Applied Geochemistry 57 (2015) 85–105

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Review

Mineralogical characterization of mine waste

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ARTICLE INFO

Article history:
Available online 9 January 2015

ABSTRACT

The application of mineralogical characterization to mine waste has the potential to improve risk assessment, guide appropriate mine planning for planned and active mines and optimize remediation design at closed or abandoned mines. Characterization of minerals, especially sulphide and carbonate phases, is particularly important for predicting the potential for acidic drainage and metal(loid) leaching. Another valuable outcome from mineralogical studies of mine waste is an understanding of the stability of reactive and metal(loid)-bearing minerals under various redox conditions. This paper reviews analytical methods that have been used to study mine waste mineralogy, including conventional methods such as X-ray diffraction and scanning electron microscopy, and advanced methods such as synchrotron-based microanalysis and automated mineralogy. We recommend direct collaboration between researchers and mining companies to choose the optimal mineralogical techniques to solve complex problems, to co-publish the results, and to ensure that mineralogical knowledge is used to inform mine waste management at all stages of the mining life cycle. A case study of arsenic-bearing gold mine tailings from Nova Scotia is presented to demonstrate the application of mineralogical techniques to improve human health risk assessment and the long-term management of historical mine wastes.

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http://dx.doi.org/10.1016/j.apgeochem.2014.12.014
0883-2927/

1. Introduction: the need for mineralogical characterization in modern mining

The fundamental processes that control whether potentially toxic elements are released or sequestered in mine waste involve mineral–water interactions. Therefore, to understand the chemical reactions involved, it is important to characterize, in detail, the reactive minerals present in fresh and weathered material. This knowledge has direct application in predictive, operational and abandoned mine waste management. Specifically, the solid form of an element of concern and prevailing geochemical conditions play a critical role in environmental mobility (e.g. solubility and sorption–desorption) and risk to environmental and human health. Although amorphous and synthetically produced phases are not "minerals" by definition (i.e. naturally occurring crystalline materials), they are referred to as such in this paper for simplicity in describing their importance in mining environments. Tables 1–3 list examples of the three types of minerals discussed in this paper and their formulae.

The most costly and serious environmental problem associated with mining and milling metallic ores is considered to be acid rock drainage (ARD) and associated metal leaching (ML). The estimated costs for total worldwide liability associated with the current and future remediation of acid drainage are approximately $100 billion (Tremblay and Hogan, 2001). Rates of mineral weathering are greatly enhanced as a result of extraction processes (e.g. blasting, crushing and grinding) that increase rock surface area and expose mineral surfaces to water and oxygen. Mineralogy provides the fundamental controls on ML/ARD due to the relative abundance and reactivity of (1) the acid-generating sulphides and related minerals that may be present and (2) the associated neutralizing minerals present in or subsequently added to mine wastes (Plumlee, 1999).

Sulphide minerals tend to oxidize rapidly in the waste rock and tailings environment if exposed to the atmosphere. This process is often catalyzed by bacteria. Although extraction is focused on ore minerals, it is the pyrite and pyrrhotite, common accessory minerals in many types of ore deposits, that are largely responsible for the generation of low-pH waters. However, once an acid environment has been established, other sulphide, oxide, silicate, and carbonate minerals dissolve and release, depending on the nature of the ore deposit, metals such as Cu, Zn, Pb, Ni, Cd, Co, Hg, Al, Mn, and U and metalloids including As, Sb and Se (Nordstrom, 2011).

Mineralogy is equally important in terms of the ability of waste materials to neutralize acidity produced by sulphide oxidation. Neutralization is provided by the dissolution of gangue minerals such as Ca carbonates (calcite) and Ca–Mg carbonates (dolomite), or through the addition of lime or crushed limestone as part of remediation. Iron carbonates in the form of siderite, ferroan dolomite and ankerite are less reactive and ultimately provide no net neutralization from the Fe fraction of the carbonate due to subsequent Fe hydrolysis under oxidizing conditions. Whereas dissolution of other non-carbonate minerals (primarily silicates and aluminosilicates) can also provide some neutralization of acidic waters, the importance of such minerals in acid-generating environments is usually limited by slow reaction rates (Plumlee, 1999).

Although acid drainage has received most of the attention, waters draining mine waste may also be circum-neutral or even high-pH, and still can carry problematic concentrations of metals and especially metalloids. Accelerated weathering of certain minerals with or without the generation of acidity can result in the release of deleterious concentrations of metal(loids)s. Thus poor-quality neutral drainage can arise from both in-situ neutralized ARD or from non-acid generating weathering reactions (MEND, 2004). Whereas many metals have low solubility (and tend to be sorbed to Fe oxyhydroxides and other substrates) at neutral pH some weakly hydrolyzing metals such as Ni, Cd and Zn may require more elevated pH (pH 8.5 or higher) to adequately limit their mobility in the environment. Other elements of potential concern under neutral drainage conditions (e.g. As, Sb, Mo, Se) are present as anionic complexes that are less effectively sorbed at neutral to high pH. Some ore deposits, such as kimberlite-hosted diamond mines or carbonatite-hosted REE deposits produce high-pH drainage from mine waste (Rollo and Jamieson, 2006; Purdy, 2014), although sulphide-bearing host rocks may lead to acidic drainage in other parts of these systems (Smith et al., 2013).

