectively. All the 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.

Table 2.1 Rock samples details.

	Mine site	Rock samples and rock type	Deposit type	Site condition
1	Mt Kasi	3 samples; M1 – volcanic breccia, M2 – silicified ore, M3 – andesitic rock	High sulfidation epithermal vein	Abandoned but under further exploration
2	Nukudamu	4 samples; N1, N2 – oxidized andesitic rock, N3 – oxidized obsidian rock, N4 – pyritic pumice	Kuroko as in volcanic massive sulfide	Completely abandoned
3	Tuvatu	4 samples; T1 – andesite, T2 – andesite, T3 – micro monazite, T4 – mod blended monzonite	Low sulfidation epithermal gold vein	Active mining lease, development stage
4	Vatukoula	4 samples; V1 – aphantic basalt, V2 – porphyritic andesite, V3 – basalt, V4 medium coarse rained monzonite	Low-sulfidation, epithermal gold veins, porphyry Cu-style mineralization	Active mining lease, full operation
5	Wainivesi	1 composite sample; W1 – silicified andesite, pyritic andesite and dacitic ore	Volcanic massive sulfidation vein	Active and under exploration license

2.3.2 Total Carbon, Inorganic Carbon and Loss on Ignition Tests

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). For TC, following the equipment calibration procedures, 0.3 g of crushed rock sample (<2 mm) were accurately weighed and spread evenly into the ceramic combustion boat, then, covered with fiber wool ready to be inserted into the combustion chamber of the carbon analyzer. A similar process was followed for IC measurements where 0.1 g of the sample without fiber wool, and the sample was then soaked with phosphoric acid (H_3PO_4) in the combustion chamber. Prior to measuring TC and IC, the equipment followed a standard calibration process where 0.05 g of glucose was used for TC and 0.088 g of sodium carbonate (Na_2CO_3) for IC. These chemical reagents were dried under 100 °C, over 24 hrs, and the combustion ceramic boats were heated at 900 °C for 1 h before use.

Loss on ignition (LOI) test was also considered and conducted to assess analytical accuracy of total volatile measurements, mainly added to other oxides totaling 100 ± 1.0%. Loss on ignition was determined through gravimetry by heating the 2 g of the sample (<2 mm) inside a furnace at 750 °C for 1 h after drying in an oven at 110 °C for 24 hrs. (JIS A 1226, 2020; Marove et al., 2020). The weight of the sample was re-weighed after heating and LOI was calculated by the difference in weight before and after the heating presented in percentage.

2.3.3 Batch Leaching Tests

The leaching experiment was based on the Environmental Agency of Japan Notification No. 46 (JLT-13, 1973), as shown in Figure 2.2, which was applied to evaluate the leaching concentrations of Al, Cu, Ca, Fe, K, Mg, Na, SO_4^{2-}, Si, Pb, and Zn from rock samples (Tabelin et al., 2014). 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 hrs. at 120 rpm. This method is widely used in excavated and hydrothermally altered rocks that simulate on-site environmental vulnerabilities via leaching (Huyen et al., 2019; Khoeurn et al., 2019; Tabelin et al., 2020). 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 of the leachates 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 (HNO_3) before chemical analysis. Alkalinity of leachates with pH > 4.8 was measured by titrating a known volume of the sample's leachate to pH 4.8 with 0.01 M of sulfuric acid (H_2SO_4). Hazardous elements and major ions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES ICPE 9800, Shimadzu Corporation, Kyoto, Japan).

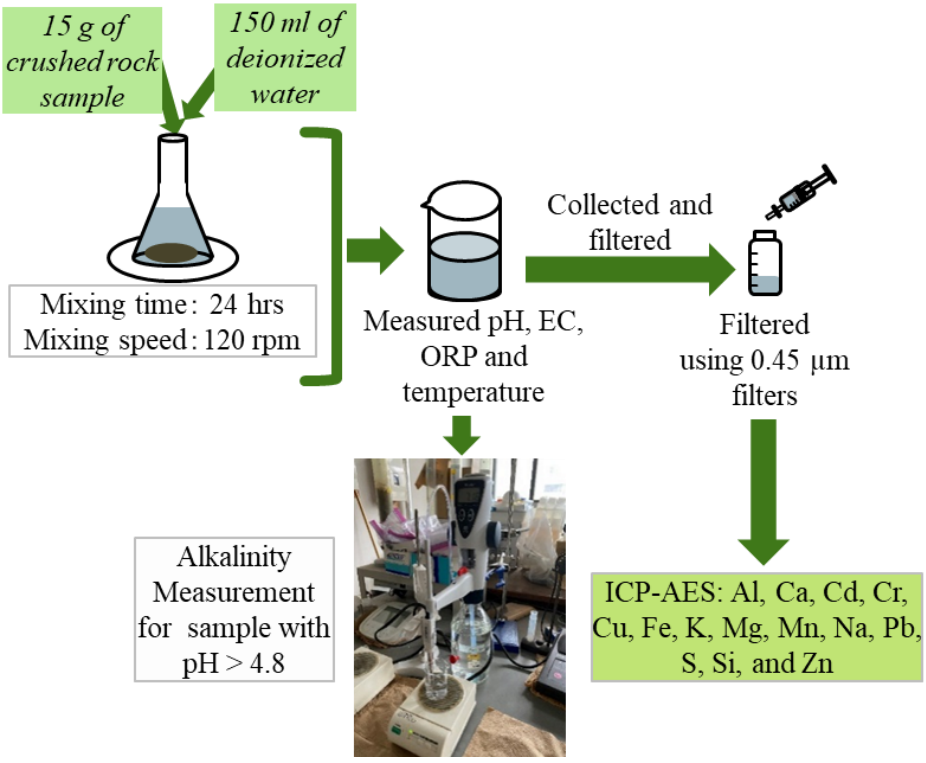


Figure 2.2 Flow diagram of batch leaching experiment procedures.

2.3.4 Quality Assurance and Quality Control

The analysis was conducted in triplicate together with certified reference materials (Table 2.2) traceable to NIST SRM® (Merck KGaA, Darmstadt, Germany) for accurate leachate concentrations. All the chemicals used were reagent grade. Blank solutions (Millipore Milli-Rx 12α 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 ± 2%–3%, detection limit 0.01–0.001 mg/L) (Mufalo et al., 2021).

Table 2.2 Quality assurance (QA) and quality control (QC).

Calibration standard for ICP-AES										
Elements	Mass concentration (w/v) ± expanded measurement uncertainty									
	Certified value (mg/L)	Uncertainty	Measured value							Traceable to SRM
			Multi Standard				SO_4^{2-} Standard			
			Std 1	Std 5	Std 10	Std 20	Std 1	Std 5	Std 10	
Ca	1009	±10	1002	996	992	1005				SRM 3109a
Cu	998	±10	970	1002	1002	997				SRM 3114a
Fe	998	±10	996	992	989	1002				SRM 3126a
Mg	999	±10	985	982	995	993				SRM 3131a
Na	1001	±10								SRM 3152a
K	1002	±10	1010	1004	1000	1005				SRM 3141a
Pb	999	±10	987	980	979	990				SRM 3128
Zn	997	±10	978	982	986	1015				SRM 3168a
SO_4^{2-}	1000						1020	996	1005	
	0.8% (coverage factor k = 2 level of confidence approximately 95% (Sulfate ion standard solution SO_4^{2-} 1,000) (ISO/IEC 17025:2017 and ISO 17034:2018)									

2.3.5 Statistical Analysis and Thermodynamic Modelling

Principal component analysis (PCA) was performed using Origin Pro® 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) (Gustafasson, 2014). The input parameters include the pH, temperature, pe, alkalinity as HCO^{3-}, and components of the leachates (Al, Cu, Ca, Fe, K, Mg, Na, SO_4^{2-}, Si, Pb, and Zn).

2.3.6 Acid-Base Accounting (ABA) Test

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 (H_2O_2)). The *ABA* test was used to evaluate the acid-neutralizing potential (*NP*) and acid-generating potential (*AP*) of rock samples as shown in Figure 2.3 (Lawrence and Wang, 1997; Wang et al., 2017). 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 hrs. The suspension was allowed to react at room temperature for 24 hrs and then titrated to pH 8.3 with 1M sodium hydroxide (NaOH). The *NP* (kg $CaCO_3$/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% H_2O_2 (pH = 7), which was kept at room temperature for 48 hrs before being heated to remove residual H_2O_2. After cooling, its acidity was determined by titration with 1 M NaOH to pH 8.3. The *AP* (kg $CaCO_3$/t) was calculated using Equation (2) from the content of sulfide sulfur ($S_{sulfide}$%), which was determined by leaching with H_2O_2 and calculated according to Equation (3). The difference between the values of *NP* and *AP* is the net acid-neutralizing potential (*NNP* = *NP* − *AP*):

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

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):

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

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

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

If the *NNP* value is below −20 kg $CaCO_3$/t, acid generation is likely to occur; if the *NNP* value is between −20 and 20 kg $CaCO_3$/t, the acid generation is uncertain; and if the *NNP* value is above 20 kg $CaCO_3$/t, the rock sample is unlikely to generate any acidity.

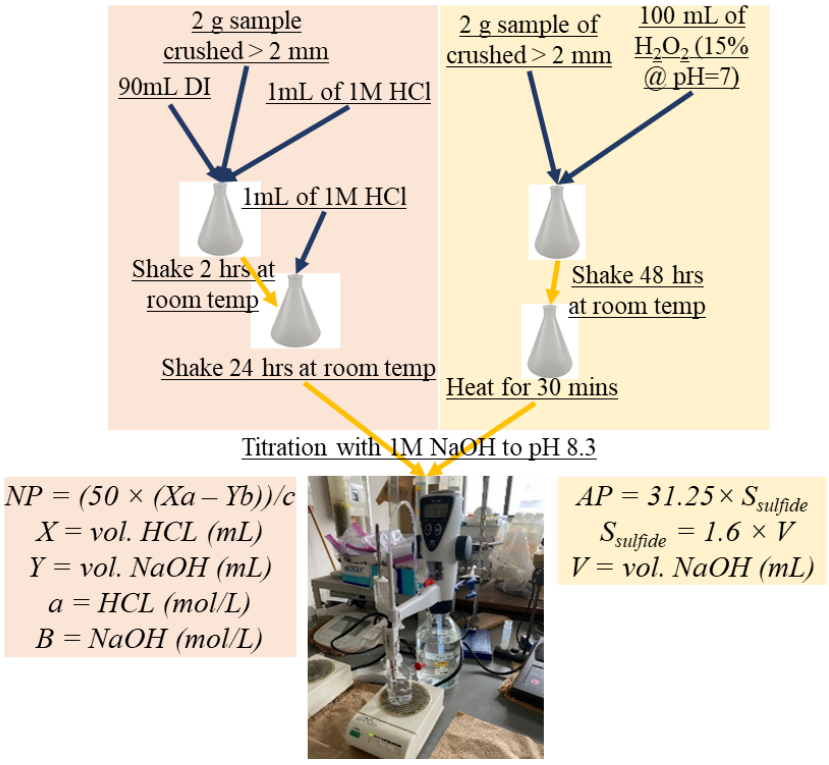


Figure 2.3 Flow diagram of the acid base accounting experiment procedures.

2.3.7 Hydrogen Peroxide and pH Acidification (pH (H_2O_2)) Test

The pH (H_2O_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, (JGS 0271-2016, 2016) 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 (H_2O_2) acidification test uses the oxidation principle, in which H_2O_2, a strong oxidant, oxidizes sulfide minerals exposed during the test.

In the experiment, H_2O_2 solution was first prepared by neutralizing a pre-determined volume of 30% H_2O_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 °C in a fume hood as shown in Figure 2.4. 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 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 (Igarashi et al., 2001; Inui et al., 2014).

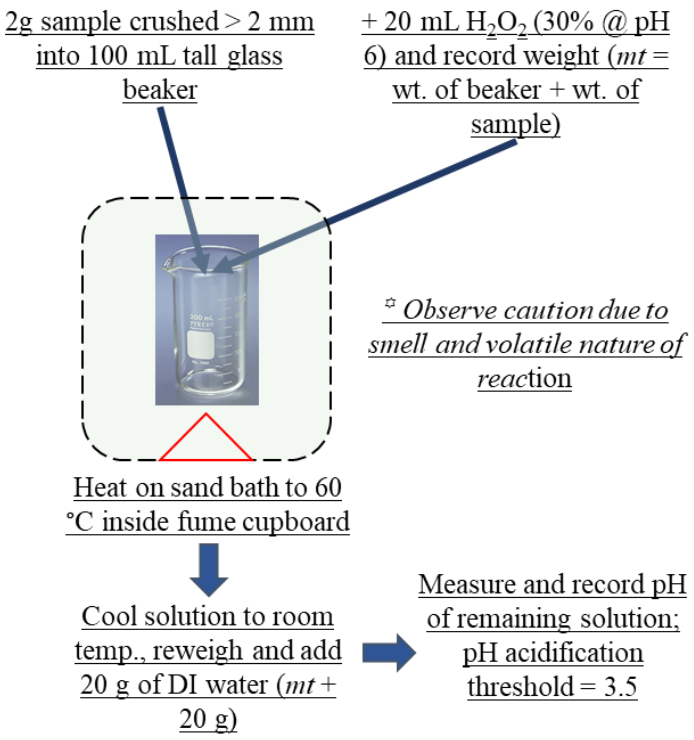


Figure 2.4 Flow diagram of the pH (H_2O_2) acidification test procedures.

2.4 Results and Discussion

2.4.1 Mineralogical and Chemical Properties of Rock Samples

The chemical and mineralogical composition of Mt Kasi (M1–M3), Nukudamu (N1–N4), Tuvatu (T1–T4), Vatukoula (V1–V4), and Wainivesi (W1), are summarized in Table 2.3 and Figure 2.2, accordingly their TC and IC contents are presented in Table 2.4. 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 quartz (SiO_2), and pyrite (Fe_2S), the identified significant minerals (Figure 2.2 (a)). Pyrite could not be confirmed in M2 with

XRD; however, an optical microscope confirmed the presence of both quartz and pyritic minerals (Figure 2.3 (a)).

Table 2.3 Chemical compositions of the rock samples from the XRF analysis results.

Sample	M1	M2	M3	N1	N2	N3	N4	T1	T2	T3	T4	V1	V2	V3	V4	W1
†SiO_2	79.3	90.4	84.1	79.1	2.88	68.5	1.84	62.7	53.7	58	62.4	43.2	57.9	46.5	59.1	23.6
†TiO_2	0.64	0.34	0.39	0.47	0.36	0.01	0.11	0.52	0.73	0.57	0.45	0.44	0.46	0.49	0.50	0.04
†Al_2O_3	17.0	2.00	12.9	13.8	1.47	0.54	6.50	21.2	16.3	18.6	20.2	11.9	20.3	12.4	19.5	3.51
†Fe_2O_3	4.90	2.76	3.79	2.35	96.5	26.4	40.0	3.89	11.4	8.05	2.69	9.93	6.47	10.2	6.82	10.7
†MnO	<0.01	<0.01	<0.01	<0.01	0.03	0.09	0.01	0.06	0.22	0.23	0.07	0.24	0.15	0.20	0.16	<0.01
†MgO	<0.01	<0.01	0.03	0.31	<0.01	<0.01	<0.01	8.27	8.21	5.49	3.18	9.16	4.89	14.0	4.93	0.02
†CaO	0.04	0.03	0.05	1.93	0.11	0.05	0.08	3.35	10.6	7.03	2.40	13.7	5.04	13.0	6.24	<0.01
†Na_2O	0.02	0.14	<1	6.51	<0.01	<0.01	0.63	5.25	2.71	3.06	3.92	1.81	3.28	1.23	4.52	<0.01
†K_2O	0.02	0.13	0.03	0.5	0.03	0.05	0.02	0.12	2.93	4.64	7.63	2.59	4.64	0.83	4.26	0.42
†P_2O_5	0.11	0.08	0.17	<0.01	<0.01	0.36	0.06	0.27	0.67	0.47	0.35	0.33	0.64	0.30	0.67	0.03
†SO_3	6.28	6.31	6.76	0.37	1.30	0.81	52.3	0.05	0.19	0.83	0.76	2.30	0.05	0.51	0.21	70.7
*Pb	15.0	28.0	11.0	5.00	208	519	21.0	<1	3.00	8.00	21.0	4.00	9.00	5.00	9.00	507
*Cd	2.00	1.00	<2	1.00	<2	<1	<1	<1	<1	<1	1	<1	1	<1	<1	1,600
*Zn	10.0	3.00	4.00	140	535	460	59.0	59.0	87.0	112	180	76.0	78.0	81.0	82.0	358,000
*Cu	61.0	29.0	67.0	50.0	986	327	83.0	6.00	152	190	30.0	144	82.0	126	161	28,700
*As	92.0	137	38	50.0	619	590	7.00	<1	6.00	4.00	66.0	4.00	1.00	3.00	2.00	80
*Cr	19.0	<3	17.0	9.00	59.0	5.00	<4	<1	34.0	24.0	8.0	260	13.0	445	41	<3
*Co	99.0	247	68.0	46.0	<62	<21	<40	<10	34.0	30.0	39.0	17.0	24.0	24.0	40.0	76.0

† (wt%) * (mg/kg)

Table 2. 4 Total carbon, Inorganic carbon and Loss on Ignition analysis results.

Sample	M1	M2	M3	N1	N2	N3	N4	T1	T2	T3	T4	V1	V2	V3	V4	W1
†TC	0.10	0.01	<0.01	0.02	0.13	0.01	0.67	0.76	0.01	0.04	0.46	1.69	0.65	0.98	0.37	<0.01
†IC	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.61	<0.10	<0.10	<0.10	1.26	0.56	0.72	0.31	<0.01
†LOI	7.06	1.26	5.46	0.99	7.01	5.91	7.60	1.68	0.52	1.17	1.11	4.87	3.51	3.97	1.36	4.41

† (wt%)

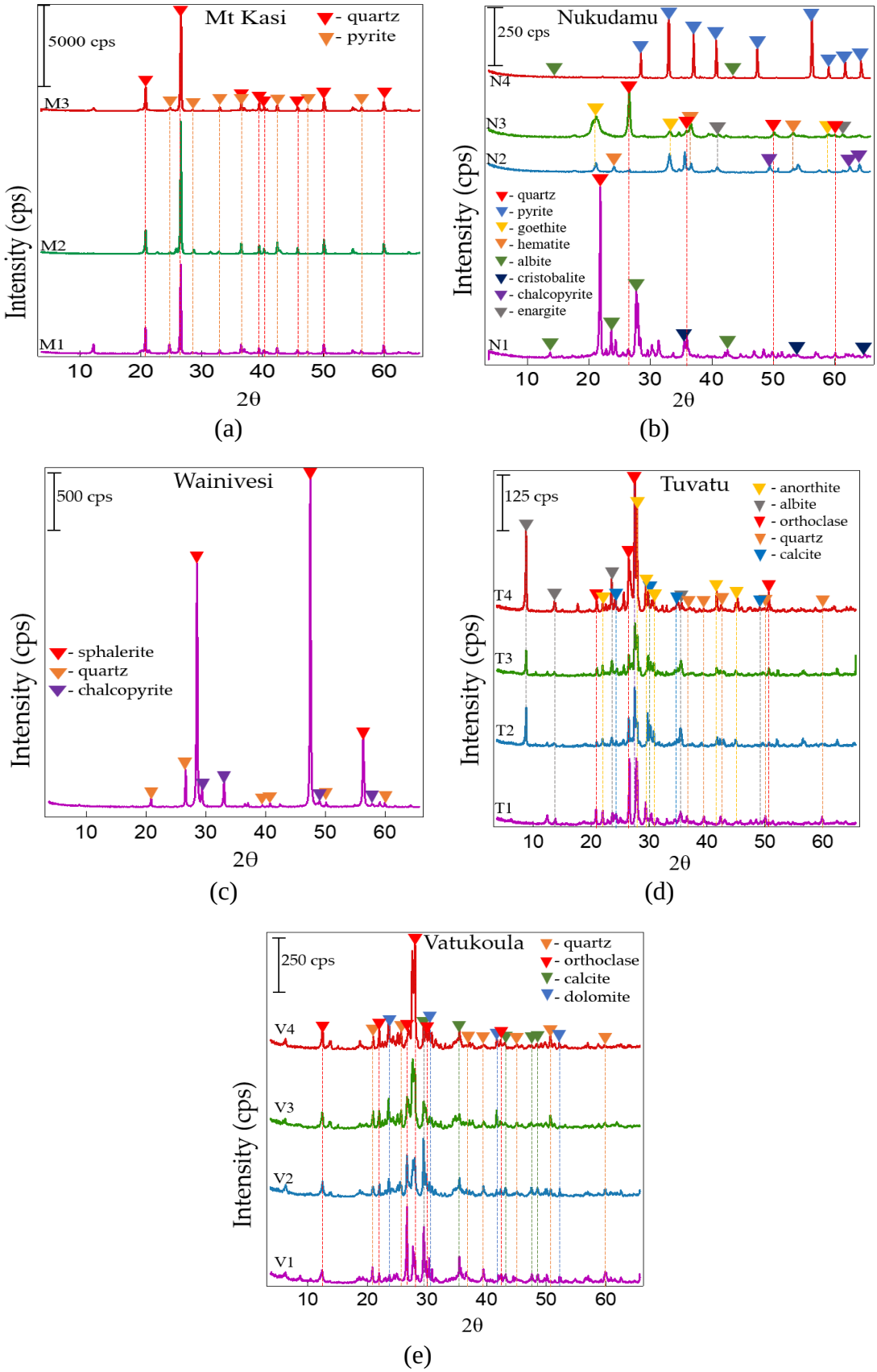


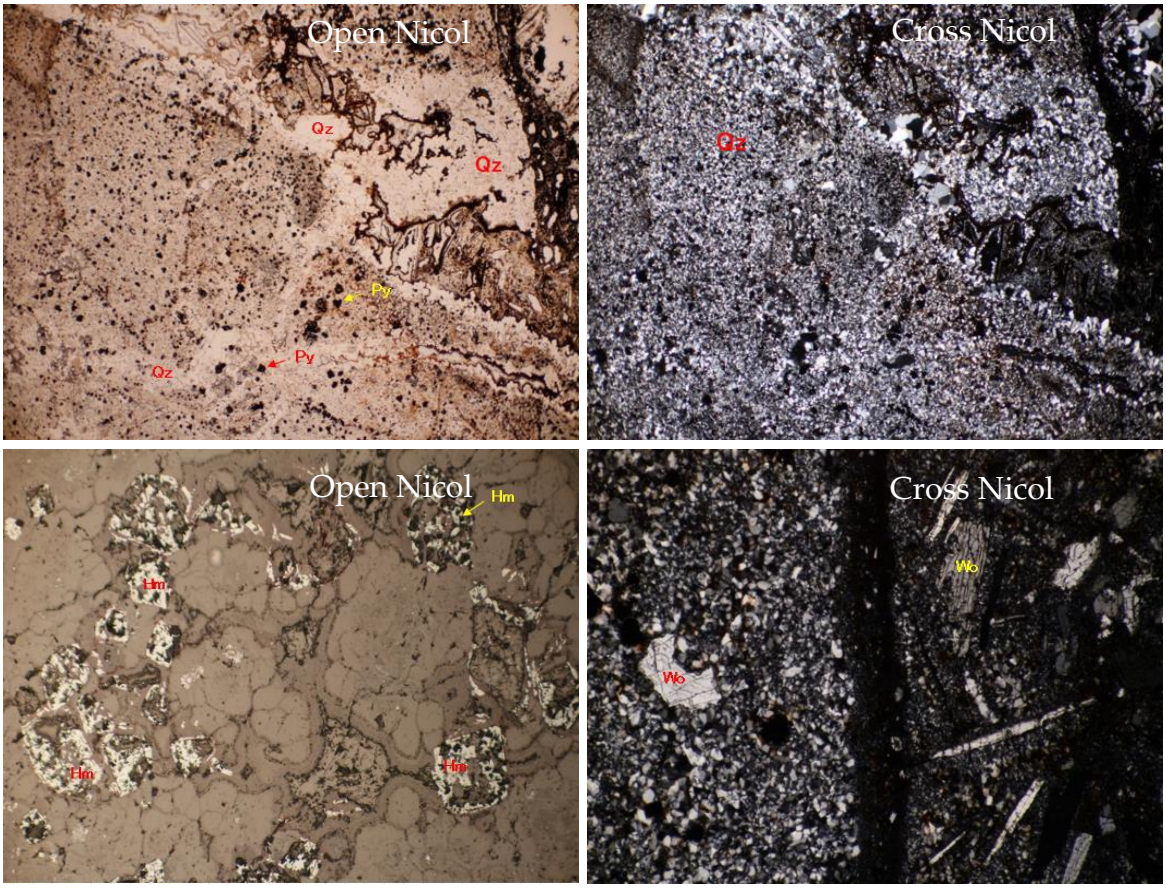
Figure 2.5 XRD patterns for the mineralogical composition of (a) Mt Kasi, (b) Nukudamu, (c) Tuvatu, (d) Wainivesi, and (e) Vatukoula.

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 2.5). Sulfide minerals such as pyrite, chalcopyrite ($CuFeS_2$), and enargite (Cu_3AsS_4) were also detected in N2 and N3 (Figure 2 (b)) 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 2.3 (b)).

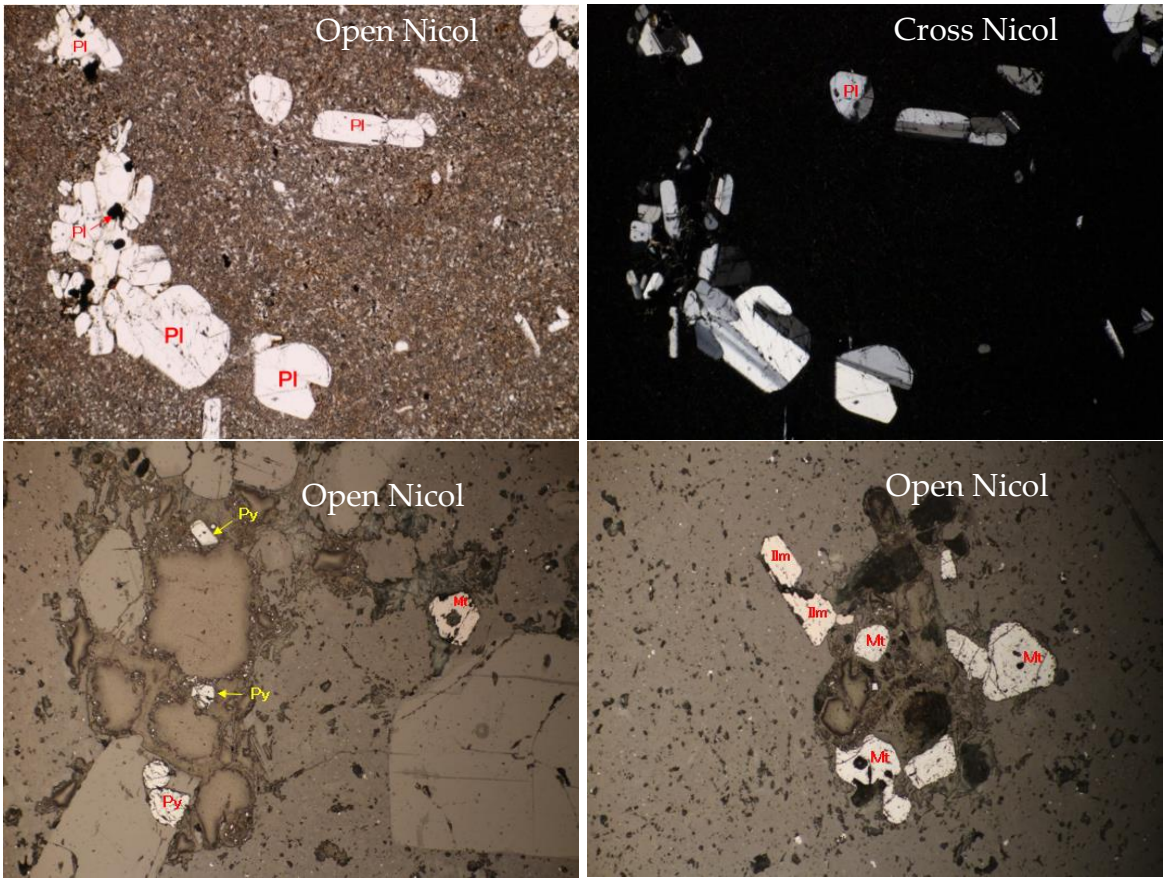
Meanwhile, the Wainivesi (W1) (Figure 2.2 (c)) sample is mainly composed of quartz and sphalerite (ZnS), with chalcopyrite as a minor mineral component. This is consistent with the high chemical contents of Zn (358,000 mg/kg), Cu (28,700 mg/kg), and S (70.7 wt%) in the sample. While pyrite was undetected by XRD, the microscopic observation in Figure 2.3 (f) showed abundance of pyritic minerals in the Wainivesi composite 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), 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 2.5 XRD diffraction percentage mineralogical abundances (%) of the rock samples