Predictive characterization of mine drainage quality involves developing an understanding of the deposit and waste material geochemistry as it relates to both the observed and future drainage quality at mine sites. This benefits from a well-structured and integrated program that continues to evolve at various stages of data collection and project development (e.g. Maest et al., 2005). Mineralogy should play a key role at all stages of an evolving environmental management program.

1.1. Objective and scope

In this paper, mineralogy will be described in the context of mining and mine waste with specific attention, application and discussion of mineralogical fundamentals as they relate to understanding and predicting ML/ARD and, more generally, element mobility and availability in the environment. Application of mineralogical techniques relevant to problems at operating and abandoned mine sites will also be discussed. The available mineralogical tools are described with emphasis on capabilities and limitations, and selection of the most appropriate techniques. The work is culminated with a case study demonstrating applications of various techniques to characterize the key processes controlling element mobility and attenuation in mine waste and mine-impacted soils and sediments.

For further information, readers are referred to other useful reviews on the subject of mine waste mineralogy and analytical methods, including Alpers et al. (1994), Bigham (1994), Jambor (2003), Weisener (2003), Lottermoser (2010), Jamieson (2011), Jamieson and Gault (2012), Wogelius and Vaughan (2013), Brough et al. (2013) and Blowes et al. (2013).

Table 1
Selected primary minerals containing potential inorganic contaminants.

Pyrite	FeS_2
Marcasite	FeS_2
Pyrrhotite	$Fe_{(1-x)}S$
Chalcopyrite	$CuFeS_2$
Sphalerite	$(Zn,Fe)S$
Pentlandite	$(Fe,Ni)_9S_8$
Enargite	Cu_3AsS_4
Galena	PbS
Molybdenite	MoS_2
Tetrahedrite–Tennantite	$(Cu,Fe)_{12}Sb_4S_{13}–(Cu,Fe)_{12}As_4S_{13}$
Cinnabar	HgS
Cobaltite	$CoAsS$
Stibnite	Sb_2S_3
Realgar	As_4S_4
Willemite	Zn_2SiO_4
Cerussite	$PbCO_3$
Uraninite	UO_2
Monazite	$(Ce,La,Th)PO_4$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Alunite	$KAl_3(SO_4)_2(OH)_6$
Goethite	α-FeO(OH)

Table 2
Selected compounds produced by ore processing.

Compound	Origin
Scorodite, $FeAsO_4{\cdot}2H_2O$	Pressure oxidation of gold ore, treatment of Fe- and As-rich effluents
Ferric-arsenate sub-hydrate, $FeAsO_4{\cdot}0.75H_2O$	Pressure oxidation of gold ore
Basic ferric-arsenate-sulphate, $Fe[(AsO_4)_{1-x}(SO_4)_x(OH)_x]{\cdot}wH_2O$	Pressure oxidation of gold ore
Arsenic trioxide, As_2O_3 (e.g. synthetic arsenolite)	Roasting of As-rich gold ore
Maghemite, γ-Fe_2O_3	Roasting or other oxidation of sulphide-hosting gold ore
Hematite, α-Fe_2O_3	Pyrometallurgical processing of Fe sulphide ores, precipitation for Fe control in metallurgical process
Iron oxyhydroxides (e.g. ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$), goethite (α-FeOOH))	Precipitation for Fe control in metallurgical process and water treatment residues
Jarosite group minerals, $(K,Na,H_3O,NH_4)Fe_3(SO_4)_2(OH)_6$	Precipitation for Fe control in metallurgical process
Elemental S	Pressure oxidation of sulphide-bearing ores
Gypsum, $CaSO_4{\cdot}2H_2O$	Precipitation from lime neutralized acid residues and waters
Slag, including synthetic glass, metal oxides, silicates and native metals	Pyrometallurgical processing

Table 3
Selected secondary minerals formed in mine waste.

Mineral	Formula
Iron (oxy)hydroxides	
Goethite	α-FeO(OH)
Akaganeite	β-FeO(OH,Cl)
Lepidocrocite	γ-FeO(OH)
Ferrihydrite	Nominally $Fe_5HO_8{\cdot}4H_2O$
Aluminium (oxy)hydroxides	
Gibbsite	$Al(OH)_3$
Böhmite	AlO(OH)
Sulphate minerals	
Gypsum	$CaSO_4{\cdot}2H_2O$
Jarosite group minerals	$(K,Na,H_3O)Fe_3(SO_4)_2(OH)_6$
Schwertmannite	$Fe_8O_8SO_4(OH)_6{\cdot}nH_2O$
Melanterite	$FeSO_4{\cdot}7H_2O$
Copiapite	$Fe^{II}Fe^{III}_4(SO_4)_6(OH)_2{\cdot}20H_2O$
Epsomite	$MgSO_4{\cdot}7H_2O$
Anglesite	$PbSO_4$

2. Mine waste characterization

2.1. The role of mineralogy in the prediction of acid rock drainage

Considerable time, effort and money are spent by the mining industry in predicting whether solid mine waste will be acid-generating or not. In most countries, regulations require that drainage falls within a narrow pH window (typically between 5.5 and 9.5) that is suitable for aquatic life. Based on an understanding that the pH of mine drainage is mainly controlled by the balance between acid-generating sulphide oxidation and acid neutralization by mineral dissolution (especially of carbonates), a commonly-used method of predicting whether a given waste material will produce acid drainage or not is based on the concept of acid–base accounting (ABA) (Jambor, 2003; INAP, 2009; Price, 2009; Blowes et al., 2013).

Acid–base accounting static tests have two parts: (1) determination of the acid-producing potential (AP) based on sulphide content (assumed to be pyrite), and (2) evaluation of the neutralization potential (NP) by titrating the sample with acid or determining the carbonate NP by measuring the carbonate content of the sample. The NP/AP ratio is also known as the neutralization potential ratio (NPR) (Price, 2009). For most current guidance, those materials with $NP/AP < 1$ are considered potentially acid generating (PAG) and those with NP/AP greater than 2 are considered non-PAG (INAP, 2009; Price, 2009). Materials with NP/AP between 1 and 2 are considered to be of uncertain potential for acid generation.

For ABA, the presence of non-sulphide S (sulphates and organically-hosted S) must be identified so that an over-estimation of AP on the basis of total S alone does not occur. More specifically, as with other ARD tests, speciation-sensitive chemical tests (Price, 2009) have evolved to address these mineralogical questions. For example, it is common to determine water or weak acid leachable sulphate to correct for the presence of moderately soluble sulphates such as gypsum. The presence of alunite–jarosite group minerals adds further challenges to S speciation for the purposes of ABA (e.g. Lapakko, 2002) because (i) their response to various S-specific leach tests may vary and are not well understood, and (ii) these minerals can be a source of stored acidity in the samples. Sulphide-specific determinations have also been developed (using pyrolysis or selective wet chemical methods); however, these tests can underestimate sulphide content due to incomplete reaction of some phases, such as chalcopyrite and galena (Lapakko, 2002). Selective dissolution methods may similarly under-predict sulphide content from chalcopyrite and galena as well as coarsely crystalline pyrite (Jennings and Dollhopf, 1995). Such empirical analytical approaches to S speciation continue to evolve (e.g. Li et al., 2007); however, overall the complexity and variety of potential S species continues to prevent the application of a single simple and cost effective analytical regimen that is applicable to all materials. Definitive interpretation of S speciation especially in complex samples requires application of direct mineralogical techniques.

In modern mining, especially at the predevelopment stage for heterogeneous materials such as waste rock, it is not uncommon for hundreds or thousands of samples of heterogeneous material such as waste rock to be subjected to ABA tests. Static testing of other waste materials such as tailings requires specific consideration and will generally involve fewer samples with representativeness largely controlled by the design of the metallurgical test work. By their nature, such static tests provide only a prediction of whether or not a material can be expected to generate acid drainage at some point in the future. Static tests provide no indication of the relative rates of acid generation and neutralization or how long it will be before the onset of acid conditions, or whether effective neutralization will be available prior to acid generation (Blowes et al., 2013). Such tests are also typically conducted on a relatively small (10s of grams) subsample of pulverized rock material. Representativeness of the material with respect to the original larger rock or tailings (usually kg or larger) sample can be managed by careful sample preparation, handling and splitting techniques. However, variations of NP and AP with waste rock grain-size are not routinely evaluated in standardized static testing methods even though grain size and mineral liberation are understood to be critical factors in controlling drainage quality.

Laboratory kinetic tests such as humidity cells and columns are routinely used to assess the potential for ML/ARD on a selected subset of mine waste samples (usually measured in a few to tens of samples per study rather than hundreds for static testing). Such kinetic tests provide additional information on the rate of acid generation and neutralizing processes and changes in drainage quality over time. Kinetic tests are typically conducted on coarsely crushed rock for waste rock samples and simulated tailings from metallurgical tests. The prepared materials are exposed to simulated weathering conditions and drainage quality indicators including pH, sulphate, dissolved metals and other solutes are monitored at set intervals (Morin and Hutt, 1997; Sapsford et al., 2009).