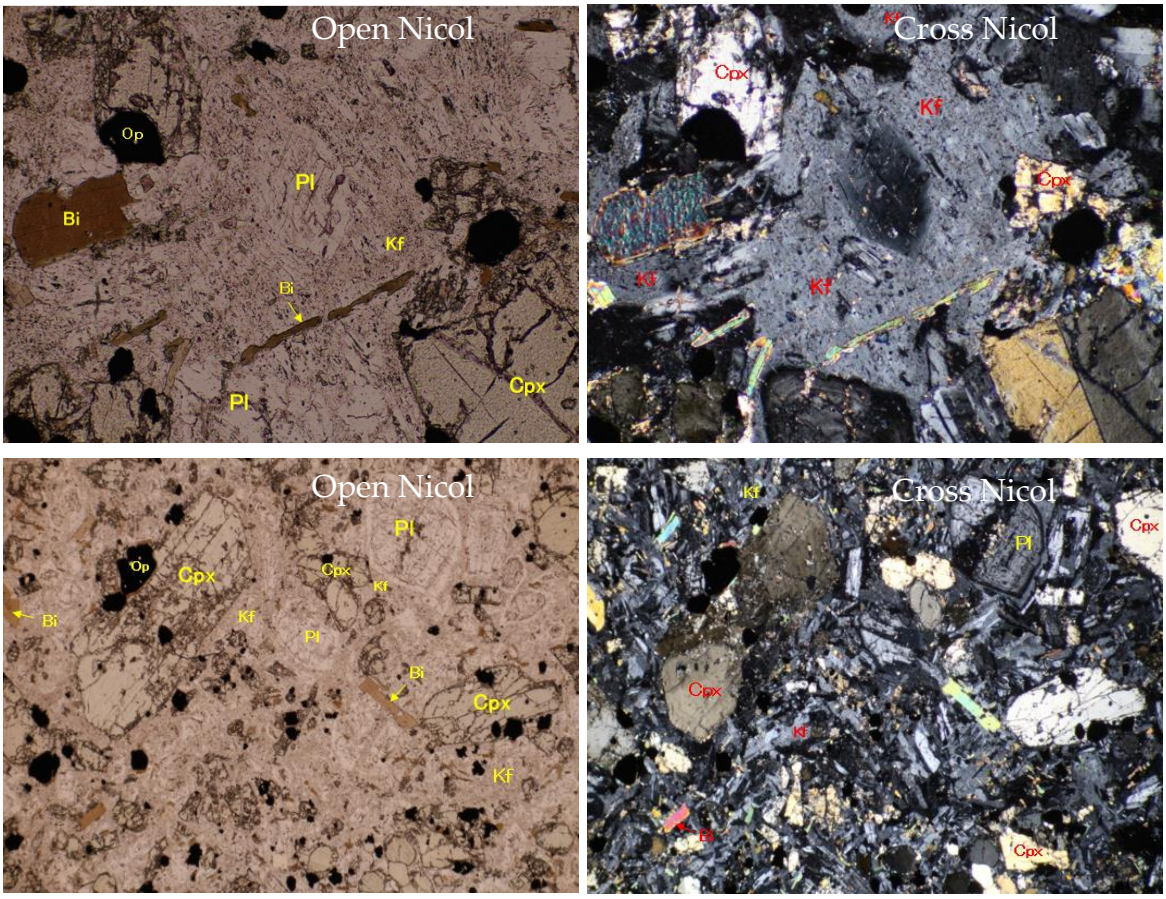
Sample	M1	M2	M3	N1	N2	N3	N4	T1	T2	T3	T4	V1	V2	V3	V4	W1
Quartz	77.5	85.9	87.6	13.8	6.40	58.8	-	23.7	14.6	-	12.3	23.2	9.8	23.7	17.2	30.8
Pyrite	5.00	-	3.50	-	4.30	-	94.6	-	-	-	-	-	-	-	-	7.70
Anorthite	-	-	-	-	-	-	-	64.6	32.0	48.8	54.8	-	-	-	37.3	-
Orthoclase	-	-	-	-	-	-	-	-	-	25.2	30.9	-	44.1	-	41.2	-
Calcite	-	-	-	-	-	-	-	8.8	-	-	-	26.1	22.7	17.3	-	-
Goethite	-	-	-	-	8.90	34.3	-	-	-	-	-	-	-	-	-	-
Albite	-	-	-	47.5	-	-	3.00	-	-	-	-	-	-	-	-	-
Cristobalite	-	-	-	38.7	-	-	-	-	-	-	-	-	-	-	-	-
Chalcopyrite	-	-	-	-	2.00	-	-	-	-	-	-	-	-	-	-	6.03
Hematite	-	-	-	-	72.4	4.60	-	-	-	-	-	-	-	-	-	-
Dolomite	-	-	-	-	-	-	-	-	-	3.40	-	-	-	-	4.30	-
Arsenopyrite		2.20	-	-	8.10	-	-	-	-	-	-	-	-	-	-	-
Sphalerite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	55.2



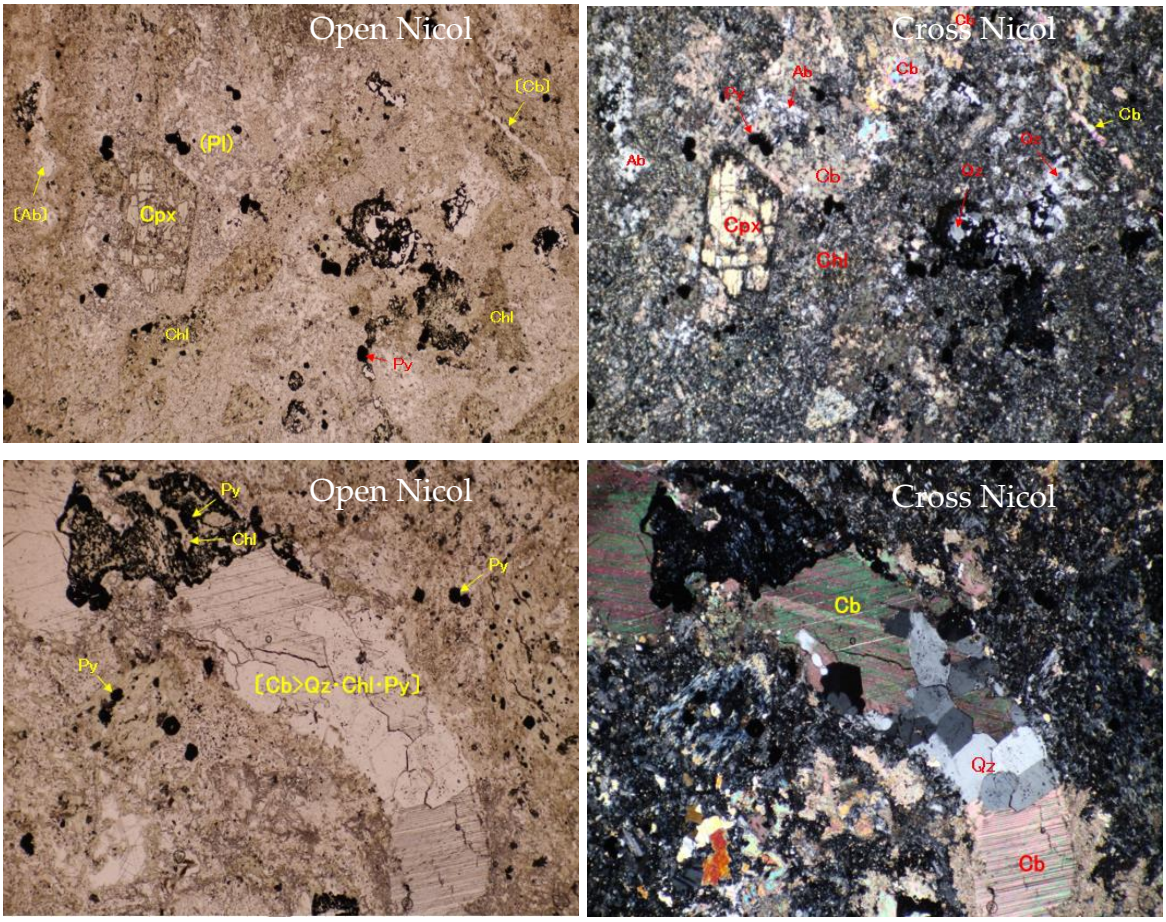
(a) M2 – Qz: quartz, Py: pyritic minerals, Hm: hematite, Wo: wollastonite.



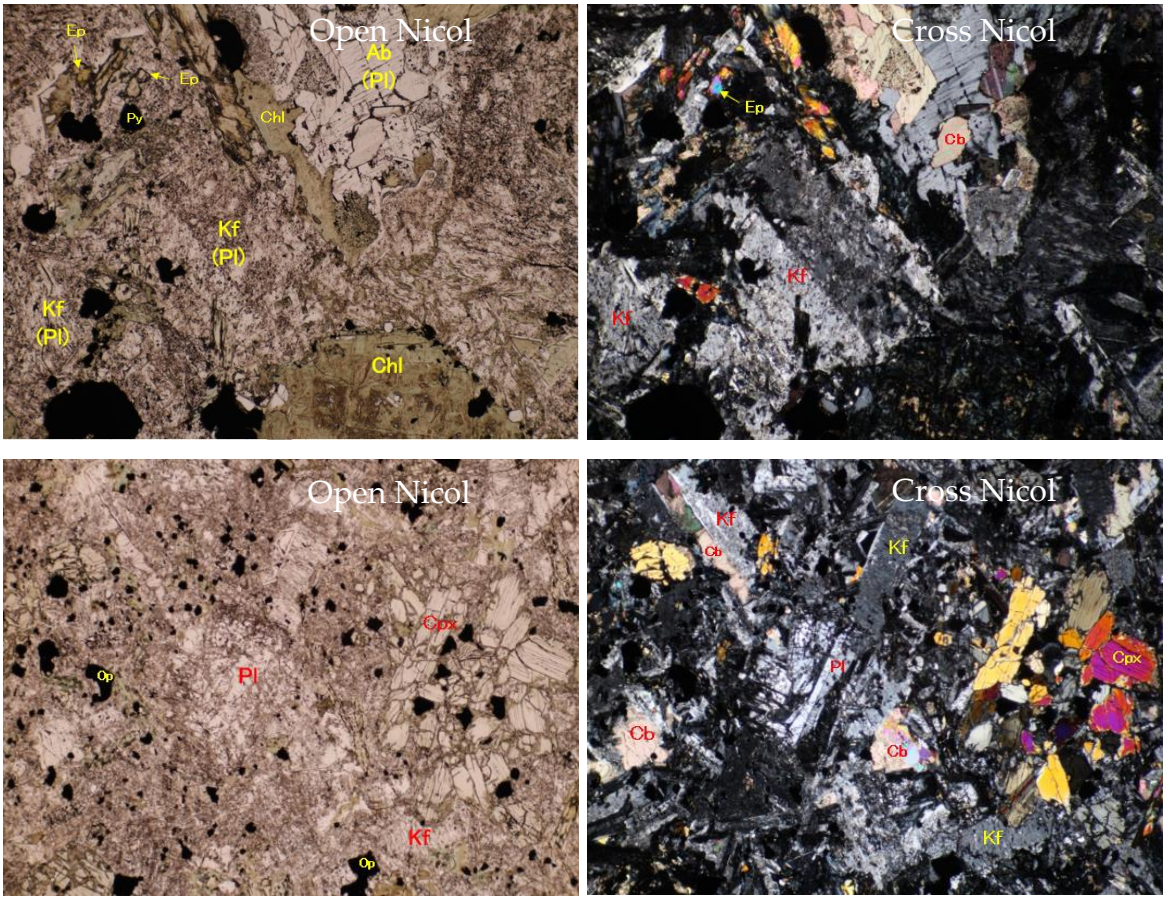
(b) N1 – Pl: plagioclase, Py, pyritic minerals, Mt: magnetite, Ilm: ilmenite.



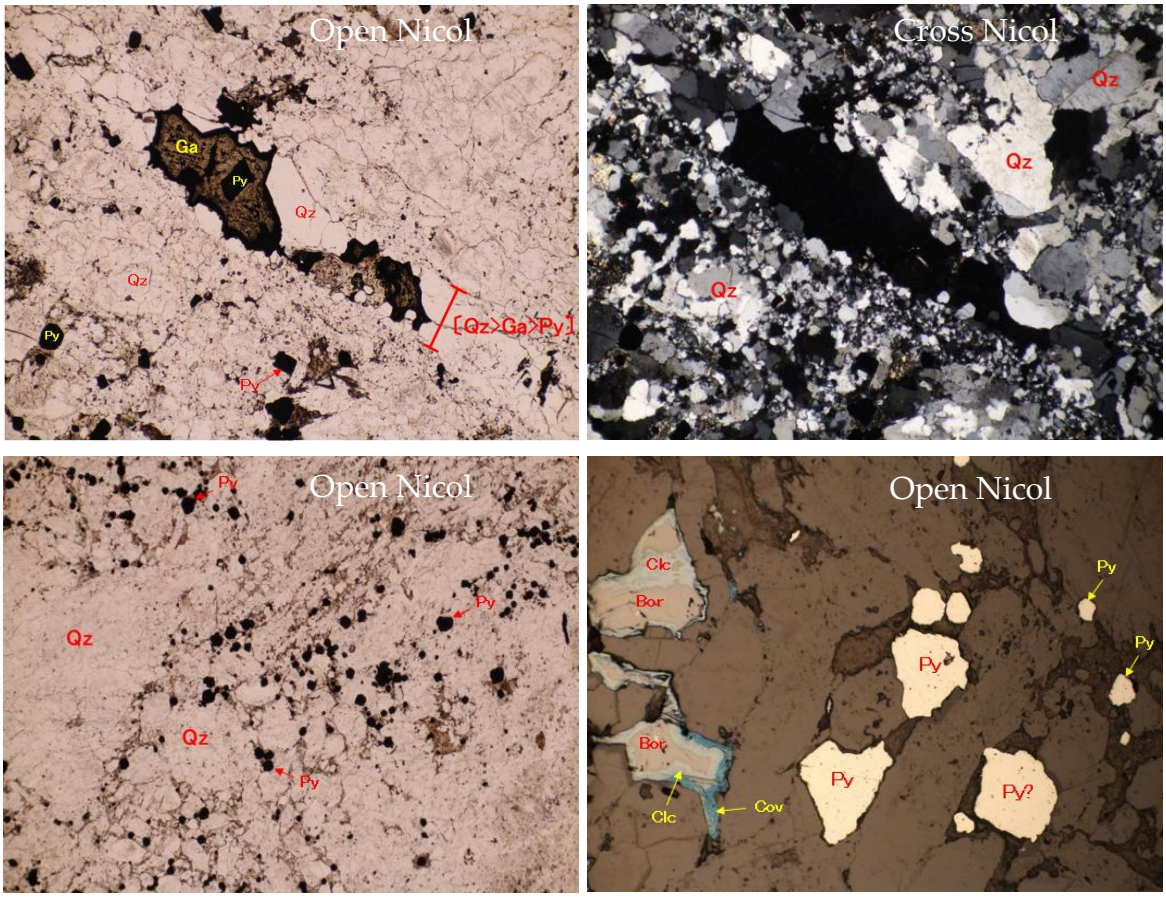
(c) T3 – Bi: biotite, Pl: plagioclase, Op: opaque minerals, Kf: potassium feldspar, Cpx: clinoaugite, Mt: magnetite, Py: pyritic minerals, Bi: biotite.



(d) V1 – Ab: albite, Pl: plagioclase, Cpx: clinoaugite, Opx: orthopyroxene, Py: pyritic minerals, Cb: carbonate minerals, Chl: chlorite, Qz: quartz, Mt: magnetite



(e) V4 –Ep: epitode, Py: pyritic minerals, Kf: potassium feldspar, Ab: albite, Pl: plagioclase, Chl: chlorite, Cb: carbonate minerals, Op: opaque minerals, Cpx: clinopyroxene.



(f) W1 – Ga: galena, Qz: quartz, Py: pyritic minerals, Clc: calcocite, Cov: covellite, Bor: bornite.

Figure 2.6 Microscopic observation of rock samples (a) M2, (b) N1, (c) T3, (d) V1, (e) V4 and (f) W1, under Open and Cross Nicol.

At Tuvatu, anorthite ($CaAl_2Si_2O_8$), albite ($Na(AlSi_3O_3)$, and orthoclase ($KAlSi_3O_8$) were the major minerals, and minor minerals included quartz, calcite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$) (Table 2.4). Surprisingly, pyritic minerals were detected with an optical microscope in T3 (Figure 2.3 (d)), but were not detected by XRD (Table 2.5). The Tuvatu samples were predominantly of silicate origin but unlike the Mt Kasi, Nukudamu, and Wainivesi samples, carbonate minerals such as calcite and dolomite were detected in minor quantities (Figure 2.2 (d)), 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. 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 quartz and orthoclase, as major mineral constituents (Figure 2.2 (e)), while calcite and dolomite (Table 2.5) are present as minor minerals, the latter minerals were also noted by Anderson and Eaton, (1990), mineralization study of Vatukoula. Evidence of pyritic minerals were detected in V1 and V4, (Figure 2.3 (d), (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 (up to 1.69 wt%).

2.4.2 Leachate Characteristics of the Rock Samples – Release and Retention Mechanism

Figures 2.4 and 2.5 illustrate pH *vs* concentrations of Cu, Fe, Pb, Zn and coexisting ions (Ca, K, Mg, and SO_4^{2-}) after batch leaching tests, which were compared with the WHO guideline values for drinking water (World Health Organization, 2011) 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 (Tabelin et al., 2018; Igarashi et al., 2020).

Pyrite is typically ubiquitous, associated with most of the base metals, and usually problematic due to AMD generation when exposed to oxic conditions. Oxidation products, such as Fe(III) hydroxysulfate (Bao et al., 2018) (pH < 3), sulfate (SO_4^{2-}), ferrous iron (Fe^{2+}), and hydrogen (H^+) ions are released into the solution, and the ferrous iron is further oxidized to ferric iron (Fe^{3+}) generating more acidity (Igarashi et al., 2020). Fe^{3+} in the acidic solution also tends to oxidize other metal sulfide minerals in the rock samples, consequently releasing more metal, H^+, and 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 (Tabelin et al., 2020).

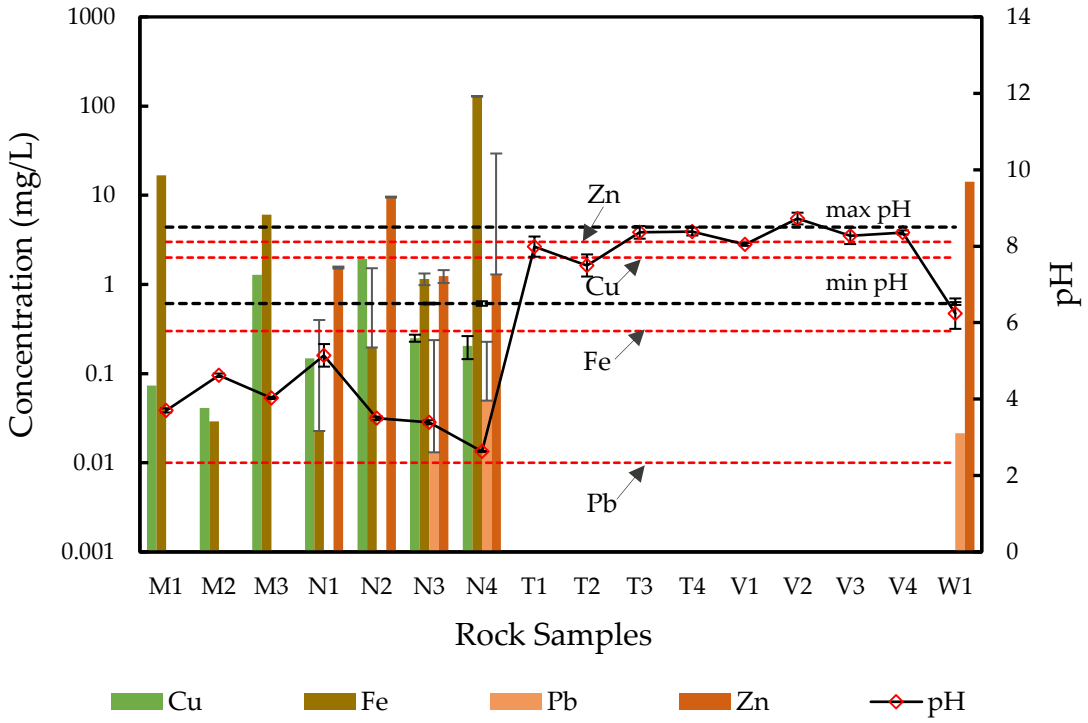


Figure 2.7 Leachate concentrations of Cu, Fe, Pb and Zn and the pH of Mt Kasi (M1–M3), Nukudamu (N1–N4), Tuvatu (T1–T4), Vatukoula (V1–V4) and Wainivesi (W1). The dotted lines indicate the WHO drinking water guidelines for Cu, Fe, Pb, Zn and pH (minimum and maximum values; 6.5, 8.5).

Sulfide oxidation is likely the most dominant release mechanism of Cu, Pb, Zn, and SO_4^{2-} (Figures 2.4 and 2.5) 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 2.6). 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 (Kelderman and Osman, 2007; Popenda, 2014).

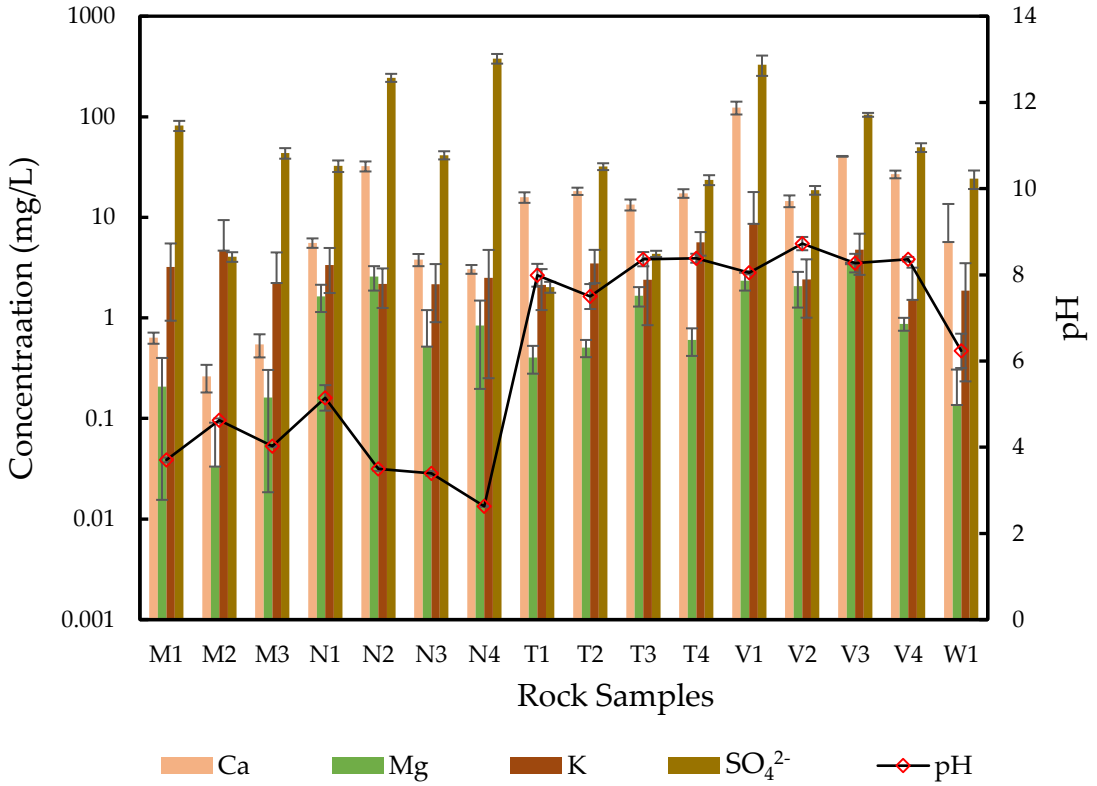


Figure 2.8 Leachate concentrations of Ca, Mg, K and SO42- and the pH of Mt Kasi (M1–M3), Nukudamu (N1–N4), Tuvatu (T1–T4), Vatukoula (V1–V4) and Wainivesi (W1) samples.

Although Cu, Fe, Pb, and Zn were detected in the leachates, they were not consistently leached from all the rock samples (Figure 2.4; Table 2.6). Higher concentrations of Fe at 16.8 ± 3.72 mg/L, 6.08 ± 1.45 mg/L, 1.15 ± 0.20 mg/L, and 129 ± 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 ± 0.41 mg/L (N2) and was around the WHO drinking water standard of 2 mg/L. High Zn concentration was observed in the leachates of samples from Wainivesi (14.2 ± 3.22 mg/L) and Nukudamu (N2; 9.54 ± 1.32 mg/L). Meanwhile, Pb leached only from two of the four Nukudamu rock samples (N3 and N4) with concentrations of 0.02 ± 0.02 and 0.05 ± 0.06 mg/L, respectively, and concentrations of 0.02 ± 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 at 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 (Kumar et al., 2022).

Table 2.6 pH, EC, ORP, and concentrations of toxic elements and coexisting ions SO_4^{2-} and Ca measured in the leachates of batch leaching experiments.

Sample	pH	EC (mS/cm)	ORP (mV)	Pb (mg/L)	Zn (mg/L)	Cu (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Ca (mg/L)
M1	3.70 ± 0.06	0.249 ± 0.02	362 ± 16.7			0.07 ± 0.11	16.8 ± 3.72	81.6 ± 9.43	0.63 ± 0.08
M2	4.62 ± 0.05	0.042 ± 0.03	338 ± 11.8			0.04 ± 0.04	0.03 ± 0.03	4.05 ± 0.45	0.26 ± 0.08
M3	4.02 ± 0.02	0.13 ± 0.01	347 ± 21.4			1.28 ± 0.27	6.08 ± 1.45	43.5 ± 5.24	0.55 ± 0.14
N1	5.14 ± 0.3	0.09 ± 0.005	311 ± 26.5		1.55 ± 0.38	0.15 ± 0.15	0.02 ± 0.04	32.5 ± 4.28	5.57 ± 0.60
N2	3.50 ± 0.05	0.55 ± 0.04	449 ± 16.2		9.54 ± 1.32	1.94 ± 0.41	0.20 ± 0.11	245 ± 22.5	32.3 ± 3.68
N3	3.39 ± 0.05	0.22 ± .005	427 ± 23.5	0.01 ± 0.02	1.24 ± 0.17	0.25 ± 0.22	1.15 ± 0.20	41.5 ± 3.87	3.79 ± 0.53
N4	2.63 ± 0.01	1.50 ± 0.04	389 ± 13.4	0.05 ± 0.06	1.29 ± 0.28	0.20 ± 0.18	129 ± 0.20	379 ± 41.8	3.05 ± 0.31
T1	7.99 ± 0.26	0.09 ± 0.002	253 ± 19.3				0.006 ± 0.01	2.03 ± 0.25	15.8 ± 1.90
T2	7.50 ± 0.29	0.13 ± 0.01	204 ± 21.4				0.001±0.002	32.0 ± 2.50	18.2 ± 1.51
T3	8.36 ± 0.17	0.08 ± 0.002	184 ± 29.3				0.003±0.005	4.34 ± 0.30	13.4 ± 1.68
T4	8.38 ± 0.10	0.16 ± 0.01	188 ± 37.7				0.002±0.004	23.6 ± 2.68	17.3 ± 1.70
V1	8.05 ± 0.04	0.69 ± 0.04	190 ± 26.0					330 ± 75.5	123 ± 18.0
V2	8.72 ± 0.15	0.12 ± 0.02	215 ± 38.7				0.001±0.001	18.6 ± 1.85	15.0 ± 1.95
V3	8.27 ± 0.22	0.31 ± 0.03	184 ± 27.8					105 ± 4.61	40 ± 0.36
V4	8.36 ± 0.05	0.19 ± 0.01	182 ± 27.4					49.6 ± 4.97	27.0 ± 2.35
W1	6.24 ± 0.40	0.06 ± 0.01	228 ± 18.5	0.02 ± 0.04	14.2 ± 3.22			24.2 ± 5.05	5.68 ± 7.90

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 2.2 (c), (e) and Table 2.6), which releases divalent cations (Ca, Mg, Fe) and 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 2.5), 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 2.7), suggesting the dissolution of these minerals. Equilibrium dissolution of calcite and dolomite consumes H^+ and generates aqueous carbonate species, e.g., hydrozincite, smithsonite, hydrocerussite, and cerussite (Tangviroon et al., 2020; Khoshraftar et al., 2022), which are later reflected in Nukudamu (N1) and Wainivesi (W1) leachates. Although the saturation indices (*SI*s) 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 H^+. This is supported by the undersaturation of hydrozincite, smithsonite, hydrocerussite, and cerussite (Table 2.6). The *SI*s 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 (Tabelin et al., 2018).

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 ($Al_2Si_2O_5(OH)_4$) as indicated by positive *SI*s for this mineral. Although the pH buffering reaction of Al-bearing phases between pH 4 to 4.5 (Gu et al., 2008) could occur through gibbsite dissolution (*SI*s < 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 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.

Table 2.7 Saturation indices (SIs) of the selected mineral phases in the leachates of the rock samples.

Minerals	M1	M2	M3	N1	N2	N3	N4	T1	T2	T3	T4	V1	V2	V3	V4	W1
Alunite	-0.60	-2.27	**0.74**	**1.58**	-0.81	-5.31	-8.79	-7.17	-1.90	-6.99	-5.34	-3.66	-3.29	-8.39	-5.08	-
Diaspore	-0.69	0.37	**0.67**	**1.97**	-0.82	-2.07	-4.51	**3.13**	**3.17**	**2.95**	**2.93**	**2.45**	**3.40**	**1.89**	**2.98**	-
Chalcedony	-0.66	-1.52	-0.82	-0.93	-0.82	-0.95	-2.23	-0.90	-0.82	-0.59	-0.82	-0.76	-1.33	-0.75	-1.01	-1.69
Cristobalite	-0.86	-1.72	-0.92	-0.60	-1.02	-1.15	-2.43	-1.08	-1.02	-0.79	-1.02	-0.96	-1.53	-0.95	-1.21	-1.89
Ferrihydride	-10.4	-9.07	-9.82	-8.53	-10.9	-10.9	-13.1	-5.70	-5.63	-5.43	-5.42	-5.69	-5.71	-5.71	-5.44	-7.46
Gibbsite	-1.15	-0.39	-0.20	**1.11**	-1.71	-2.94	-5.31	**2.61**	**1.80**	**2.07**	**2.04**	**1.57**	**2.53**	**1.01**	**2.11**	-
Goethite	-7.56	-6.25	-7.02	-5.70	-8.03	-8.09	-10.3	-2.87	-2.88	-2.60	-2.59	-2.86	-2.88	-2.88	-2.61	-4.63
Gypsum	-3.23	-4.18	-3.45	-2.89	-1.62	-2.99	-2.52	-3.62	-2.41	-3.36	-2.56	-0.92	-2.72	-1.69	-2.10	-3.01
Quartz	-0.20	-1.06	-0.30	0.06	-0.90	-2.26	-1.78	-0.42	-0.36	-0.13	-0.37	-0.30	-0.87	-0.27	-1.09	-1.23
Kaolinite	-3.43	-3.04	-3.12	2.40	-4.03	-6.79	-14.2	**3.77**	**3.97**	**3.99**	**3.47**	**2.64**	**3.42**	**1.55**	**3.22**	-
Hydrozincite	-	-	-	-22.4	-	-	-	-	-	-	-	-	-	-	-	-11.0
Smithsonite	-	-	-	-3.96	-	-	-	-	-	-	-	-	-	-	-	-2.99
Calcite	-	-	-	-5.63	-	-	-	-3.04	-2.98	-2.91	-2.56	-1.76	-3.27	-1.68	-2.95	-5.61
Dolomite	-	-	-	-11.5	-	-	-	-7.40	-7.27	-6.44	-6.30	-4.95	-1.53	-4.13	-7.11	-12.6
Anglesite	-	-	-	-	-	-3.10	-1.91	-	-	-	-	-	-	-	-	-3.00
Hydrocerrusite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-10.4
Cerrusite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-3.99

* Bold text indicates oversaturation

2.4.3 Rock Sample 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, SO_4^{2-}, and Si) (Table 2.8, Figure 2.6). 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 EC, ORP, Fe, Pb, and to some extent also Cu

and 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 SO_4^{2-} was associated with the higher ORP and more acidic pH of the rock samples, which was attributed to the enhanced oxidation of sulfide minerals (Tabelin et al., 2018).

Table 2.8 Principal component analysis (PCA) including total variance, eigenvalue, and cumulative frequency for the leachates of rock samples.

Variables	PC1	PC2	PC3	PC4
pH	**−0.381**	0.141	−0.078	−0.276
EC	**0.308**	**0.393**	−0.082	0.103
ORP	**0.362**	−0.171	0.181	**0.310**
Al	0.253	−0.049	**0.471**	−0.081
Cu	0.238	−0.097	**0.469**	−0.077
Fe	**0.317**	0.220	−0.299	0.166
Mg	−0.076	**0.325**	**0.345**	−0.062
Mn	0.121	−0.186	0.049	**0.316**
Pb	**0.331**	0.129	−0.358	−0.058
Zn	0.178	−0.111	0.139	−0.618
Ca	−0.123	**0.452**	0.209	−0.125
K	−0.163	**0.395**	0.072	0.143
Na	−0.297	0.052	0.047	0.290
SO_4^{2-}	0.262	**0.451**	0.097	0.021
Si	−0.216	−0.008	**0.306**	**0.410**
Eigenvalue	5.00	3.03	2.42	1.30
Variance%	31.6	21.1	16.6	8.60
Cumulative%	31.6	52.7	69.2	77.5

* Bold text indicates variables that accounts significantly under each PC.

The PC2 (21.1%) indicated high loadings of EC, Mg, Ca, K, and SO_4^{2-}. The highest contribution of Ca and 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.

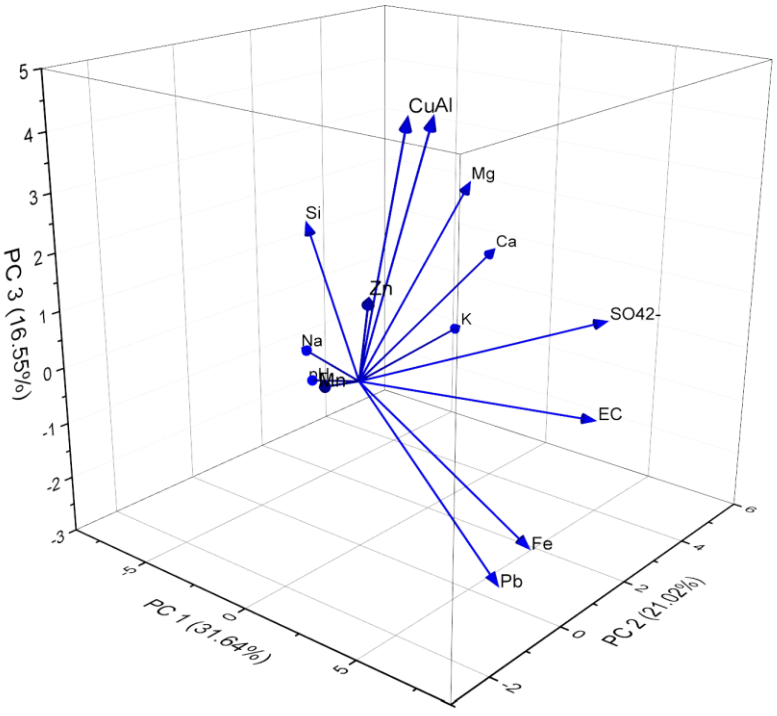


Figure 2.9 Graphical presentation of the PCA results showing the first 3 components with significant inter-correlated dependent variables.

The *ABA* test results in Figure 2.7 show that rock samples from Mt Kasi, Nukudamu, Wainivesi, Tuvatu (T1), and V4 from Vatukoula had negative *NNP* values (<−20 kg $CaCO_3$/t). This means that such rock samples from these sites were likely to generate acidity when exposed to oxic 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* of 20.5 $CaCO_3$/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 $CaCO_3$/t, suggesting uncertainty to generate acidity.

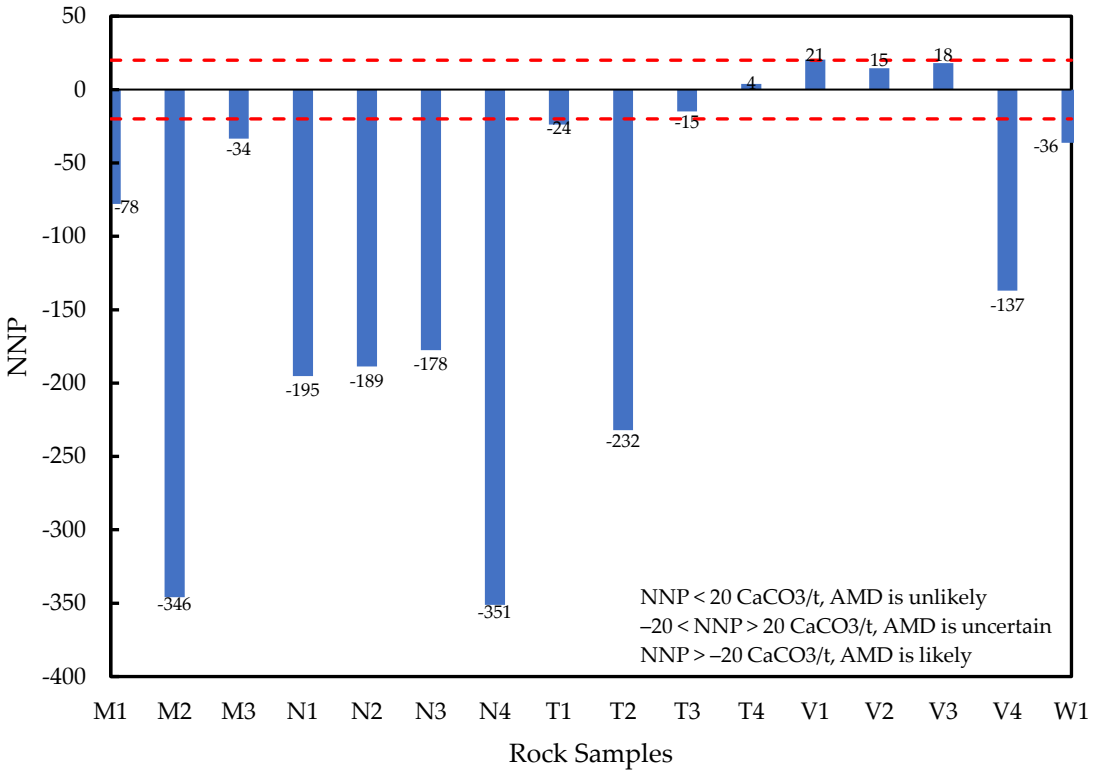


Figure 2.10 Acid–base accounting (ABA) for Mt Kasi (M1−M3), Nukudamu (N1−N4), Tuvatu (T1−T4), Vatukoula (V1−V4), and Wainivesi (W1) rock samples.

The pH (H_2O_2) acidification test results are illustrated in Figure 2.8. 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 (H_2O_2) test showed a pH of 3.2. This implies that the sample is 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 (H_2O_2) test. This implies that a single acid test could not completely provide the certainty of acid production of rock samples 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 (Gunsinger et al., 2006; Brady and Cravotta, 1992). 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 (Igarashi et al., 2001; Inui et al., 2014).

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, causes the dissolution of carbonates for neutralization. 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.

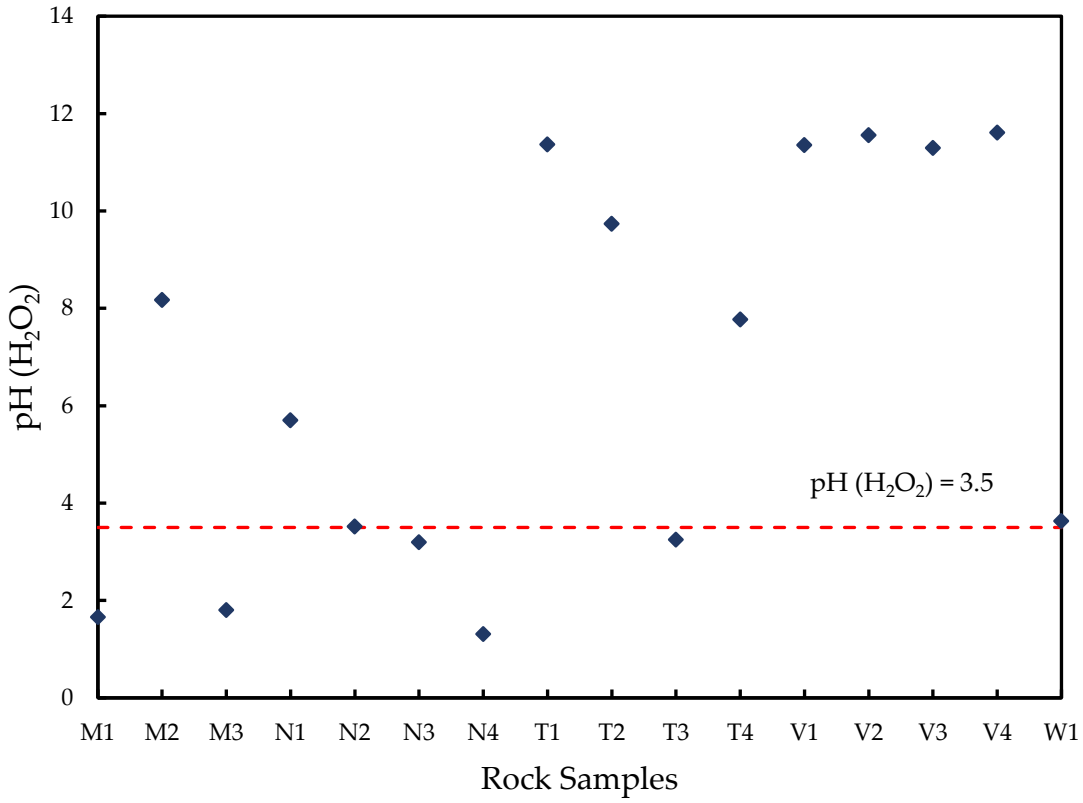


Figure 2.11 Hydrogen peroxide pH test (pH (H_2O_2)). The dotted line indicates the threshold for acidification potential (pH = 3.5).

Incorporating the two methods coupled with chemical and mineral characterization and thermodynamic calculation provides 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 chemical and mineral 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 (Akcil and Soner, 2006; Stewart et al., 2006; Simate and Ndlovu, 2024; Assawicharoenkij et al., 2018). Thus, close attention should be paid to the abandoned sites and proper environmental management practices should seriously be 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.

2.5 Conclusions

The chemical and mineral 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 chemical and mineral 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 had 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 especially chemical and mineral characteristics 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.

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Chapter 3 CHEMICAL AND MINERAL CHARACTERIZATION OF NUKUDAMU ABANDONED MINE

3.1 Introduction

This chapter covers the detailed chemical and mineral characterization study of rock and water samples collected from Nukudamu abandoned mine site. The site was selected for more comprehensive geochemical examination since it was evaluated with high environmental vulnerability from the initial study in chapter 2. A summary of the Nukudamu mine geology is provided, so there was reflection on the short history of mining that was undertaken on site and its current state. The chapter then discusses the water and rock sampling, the experimental methodology used which were primarily XRD, XRF and leaching as the main characteristic laboratory tests with sequential extraction, scanning electron microscope, pH (H_2O_2) test, supported by the statistical PCA and thermodynamic modeling. Then the results obtained with discussion reflecting on the findings with reference to available published work are presented. The detailed geochemical properties of the samples that intended to offer a clear understanding of the minerals and chemical composition, their nature of occurrence, their interactions, movements, and behavior, especially elements of significant interest such as heavy metals and metalloids, i.e., hazardous or potential toxic elements distinctive to the geology of Nukudamu and disturbed landform onsite are provided. Specifically, hazardous elements, As, Cu, Fe, Pb, Zn, and co-existing major ions, such as Ca, Mg, Na, K, SO_4^{2-}, and Si, contained in the rock samples were analyzed. As highlighted in chapter two, there is evidence of AMD from the exposed open cut and it is a further intention of this chapter to explore the geochemical characteristics of the site to seek the most appropriate strategy for countermeasures.

The content of this chapter not only characterize Nukudamu abandoned mine's geochemistry but supports the study's overall goal and rationale of using chemical and characterization to raise awareness of the mine site potential impacts. When such knowledge is lacking, mining

approval processes is compromise, as well as management of mines, mining waste and mine rehabilitation. Thus, the needs of jurisdictions in developing countries like Fiji to strengthen their mineral development and sustainable strategies via a thorough understanding of the geochemical characteristic of orebodies are critical. Apart from making available new information about Nukudamu mine, it contributes to and plays an important role in mining administration, particularly in improving mining approval processes.

3.2 The History and Geological background of Nukudamu abandoned mine site.

The Nukudamu abandoned mine is located about 10 km SW of tip of Udu peninsula and 1 km SW of Nukudamu village, northeast of Vanua Levu. Mining at Nukudamu ceased more than 50 years ago, even though periodic drilling exploration have been carried out on site, no rehabilitation work was ever conducted and the site remains abandoned for most of its existence till to date. Once open cut mine face has been left exposed and barren over the years, the mine has resulted in significant erosions that have badly damaged the landscape. Also, there is evidence of AMD occurring on site (Soro et al., 2023).

The geology and rock formation of Nukudamu was best described by geologist Colley and Rice in their published manuscript by the Economic Journal in 1975, which they reproduced again in 1978 in the New Zealand Journal of Geology and Geophysics, 1978. Colley then together with Flint (1995) also summarized the same in the compilation of the book, Metallic Mineral Deposits of Fiji (Colley and Flint, 1995). In these records, it described that the Nukudamu mine sits on the Udu volcanic rock group, which is made up of massive flows, breccias, tuffs, and associated sediments, mostly of submarine origin. The lower part of this group is referred to as the Nasavu Formation (or Nasavu Dacites) and contains massive flows, autoclastic breccias, and tuffs, with minor intercalations of turbiditic marine sediments, carbonate beds and some welded tuffs. Rickard (1961) suggested that part of the Nasavu dacites was subaerial. The upper part of the Udu Group is referred to as the Malau Formation (or Malau Breccias) and consists mainly of massive and well-bedded pumiceous tuffs and

breccias having the characteristics of subaqueous pyroclastic flows (Fiske and Matsuda, 1964). Rare massive flows of dacite and rhyodacite also occur and the upper horizons show an increase in volcano-clastic sedimentation indicative of waning volcanism.

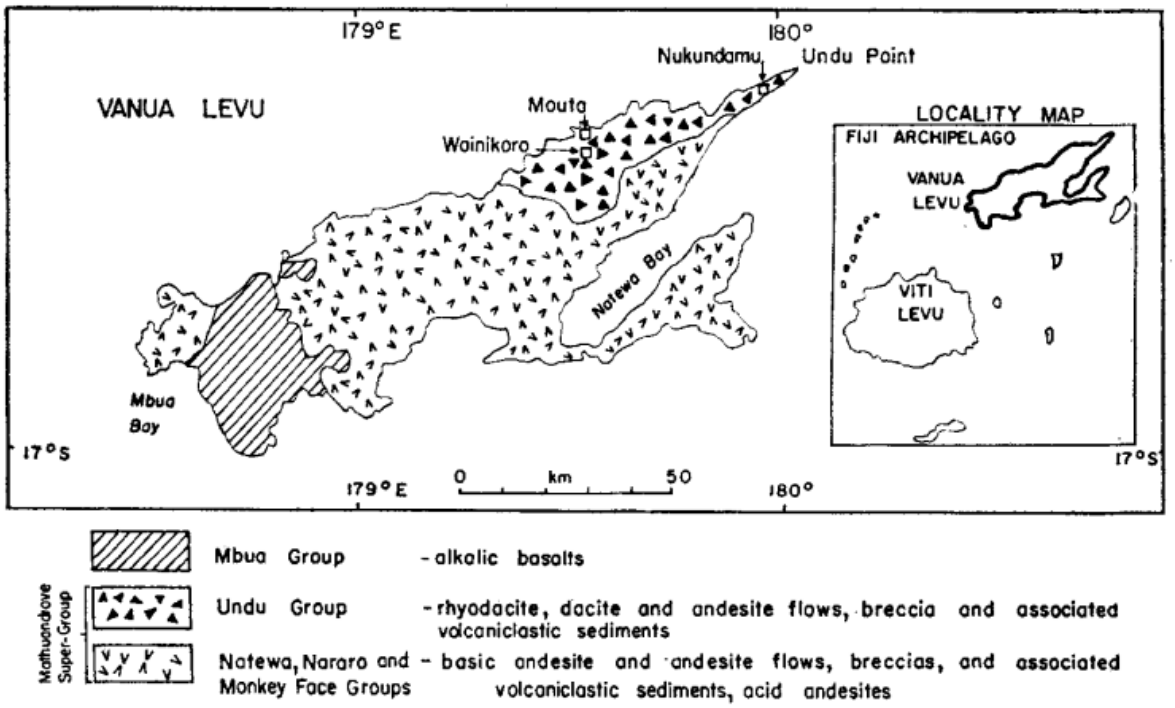


Figure 3.1 Geological sketch-map of Vanua Levu by Colley and Rice, (1975).

The Nukudamu mineral deposit was first discovered in 1957 by a local prospector, who carried out pitting and trenching operations, which revealed a thin zone of supergene ore beneath the gossan (Colley and Rice, 1975; Colley and Flint, 1995). The deposit later confirmed to be mixed-sulfide deposit, closely resembling the kuroko ore deposits of Japan, which are found in pockets of the Udu rock group (Colley and Rice, 1975, 1978). In 1959, a local subsidiary of Banno Bros. of Japan entered into an agreement with the prospector and conducted intensive exploration involving drilling. Banno assumed control of the operation in 1961 and later entered into an agreement with the Dowa Mining Company. The drilling exploration estimates the deposit of base metals (Cu and Zn) at 150,000 tons, which convince the company to commenced mining in early 1968. It had been assumed that the ore formed a sheet like body, but opencast mining showed that the massive ore occurred only in isolated

pockets and estimates fell to 40,000 tons. Mining operations ceased at the end of 1968 with a final production figure of 32,435 tons of concentrate containing 5.9% Cu and 6.7% Zn (Colley and Rice, 1975; Colley and Flint, 1995).

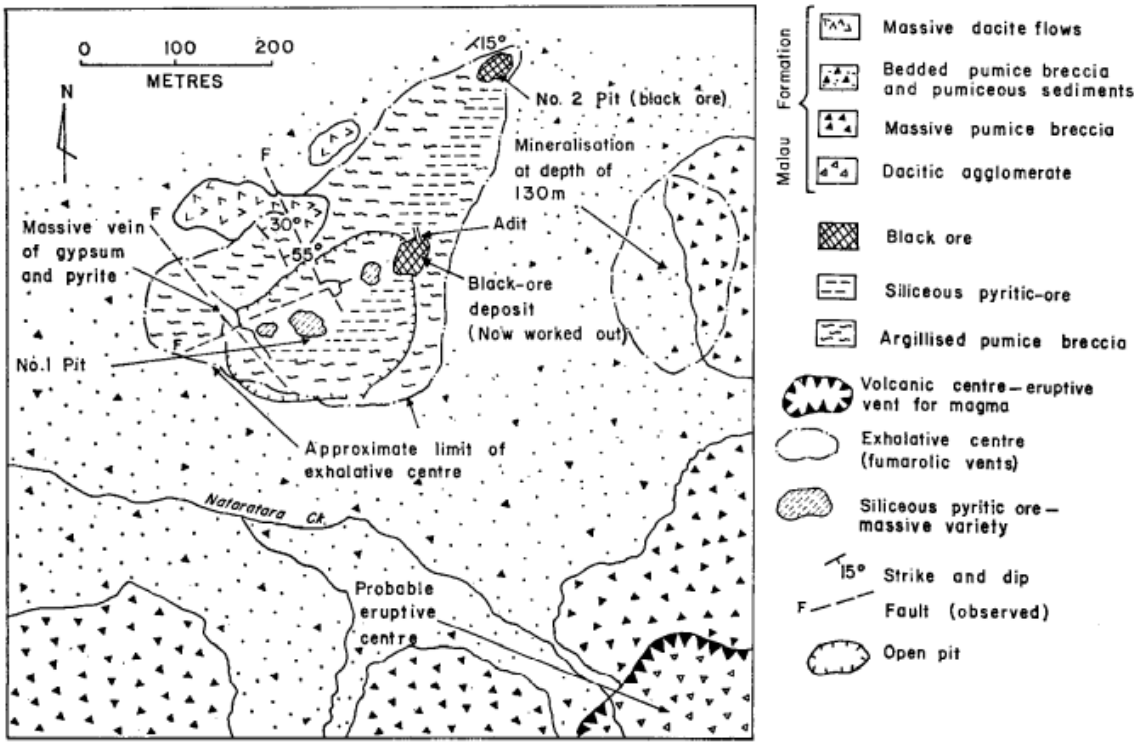


Figure 3.2 Geological sketch-map of Nukudamu mine from Colley and Rice, (1978).

The main sulfide minerals are sphalerite, chalcopyrite, and pyrite with lesser quantities of galena, bornite, enargite, tennantite, covellite, and possibly idaite. Gypsum, anhydrite, and baryte were identified as common gangue minerals. Similar Japanese Kuroko type deposits of predominantly siliceous ores were found to occur in places of black and yellow ore types with remnants of Cu-rich pods of siliceous pyrite ore that occurs beneath an extensive gossan. Colloform textures are particularly abundant in the upper part of the deposit, whereas replacement textures become more important with depth. Brecciation of the ore is ubiquitous and the fractures are usually infilled by chalcedony. Sphalerite contains very little Fe (maximum recorded = 0.7%) and, unlike the Japanese deposits, tennantite is not a major carrier of Ag (Colley and Rice, 1978).

Figure 3.3 Composite pictures of the general landscape disturbances at Nukudamu abandoned mine site.

Since its abandonment in 1969, a number of investors have conducted further drilling explorations and extensive geophysics studies to improve the site's resource feasibility but none has been able to transit into mining. It is also hoped that this study can share valuable information that may contribute to the feasibility of the site.

3.3 Materials and Methods

3.3.1 Rock and Water Samples

Rocks were collected from the abandoned Nukudamu open cut mine with sample details and locations of collection provided in Table 3.1 and Figure 3.4. The samples were selectively collected from outcrops and boulders over the face of the open cut mine and were assumed to be representative of the site's geology based on in situ inspection and observation considering their dominance and abundance on site (Figure 3.5).

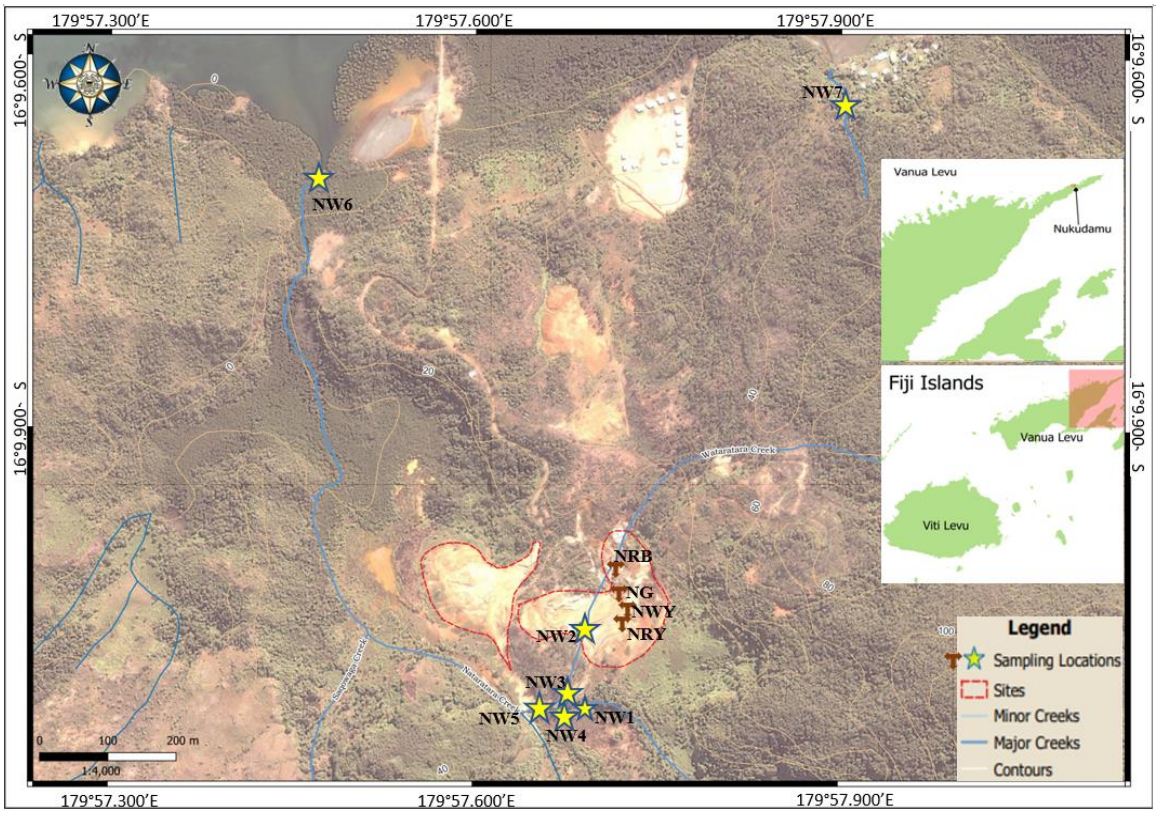


Figure 3.4 Map showing the water and rock sample collection location at Nukudamu abandoned mine site on google map backdrop.

Based on these assumptions, two rock types were considered according to their occurrence as altered and weathered rocks type 1 (NG1, 2, 3, NWY1, 2, and 3) and hard, solid Kuroko rock type 2 (NRB1, 2, 3 and NRY). A total of ten samples were collected (Figure 3.4 and Table 3.1). Two further creek bed rock samples (NCB1 and 2) were collected from Nataratara creek few meters from the open cut mine discharge to verify leachate precipitation. All samples collected were packed in seal plastic bags and label according to their rock type, sample number and location.

Table 3.1 Rock samples and related details.

Sample	Rock type, location	Sample description and field observation
NG1, NG2, NG3	Altered and weathered rock type, collected from bottom east edge of the open cut	Dark grey to greyish color, heavily weathered, soft to medium hardness, easy to crumble when pressed by hand, easy to break with geological pick, fine to coarse particle sizes
NWY1, NWY2, NWY3	Altered and weathered rock type, at the bottom east end of the open cut	White yellowish color, soft to medium hardness, easily broken with geological pick, fine grain particles
NRB1, NRB2, NRB3	Hard and solid rock type, collected from the northern slope face of the open cut	Black to dark brown-reddish color, very hard, broken only after several attempts with geological pick, coarse grain particles
NRY	Hard and solid rock, southeast side at the bottom of the open cut	Dark reddish and yellowish color, hard but can be broken with geological pick
NCB1, NCB2	Creek bed sample, along Nataratara creek downstream from open cut surface water discharge	Grey with yellowish brown flat compressed layered rock, semi hard, broken with one strike by geological pick, coarse grain

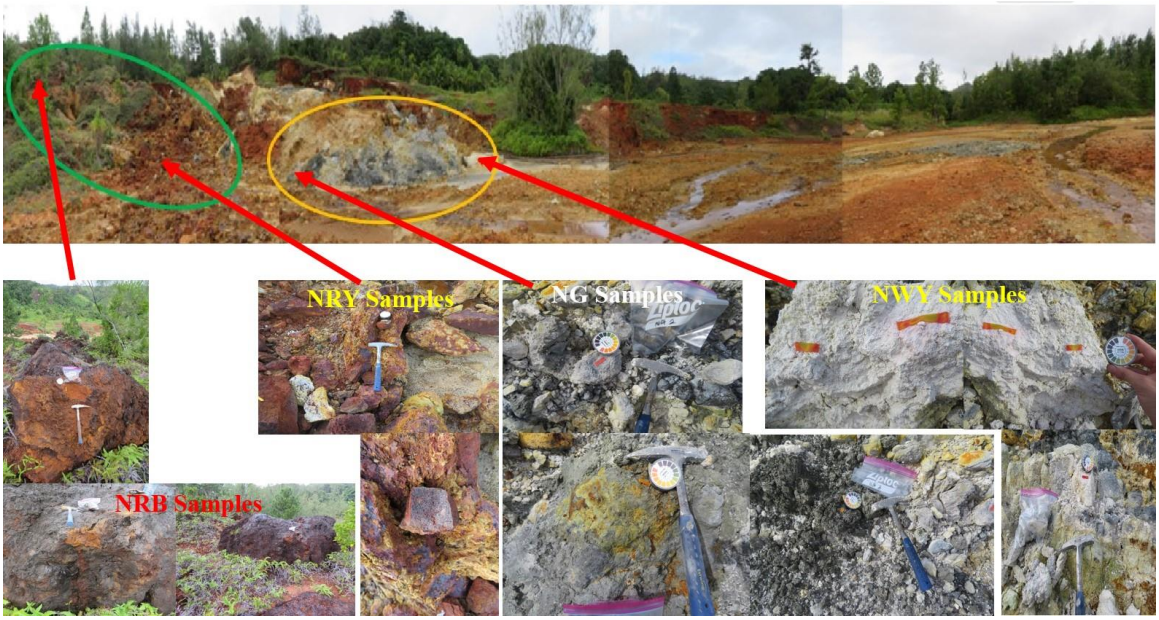


Figure 3.5 Rock samples mapping at the Nukudamu mine site.

Water samples were collected from the surface water flows within the open cut mine site and its surrounding environment according to drainage pattern of the area, considering the open cut drainage, discharge, and natural tributary flow. The intention was to understand the

migration of minerals and chemicals due to surface water flow of the mine and to the nearby environment. The water samples were collected and label in order of creek and mine surface runoff flows from upstream of the creek at location NW1 of Nataratara creek as background control water sample to downstream to estuary at location NW6. The mine water surface runoff samples were also collected likewise from NW2 at the top of surface runoff flow through NW3, which was collected at the tail of the mine surface runoff before discharging into Nataratara confluence at location NW4 and NW5 about 10 m downstream of Nataratara creek from the confluence point. A second background water sample (NW7) was also collected from another creek, east of the mine as a further reference and background sample.

About 100 mL each of raw and filtered water samples were collected from seven locations (Figure 3.4 and Table 3.2). Raw water samples were collected straight into the 100 mL plastic sampling bottles after first washing the bottles with raw water, then filled to the top and closed tightly. For filtered samples, a 50 mL syringe was used to extract the water on site, a 0.45 µm Millex syringe-driven filter unit was then attached and filtered water was injected into 100 mL sampling bottle, washed first then filled until full and closed tightly. All samples were then labelled by number according to location and water sample type (raw or filtered) and kept under cool temperature. The samples were packed and stored appropriately for overseas transportation via plane to Hokkaido University for respective sample preparation and analysis. Analysis of water samples was conducted using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) using ICPE 9800 (Shimadzu Corporation, Japan) after proper dilution. Results and discussion were presented in Figure 3.9 in 3.4.3.

Table 3.2 Water samples and relevant details.

Sample ID	Location	Sample description from field observation
NW1	Upstream of Nataratara creek, 20 meters from the mine surface discharge confluence	Sample is assumed to be the control point and background sample for water samples collected at Nukudamu mine
NW2	Mine site open cut surface runoff, top of main flow	Sample was collected from the main surface runoff of mine open cut at top end of the flow
NW3	Mine site discharge before Nataratara creek	Sample was collected from the main surface runoff at the tail end of the flow before discharges into Nataratara creek
NW4	Nataratara creek and mine face discharge confluence	Sample was collected from the confluence of the mine open cut discharge and the Nataratara creek
NW5	Nataratara creek, ten meters downstream from the confluence (NW3)	Sample was collected along Nataratara creek, about ten meters down creek from sample NW3 location
NW6	Mouth of Nataratara creek at the estuarine	Sample was collected at the estuarine of Nataratara creek as it flows into the sea.
NW7	Old village water source, different tributary from north-east of the mine site	Sample from a creek to the east over a ridge from Nataratara creek and the mine site as an alternative background sample

3.3.2 Characterization of rock samples

The X-ray powder diffraction (XRD) analysis was carried out to identify the mineralogical properties of the rock samples whereas X-ray fluorescence spectroscopy (XRF) analysis was conducted to determine its chemical composition. The sample for XRD analysis was prepared by crushing 10 g of rock samples to finer than 50 μm, the powder (≈ 1.5 g) was then transferred into standard ten-yen coin size aluminium ring and power pressed at ≈ 50 MPa into round pellets and then analyzed by XRD (MultiFlex, Rigaku Corporation, Japan). For XRF analysis, similar quantity of the sample powder was transferred into ring pallets and manually pressed using glass to achieve a smooth flat face, then analyzed by XRF (SpectroXepos, Rigaku Corporation, Japan). The fundamental parameter (FP) method was used for XRF analysis, which relies on built-in algorithms that describe the physics of the detector's response to pure elements. Such method typically achieved detection limits between 0.3 and 2,000 mg/kg depending on the element analyzed and the sample matrix.

The XRD signature patterns obtained from the analysis of rock samples were further evaluated using the Match!® software (Crystal Impact, Germany) to identify the dominant minerals as well as minerals of significant interest.

3.3.3 Batch Leaching Tests

The batch leaching experiments were conducted to evaluate metallic element leachates (As, Cu, Fe, Mn, Pb, and Zn) and coexisting ions (Ca, Mg, Na, K, and SO_4^{2-}) from the collected rock samples (Table 3.1 and Figure 3.4). The leaching experiment used in this part of the study follows the same procedures described in 2.3.3 for rock samples. The same inductively coupled plasma atomic emission spectroscopy (ICP-AES) using ICPE 9800 (Shimadzu Corporation, Japan) was also used for the analysis of water samples after proper dilution.

3.3.4 Sequential Extraction (SE)

The sequential extraction procedure used for this part of the study followed the methodology developed by Marumo et al. (2003), a streamlined version based on the earlier work by Tessier et al. (1979) and Clevenger (1990). The sequential extraction analysis technique is most commonly used to identify the solid-phase partitioning for contaminated soil and sediment samples (Gleyzes et al., 2002; Abollino et al., 2006; Qayyum et al., 2016; Matabane et al., 2021). Although the sequential extraction may not always be applied to solid rock samples since toxic or trace elements are solidly bounded and immobilized. However, it was considered valid based on previous studies (Filguiras, et al., 2002; Rodgers et al., Liang and Zhu, 2016; Junussov et al., 2018; Junussuv wt al., 2019). The designed laboratory procedures manifest the extraction of partitioned elements in different predetermined fractions using known reagents to identify their chemical forms (Tessier at al., 1975; Clevenger, 1990; Marumo et al., 2003). Hence predicting how such elements mobilize through processes like

weathering or mining adds important geochemical characteristics of rock samples as well as the mine sites.

The detailed procedure applied such as volume of extractants, temperature, pH, mixing rate, and extraction time is listed as follows:

1. Fraction 1 (Exchangeable): One gram of crushed rock sample was mixed with 20 mL of 1 M NaH_2PO_4 at pH 5. The mixture was shaken at 200 rpm for 1 hour at room temperature.

2. Fraction 2 (Bound to carbonates): The residual crushed rock sample from fraction 1 was extracted and added with 20 mL of 1 M CH_3COONa at pH 5, and the mixture was shaken at 200 rpm for 5 hours at room temperature.

3. Fraction 3 (Bound to iron and manganese oxides): The residual crushed rock sample from fraction 2 was mixed with 20 mL of 0.04 M NH_2OH. HCl in 25% acetic acid. The mixture was continuously shaken at 100 rpm for 5 hours at 80 °C.

4. Fraction 4 (Bound to organic matter and sulfide minerals): The extractants of this fraction was the mixed solution of 20 mL of 0.04 M NH_2OH. HCl in 25% acetic acid, 8 mL of 30% H_2O_2, and 8 mL of 0.02 M HNO_3, which was mixed with the residual crushed rock sample from fraction 3 by shaking at 100 rpm for 5 hours at 80 °C.

5. Fraction 5 (Residual): 20 mL of HNO_3 60% was used to dissolve any leftover or undissolved minerals, and the mixture was boiled for 1 hour using a hot sand plate.

The mixtures after shaking for all fractions from 1 to 5 were centrifuged at 3,000 rpm for 40 minutes using a centrifuge s300 series (Kubota Corporation, Japan). The supernatant was then decanted while the residues were washed with 10 mL of DI water. At each fraction from 1 to 4, the supernatants were diluted to 50 mL, while at fraction 5 they were diluted to 100

mL. The diluted solutions were filtered using 0.45 µm Millex® membrane filters, which were then analyzed by ICP-AES.

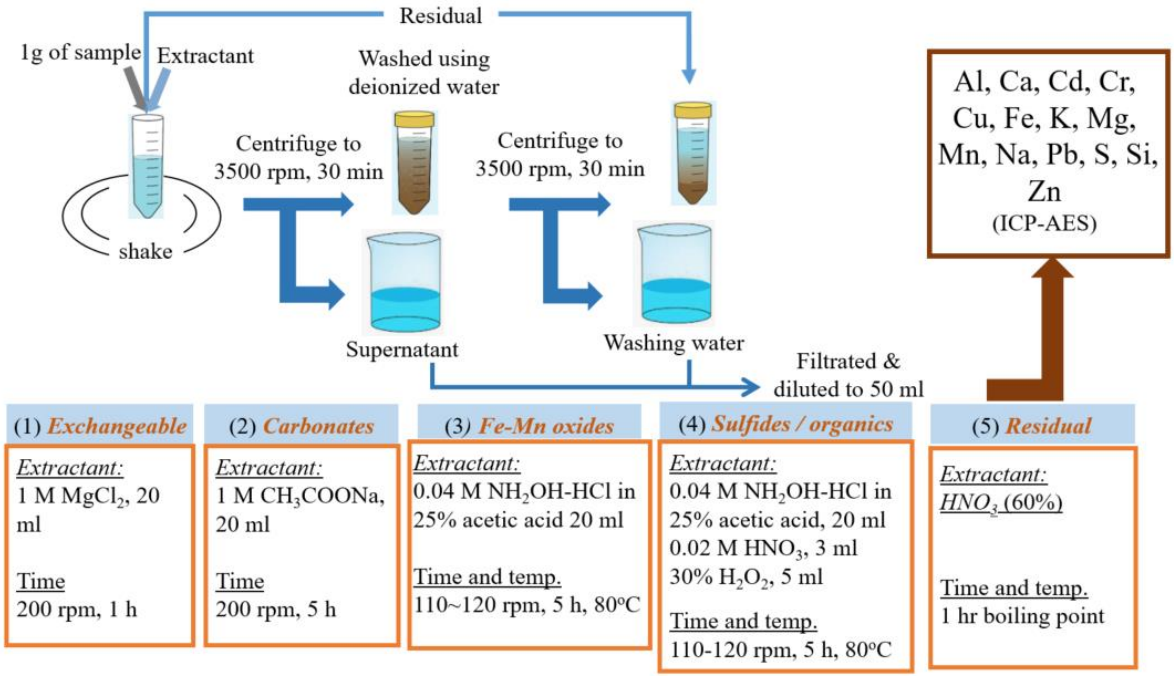


Figure 3. 6 Schematic process of sequential extraction.

3.3.5 Hydrogen Peroxide pH Acidification (pH (H_2O_2)) Test

The pH (H_2O_2) acidification test technique used for this part of the study follows the same procedures described in 2.3.7 with the results provided 3.4.5.

3.3.5 Statistical Analysis

Principal component analysis was performed to understand the correlations between the different variables and identify the dominant factors for the XRF and leaching results. It follows the same method used earlier in 2.3.5 above using 0.3 as the acceptable loading factor. The results with discussion are provided in 3.4.6. .

3.3.6 Thermodynamic Modelling

Thermodynamic calculations of leachates were determined using Visual MINTEQ 3.1 (USEPA, Stockholm, Sweden) by Gustafsson, (2014). The model uses the input physical parameters that include pH, temperature, pe, alkalinity as HCO_3^-, and the components of the leachates (Al, As, Cu, Fe, K, Mg, Mn, Na, Pb, SO_4^{2-}, Si, and Zn).

3.3.7 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) technology was explored to verify the mineralogy of the creek bed samples NCB1 and NCB2 collected from Nataratara creek. The technology provides high resolution imagery of observed rock samples by using back scatter electron detection, secondary electron detection and energy dispersive X-ray spectroscopy (Schulz et al., 2020). The intention was to verify the XRF analysis results of the two samples to identify possible secondary minerals that may influence the leachate chemistry by Fe oxide precipitation.

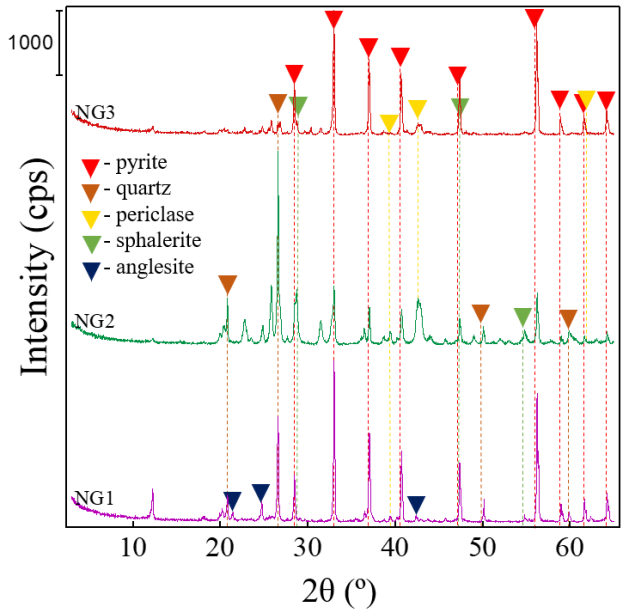
3.4 Results and Discussion

3.4.1 Mineralogical and Chemical Properties of Rock Samples

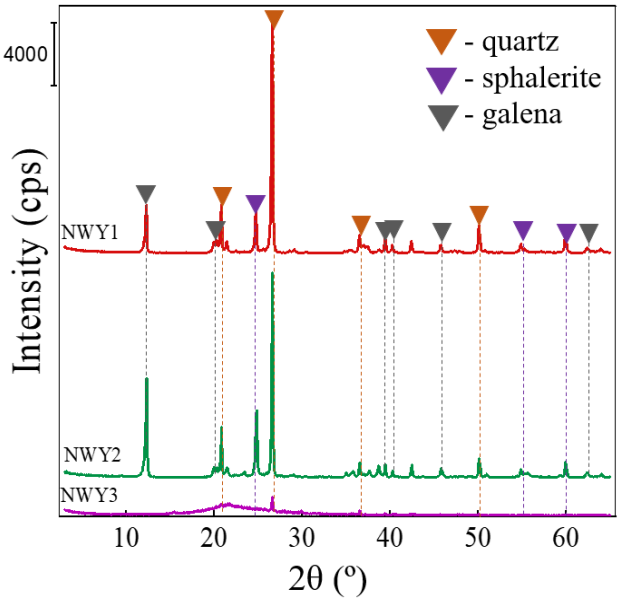
The chemical composition and the mineralogy of rock samples are summarized in Table 3.3 and illustrated in Figure 3.6. According to the XRD analysis, rock samples NG1, 2, and 3 were dominated by pyrite (FeS_2), quartz and periclase (MgO) minerals. Sphalerite and anglesite were observed as minor minerals in samples NG1 and 2. The chemical composition test showed significant contents of SiO_2 (47 wt%), MgO (7.2 wt%), SO_3 (15.7 wt%), Pb (7,190 mg/kg), Zn (27,200 mg/kg). The samples NYW1, 2, and 3, altered and heavily weathered rocks, were dominated by quartz, while sphalerite and galena were also found as

minor minerals. Again, the mineralogy was well corroborated by the chemical compositions of elements responsible for the makeup of such minerals, which were detected in significant quantities by the XRF results such as SiO_2 (81.4 wt%), Al_2O_3 (18.4 wt%), and Zn (2,590 mg/kg) in average contents. The overall mineral compositions of rock samples collected from Nukudamu mine site indicate that they are more associated with silicate as well as sulfide minerals which are significant since they are known to be acidic in nature of existence, which agrees with the early study in Chapter 2 (Soro et al., 2023).

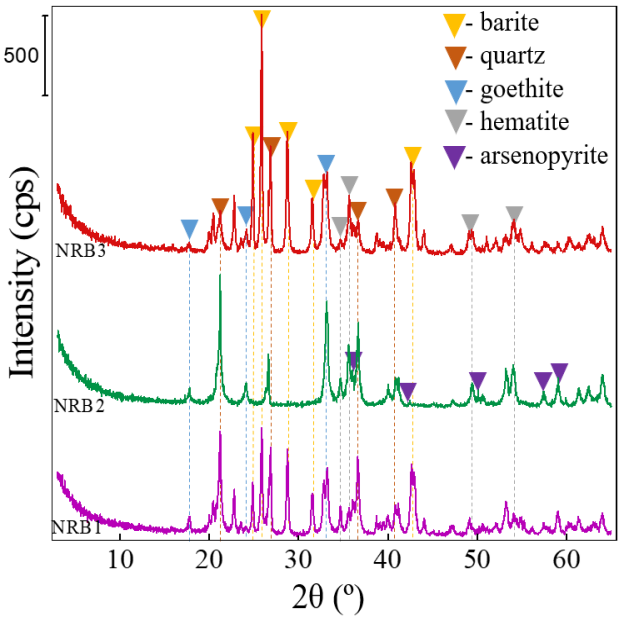
The hard, solid rock samples NRB1, 2, and 3 were dominated by barite ($BaSO_4$), and quartz (SiO_2) with iron minerals of hematite (Fe_2O_3) and goethite (FeOOH). In addition, sphalerite (ZnS) mineral was significant but in trace amount of a minor mineral for NRB1 sample, while arsenopyrite (AsFeS) and calcite ($CaCO_3$) were significant for sample NRB2 and NRB1, respectively. The XRF analysis results agreed with the mineralogy assessment having high chemical compositions of SiO_2 (38.9 wt%) and Fe_2O_3 (51.8 wt%) on average for all NRB samples. It was also noted that sample NRB1 had high composition of Zn (1,290 mg/kg) and NRB 2 with Pb (1,360 mg/kg), and As (3,230 mg/kg). NRY rock, which shares similar geological features to NRB rock sample has similar mineralogy with the dominant presence of goethite, quartz, and hematite as major minerals. There were also minor presence of arsenopyrite and sphalerite which was equally supported by its chemical composition to be high in Fe_2O_3 (52.7 wt%), quartz (39.1 wt%), and significant trace of Zn (5,850 mg/kg). Calcite was also detected with trace presence abundance of 4.9%.



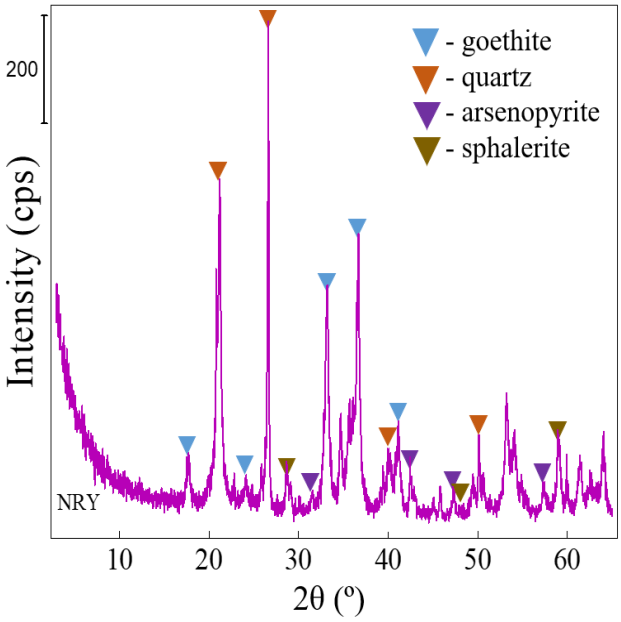
(a) NG samples



(b) NWY samples



(c) NRB samples



(d) NRY samples

Figure 3.7 XRD profile of mineralogical composition of (a) NG1, 2, 3 rock samples, (b) NWY1, 2, 3 rock samples, (c) NRB 1, 2, 3 rock samples and (d) NRY rock samples.

Table 3.3 Chemical compositions of the rock samples from the XRF analysis results.

Sample	NG1	NG2	NG3	NWY1	NWY2	NWY3	NRY	NRB1	NRB2	NRB3	NCB1	NCB2
†SiO_2	44.2	55.5	41.4	75.2	63.1	92	39.1	39.2	38.3	39.2	38.0	57.2
†TiO_2	<1	<1	<1	<1	<1	<1	1.35	5.79	<1	6.89	1.17	<1
†Al_2O_3	9.97	4.08	6.24	23.3	28.0	4.01	4.00	2.85	2.86	2.73	11.4	10.8
†Fe_2O_3	25.3	3.04	20.0	0.53	1.14	4.00	52.7	48.1	63.2	44.0	53.9	18.6
†MnO	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
†MgO	9.90	6.74	5.37	<1	<1	<1	4.44	4.63	5.14	4.19	3.96	1.91
†CaO	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1.33
†Na_2O	<1	1.18	<1	<1	<1	<1	<1	<1	<1	<1	<1	2.66
†K_2O	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
†P_2O_5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
†SO_3	18.9	14.7	13.5	<1	<1	2.60	<1	1.74	<1	1.36	<1	<1
*Pb	3,580	<1	<1	103	2,679	2,653	2486	<1	1,362	<1	2,145	381
*Cd	<1	<1	<1	2.89	<1	5.24	1.48	<1	<1	<1	<1	<1
*Zn	1,150	75,947	4,617	631	1,293	5,854	1,004	3527	118	231	454	1,599
*Cu	297	9,811	2,313	1.17	135.2	255	852	912	569	299	820	294
*As	156	<1	664	39	659	748	1,592	<1	3,232	<1	2,730	532

† (wt%) * (mg/kg)

The geological features of NGs and NWYs rocks were altered, heavily weathered and relatively soft in comparison to the unaltered, hard, and solid NRBs, and NRY rock samples. The red-brown rocks (NRB1, 2, and 3) were observed to also have significantly high composition of Fe ($Fe_2O_3 \approx 51.8$ wt%) on average respectively to indicate dominant Fe rock sample. Interestingly, white-yellow rock samples NWY1, 2, and 3 detected high composition of silica (SiO_2 = 81.4 wt%) and Al_2O_3 (18.4 %wt) on average but were significantly low in sulfur at 0.56 wt% whereas NG1, 2 and 3 had high silica as well as sulfur. However, both rock types were composed of significant trace elements of Pb, Zn and Cu and they predominantly existed as sulfides as discovered by XRD, which contributes to their altered and heavily weathered features. The distinguished geological features of the rock samples as highlighted above and described in Table 3.1 also contribute to their mineralogical and chemical composition, which was further corroborated by the leaching and SE tests.

3.4.2 Batch Leaching Experiments and Mechanism of Hazardous Element Mobility

The leachates of rock samples collected from Nukudamu mine are presented in Table 3.4. It provides measured physical parameters of pH, EC, and ORP, the metal(loid)s (Al, As, Cu, Fe, Pb and Zn) and coexisting ions (Ca, K, Mg, Na, SO_4^{2-}) concentrations. Low pH range, 2.9–4.9 were obtained for all leachates to indicate naturally acidic based rock. High acidic range (pH 1.9–3.2) were recorded for the altered and weathered NGs and NWYs rock samples whereas the unaltered, hard, solid NRBs and NRY rocks recorded weakly acidic (pH 3.8–4.9). pH is a unique parameter that has a dominant influence on the behavior of individual elements or compounds (Lawrence and Wang, 1997; Wang et al., 2017). It is prevalent in mining and more important if the mined rocks contain high levels of hazardous elements. Sulfide minerals are the most common mined minerals in which most target minerals exist together with hazardous elements. Pyrite mineral is one classic example of such sulfide mineral that when exposed to oxygen or comes in contact with water forms acid to lower the pH of the water draining through mine sites commonly known as acid mine drainage (AMD) (Xu et al, 2021; Worlanyo and Jianfeng, 2021; Huyen et al., 2019; Lawrence and Wang, 1997).

Table 3.4 pH, EC, ORP, and concentrations of hazardous elements including coexisting ions measured in the leachates of batch leaching experiments.

Sample	**pH**	**EC (mS/cm)**	**ORP (mV)**	**Al (mg/L)**	**As (mg/L)**	**Cu (mg/L)**	**Fe (mg/L)**	**Pb (mg/L)**	**Zn (mg/L)**	**Ca (mg/L)**	**K (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**SO_4^{2-} (mg/L)**
NG1	2.11 ± 0.02	457 ± 8.6	387 ± 5.1	18.2 ± 1.96	0.50 ± 0.29	5.55 ± 0.65	619 ± 193.6	2.98 ± 0.1	18.8 ± 1.39	3.00 ± 025	4.57 ± 5.5	5.91 ± 0.28	4.54 ± 2.34	1600 ± 20
NG2	3.05 ± 0.02	197 ± 3.78	362 ± 3.4	1.69 ± 1.2	0.19 ± 0.02	229 ± 3.56	264 ± 9.63	2.38 ± 0.15	234 ± 8.16	-	2.05 ± 2.89	1.85 ± 2.62	3.67 ± 2.29	1,223 ± 45
NG3	2.17 ± 0.03	395 ± 3.74	430 ± 0.82	13.5 ± 1.49	0.71 ± 0.07	8.77 ± 0.52	436 ± 18.4	3.30 ± 0.17	9.88 ± 0.16	2.27 ± 0.8	2.08 ± 2.94	2.89 ± 0.02	3.90 ± 2.05	1,423 ± 26.3
NWY1	3.23 ± 0.02	46.8 ± 1.26	504 ± 2.87	7.1 ± 0.37	0.004 ± 0.003	-	1.36 ±0.18	-	10.4 ± 0.24	4.19 ± 0.11	2.62 ± 3.71	9.26 ± 0.15	4.13 ± 2.32	138.3 ± 2.49
NWY2	2.35 ± 0.02	265 ± 1.7	559 ± 1.25	18.77 ± 2.3	2.07 ± 0.13	21.8 ± 0.14	553 ± 195.2	3.73 ± 0.22	10.5 ± 0.12	2.98 ± 0.17	1.82 ± 2.57	6.94 ± 2.62	3.47 ± 2.05	1,450 ± 30
NWY3	1.87 ± 0.02	700 ± 5.89	620 ± 2.62	5.98 ± 0.2	2.98 ± 0.10	11.2 ± 0.62	1138.3 ± 14.3	2.36 ± 0.12	119.6 ± 1.7	1.12 ± 0.07	2.27 ± 2.53	-	4.29 ± 1.73	4,058 ± 101
NRY	3.38 ± 0.02	23.47 ± 0.83	482 ± 18.5	-	0.005 ± 0.001	-	-	-	-	1.49 ± 038	2.44 ± 2.73	0.41 ± 0.58	3.07 ± 1.44	37.7 ± 082
NRB1	4.86 ± 0.14	2.61 ± 0.3	596 ± 3.8	-	0.048 ± 0.001	-	-	-	-	-	1.78 ± 2.51	-	3.70 ± 1.81	-
NRB2	4.74 ± 0.02	1.77 ± 0.05	368 ± 15.6	-	0.024 ± 0.027	-	-	-	-	-	1.78 ± 2.52	-	3.07 ± 1.81	-
NRB3	4.93 ± 0.01	2.2 ± 0.22	338 ± 22.2	-	0.019 ± 0.011	-	-	-	-	-	1.86 ± 2.64	-	3.25 ± 2.07	-
***FNLWS**	7 – 9				0.05	0.5	5	0.05	1					500

**Fiji National Liquid Waste Standards*

The ORP of the leachates were highest for NWY samples at an average of 561 mV, followed by NRB samples at 434 mV then NRY at 482 mV and NG at 393 mV. The highest EC of the leachates was recorded for NWY3 sample at 700 ± 5.89 and the lowest from NRB2 at 1.77 ± 0.05. The average EC values for the rock samples were 349 mS/m for NG samples, 337 mS/m for NWY samples, 2.19 mS/cm for NRB samples, and 3.38 mS/m for NRY sample. EC values indicate dissolved materials in the aqueous solution of the samples (Tabelin et al., 2018; Igarashi et al., 2020). It is also an indirect indication of weathering of rocks, as more elements are released and available to mobilize (Bao et al., 2018; Kelderman and Osman, 2007). The altered and weathered rock samples NGs and NWYs recorded high EC values on average of 346 mS/m which was 80 times more than the EC average of unaltered, hard, solid rock samples NRBs and NRY (4 mS/m).

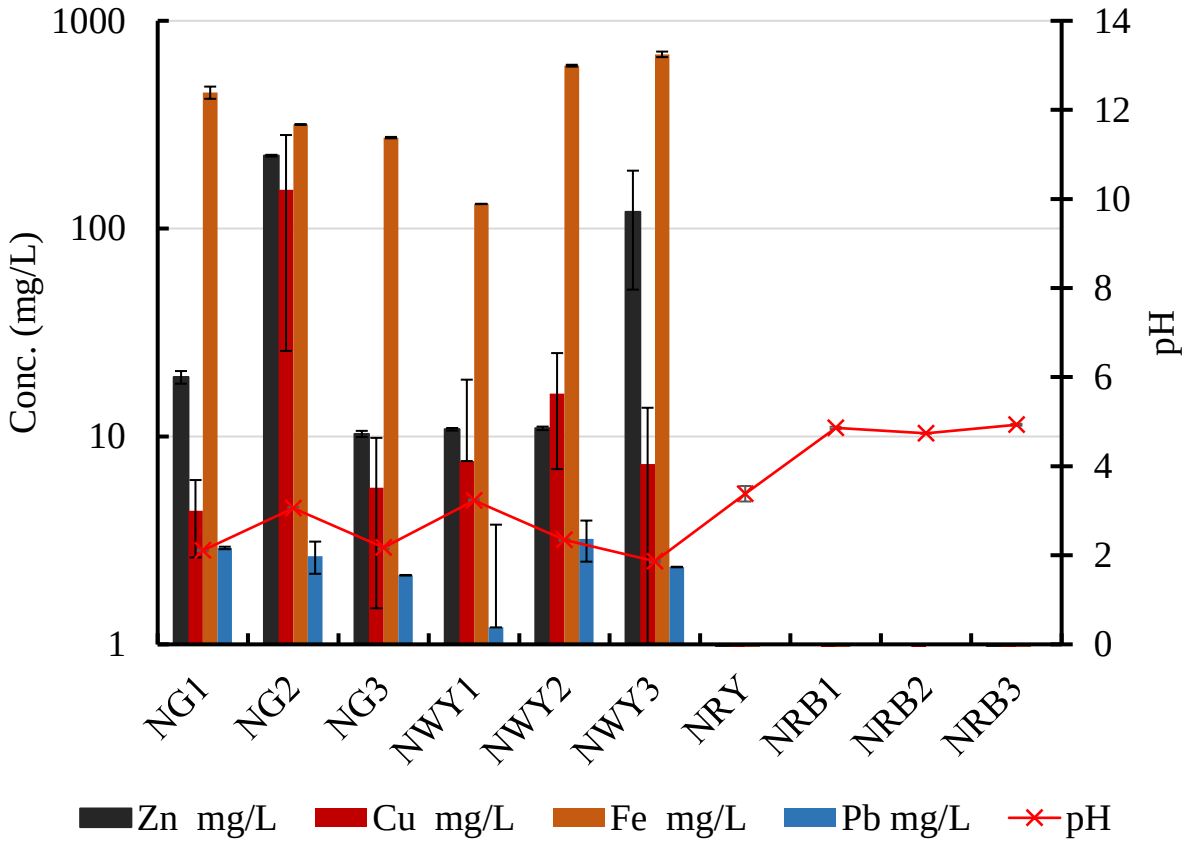


Figure 3.8 Leachate concentrations (mg/L) of hazardous elements Cu, Fe, Pb, and Zn with the pH of Nukudamu rock samples.

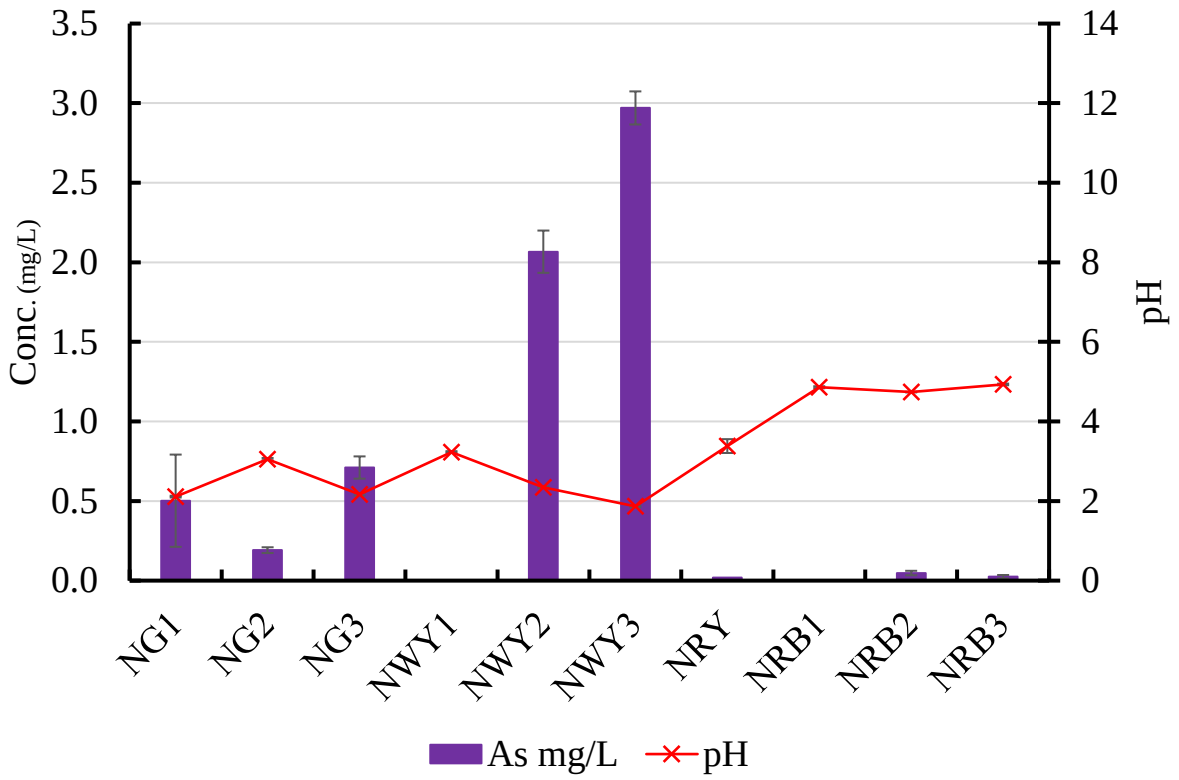


Figure 3.9 Leachate concentrations of As and pH of Nukudamu rock samples.

Significantly high leachates of hazardous elements Cu, Fe, Pb, and Zn were recorded at lower pH (pH < 3.5) for altered and weathered rock samples (NGs and NWYs) as recorded in Table 3.4. Whilst As leached from all rock samples at trace concentrations, no leachates of Cu, Fe, Pb, and Zn were observed for the unaltered, hard, solid NRBs and NRY rock samples. Figure 3.7 clearly demonstrates such occurrence at lower pH below 4, and leachate concentrations of As, Cu, Fe, Pb, and Zn were high, indicating more leaching and higher mobility whereas the opposite was experienced as pH increased. It clearly illustrates the significance of pH in the leaching tests, confirming increased mobility of hazardous elements at lower pH but decreased with raise in pH for rock samples NG 1, 2, 3, NWY1, 2, and 3 (Xu et al, 2021; Igarashi et al., 2001; Inui et al., 2014; Tabelin et al., 2018; Igarashi et al., 2020). This could be attributed to the oxidation of sulfide minerals, which were observed in abundance in these samples to release high leachate concentrations. However, for the hard, solid rock samples NRY and NRB1, 2, and 3, even though recorded weakly acidic leachates (pH 3.4–4.9) no hazardous elements were leached except for As

(Table 3.4, Figure 3.8). According to the XRF analysis (Table 3.3), NRY and NRBs rock samples, had high contents of Fe and O, but severely lacked S that restricts formation of common sulfide minerals to oxidize and provide conducive condition for such elements to leach. Also, traces of calcite minerals were observed in these samples that could contribute to the dissolution process by counteracting causing low oxidation, hence low mobility.

The phase distribution according to the SE test, further supports the above discussion whereby the partitioned hazardous elements in these unaltered, and hard, solid samples strongly favored insoluble residuals and sulfide phase further restricting their mobility (Figure 3.10). Moreover, the hard and solid geological features of the NRBs and NRY rocks having strong holding capacity and lacking alteration contribute to the restriction of oxidation and abilities of these rock types preventing hazardous element mobility. This is evident on site, after 50 years for exposure, little weathering can be observed on these rock types. The opposite is observed for the altered and weathered NGs and NWYs rock samples.

In addition, lower pH induces hazardous elements present in coexisting minerals to mobilize exposing receiving ecosystems to detrimental impacts (Tabelin et al., 2014; Huyen et al, 2019). This is evident from the leaching experiment in this study and it is noted that leachate levels for hazardous elements As, Cu, Fe, Pb and Zn were significantly higher for the weathered and altered NG and NWY rocks at exceptionally high concentration especially As due to its high toxicity level, even at low concentration. These leachates were all above the standards for wastewater discharge by the government of Fiji (FNLWS) as well as the WHO drinking water standards. The water sample analysis results agreed with the lower leachate pH for water samples collected within the mine open cut or disturbed area's surface runoffs to detect high concentrations of As, Cu, Fe, Pb and Zn. However, it was also noted that the water analysis results of sample collected down creek from the mine surface runoffs discharge was diluted since it joins the Nataratara Creek and recorded circumneutral pH without hazardous elements detected as it flows northward to the open sea. The SEM observation of the Nataratara creek bed samples (NCB1 and 2) reveal presence of Fe and O with S (Figures 3.14 and 3.15) suggesting Fe precipitations of oxides and/or hydroxides. Iron precipitation is likely to adsorb hazardous elements discharged through the surface water runoffs from the mine, contributing to natural attenuation by reducing their concentrations and raising the pH levels of water samples flowing down Nataratara creek.

Another important aspect to consider is the coexisting ions (SO_4^{2-}, Ca, K, Mg, and Na) that associate in minerals since the role that they play have an influence on the behavior of hazardous elements. Sulfate (SO_4^{2-}) is a coexisting ion with such influence and in this case was quite dominant anion in the leaching test for samples NG1, 2, 3, NWY 1, 2, and 3 (Table 3.4) even though SO_3 was not so prominent in the XRF chemical composition test (Table 3.3), but the presence of sulfide minerals such as pyrite, sphalerite, arsenopyrite and anglesite in these samples compensates to further contribute to the oxidation process in leaching. The sulfate ion provides a favorable condition for acid generation where hazardous elements are mobilized, which were reflected by the high leachates of As, Cu, Fe, Pb and Zn from these samples. Such occurrence was explained in Chapter two and published by Soro et al. (2023), reflecting on earlier work by Kelderman and Osman, (2007) and Popenda (2014) as well as publications by Bao et al. (2018), Igarashi et al. (2020), and Tabelin et al. (2020). It was noted that no carbonate minerals were detected but only minor silicates and it also reflects in the leaching results with low leachates of Ca, K, Mg, and K anions.

The above condition may differ if carbonate minerals are present to neutralize such oxidation process via dissolution of carbonate, oxy-hydroxide, and silicate minerals (Holmstrom et al., 1999; Soro et al., 2023). Carbonate dissolution may be contributing to the process occurring in the unaltered and hard, solid rock samples NRY, NRB1, 2, and 3 which identify the traces of calcite mineral by XRD. Even though the leachate pH of NRY and NRBs samples were weakly acidic (pH 3.8–4.9) the low presence of calcite mineral could contribute to the increased pH compared to strong acidic leachates of NGs and NWY samples (pH 1.9–3.2).

Table 3.5 shows the dominant secondary mineral phases in the Nukudamu leachates after modelling using Visual MINTEQ software. The model indicates that anglesite by using $SI = \pm 0.5$ as the mineral responsible for controlling the leachate system of the altered and weathered rock samples (NGs and NWYs) contribute to the precipitation of Pb while quartz was controlling the unaltered hard rocks NRBs and NRY samples.

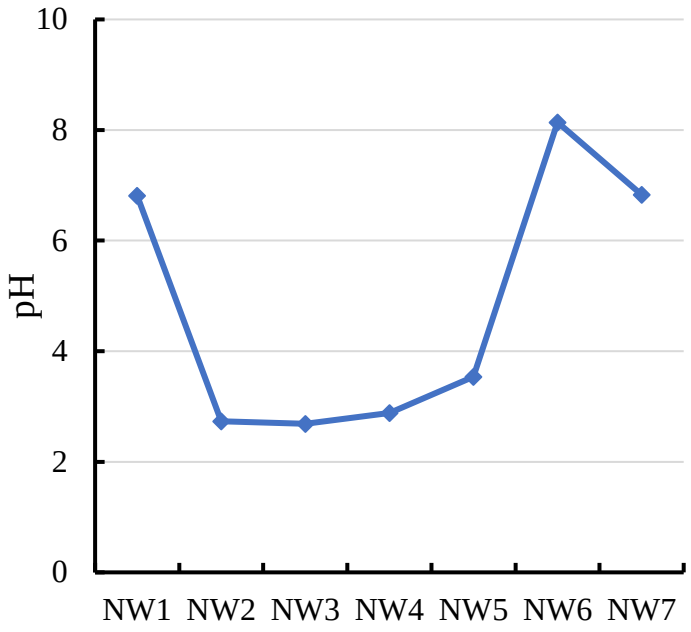
Table 3.5 Saturation indices (SIs) of the selected mineral phases in the leachates of the Nukudamu rock samples.

Minerals	NG1	NG2	NG3	NWY1	NWY2	NWY3	NRB1	NRB2	NRB3	NRY
Anglesite ($PbSO_4$)	-0.053	-0.065	-0.232	-0.488	**0.046**	-0.121	-8.788	-	-	-
Anhydrite ($CaSO_4$)	-2.704	-2.751	-3.175	-2.807	-2.611	-3.174	-4.349	-4.466	-3.981	-3.778
Alunite ($Kal_3(SO_4)_2(OH)_6$)	-9.211	-9.272	-5.197	-2.916	-8.573	-12.37	-	-	-	-
Arsenolite (As_4O_6)	-6.959	-8.560	-6.666	-11.16	-5.728	-5.411		-9.008	-9.609	-9.812
Chalcedony (SiO_2)	-1.573	-	-1.695	-1.331	-0.551	-0.302	-1.356	-1.408	-0.935	-0.673
Cristobalite (SiO_2)	-1.773	-	-1.895	-1.531	-0.751	-0.502	-1.556	-1.608	-1.135	-0.873
Diaspore (AlO(HO))	-5.454	-3.140	-5.278	-2.036	-5.056	-6.752	-	-	-	-
Gibbsite ($Al(OH)_3$)	-6.321	-4.007	-6.146	-2.903	-5.923	-7.62	-	-	-	-
Gypsum ($CaSO_4.2H_2O$)	-2.455	-2.927	-2.504	-2.558	-2.363	-2.926	-4.100	-4.216	-3.731	-3.529
Kaolinite	-14.84	-	-14.74	-7.523	-12.00	-14.900				
Quartz	-1.123		-1.246	-0.881	-0.101	**0.147**	-0.906	-0.958	-0.485	-0.223
Silica gel	-2.413		-2.534	-2.170	-1.390	-1.142	-2.195	-2.248	-1.775	-1.513
Silica glass	-2.383		-2.505	-2.140	-1.360	-1.112	-2.615	-2.218	-1.745	-1.483

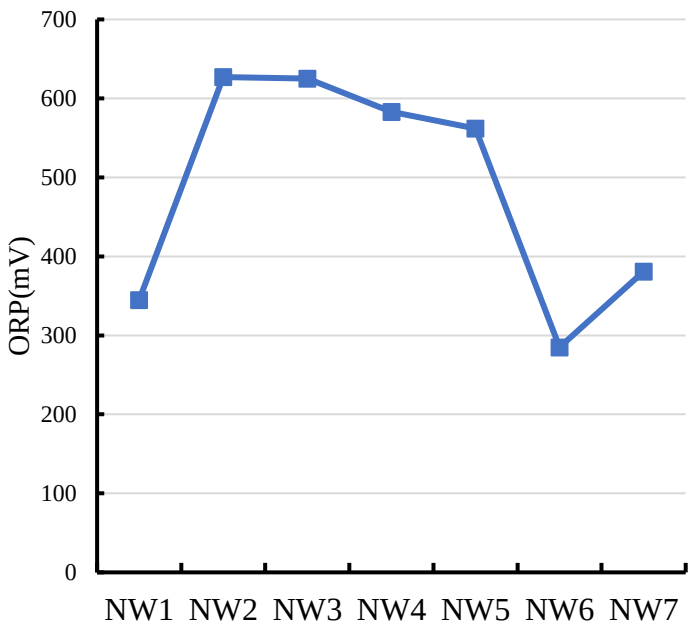
* Bold text indicate oversaturation

3.4.3 Water Analysis Results, Dilution and Natural Attenuation

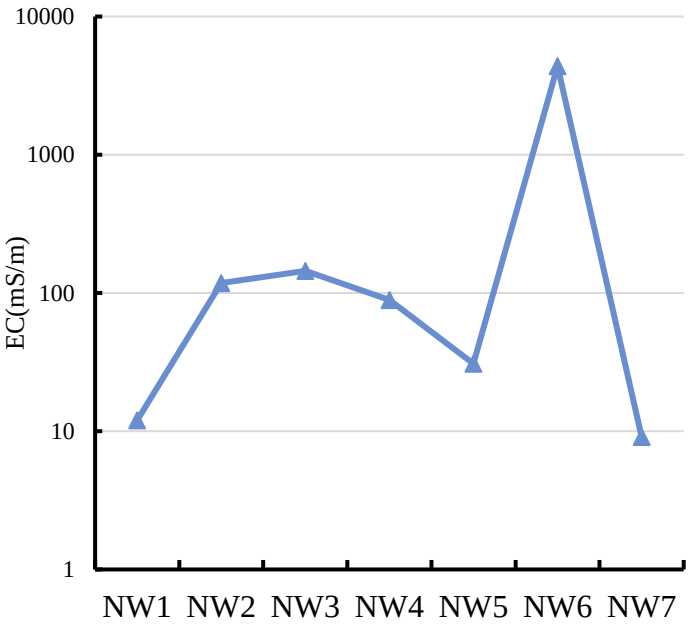
Analyzed results of water samples collected from Nukudamu are presented in Figures 3.8 (a) to (j). The graphs represent measured parameters (pH, EC, ORP) and analyzed elements contents (Al, As, Cu, Fe, Pb, SO_4^{2-} and Zn) arranged in order of creek and mine surface runoff flows as described in 3.1 and Table 3.2. It confirms that water samples (NW2–NW4) collected from the mine open cut surface runoffs and its discharges (Figure 3.4) were highly acidic with lower pH (pH < 3.6) whereas NW1 and NW6 were circumneutral as well as NW7. Similarly, EC and ORP measurements follow the standard inverse trend to pH of each sample. The analysis result also shows high concentrations of hazardous elements (As, Cu, Fe, Pb and Zn) in the mine runoffs water samples NW2 and 3. These indicate AMD occurrence as noted in Chapter 2 (Soro et al., 2023). As highlighted earlier from the XRD and XRF analyses the major influencing factor were the high sulfide minerals supported by relative high compositions of related compounds and elements in the altered and weathered rock samples that are oxidized and decreased the pH, and causes hazardous elements to dissociate and mobilize.



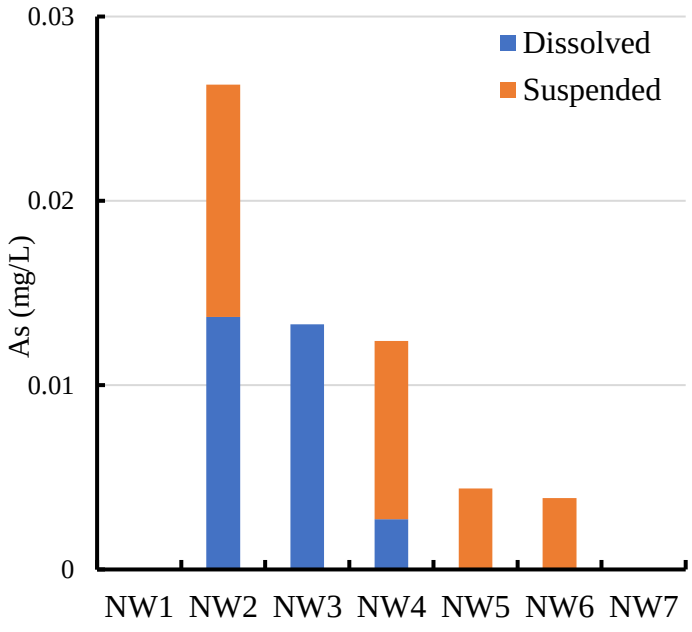
(a) pH



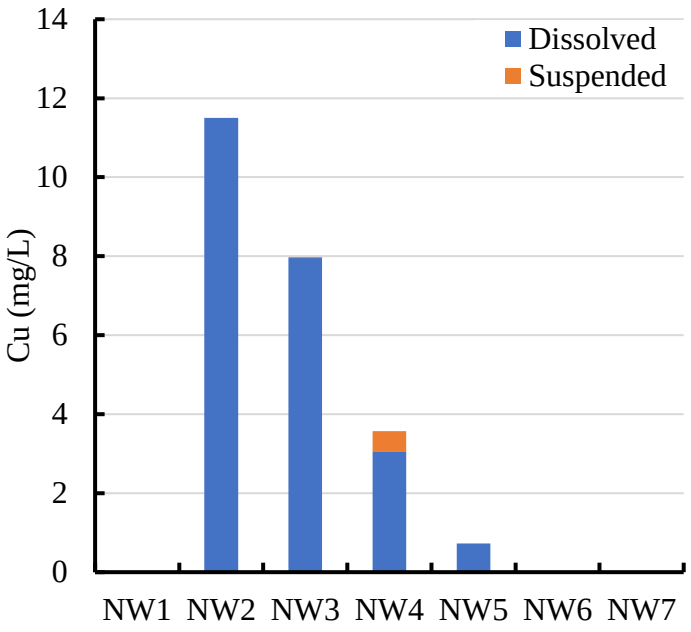
(b) ORP



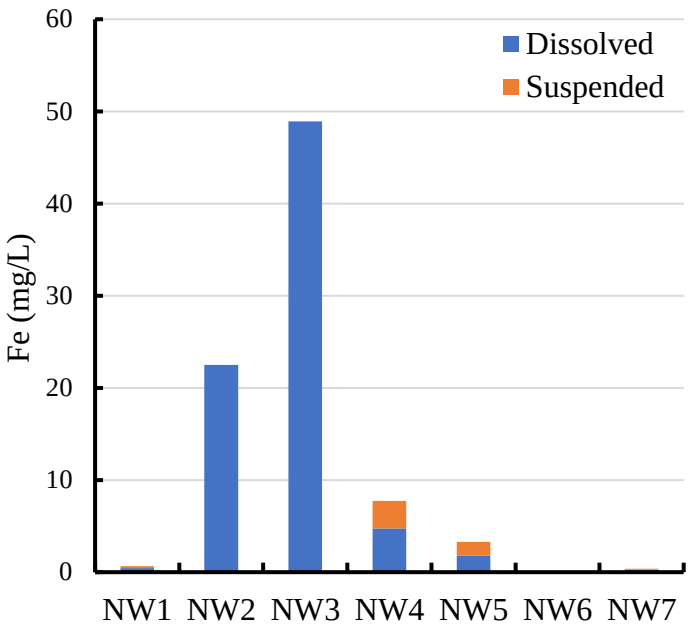
(c) EC



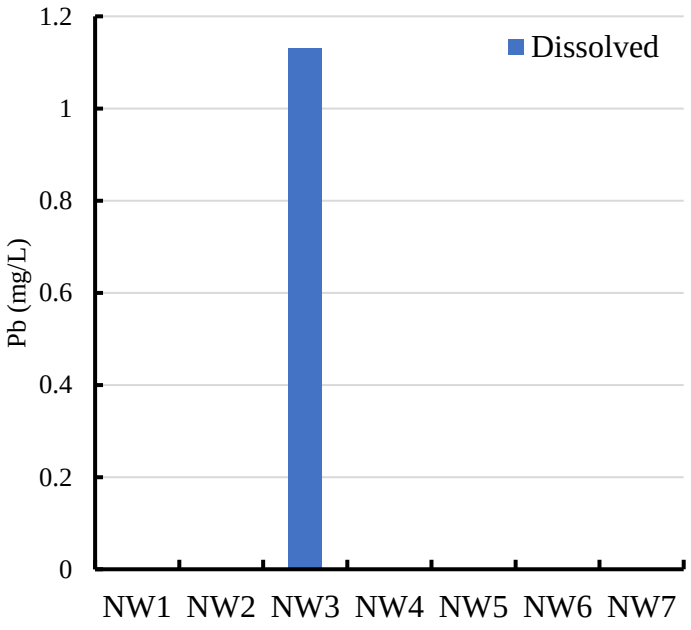
(d) As



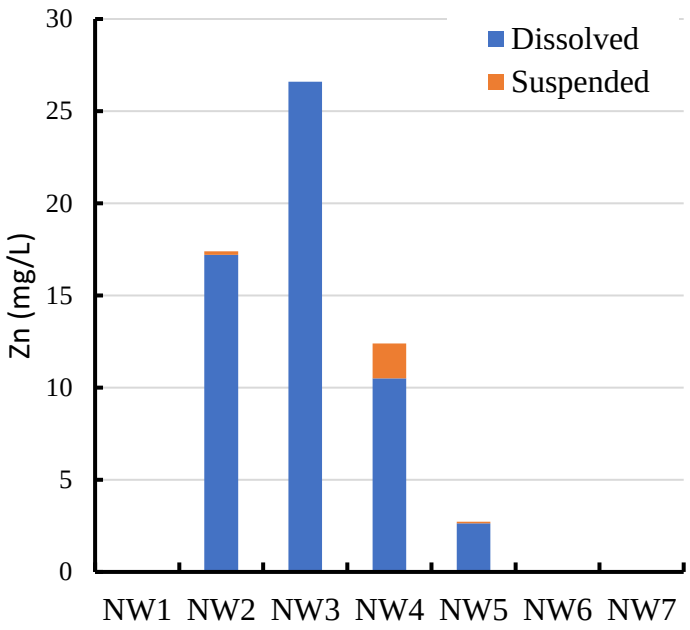
(e) Cu



(f) Fe



(g) Pb



(h) Zn

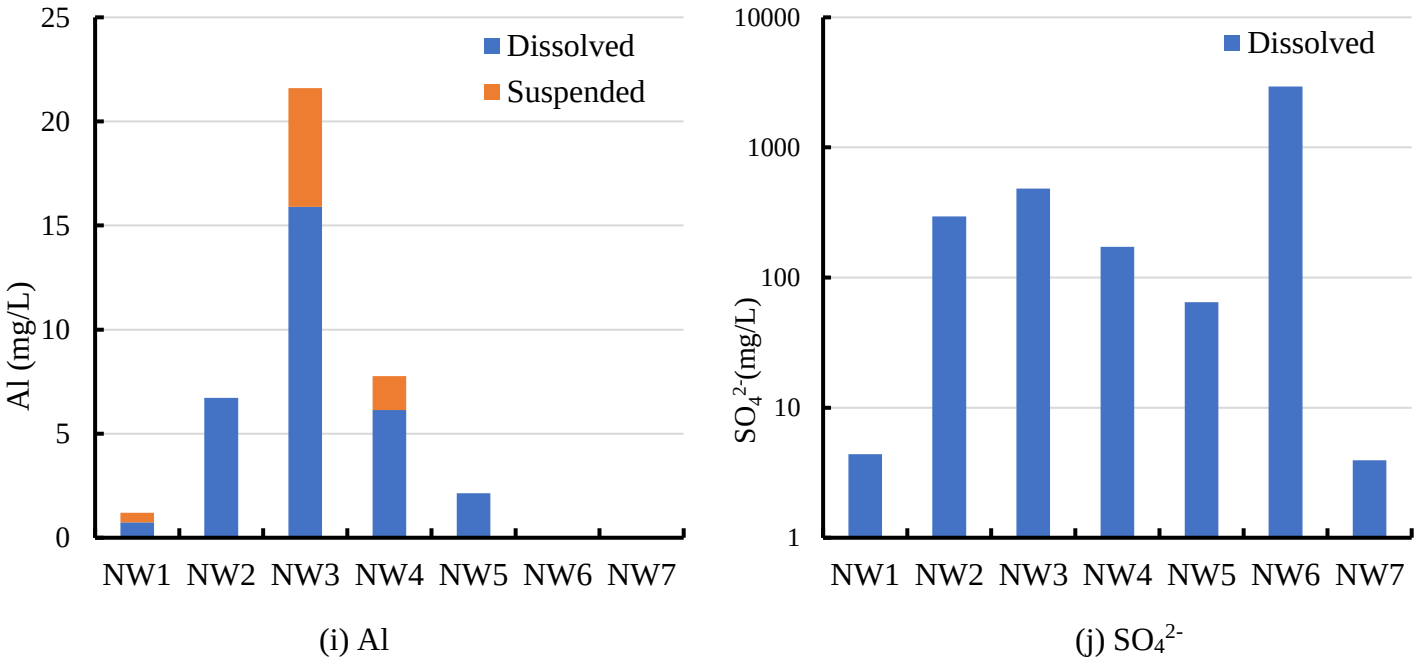
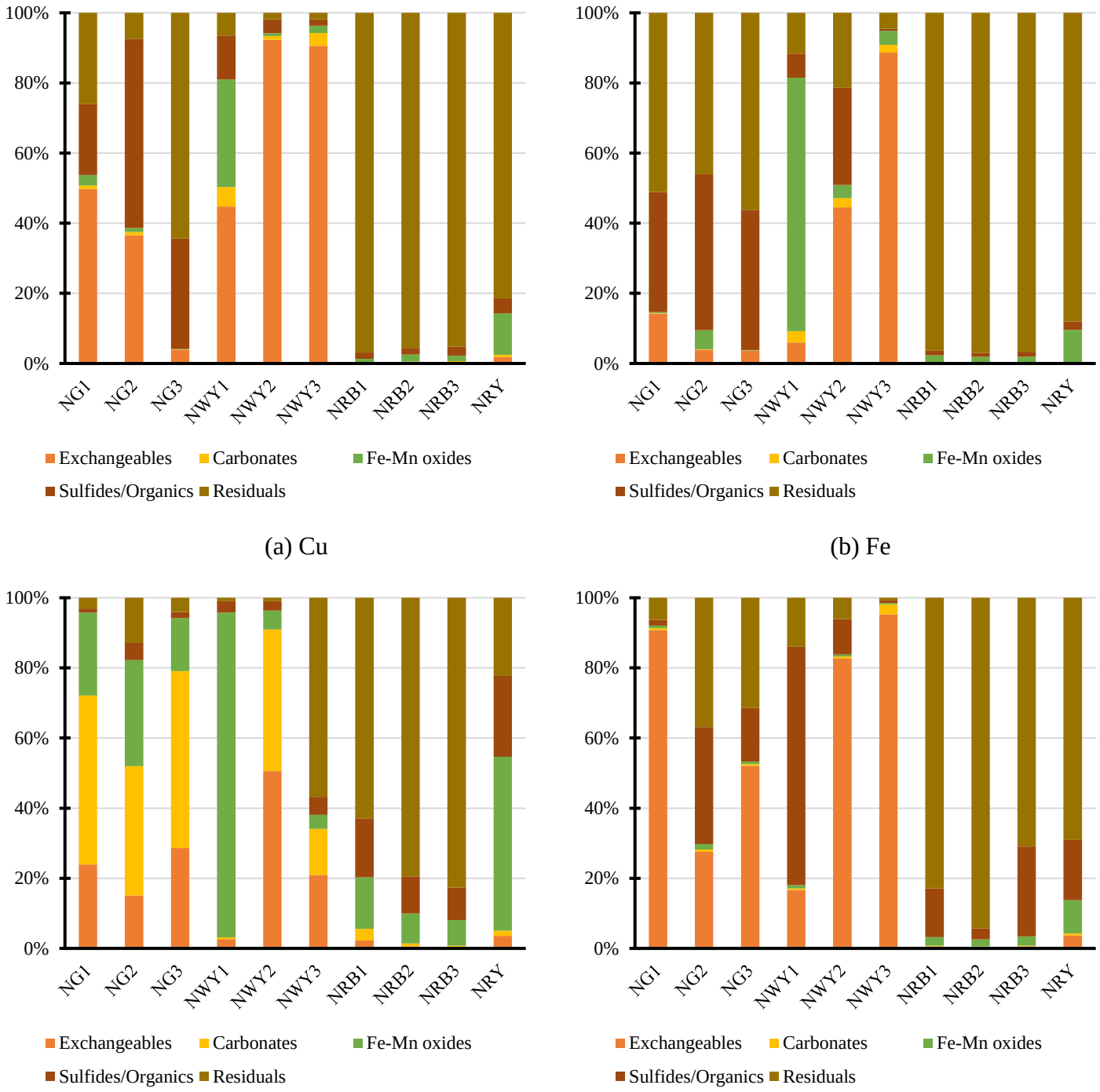


Figure 3.10 Water analysis results showing the physical parameters (a) pH, (b) EC, and (c) ORP as well as significant elements (d) Al, (e) As, (f) Cu, (g) Fe, (h) Pb, and (i) Zn in dissolved and suspended samples with dissolved (j) SO_4^{2-} from Nukudamu.

However, the graphs also show that the pH increases as the water flows down through Nataratara creek, even though pH at NW7 may be influenced by seawater. The levels of As, Cu, Fe, Pb, and Zn from the mine open cut surface runoff discharge also decreased as it flows into Nataratara creek confluence point NW4 before continuing flowed to the sea (Figure 3.4). This indicates that Nataratara creek water contributes as a neutralizing agent to dilute the pH level. It should be noted that the lower reach of Nataratara creek has formed into a wetland over the years before creek water finally flows to the sea. The hazardous elements, on the other hand, were also adsorbed mainly due to Fe precipitates acting as adsorbents to these elements, reducing their concentrations. SEM analysis of creek bed samples (NCB1 and 2) in Figures 3.11 (a) and (b) indicates prominent presence of Fe, O and S. These elements are primarily responsible for iron-oxide/oxy-hydroxide, and hydroxy sulfates phases to precipitate and adsorbed elements released from the altered weathered rocks, subsequently neutralize acidity of the mine discharges to acceptable levels as natural attenuation (Moncur et al., 2005).

3.4.4 Sequential Extraction (SE)

Sequential extraction test results from the ICP-AES are displayed in Figure 3.10 for selected hazardous elements found to leach during the leaching experiment, i.e., Cu, Fe, Pb and Zn. It shows that Cu persisted to be partitioned more as residuals for NRB samples, which are hard and solid type rocks. In fact, Fe, Pb and Zn share similar distribution for NRB samples to be favorably portioned as residuals. The same portioning trend was observed for the NRY rock samples, which is also a hard rock but mildly weathered, however Pb was observed to be distributed favoring Fe-Mn oxides amongst sulfide/organics and residuals. The Cu in the altered and weathered NG1, 2, and 3 rock samples, was found to be distributed more as exchangeables for NG1 followed by residuals and sulfide/organics; Cu was evenly distributed between sulfides/oxides and exchangeables for NG2 but dominantly persisted as residuals then sulfide/organics for NG3. In NWY2 and 3 samples, Cu was favorably partitioned as exchangeables, in NWY1 sample. Copper was also largely distributed to the same but also as Fe-Mn oxides.



(a) Cu

(b) Fe

(c) Pb

(d) Zn

Figure 3.11 Sequential extraction results of (a) Cu, (b) Fe, (c) Pb and (d) Zn from the Nukudamu rock samples.

Iron was found to be highly distributed as sulfides/oxide and residuals for NG rock samples. It was portioned favorably as Fe-Mn oxides in sample NWY1 and exchangeables for NWY3 and NWY2, but was then evenly distributed between sulfides/organics and residuals for the latter. Lead was distributed largely in the order of carbonates, exchangeables and Fe-Mn

oxides for the NG samples. It's dominantly existed as Fe-Mn oxide for sample NWY1, but allocated evenly between exchangeables and carbonates for NWY2 sample and persisted more to residuals for NWY3 sample. The NRY sample partitioned Pb more as Fe-Mn oxides then evenly between the sulfides/organic and residual phase. For Zn, it was favorably portioned as exchangeables for NG1 sample as well as NWY 2 and 3 but partitioned highly as residuals for NRY sample. It was dominantly portioned as sulfides/organics for sample NWY1 then evenly between exchangeables and residual phases. Pb in sample NG2 was evenly distributed among residuals, sulfides/organics and exchangeables; for NG3 it was also distributed largely among the same phases in the order, exchangeables > residuals > sulfide/organics.

The phase distribution by the SE experiments purely partitioned Cu, Fe Pb and Zn according to the extent of the sulfide mineral oxidation process occurring in the two respective rock types. The NGs and NWYs altered and weathered rock samples, favorably partitioned Cu, Fe, Pb, and Zn as exchangeables and carbonates. These phase distributions are easily solubilized exposing these hazardous elements to lesser restrictions making them more accessible and freer to dissociate and mobilize. This is in contrast to the unaltered, solid rock samples NRBs and NRY, which are low in sulfides, distributing more to residuals and sometimes sulfide/organics that restrict their exposure and mobility.

Apart from the geochemical characteristics of the rock samples, the SE test results also show the contribution of the geological and physical properties of rocks from Nukudamu. The degree of alteration and heavy weathering occurring on site for these rock types contributes to high exposure of sulfide minerals stimulating oxidation that promotes mobilization of hazardous elements being distributed largely as exchangeable. Compared to the hard, solid rock samples of NRBs and NRY have much stronger hold and control to bind and restrict mobility to retain these elements. Thus, the SE results for Cu, Fe, Pb, and Zn are well supported by the high leachates of these elements from the altered and weathered samples of NGs and NWYs, but no leachates of the same elements were observed from the NRBs and NRY rock samples.

3.4.5 Hydrogen Peroxide pH Acidification (pH (H_2O_2)) Test and AMD Generation

The results of hydrogen peroxide acidification tests pH (H_2O_2) are illustrated in Figure 3.10. The results show that rock samples NG1, 2, 3, NWY2 and 3 had pH < 3.5 indicating their potential to generate acid. Even though the leachates of all rock samples showed acidic pH < 5 (Table 3.3), pH (H_2O_2) tests indicate that the above-named rock samples are likely to produce AMD in the long term. It further verifies that weathered and altered rocks exposed on site are the main contributors of AMD. As earlier explained, AMD generation further contributes to the release of hazardous elements through oxidation of sulfide minerals which were evident from the high leachates concentrations of As, Cu, Fe, Pb, and Zn from NG and NWY rock type.

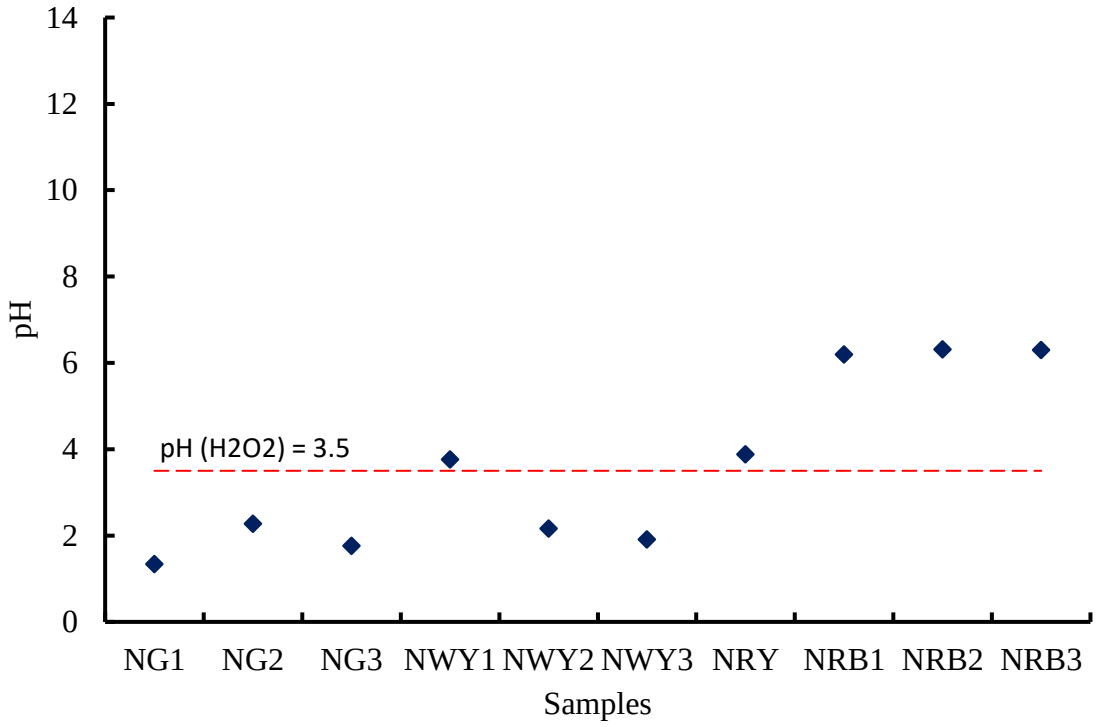


Figure 3. 12 Hydrogen peroxide pH tests (pH (H_2O_2)). The dotted line indicates the threshold for the acidification potential (pH = 3.5).

The pH (H_2O_2) test on the other hand also suggests that NRB and NRY rock type has low potential of generating AMD in the long term, even though the leaching test recorded weakly acid at the pH range of 3.4–4.9. The presence of calcite as detected by XRD could be a factor via the dissolution process of carbonates and the stable geological features of these rock types are another contributing factor. This is evident on site, after 50 years of exposure of weathering processes these rock remains unaltered, intact, and solid without hazardous leachates to indicate low dissolution risk of hazardous elements.

All the above geochemical tests have confirmed that AMD is the most high-risk impact at Nukudamu, and tests further confirmed that possible countermeasures is through management of surface water discharged from the weathering of exposed altered rocks in mine open cut. Passive remediation technique is the best approach given the isolated location of the site and the likelihood remain viable for possible redevelopment in the future for example, covering exposed altered rocks and lining the open cut surface runoff waterways with limestone boulders.

3.4.6 Principal Component Analysis (PCA)

The PCA results for the leaching experiment result are presented in Table 3.6. It simplifies the distribution of sixteen leaching variables (pH, EC, ORP, Al, As, Ca, Cu, Fe, K, Mg, Mn, Na, Pb, SO_4^{2-}, Si, and Zn) by categorizing them into four principle components to determine the important and inter-correlated dependent variable that influences the leachates. The PCA results showed that the 4 PCs accounted for 95% of the leachate results where PC1 accounting for 55.4% of the PCA results confirms the significant of Fe and SO_4^{2-} as the major constituents of sulfide minerals controlling the pH to strong acidic indicated by negative (-0.297) PC1 coefficients and high EC. This is due to the oxidation of sulfide minerals such as pyrite in most Nukudamu altered and weathered NGs and NWYs rock samples. PC2 indicates Al, Ca, Mg and K to be significant with positive PC coefficients due to their contributions as

coexisting ions with potentials to neutralize the acidic nature of the hard, solid rock NRB and NRY samples by raising the pH.

Table 3.6 Principal component analysis (PCA) including total variance, eigenvalue, and cumulative frequency for the leachates of Nukudamu rock samples. Bold values are coefficients with significant influence in this particular leaching experiment.

Variables	PC1	PC2	PC3	PC4
pH	**-0.297**	-0.114	0.006	-0.053
EC	**0.295**	-0.003	0.009	**-0.378**
ORP	0.234	-0.139	**0.350**	**0.364**
Al	0.238	**0.351**	-0.034	0.117
As	0.278	-0.172	0.202	-0.083
Ca	-0.025	**0.457**	0.263	0.146
Cu	0.052	-0.122	**-0.614**	0.274
Fe	**0.320**	-0.012	-0.015	-0.058
K	0.101	**0.377**	-0.084	**-0.598**
Mg	0.123	**0.403**	0.054	**0.470**
Mn	0.261	-0.258	0.084	0.010
Na	**0.314**	0.024	0.102	0.024
Pb	0.290	0.143	-0.206	0.079
SO_4^{2-}	**0.320**	-0.041	-0.025	-0.028
Si	0.186	**-0.320**	**0.349**	-0.044
Zn	0.204	-0.263	**-0.391**	0.092
Eigenvalues	9.417	3.603	2.228	0.91
Variance %	55.39	21.2	13.11	5.36
Cumulative %	55.39	76.59	89.7	95.05

*Bold text indicates variables that accounted for significantly under each PC

The PCA of the XRF test results is presented in Table 3.7. PC1 indicates the high composition of Zn, Cu, in the altered and weathered rocks as sulfides, contributing their sulfide mineral oxidation that accounted for 27.6% of such manifestation. PC2 highlights SiO_2, Al_2O_3 and K_2O having positive coefficients indicating the significant role of nacrite minerals specifically in NWY samples. PC3 and 4 accounted for less than 20% of the variance for each and their contribution were less significant under the XRF tests.

Table 3.7 Principal component analysis (PCA) with total variance, eigenvalue, and cumulative frequency for the XRF results of Nukudamu rock samples.

Variables	PC1	PC2	PC3	PC4
SiO_2	-0.016	**0.399**	-0.223	-0.030
TiO_2	-0.009	-0.205	0.276	**-0.545**
Al_2O_3	-0.166	**0.304**	-0.234	-0.046
Fe_2O_3	-0.147	-0.460	0.154	-0.045
MnO	0.273	0.028	0.246	-0.259
MgO	0.222	**-0.332**	0.119	**0.306**
CaO	-0.106	0.282	**0.410**	0.192
Na_2O	-0.127	0.104	**0.490**	0.298
K_2O	-0.090	**0.393**	**0.362**	0.127
P_2O_5	0.121	-0.177	0.081	0.201
S	**0.319**	-0.058	-0.003	**0.405**
Pb	-0.165	-0.045	-0.273	**0.372**
Zn	**0.419**	0.086	-0.078	0.010
Cu	**0.426**	0.018	-0.051	0.047
As	-0.215	-0.271	-0.153	0.212
Eigenvalues	4.686	3.490	2.936	1.849
Variance %	27.58	20.53	17.27	10.88
Cumulative %	27.58	48.11	65.380	76.260

3.4.7 Scanning Electron Microscope (SEM)

The representative SEM images of Nataratara creek bed samples NCB1 and 2 are presented in Figure 3.11(a) and 3.11(b). They show the samples to be rich in Fe and O with S also visible. The presence of such elements suggests Fe precipitates of oxides, and hydroxides which are likely to adsorb hazardous elements discharged through the surface water runoffs from the mine. It is possible that such processes contributes to the natural attenuation of hazardous elements by reducing their concentrations and raising the pH levels of water flowing from the mine surface through Nataratara creek.

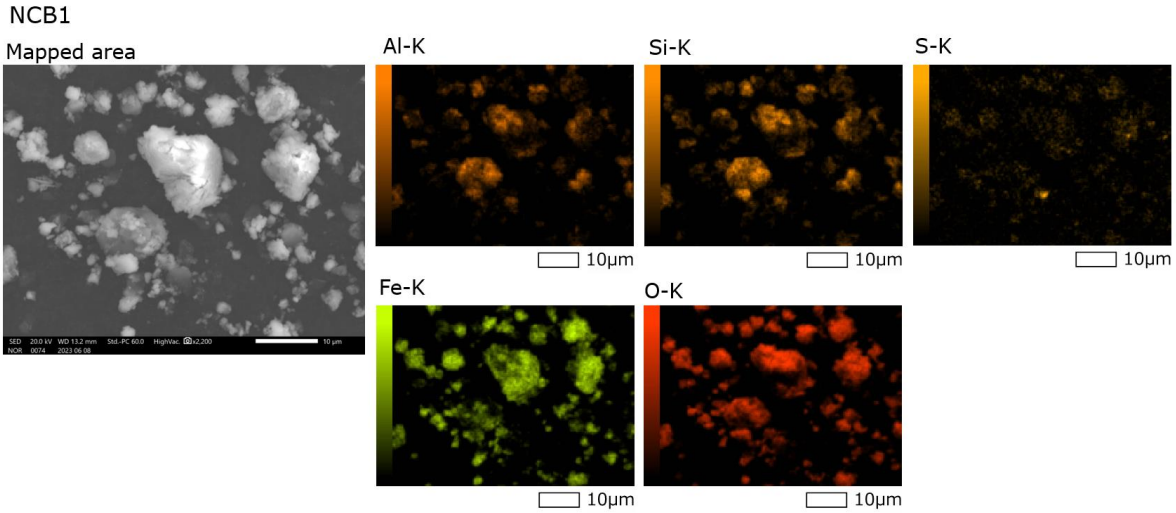


Figure 3.13 SEM images of NCB1 sample.

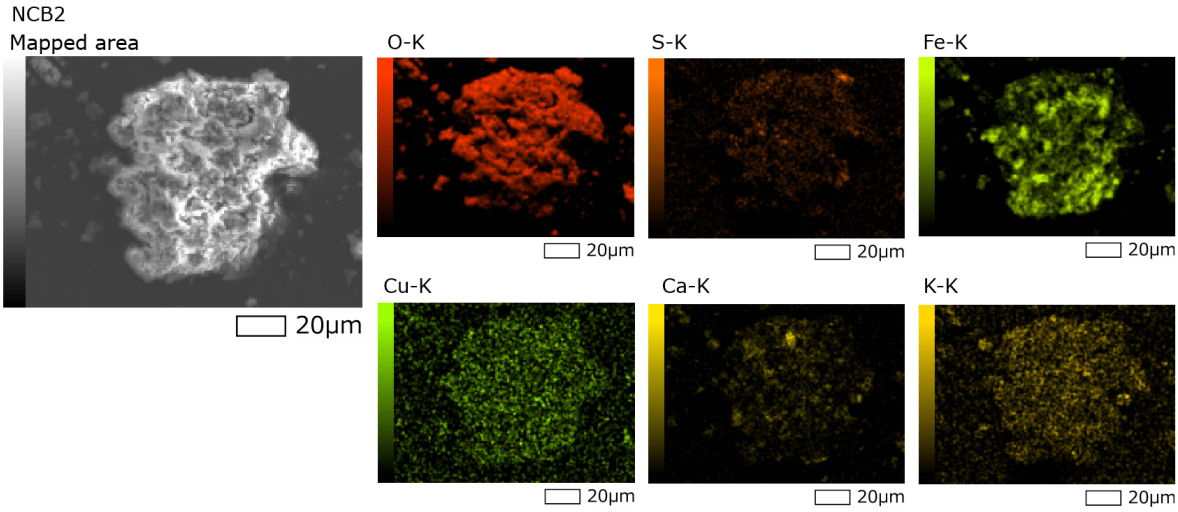


Figure 3.14 SEM images of NCB2 sample.

3.5 Conclusions

The chemical and mineral characterization of Nukudamu rock samples examined in this study confirmed that there existed a contrast difference between the two major rock types, i.e., the altered and heavily weathered grey and whitish-yellow rock samples (NG1, 2, 3, NWY1, 2, and 3) and the hard, solid Kuroko type, red brownish and yellow rocks (NRB1, 2, 3, and NRY). Mineralogy and chemical compositions confirmed the former to be abundant with sulfide minerals and devoid of carbonates while the latter had less sulfide with traces of carbonates. The risk of AMD and hazardous elements leaching are high for altered and weathered rock samples but less likely and low for the unaltered hard and solid rocks. This was supported by the strong acidic leachates with high concentrations of hazardous elements (As, Cu, Fe, Pb, and Zn) generated from the altered rocks exposed to weathering and mobilized as mine surface water runoffs discharging into the nearby Nataratara creek. However, the acidic surface water was diluted and neutralized after mixing with the creek water as it flow to the sea. Iron deposits formed on Nataratara creek bed were identified as hematite and goethite suggesting that Fe precipitates contribute to the immobilization of hazardous elements by the creek water. The sequential extraction tests verified that the difference in leachate risk were caused largely by the dissimilar partitioning phases and existence form of each hazardous element. The partitioning pattern for the leachates in altered and weather rock samples favored the easily soluble exchangeables and carbonates phases whereas the hard, solid Kuroko rocks portioned them largely to the less soluble residuals. The study confirms that Nukudamu abandoned mine carries a high environmental risk to the immediate vicinity of its location. However, based on the findings of this detailed study about the current condition of the site, the natural attenuation capacity of Nataratara creek is sufficient to warrant a prudent monitoring than a countermeasure approach. In the event that the site is to be re-developed, then countermeasure approach is to be seriously considered. Also, an evaluation of the Nataratara creek hydrology is important to establish its carrying capacity in neutralizing the generation of more AMD and reducing the likelihood of increased concentration of hazardous elements if site redevelopment is proposed.

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Chapter 4 CHEMICAL AND MINERAL CHARACTERIZATION OF VATUKOULA GOLD MINE

4.1 Introduction

Vatukoula gold mine is the longest operating mine in Fiji, with more than 80 years of active mining. Over the years, the operation of the mine has attracted various studies about it geology, geochemistry, and geotechnical characteristics of its orebody with matching mining techniques, and economic benefits. Also, studies reflecting its social and environmental impacts are available. However, there remains a gap in specific studies to provide knowledge about the nature of mined rocks and the geochemical properties of the Vatukoula orebody. Thus, the connection of the impacts generated from exposing such mineral deposits during mining is still not well understood.

This chapter examines the chemical and mineral characterization of rocks, tailings, and water samples collected from Vatukoula mine site to understand the detailed geochemical properties of the samples, i.e., the minerals and chemical composition, their nature of occurrence, their interactions, movements, and behavior, especially elements of significant interest such as hazardous elements / heavy metals distinctive to the geology of Vatukoula mine. Specifically, trace elements, As, Cu, Fe, Pb, and Zn, and co-existing major ions or elements such as Ca, Mg, Na, K, SO_4^{2-}, and Si, contained in the rock samples were analyzed. In a preliminary characterization study in chapter 2 (Soro et al., 2023), Vatukoula mine poses manageable threats and is less vulnerable to environmental from the impacts of mining. Hence, this chapter further explores to verify such fact and specific concerns that may emanate from its detailed chemical and mineralogy characterization study.

The Vatukoula gold mine was selected for further detail investigation as part of this research as an active mine with > 80 years in operation to examine its mined rocks and assess how mining has affected the surrounding environment and to what extent, if any. Hence, there is a need to explore and understand more about the Vatukoula orebodies, the impacts due to

ongoing mining operation and how the minerals and elements alike persists once exposed due to extraction activities. The water samples were collected to understand the chemical contents of the water and the migration pattern of chemicals due to mining transported via surface water flow within the mine surrounding environments and further on. It is also the intent of this chapter to explore how chemical and mineral characterization is used to evaluate the exposed minerals from the mining operation and assess their potential to generate AMD or otherwise.

The outcome of this chapter will contribute to overall ambition and rationale of this work, which is to explore how chemical and mineral characterization knowledge can strengthen mining administration for safer mining and prudent mine waste management in Fiji. This study aimed to offer thorough understanding of such characteristics and their impacts from mining the Vatukoula orebodies, and such knowledge once recognized and understood plays an important role in improving the regulation of mining particularly mining approval processes. The contents of this paper is also effective in raising awareness for mining jurisdictions in developing countries like Fiji to build capacity and strengthen its mineral development and waste management strategies with matching mine closure and post mining plans.

4.2 The History and Geological background of Vatukoula gold mine.

Vatukoula, which traditionally translates as ‘rocks of gold,’ is a mining settlement generated due to mining and is located less than 10 km inland south of Tavua town, a coastal town along the northern shoreline of Viti Levu, the main island in Fiji group of islands (Figure 4.1). Interest for mineral exploration in the Vatukoula region started back in 1872 after the discovery of Au along the Nasivi River (Flint and Htay, 1994; Lum, 1995). It was not until 1932 after William Borthwick, a Scottish prospector discovered Au while panning along Lololevu creek that mining eventuated which led to the establishment of what is now known the Vatukoula Au mine It subsequently paved the way in the setting up of a number of mining

ventures around the discovered deposits that were eventually consolidated into the well-known Emperor Gold Mining Company Limited (Colley and Flint, 1995). Mining has continued unabated at Vatukoula since 1933 to become the premier mine in Fiji and has to date produced over seven million ounces of Au and two million ounces of Ag (Vatukoula Gold Mines, 2009).

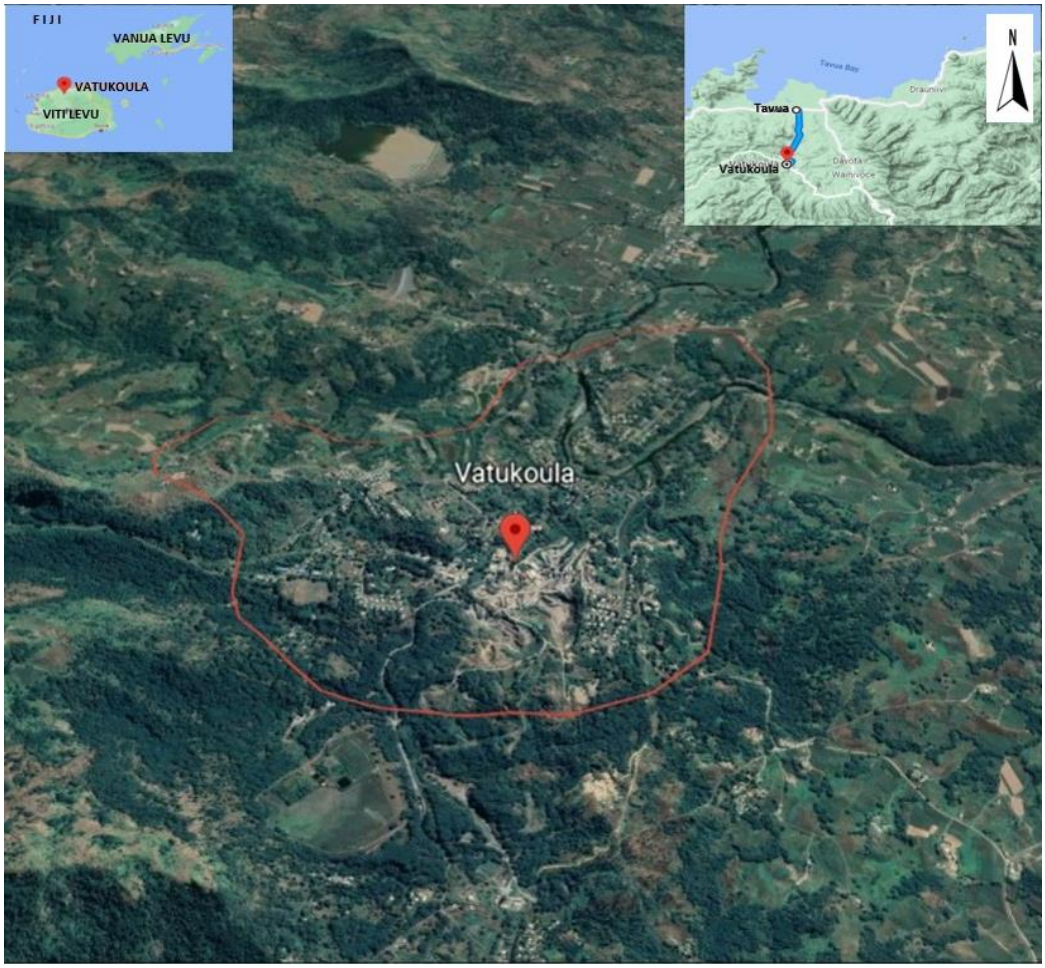


Figure 4.1 Location map of Vatukoula from the google earth image with amendments by the author (https://earth.google.com/web/search/Vatukoula+Gold+Mines,+Vatukoula,+Fiji...)

The mine was closed temporarily due to lack of viable returns in December 2006 and was sold to Westech Mine of Australia who operated it until River Diamond assumed management in 2008 through majority shareholder status (Soro, 2013). In 2010, a new

Chinese management team acquired the sole ownership of the mine and is now operating as the Vatukoula Gold Mine Limited (VGML).

According to Colley and Flint (1995), the rocks of Vatukoula originates from a series of volcanic activities in which potassium-rich magma of shoshonitic association with an apparently relatively simple evolution from absarokite (olivine basalt) parent magma to shoshonite, banakite (trachyangesite) and monzonite derivatives. Vatukoula Au mine is presently located in a collapse caldera and the present Au activity is located within 2 km^2 of fractured block up to a depth of 600 meters (Ahmad et al., 1987; Anderson and Eaton, 1990; Colley and Flint, 1995). Gold is found primarily in three basic structural settings that are steeply dipping northwest at striking shears; flat dipping (flatmakes) fractures, and shatter blocks between shears (Ahmad et al., 1987; Anderson and Eaton, 1990; Eaton and Setterfield, 1993; Colley and Flint, 1995). The Au deposits of Vatukoula are known to be low sulfidation epithermal of two major types: low sulfidation (LS) and high sulfidation (HS). Each of these is formed from waters of varying chemical composition, and in an appropriate volcanic environment. The presence of LS epithermal Au deposits are commonly related with the presence of the following metals: Ag, Pb, Cu, Zn, As, Hg, Se, Cd, and sometimes Sb (Colley and Flint, 1995; Ackely, 2008: Rabuku and Malik, 2020). Additional mineralogical study confirmed Au mineralization at Vatukoula to also exist in the form of arsenian pyrite (arsenopyrite), which is part of the target mineral mined at VGML (Pals and Spry, 2003; Anderson and Eaton, 1990; Kwak, 1990). The Vatukoula Au mine deposits represent one of the best-known examples of low-sulfidation epithermal mineralization hosted by alkaline basic and intermediate volcanic and localized by structures marginal to a caldera and is a world-class Au telluride deposits (Ahmad et al., 1987; Anderson and Eaton, 1990; Eaton and Setterfield, 1993; White et al., 1995). Such deposit in volcanic setting is typical of other major gold mines in the southwest Pacific region including Grasberg mine in Indonesia, the Porgera and Lihir in Papua New Guinea (Anderson and Eaton, 1990; WH Ireland, 2012).

Since its establishment, VGML has grown considerably and during its peak operation phase in the 1990s it was the largest single employer in Fiji. Workers migrated to Vatukoula to start a new life, creating a town-like community, and in the 2007 census, Vatukoula recorded a population of approximately 5,700 (Fiji Islands Bureau of Statistics, 2008) although the population had a sudden drop after the temporary closure of the mine late that year. The closest commercial center is Tavua town, located along the northern coast of Viti Levu, was also founded because of the mine, and had a much smaller population of about 2,500 people (Fiji Islands Bureau of Statistics, 2008). Hence, till to date, residents of Vatukoula are optimistic that life will continue in the mining community well, post mining.

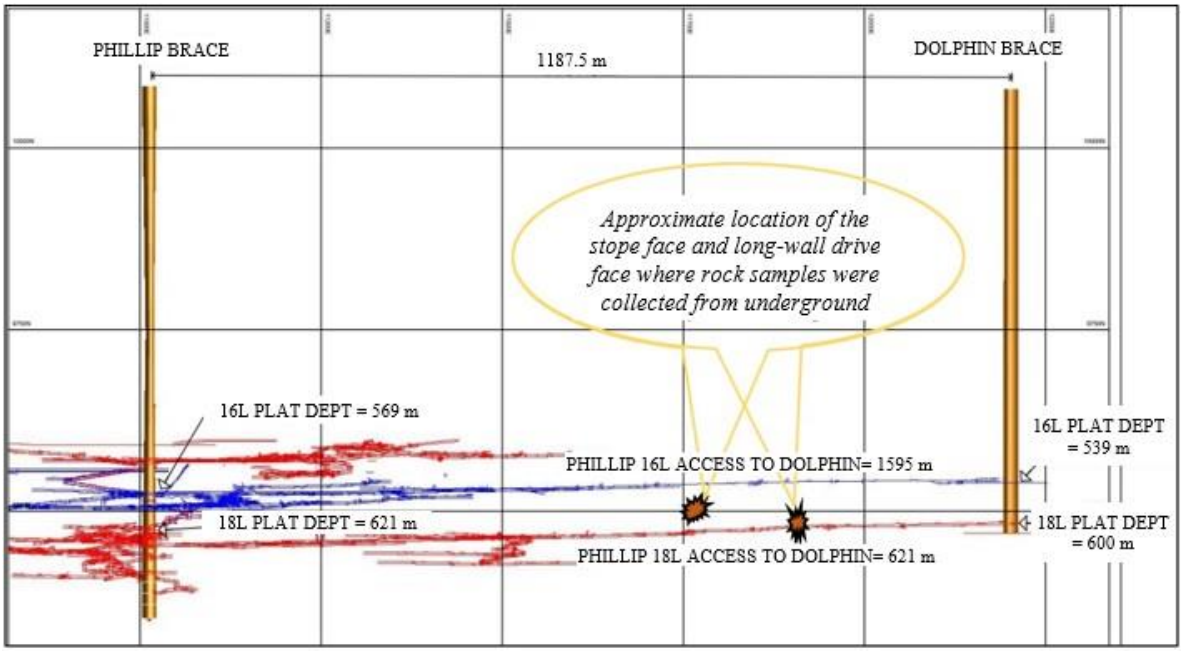


Figure 4.2 Cross-section schematic of underground access and workings between Phillip and Dolphin shaft indicating the approximate location where rocks samples were collected.

4.3 Materials and Methods

4.3.1 Rock and Water Samples

Rock samples from Vatukoula Au mine were collected from two locations along the underground long wall drive at level 18, about 600 m deep (Figure 4.2). The drive provides an access from the Phillip shaft to Dolphin shaft in the southeast direction. The samples were selectively collected under the assumption that they represents the typical geology of the Vatukoula mined orebody based on in situ inspection and observation in consultation with the underground mine officers. Based on these assumptions, two rock types were considered according to their occurrence as host rocks, and altered, mineralized rocks. A total of 10 samples were collected with details listed in Table 4.1.

Table 4.1 Vatukoula rock samples and related details.

Sample	Rock type, location	Sample description and field observation
VH1, VH2, VH3	Host rock, collected from the stope face	Greyish rock, fine to coarse grain and hard to break with geological hammer
VH2-1, VH2-2	Host rock, collected from the long-wall drive	Greyish rock, fine to coarse grain and hard to break with geological hammer
VAM1, VAM2, VAM3	Altered and mineralized rock, from the stope face	White yellowish color, crystalline and hard to break with geological hammer
VAM2-1, VAM2-2	Altered and mineralized rock, from the stope face	White yellowish color, crystalline and hard to break with geological hammer
VTD1, VTD2, VTD3, VTD4	Tailings sample from Toko tailings dam facility	Pinkish grey in color, coarse to fine clayish grain

The first set of samples were collected from a stope located about 300 m from Dolphin shaft. The stope face was approximately 1.5 m × 1.5 m with a clear heavily mineralized vein running horizontally at its center. Three host rock samples were extracted using the geological hammer from the top, middle and bottom labelled VH1, VH2 and VH3 of the face, respectively. Similarly, three altered and mineralized samples were collected along the horizontal vein at the center of the stope face, from the right, middle, and left of the stope face labelled VAM1, VAM2, and VAM3 (Figure 4.3).

Figure 4.3 Rock sampling pictures from a typical working face underground Vatukoula mine showing typical host rocks and altered, mineralized rocks.

The second set of rock samples were collected from the long-wall drive about 250 m from Dolphin shaft, at which a similar face to the stope sampling face was identified. Two samples of host rock (VH2-1 and VH2-2) and two samples of altered and mineralized rock (VAM2-1 and VAM2-2) were gathered. Also, an additional four tailings samples were collected from Toko tailings storage facility where the mine was currently dumping tailings after mineral processing from the mill (Figure 4.4).

The water samples were collected from the surface water flows within the mine site and its surrounding environment according to drainage pattern of the area, considering the mine shaft and mill discharge and drainage, and the natural surface tributary flow. The intention was to understand the migration pattern of minerals and chemicals transported via water flow from the mine to the nearby environment and further on. About 100 mL each of raw and filtered water samples were collected from eight locations as shown in Figure 4.4b and their respective details are listed in Table 4.2.

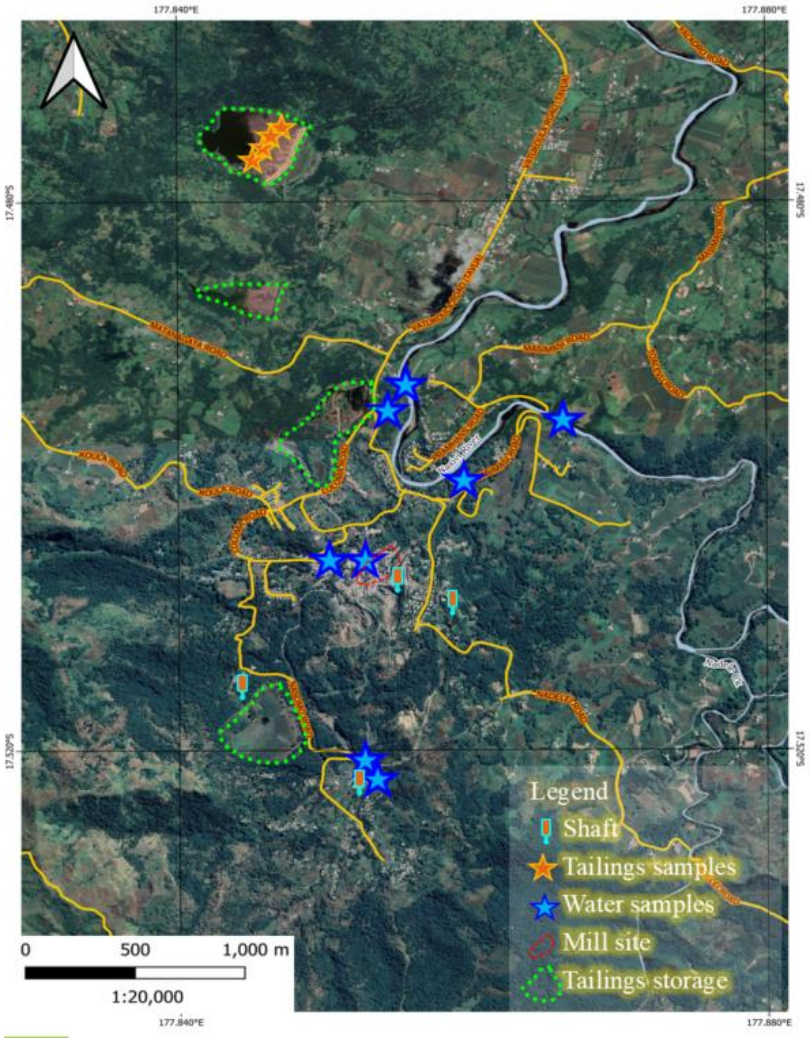


Figure 4.4 Map showing the water and rock sample collection location at Vatukoula on google map backdrop. Map is source from google earth and added features by the author (https://earth.google.com/web/search/Vatukoula+Gold+Mines,+Vatukoula,+Fiji...)

Raw water samples were collected straight into the 100 mL plastic bottles after first washing the bottles with raw water then filled to the top and closed tightly. For filtered samples, a 50 mL syringe was used to extract the water on site, a 0.45 µm Millex syringe-driven filter unit was then attached and filtered water was injected into 100 mL sampling bottle, washed first then filled until full and closed tightly. All samples were then labelled by number according to location and water sample type (raw or filtered) and kept under cool temperature.

Table 4.2 Descriptive detail of water samples collected from Vatukoula mine site and its surrounding.

Sample ID	Location	Sample description from field observation
VW1	Upstream of Lololevu creek and the Phillip shaft discharge confluence	Location is assumed to be control point for Lololevu creek, before Phillip shaft discharge
VW2	Phillip shaft discharge	Discharge from underground workings.
VW3	Downstream of Lololevu creek before joining Nasivi River	Location is just before Lololevu creek joins into the Nasivi River
VW4	Upstream Vunidraviloa creek before mill discharge	Location is assumed to be control point for Vunidraviloa creek, before mill discharge
VW5	Mill discharge before joining Vunidraviloa creek	Directly collected from the mill discharge, assumed to be the mill processing water.
VW6	Downstream of Vunidraviloa creek before joining Nasivi River	Location is just before Vunidraviloa creek joins the Nasivi River.
VW7	Upstream of Nasivi River	Control point for Nasivi River,
VW8	Downstream of Nasivi River	Location is assumed to be the last neutralizing point along Nasivi River

The samples were packed and stored appropriately for overseas transportation via plane to Hokkaido University for respective sample preparation and analysis. In situ measurements of physical water parameters such as temperature, EC, pH and ORP were measured and recorded using Horiba U-50 Multiparameter water quality meter (Thermo Fisher Scientific, Japan). All samples were properly wrapped, packed safely, and transported by airplane to Hokkaido University where chemical and mineral characterization test were conducted. Analysis of water samples was conducted using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) using ICPE 9800 (Shimadzu Corporation, Japan) after proper dilution.

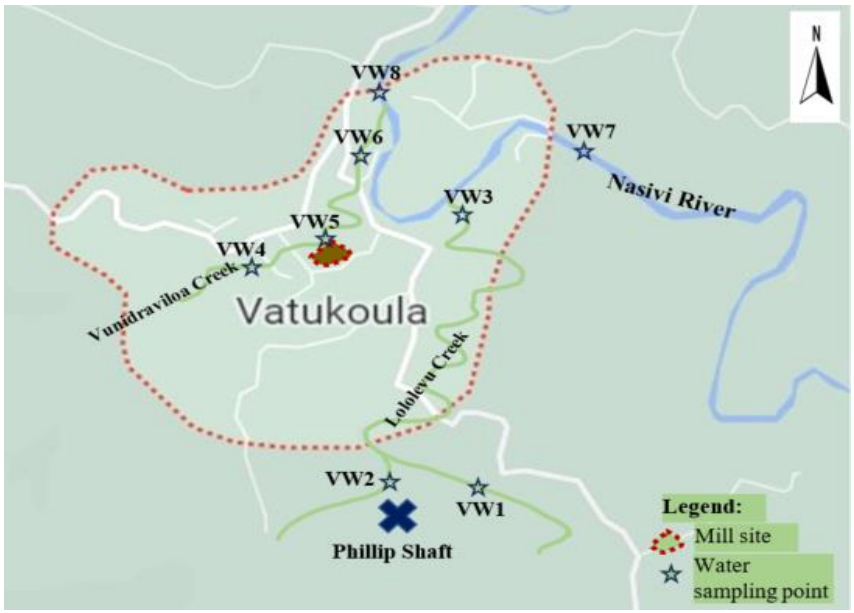


Figure 4.5 Vatukoula water sampling map.

4.3.2 Characterization of rock samples

The X-ray powder diffraction (XRD) and X-ray fluorescence spectroscopy (XRF) analysis was conducted to identify the mineralogy and to determine the chemical composition of the rock and tailings samples, respectively. The experimental procedures were the same in 2.3.1 with the results discussed in 4.4.1.

4.3.3 Batch Leaching Tests

The batch leaching experiments were conducted to evaluate metallic element leachates (As, Cu, Fe, Mn, Pb, and Zn) and coexisting ions (Ca, Mg, Na, K, and SO_4^{2-}) from the Vatukoula rock and tailings samples (Table 3.1 and Figure 3.4). The leaching experiment used in this chapter followed the same procedures described in 2.3.3 with the analysis results presented and discussed in 4.4.2.

4.3.4 Sequential Extraction (SE)

The same sequential extraction procedures used in 3.4.3 was applied in this part of the study to describe the partitioning of metal(loid)s in the Vatukoula rock samples. Analysis results are presented in 4.4.4.

4.3.5 Hydrogen Peroxide pH Acidification (pH (H_2O_2)) Tests

The pH (H_2O_2) acidification tests were considered in this part of the study to evaluate the AMD generation potential of the rock and tailing samples, using the same procedures applied in 2.3.7 with the test results presented and discussed in 4.4.5.

4.3.6 Statistical Analysis

Principal component analysis using Pro software (OriginLab Corporation, USA) based on the XRF and batch leaching test results was conducted following the procedures described in 2.3.5 with the results discussed in 4.4.6.

4.4 Results and Discussion

4.4.1 Mineralogical and Chemical Properties of Rock and Tailings Samples

According to the XRD analysis of the Vatukoula rock samples, quartz (SiO_2) was identified as the major mineral to be widely available in all the rock samples and was predominant in the mineralized and altered samples (VAM1, VAM2, VAM3, VAM2-1, VAM2-2) as noted by the percentage abundance in Table 4.3. Orthoclase ($KalSi_3O_8$) and dolomite ($CaMg(CO_3)_2$ were the other minor minerals with anorthite ($CaAl_2Si_2O_8$), sphalerite and calcite as trace minerals. Pyrite was detected in samples VAM1, 3, and 2-1 but in trace quantities. Augite and quarts as the dominant major mineral, with anorthite and dolomite as minor were

identified in the host rocks (VH1, VH2, VH3, VH2-1, and VH2-2). In tailings samples (VTD1, VTD2, VTD3, and VTD4) orthoclase mineral was dominant, quartz, augite, and dolomite as minor and traces of arsenopyrite, calcite and pyrite were identified.

Table 4.3 XRD mineralogical abundances (%) of the Vatukoula rock samples.

Samples	**VH1**	**VH2**	**VH3**	**VH2-1**	**VH2-2**	**VAM1**	**VAM2**	**VAM3**	**VAM2-1**	**VAM2-2**	**VTD1**	**VTD2**	**VTD3**	**VTD4**
Quartz	18.9	16.8	19.9	69.2	-	67.9	50.9	85.6	51.8	91.08	23.9	22.3	23	41.7
Dolomite	22.8	10.8	24.8	4.30	12.6	12.2	46.2	3.80	4.90	3.60	11.2	26.6	23.2	22.8
Orthoclase	-	72.4	-	-	-	13.9	-	6.60	22.3	-	28.9	30.1	34.6	22.2
Augite	23.7	-	27.7	23.4	38.7	-	-	-	-	-	13.1	13.5	15.5	12.5
Pyrite	1.58	-	-	-	5.10	4.72	-	1.90	5.80	-	-	-	1.90	0.80
Calcite	5.92	-	-	3.10	-	-	1.50	1.70	2.90	-	6.00	7.50	-	-
Anorthite	27.1	-	27.6	-	43.6	-	-	-	12.3	-	16.9	-	-	-
Arsenopyrite	-	-	-	-	-	0.77	-	-	-	3.50	-	-	1.80	-
Sphalerite	-	-	-	-	-	0.51	0.90	0.4	-	-	-	-	-	-
Smithsonite	-	-	-	-	-	-	-	-	-	0.40	-	-	-	-
Chalcocite	-	-	-	-	-	-	-	-	-	0.70	-	-	-	-
Cuprite	-	-	-	-	-	-	0.50	-	-	0.72	-	-	-	-

The XRF chemical composition analysis results are presented in Table 4.3. On average for the major ions composition, quartz was dominant (SiO_2 >50 wt%) in all the three rock sample types but more in altered and mineralized samples (>70 wt%) compared to the host rock (52.8 wt%) and tailings samples (53.5 wt%). The compositions of MnO, MgO, CaO, Na_2O, K_2O, and P_2O were observed to be comparatively low on average for all samples. It was observed that a distinguishable pattern of the three rock samples with composition of the major compounds (TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, and SO_3) were noticed to be twice to three times less in average composition for altered, mineralized rocks compared to host rocks and tailings samples but in minor composition (≤ 10 wt%) in order of host rock > tailings > altered and mineralized samples. In describing the compositions of detected trace elements (Pb, Zn, Cu, As, Cr, and Ni), a different trend was observed in their average compositions. The trace elements in altered, mineralized rocks were higher than those in host rocks and tailings samples (i.e., altered, mineralized rocks > host rocks > tailings samples).

The average content of trace elements was high for altered, mineralized rock samples as expected showing Zn (2,450 ma/kg), Cu (1,570 mg/kg), As (438 mg/kg) and Cr (357 mg/kg) as dominant, whilst Pb (122 mg/kg) and Ni (31 mg/kg) in trace quantities. The results showed that the average composition sequence was altered, mineralized rocks > host rocks > tailings samples except for As, which was observed to be high in tailings samples than host rocks.

Table 4.4 Chemical compositions of the rock samples from the XRF analysis results.

Sample	VH1	VH2	VH3	VH2-1	VH2-2	VAM1	VAM2	VAM3	VAM2-1	VAM2-2	VTD1	VTD2	VTD3	VTD4
†SiO_2	47.9	54.7	48.6	65.0	47.9	66.3	63.9	90.4	65.4	85.8	53.3	53.9	52.8	54.1
†TiO_2	0.49	0.22	0.51	0.21	0.53	0.20	0.04	0.09	0.23	0.11	0.54	0.48	0.53	0.53
†Al_2O_3	10.2	15.4	11.3	7.34	10.4	9.69	2.85	6.55	9.29	6.00	12.4	12.9	13.0	11.5
†Fe_2O_3	1.39	0.97	1.83	3.90	4.34	9.03	7.78	8.36	4.79	2.28	6.70	5.85	6.63	6.66
†MnO	0.26	0.25	0.16	0.39	0.21	0.10	0.32	0.10	0.17	0.17	0.18	0.17	0.19	0.19
†MgO	11.4	1.38	12.1	4.52	12.9	<1	9.09	<1	<1	<1	6.51	6.11	5.94	5.53
†CaO	14.3	1.51	10.5	5.88	10.5	3.76	16.9	2.29	3.01	1.61	8.58	8.15	8.08	7.82
†Na_2O	1.10	0.32	1.66	0.91	1.67	0.30	0.25	0.15	0.27	0.46	1.33	1.12	0.98	0.92
†K_2O	2.80	14.8	3.14	2.33	2.64	5.10	0.11	2.04	5.97	2.21	5.08	5.28	5.56	5.57
†P_2O_5	0.27	0.22	0.29	0.24	0.32	0.46	0.11	0.27	0.44	0.26	0.33	0.34	0.35	0.34
†S	0.10	0.11	0.09	0.23	0.11	2.10	0.02	0.76	2.93	1.48	0.26	0.19	0.24	0.33
*Pb	18.4	7.51	4.50	59.2	13.2	174	86.5	30.2	53.0	269	18.2	15.3	27.4	16.7
*Zn	216	501	568	3,738	469	1,840	3,029	3,697	842	2,843	262	428	375	385
*Cu	151	58.0	104	2,292	117	604	1,650	428	481	4,667	147	117	164	133
*As	4.50	<1	<1	438	1.69	518	401	224	181	868	192	201	305	228

† (wt%) *(mg/kg)

In matching the significant chemical composition to the mineralogical analysis, the host rocks contained high CaO and MgO and had abundance of calcite and dolomite, whilst altered and mineralized rocks had significant pyrite supported by positive correlation between Fe and S contents. However, Fe and S composition were less in the tailings compared to the rock samples.

4.4.2 Batch Leaching Experiments and Behavior of Detected Sulfide and Carbonates Minerals

The chemistry of the rock and tailings sample leachate collected from Vatukoula is summarized in Table 4.4 showing their mean values and its graphical representation in Figure 4.6. Except for sample VAM1 which had a mean weakly pH of 5.7, all other samples recorded circumneutral to weakly alkaline pH (7.5–8.6) range. The EC of the host rock leachates were < 60 mS/m, altered and mineralized rocks recorded an average EC of 130 mS/m and the tailings samples had an average of 101 mS/m. The average ORP for the leachates of altered and mineralized rocks was 207 mV, whilst 175 mV and 178 mV were measured for the host rocks and tailings samples, respectively.

Table 4.5 pH, EC, ORP, and concentrations of detected trace elements including As and Fe with major ions (SO_4^{2-} and Ca) measured in the leachates from rocks and tailings collected at VGML mine site.

Sample	pH	EC (mS/m)	ORP (mV)	As (mg/L)	Fe (mg/L)	Zn (mg/L)	Ca (mg/L)	SO_4^{2-} (mg/L)
VH1	8.53 ± 0.05	14.0 ± 0.73	169 ± 17.9	0.004 ± 0.002	0.41 ± 0.43		9.95 ± 0.44	
VH2	8.01 ± 0.04	58.3 ± 0.92	187 ± 10.1	0.001 ± 0.001			5.39 ± 0.13	
VH3	8.60 ± 0.08	15.7 ± 3.60	173 ± 14.7	0.006 ± 0.004			45.1 ± 1.25	148 ± 3.86
VH2-1	8.16 ± 0.10	38.9 ± 1.25	178 ± 4.78	0.009 ± 0.006			36.6 ± 1.60	145 ± 5.44
VH2-2	8.51 ± 0.025	36.3 ± 1.46	167 ± 6.48	0.001 ± 0.002			14.9 ± 1.56	105 ± 2.83
VAM1	5.71 ± 0.27	246 ± 32.7	263 ± 11.3	0.01 ± 0.003	0.192 ± 0.14	6.11 ± 0.05	389 ± 40.5	1,910 ± 99
VAM2	7.93 ± 0.23	21.3 ± 0.34	169 ± 14.8	0.016 ± 0.009	0.187 ± 0.13		22.7 ± 0.26	57.3 ± 1.8
VAM3	7.50 ± 0.05	131 ± 5.25	196 ± 13.7	0.004 ± 0.003	0.188 ± 0.13		173 ± 11.8	775 ± 50.6
VAM2-1	6.81 ± 0.29	196 ± 5.33	218 ± 16.4	0.001 ± 0.001	1.06 ± 0.13		337 ± 35	1,387 ± 77.6
VAM2-2	7.49 ± 0.10	92.7 ± 0.61	194 ± 8.96	0.002 ± 0.002	0.29 ± 0.21		89.7 ± 1.25	477 ± 5.89
VTD1	7.71 ± 0.03	78.4 ± 2.02	183 ± 11.4	0.007 ± 0.006			89.1 ± 3.75	446 ± 104
VTD2	7.80 ± 0.05	97.3 ± 4.06	198 ± 7.59	0.008 ± 0.005	0.56 ± 0.39		130 ± 15.3	471 ± 41
VTD3	7.77 ± 0.05	120 ± 2.87	172 ± 3.09	0.026 ± 0.007			132 ± 21.6	683 ± 24.1
VTD4	7.84 ± 0.05	112 ± 2.18	159 ± 15.2	0.018 ± 0.001	0.42 ± 0.24		133 ± 10.5	577 ± 24.8

These physical parameters are indicators of physical and chemical processes that can contribute to the negative impacts of mining as the result of exposing minerals during its extraction. For example, pH is a single parameter that has a dominant influence on the behavior of individual elements or compounds (Skousen et al., 2002, Lengke et al., 2010). It generally indicates if a sample is acidic or basic in their nature of origin and it is a well-known indicator that leads to oxidation of sulfide minerals and mobilization of hazardous elements through chemical processes described in 1.5. Sulfides, especially pyrite (FeS_2) when exposed to oxygen or comes in contact with water decreases the pH of the water draining through mine sites commonly known as acid mine drainage (AMD) (Lawrence and Wang, 1997; Lapakko, 2002; Skousen et al., 2002; Lengke et al., 2010; Simate and Ndlovu, 2014; Jamieson et al., 2015; Nordstrom, 2015; Tomiyama et al., 2019; Fosu et al., 2020; Manchisi and Ndlovu, 2021). Also, EC values indicate dissolved materials in the aqueous solution of the samples (Younger et al., 2002, Shalkowski et al., 2009). It is also an indirect indication of weathering of rocks, as more elements are released and available to mobilize (Karato and Wang, 2013; Oliveira and Zuquette, 2014) whilst ORP is a general indicator of the oxidizing and reducing potential of the measured medium.

It is interesting to note according to the leaching experiments that the rocks of Vatukoula gold mine showed poor leaching of hazardous elements, only Zn and Fe was detected in nominal concentration; Zn from a single altered and mineralized rock sample VAM1 and Fe from altered, mineralized rocks and tailing samples (Table 4.5, Figure 4.6). However, As was detected in leachates of all samples (Table 4.5, Figure 4.7) but all considered safe under the FNLWS (Environment management Act, 2005). Such results generally indicate that the mined rocks at Vatukoula are alkaline in origin and even though sulfide oxidation is overwhelmed by the dissolution effect of carbonate minerals. The mineralogy and chemical composition analysis equally support such assumption/trend since the dominant minerals were identified to be silicates (quartz, anorthite, orthoclase) and carbonates (calcite and dolomite). Calcium ion was also prominent in the leachates of altered-mineralized and tailings samples under alkaline conditions. Calcium ion has the affinity to attract carbonate to form dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$). The minerals known for their ability

to neutralize acid were confirmed in abundance by the XRD tests (Table 4.3). Even though the major minerals in these samples according to the XRD analysis were silicates and carbonates, sulfides still persist in altered and mineralized samples as well as tailings.

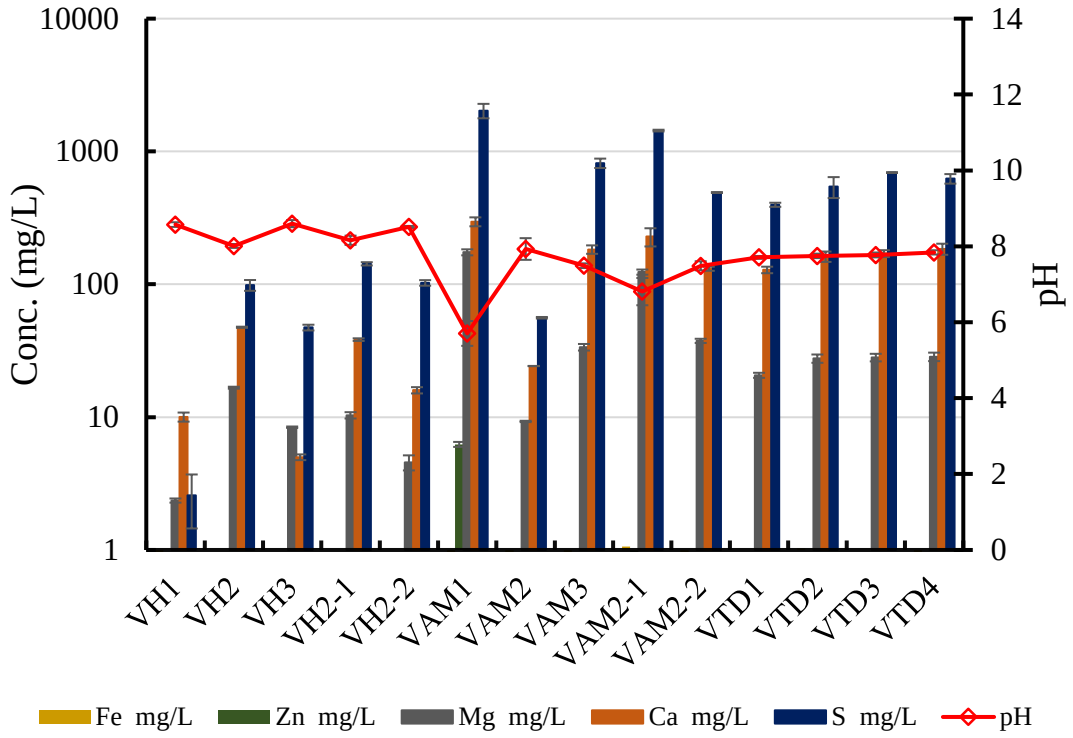


Figure 4.6 Leachate concentrations (mg/L) of significant elements Fe, Zn, Mg, Ca, S and pH in the Vatukoula leaching test.

Figure 4.6 also shows the average leached Ca and SO_4^{2-} from the samples in consideration of their pH. It shows that whilst the pH was mostly within the neutral to weakly alkaline range, Ca and SO_4^{2-} leached more from altered-mineralized rock samples then tailings and host rocks. Thus, it is important to also consider the roles of coexisting ions that associate with hazardous elements since they have an influence on the behavior of toxic elements, i.e., Ca and SO_4^{2-}. Sulfate was the dominant anion in the leachates of the altered-mineralized rock and the tailings samples as presented in Figure 4.6.

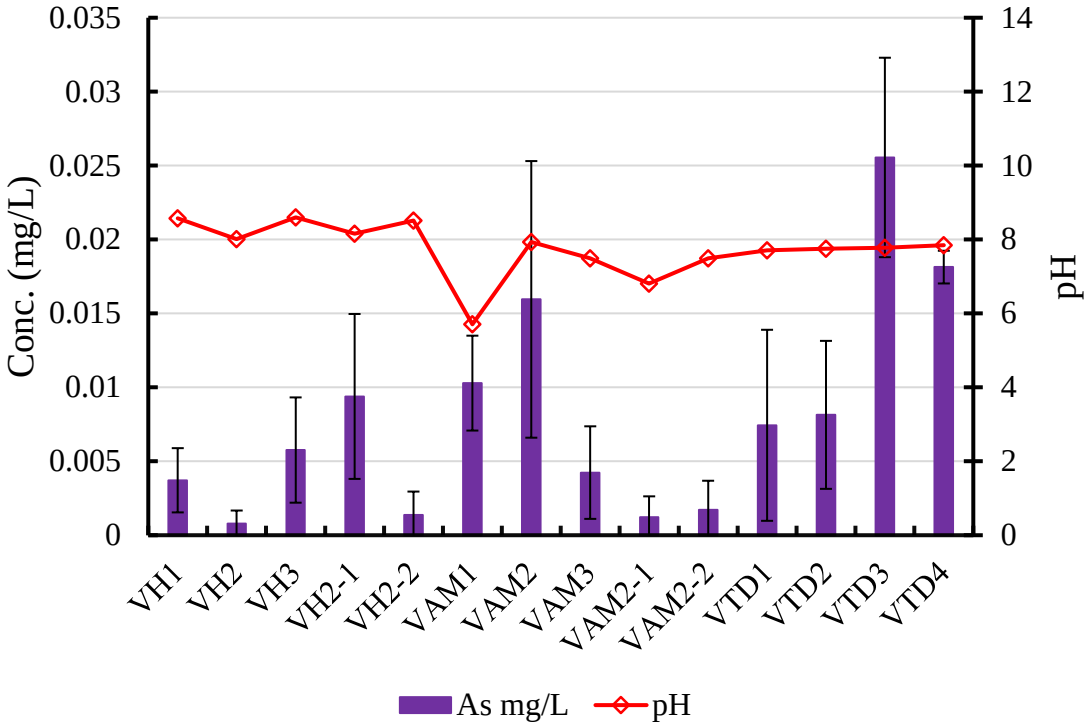
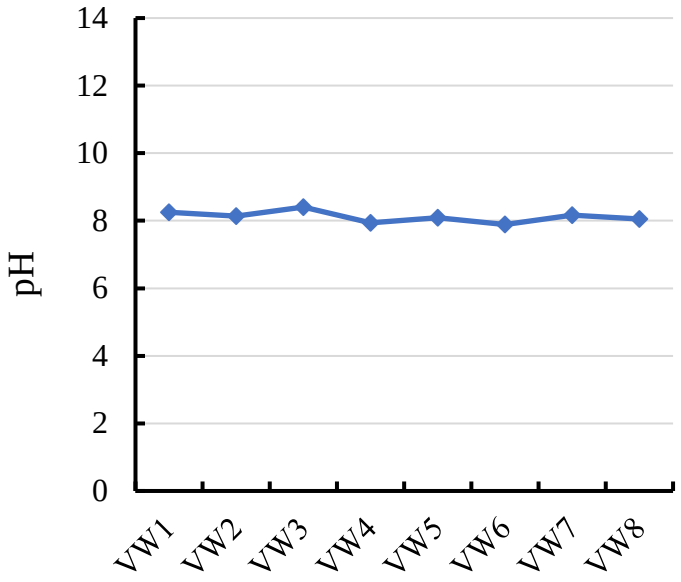


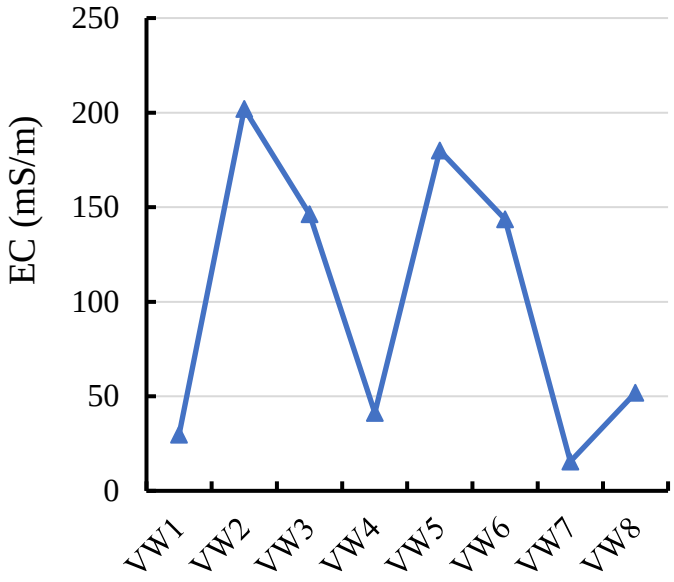
Figure 4.7 Leachate concentrations (mg/L) of As and pH in the Vatukoula leaching test.

4.4.3 Water Analysis Results

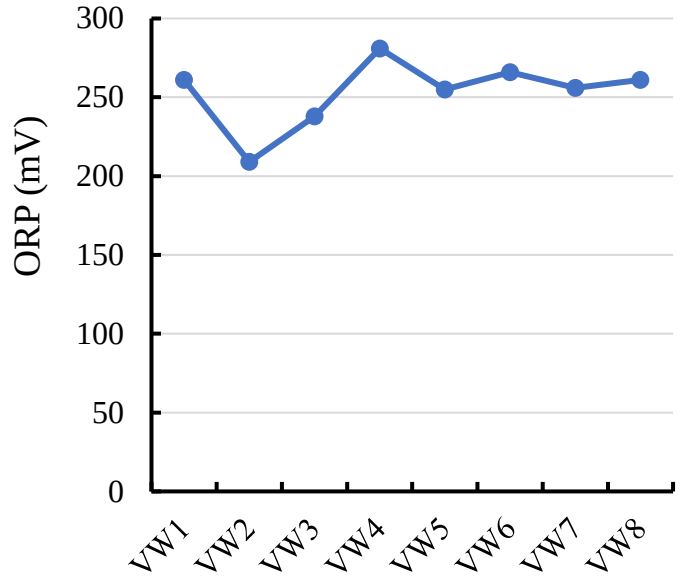
The detail results of the water samples analysis collected from within Vatukoula mine site surface water drainage are illustrated in Figure 4.7. The various graphs show the physical and chemical quality of water samples along the natural waterways as described in Table 4.2 and mapped in Figure 4.5. According to FNLWS As concentration from the mill discharge (VW5) was above the national set standard for both the original and filtered water samples (0.055 and 0.051 mg/L) respectively. However, it decreases to 0.041 and 0.044 mg/L respectively, as it flowed down Vunidraviloa creek before joining the main Nasivi River at NW6 which is below 0.05 mg/L, the safe discharge level according to FNLWS standard but above WHO drinking water guideline of 0.01 mg/L (World Health Organization, 2011).



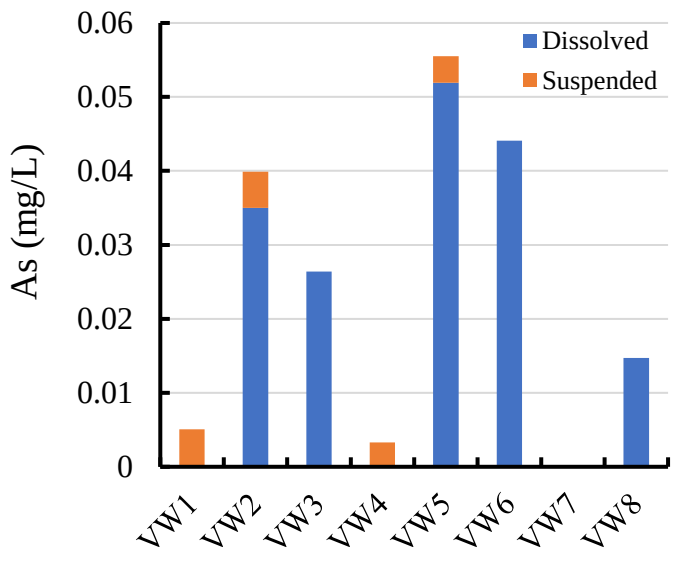
(a) pH



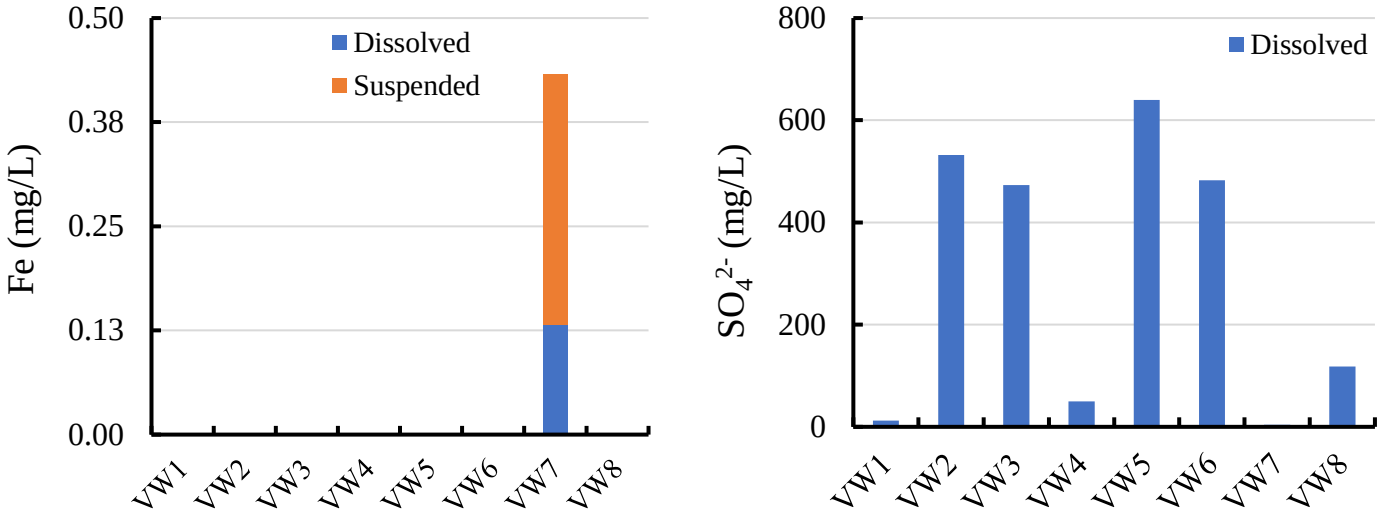
(b) EC



(c) ORP



(d) As



(e) Fe (f) SO_4^{2-}

Figure 4.8 Water analysis results of physical parameters – (a) pH, (b) EC (c) ORP as well as significant detected elements (d) As, and (e) Fe in dissolved and suspended samples with (f) SO_4^{2-} in dissolved samples.

4.4.4 Manifestation of Arsenic (As) in mined rocks and tailings of Vatukoula

This study acknowledges the elevated levels of As in the leachates of rock and tailings samples as well as the water samples. The chemical and mineralogy compositions supported that As was a naturally occurring element in the mined rocks of Vatukoula. The study attributes As to be sourced largely from the altered and mineralized rocks according to the XRF tests which sporadically leached from all samples but noted high in altered, mineralized rocks, and persisted to accumulate more in the tailings (Table 4.5, Figure 4.7). A mineral exploration study of the Vatukoula orebody by Pals et al. (2001, 2003) described that Au was largely 'invisible' in arsenian pyrite. Further studies also confirm elevated level of As in water and sediment samples collected along Nasivi River because of mining at Vatukoula as the main source (Ko et al., 2008; Singh and Mosely, 2003; Matanitobua et al., 2010). Even though the As levels detected in this study were mostly within the FNLWS, it remains a concern due to its toxic nature. Arsenic is a known carcinogen and highly toxic under inorganic form, and is often ingested by drinking water contaminated with elevated concentration of As (World Health Organization, 2011).

Given that As is mobilized under both low and high pH (Tabelin and Igarashi, 2009; Gersztyn et al. 2013), it is important to understand it chemical species. Such tests will be equally useful in gaining deeper understanding about the retention mechanism occurring in the tailings storage facility because high concentrations of As in the leachates were observed in tailings samples. The water study also indicate high levels of As from Phillip shaft underground water discharge at sampling point NW2 and mill discharge sample at NW5 as shown in Figure 4.8(d), though diluted as it flowed downstream satisfying the FNLWS. However, in the event, national discharge guideline for As may be revised to a more stringent standard, additional countermeasure options should be investigated by VGML to ensure compliance. This is important since the present study noticed a lack of significant natural attenuation of mine discharge water in Vatukoula unlike Nukudamu which demonstrate Fe precipitate capacity of oxides and hydroxides to the mine surface water runoff discharge. This study has highlighted the importance of conducting chemical and mineral property tests to make available pertinent information that can assist stakeholders to explore strategies to best manage the condition at Vatukoula. It also recommend for a more focus and specialized monitoring system be implemented to ensure prudent control and management of As mobilization off site.

4.4.5 Sequential Extraction (SE)

The SE results of the rock samples from Vatukoula are presented in Figure 4.7 for Cu, Fe, Pb and Zn. However, only leachates of As, Fe and Zn were observed in the leaching tests in which As was leached from all samples, Fe from altered, mineralized and tailings samples and Zn from sample VAM1 only. Iron was distributed randomly among the three phases but portioned more as residuals, then Fe-Mn oxides and sulfides/organics in all samples and minimally as carbonates with the exception of tailings samples. This indicates the propensity of Fe, especially ferrous hydroxide to precipitate even at circumneutral pH.

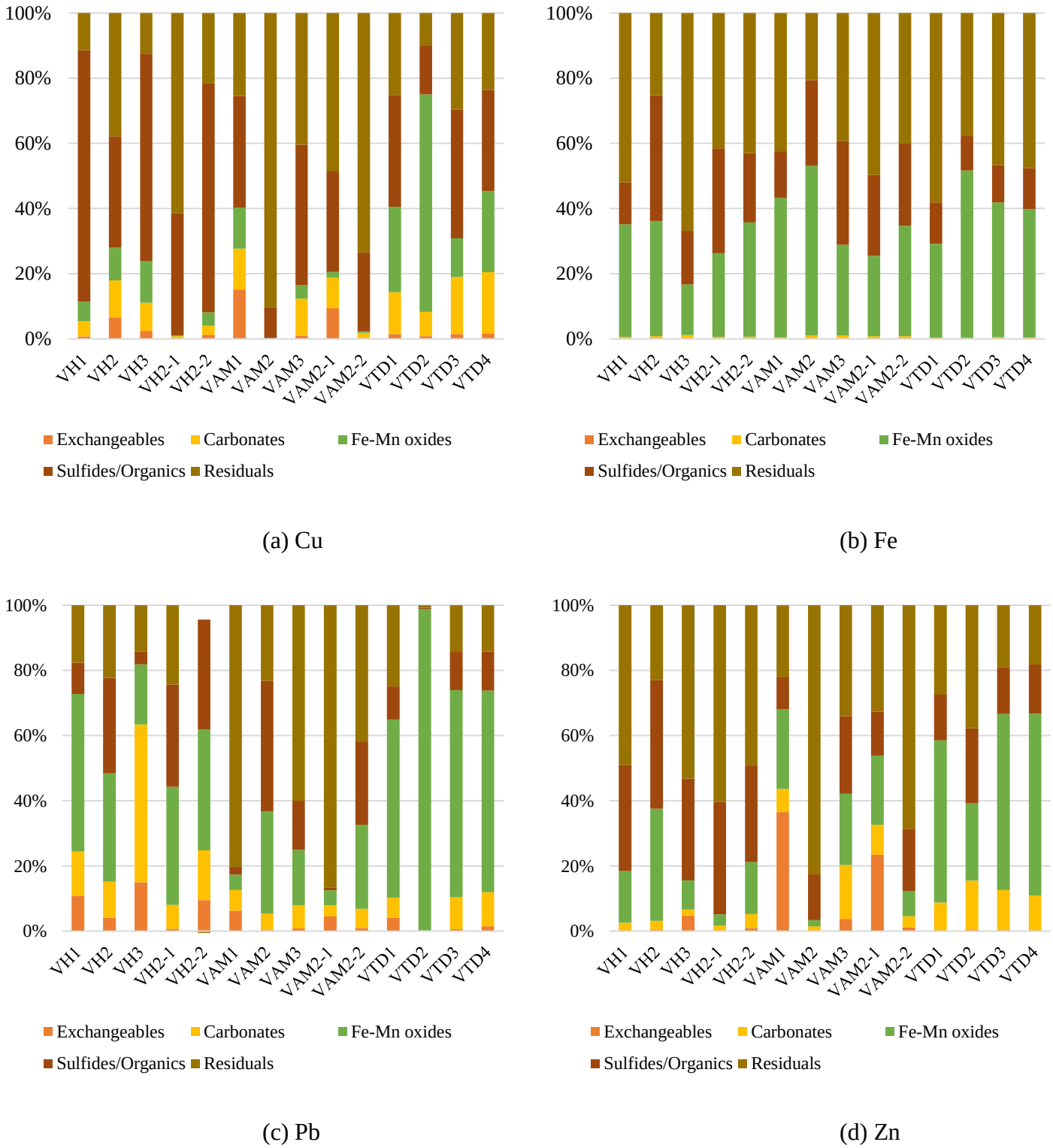


Figure 4.9 Sequential extraction results of (a) Cu, (b) Fe, (c) Pb and (d) Zn from the Vatukoula rock and tailings samples.

Zinc on the other hand also have the similar phase partitioning distribution pattern. Zinc was portioning as exchangeable phases in the altered, mineralized rocks, but still favored residual phase overall, more for host rocks, followed by sulfides/organics phase then Fe-Mn oxides. It is possible that the leached Zn in sample VAM1 was bound to exchangeables as depicted in Figure 4.7 (d) but was relatively stable and not easy to precipitate at circumneutral pH. Lead on the other hand was distributed favorably as Fe-Mn oxides for tailings samples, and residuals for altered samples and carbonates and Fe-Mn oxides for the host rock samples.

4.4.6 Hydrogen Peroxide pH Acidification (pH (H_2O_2)) Test and AMD generation

The hydrogen peroxide acidification test (pH (H_2O_2)) results are illustrated in Figure 4.8. It shows that rock samples VAM1, 3, VAM2-1, 2-2 and VH3 had acidification pH < 3.5 to indicate their potential to generate acid. Even though leachates of all rock samples showed acidic pH > 5 (Table 4.5), the pH (H_2O_2) tests indicate that the above-named rocks are likely to produce AMD in the long term. That is the alteration and mineralization processes occurring in these samples VAM1, 3, 2-1 and 2-2 induce low pH by oxidation of sulfide minerals, i.e., pyrite in these samples.

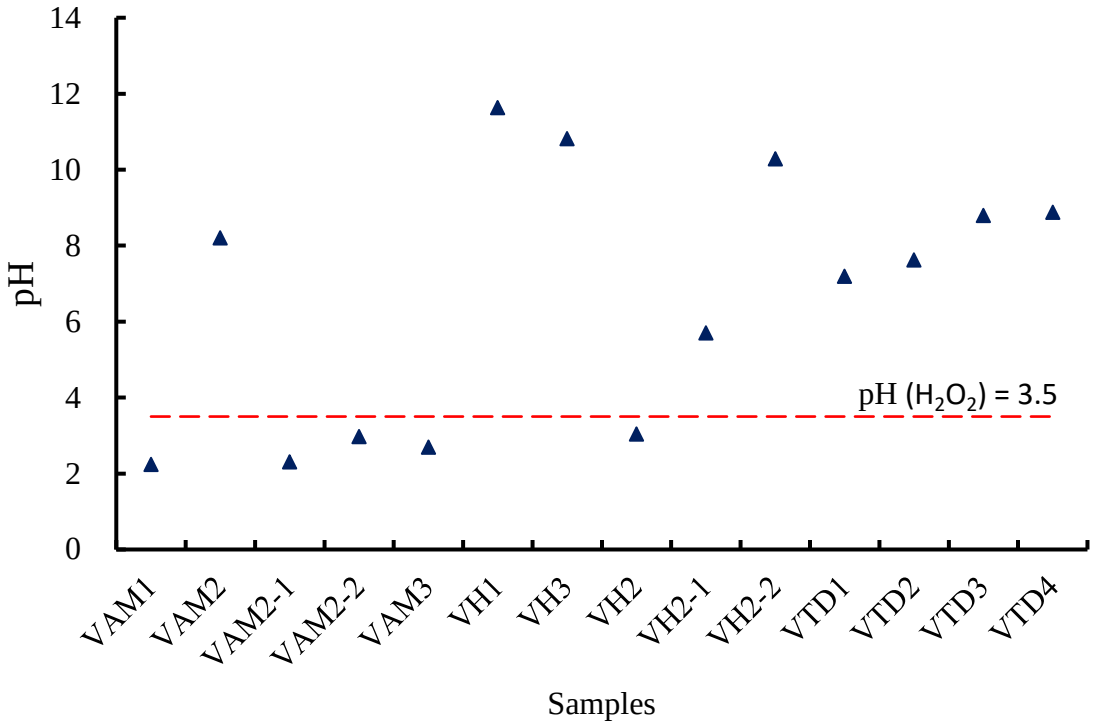


Figure 4.10 Hydrogen peroxide pH test (pH (H_2O_2)). The dotted line indicates the threshold for the acidification potential (pH = 3.5).

The pH (H_2O_2) tests confirm that despite the alkaline nature of the mined rocks and tailings at Vatukoula, the potential of AMD generation still remains. This is due mainly to contained sulfide minerals. Once exposed to oxidizing condition, the minerals can initiate a chain of oxidizing reactions explained in 2.4.2. The XRD tests confirm the presence of pyrite, arsenopyrite, sphalerite and chalcocite mostly in altered, mineralized rock and tailings samples (Table 4.3). Fortunately, the mineralogy of Vatukoula mined rocks analysed in this study also confirmed the relative abundance of carbonate minerals with dolomite and calcite dominant, and this was supported by the circumneutral leachates pH range 5.7–8.6 (Table 4.5). Such minerals are primary ingredients for dissolution that releases divalent cations (Ca, Mg, Fe) and HCO_3^-, causing pH leachate to circumneutral to weakly acid alkaline range.

The above oxidation and dissolution effect may also pose the unlikely situation where low or high pH condition favors the mobilization of As. Thus, prudent monitoring remains the

important tool to ensure optimum conditions for AMD generation and As mobilization are avoided.

4.4.7 Principal Component Analysis (PCA)

The PCA results of the Vatukoula rock sample's leaching tests in Table 4.6 show the leading four PCs that accounted for 91.7% of the total variance was dominated by PC1 at 61.7%. PC1 showed that EC, ORP, Ca, Mg, Mn, and S were responsible for the circumneutral pH of the rock samples with positive coefficients largely through dissolution as the main leaching mechanism at Vatukoula. The negative pH may be attributed to the alteration effect of dissolution where sulfides are also released, slightly reducing the pH. PC2 is related to the significant presence of As to be predominantly in Si. PC3 reflected that Ca, K, and Na coexisting ions also influenced the dissolution process within the rocks of Vatukoula, to leach profusely from all samples whereas Fe was oxidized and leached only from altered, mineralized rock and tailings. PC4 again showed As, K, Na, and Si to be relevant supporting PC2 and 3 with 6.86% overall contribution.

Table 4.6 Principal component analysis (PCA) including total variance, eigenvalue, and cumulative frequency for the leachates of Vatukoula rock samples.

Variables	PC1	PC2	PC3	PC4
pH	**-0.345**	0.025	-0.088	0.105
EC	**0.336**	-0.036	0.058	0.039
ORP	**0.323**	0.190	0.109	-0.234
As	0.016	**-0.671**	0.189	**0.391**
Ca	**0.329**	-0.119	0.048	0.056
Fe	0.165	0.125	**-0.665**	0.191
K	-0.215	0.172	**0.308**	**-0.552**
Mg	**0.341**	0.129	0.080	0.032
Mn	**0.331**	0.221	0.005	0.063
Na	-0.199	0.176	**0.462**	**0.439**
S	**0.347**	0.011	0.072	0.083
Si	-0.135	**0.593**	0.039	**0.477**
Zn	0.277	0.070	**0.418**	0.055
Eigenvalues	8.02	1.70	1.31	0.89
Variance %	61.7	13.1	10.1	6.86
Cumulative %	61.7	74.7	84.8	91.7

* Bold text indicates variables that accounted for significantly under each PC

PCA for the XRF result is presented in Table 4.7. This table shows the groupings of 15 mineralogical variables into 4 principal components to accounts for 86.7% of the total variance. Each PC group represented a certain level of significance due to the chemical composition of each variable, depicted by their coefficient values. PC1, which accounted for 43.3% of the total variance describes a feature of the host rocks chemical composition to be less on average in SiO_2 and Zn, but high in TiO_2 and Fe_2O_3, compared to the altered, mineralized rocks and tailings. These particular compositional features are the chemicals that majorly influence the mineral composition of host rock samples, negative coefficient values for SiO_2, and Zn may indicate that Zn exists mostly with silica while TiO_2 and Fe_2O_3 could be responsible for oxidation. PC2 also shared similar characterization by noting higher composition on average for MnO and CaO in host rocks, but negative coefficient values indicate that they contribute less influence to the mineralogy of this particular rock type. But the positive coefficient values of P_2O_5 and S, showed the contribution to mineralogy of host

rocks. PC3 and 4 had less overall contribution but positive coefficients of Fe_2O_3 in PC3, and As in PC 4 indicates their significance in the chemical composition due to their respective role in oxidation for Fe_2O_3 and As.

Table 4.7 Principal component analysis (PCA) including total variance, eigenvalue, and cumulative frequency of the mineralogy of Vatukoula rock samples.

Variables	PC1	PC2	PC3	PC4
SiO_2	**-0.338**	0.050	0.015	0.031
TiO_2	**0.340**	0.076	0.129	0.187
Al_2O_3	0.259	0.259	-0.252	0.164
Fe_2O_3	**0.303**	0.059	**0.345**	-0.018
MnO	0.009	**-0.377**	-0.077	-0.071
MgO	0.267	-0.299	0.202	-0.074
CaO	0.184	**-0.366**	0.173	-0.060
Na_2O	0.299	-0.082	0.250	0.180
K_2O	0.079	0.257	**-0.480**	0.015
P_2O_5	0.074	**0.462**	0.209	-0.045
S	-0.192	**0.361**	0.176	-0.226
Pb	-0.287	0.064	0.235	0.238
Zn	**-0.311**	-0.187	0.041	-0.053
Cu	-0.280	-0.124	0.195	0.285
As	-0.293	0.007	0.199	**0.405**
Eigenvalues	7.36	3.70	2.48	1.21
Variance %	43.29	21.76	14.61	7.10
Cumulative %	43.29	65.05	79.66	86.76

* Bold text indicates variables that accounted for significantly under each PC

The PCA analysis focuses largely on host rocks, but the relevance of altered, mineralized rocks and tailings are not overlooked, since they behave opposite to host rocks in many ways through oxidation processes even under high pH condition due to presence of carbonate minerals.

4.5 Conclusions

The chemical and mineral characterization of rock and tailings samples analyzed in this part of the study revealed that the host rocks had predominantly high Ca and Mg contents, and low levels of hazardous elements (As, Cu, Pb and Zn) with low leaching and acidification risk. It is expected that the high carbonates is responsible for neutralizing AMD generation. Amongst the altered-mineralized rocks, the presence of sulfide minerals such as pyrite was noticeable and there was a positive correlation between Fe and S contents. Hazardous element contents were relatively high but had low leachate concentrations. The pH (H_2O_2) acidification potential test indicated that such rocks were the likely sources of AMD generation in future. The tailings demonstrated low acidification risk, although As content was high. The leaching tests showed high concentration of As from two of the four tailings samples, which are below the Fiji environmental standard. Thus, it is safe to conclude that the mined rocks at Vatukoula has low acidification risk. Although altered and mineralized rocks did not show high concentrations of hazardous elements containing sulfur, these were somehow extracted during beneficiation process with the tailings revealing reduced risk of acidification. The host rock contains large amount of dolomite and calcite and is speculated to contribute to neutralizing acid formation. The above-mentioned chemical and mineral characterization confirms the need of conducting such study even when no significant environmental impacts are observed and is likely important for mine development expansion. It also justifies the relevance of instituting a robust environmental monitoring system especially for surrounding rivers and also groundwater.

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Chapter 5 GENERAL CONCLUSION

5.1 Summary of each Chapter

This research has provided an opportunity to study rocks, tailings, and water samples from selected mine sites in Fiji by conducting chemical and mineralogical characterization. It explores, and produce pertinent information that are beneficial to the mineral sector and its management of environment. The lack of such specific research in mining and mine sites in Fiji to gain thorough understanding and improve knowledge about these mines. It also contributes to building capacities for workers in government agencies and the sectors alike that are involved in mineral exploration and exploitation as well as environmental management to ensure sustainable development of Fiji's mineral resources.

Chapter 1 covers the desktop reflection of mining globally and in Fiji, its important contribution to Fiji's growth and economic benefits. Chemical and mineral characterizations as the main study methodology was explored, to understand its relevancy and deliver the necessary data important to meet the objectives of the study. AMD was also researched as a possible threat when chemical and mineral characterizations are not fully understood of rocks and liquid waste management in mines.

In chapter 2 the preliminary chemical and mineral characterization of rock samples from the five studied mine sites concluded that Mt Kasi, Nukudamu and Wainivesi mines had acidic based orebody rocks via dominant sulfide mineral contents. This is primarily attributed to the oxidation of sulfide minerals, which was confirmed by the leaching experiments. Acidic pH and high redox potential of the rock samples were found to be key factors contributing to the release of hazardous elements (Cu, Fe, Pb and Zn). It is also the basic mechanism that manifests to generate AMD in the rocks from the same mines as corroborated by the *ABA* and pH (H_2O_2) tests further contributing to release of hazardous elements and are likely to persist. 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 via the dissolution

by these carbonate minerals. Overall, the study highlights the importance of conducting thorough geochemical studies to identify potential environmental risks. Thus, it should be considered mandatory requirements for mining approval to strengthen and improve mining development, waste management, and post-mining rehabilitation in developing countries such as Fiji.

Chapter 3 focuses on the detailed chemical and mineral characterization of rock samples from Nukudamu mine as an abandoned site and was identified in chapter 2 being highly vulnerable and also considered a worst-case scenario from mining in Fiji. The study confirmed the difference between the two major rock types i.e., the altered and heavily weathered grey and whitish-yellow rock samples and the hard, solid, Kuroko type red brownish rocks. The altered and heavily weathered rocks had high contents of sulfide minerals and were devoid of carbonates while the latter had less sulfides with traces of carbonates. Such high sulfide mineralogy contributes to AMD generation and thus releases hazardous elements under acidic condition in altered, weathered rock samples. For hard, solid, Kuroko type rock samples no hazardous elements were detected in the leachates even at low pH to confirm low sulfide mineral contents. These were well supported by the sequential extraction test verifying the leachates in altered, weathered rock samples favored the easily soluble exchangeables and carbonates phases whereas the hard, solid, Kuroko rocks portioned them largely to the less soluble residuals. The strong acidic leachates with high concentrations of As, Cu, Fe, Pb, and Zn from the altered rocks being exposed to weathering mobilizes via mine surface water runoffs and discharged into the nearby Nataratara creek. However, the creek water diluted the mine surface discharge and iron oxide deposition on the creek bed contributed to neutralize the discharge and further attenuated as it flowed through the lower reach of Nataratara creek which has formed into a wetland before it joins the sea. Thus, the study confirmed that Nukudamu abandoned mine site and its immediate vicinity remained highly vulnerable to environmental risk, which should be a key consideration in deciding future mineral development or alternative land use. The study further reveal that despite the mine site's environmental vulnerable condition, it has relevant attenuation capacities to keep

such risk localized. Thus, it is important that a good monitoring strategy is recommended, whereas countermeasures may be applicable if the mine is redeveloped.

The study approach for chapter 4, which studied host rocks, altered, mineralized rocks, tailings, and water samples from Vatukoula mine, was similar to chapter 3 and revealed that the host rocks had predominantly high Ca and Mg contents, and low levels of As, Cu, Pb, and Zn. The study confirmed low leaching and acidification risks, which contributes to low AMD potential. This is further supported by high carbonate presence acting as neutralizers. Even though sulfide minerals were present in the altered, mineralized rocks, low leachate concentrations of the hazardous elements were observed. Similarly, tailings samples demonstrated low acidification risk, although As content was high in two samples. Altered, mineralized rock samples were confirmed by the pH (H_2O_2) acidification tests to be the likely sources of AMD generation in future but the dominant presence of dolomite and calcite is speculated to act as neutralizers. Thus, it is safe to conclude that the mined rocks at Vatukoula has low acidification risk, however, As levels remains a concern, so relevant environmental monitoring system to ensure safety of surrounding rivers and also groundwater is required.

5.2 Study Impacts and Contributions

The present study has justified the relevance of applying chemical and mineral characterization in studied mines in Fiji by confirming the high presence of sulfide minerals in the rocks of Mt Kasi, Nukudamu and Wainivesi. It demonstrates that the exposure of these sulfides through mining activities promotes its oxidization and reduces the pH causing hazardous elements to mobilize and are released (i.e., release mechanism) from the sulfides in rocks of these mines. The sulfide oxidation occurring in these sites further generates AMD which is detrimental to the environment. Surface water runoffs from these sites provide mediums in which leachates containing hazardous elements are transported, and without natural attenuation mechanism can have larger harmful environmental footprint. The study also reveal the contrast phenomenon in rocks from Tuvatu and Vatukoula to have low sulfide

mineral contents but significant carbonate minerals most notably calcite and dolomite. Carbonate minerals have strong neutralization capacity through dissolution effects and are able to diffuse the acidity of sulfide oxidation by raising the pH to neutral or alkaline, nullifying formation of AMD. Also, at such pH, hazardous elements are immobilize and retained (i.e., retain mechanism). The aforementioned mineral occurrences and chemical manifestation mechanisms within the studied mines, whilst its common in mines globally, this study is the first to confirm such occurrences in Fiji which has never been realized and is in fact a new addition to local knowledge.

The study has also demonstrate the applicability of the experimental test methods used in this research to be relevant in providing results that confirmed the above conclusions. It further revealed that mineral deposits which shares similar characteristics to the sites studied in this research either locally or overseas can apply the same analytical techniques to gain understanding of the chemical and mineralogical properties in their respective mine sites. Most notable comparison were Porgera, and Lihir mines in Papua New Guinea, Grasberg mine in Indonesia in the southwest Pacific and even Cripple Creek in Colorado, USA which shares similar mineral deposits as Vatukoula of low-sulfidation epithermal gold vein deposit associated with alkaline type igneous rock (Anderson and Eaton, 1990; WH Ireland, 2012, Rose et al, 2023). The Nukudamu mixed-sulfide deposit was assumed to share similarities with the Kuroko ore type deposit of Japan (Colley and Rice 1975, 1978). Thus, methodologies used in this study have a wider application potential outside of Fiji.

A worthy contribution from this study is the bridging of the knowledge gaps pertinent to mining administration and management in Fiji. Such information provides a good platform to improve systems and processes and much needed policies to strengthen mining administration and management. Decision making in mining approvals or permitting processes carries enormous responsibility and requires sound understanding of the mineral deposit's chemical and mineralogical properties. Developing countries like Fiji where geological information are archaic and studies are relatively rudimentary, likewise mining knowledge, the present research provides fundamental understanding to assist making just

and sound decision to permit mine development or otherwise. A systematic decision matrix guideline can be developed based on this study to indicate low sulfide deposits may be accepted for streamline processing whereas high sulfide may need further screening. Likewise for deposits that contain low and high carbonate minerals, provided that other standard requisites have been satisfied.

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