For waste rock, long-term field-based tests can also be constructed that range from small field cells containing 10s to 100s of kg of rock drill core to larger test pads containing tonnes of blasted or crushed mine rock material with pore-water sampling instruments installed. The objective of such tests is to sample and analyze drainage from waste rock exposed to actual field climatic conditions at grain sizes more closely approximating future storage conditions in the environment. If started early in mine development such tests can provide guidance on future drainage evolution and perhaps more importantly, the tests can be designed to evaluate and test assumptions regarding the scale-up and extrapolation from laboratory experiments to field operations.

As pointed out by Jambor (2003), in reference especially to the standardized lab-based ABA and kinetic tests, the remarkable thing about these prediction techniques is that "Both are similar insofar as they are chemical tests independent of determinative mineralogy even though their purpose is to predict the weathering behaviour of the minerals in the tested samples." Traditional mineralogical techniques such as petrographic microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA) are fairly routine methods in the academic and government research communities, but have had limited application on industry projects. Guidance documents on international best practices in predicting mine drainage quality categorize mineralogical testing as "a required, not optional, analysis" to better understand the acid-generating and metal leaching source materials and potential neutralizing minerals (e.g. Price, 2009; INAP, 2009). However, from the point of view of many mining companies and their consultants, mineralogical work is considered relatively time-consuming and laborious with the quality of results determined by the specific expertise and experience available. These techniques also may not always provide a simple explanation or prediction of mine drainage geochemistry, especially if the critical minerals involved are poorly crystalline or present in small amounts. Given that mining companies, regulators and other decision makers have, for several decades, generally relied on predictive techniques based on chemical tests that do not involve mineralogy and that traditional mineralogical techniques have inherent limitations, when is a more comprehensive application of mineralogical characterization warranted? How can modern mining benefit from the current state of the art in mineralogical characterization of mine waste to predict drainage quality and design short-term controls and long-term closure plans? What needs to be examined and by what analytical techniques?

The answer emerges from the concept expressed in the opening sentence – if the release and attenuation of potentially hazardous elements from solid mine waste is the result of mineral–water interaction, then a comprehensive understanding of the controlling factors requires identification and characterization (meaning a description of the chemical composition, grain size, crystallinity, texture, encapsulation and grain-scale heterogeneity) of the reacting minerals and mineral products (surface residues and precipitates). This knowledge can lead to more accurate environmental predictions, less expensive mitigation, quicker project approvals, and an overall decrease in environmental risks (Price, 2009).

Modern mining professionals understand the role of mineralogy in prediction, for example, in the context of improving the interpretation of kinetic and static tests. As already identified, complexity in S mineralogy and NP minerals may require direct mineralogical analysis to verify the important forms present at a specific site because of limitations in traditional chemical techniques (Paktunc, 1999). More specifically, pyrite may be assumed to be the dominant oxidizing sulphide, but framboidal pyrite, marcasite and pyrrhotite are known to oxidize more rapidly than coarsely crystalline pyrite. As a further example, quantifying trace and minor element substitution in specific sulphide minerals is also important for estimating the release rates of potential elements of concern (Kwong, 1993).

As discussed previously, the rate of carbonate neutralization is known to depend on the identity of the carbonate mineral present. For example, in tailings impoundments, calcite has been observed to be the most soluble carbonate and shown to dissolve rapidly, while dolomite and ankerite dissolve more slowly but can still provide neutralizing capacity (Jambor and Blowes, 1998). Predictive testing can be improved by identification of all carbonate minerals present.

More broadly, mineralogical analysis can be used to explain disparities between static and kinetic test results, for example where a PAG sample determined by static testing is classified as non-PAG in kinetic testing. It can also aid in understanding site-specific factors affecting future drainage quality for projects where a significant quantity of material has been identified as PAG (conservatively assumed for all material with an NPR of <2). At such sites, relatively small downward adjustments in cut-off limits for PAG (NPR between 1 and 2) or identification of longer times to onset of acid conditions can have substantial financial implications for projects (INAP, 2009). Detailed interpretation of the mineralogical factors affecting sulphide reaction rates and effective neutralization potential as they relate to static test results can be used to support environmental predictions and management strategies. Government regulators are more likely to accept such modifications to waste management planning where a clear mineralogical basis is provided. When there is little or no carbonate neutralization potential, but no overall acid generation apparent from kinetic tests and low sulphide oxidation rates, it may be inferred that silicate or aluminosilicate minerals are providing adequate neutralization to prevent acid onset. Mineralogical analyses can help to identify the specific silicates present and the alteration reactions that may be occurring (Sherlock et al., 1995; Paktunc, 1999; Jambor et al., 2009; Lottermoser, 2010; Brough et al., 2013). Mineralogical work can also identify factors that may be limiting sulphide oxidation rates in laboratory tests and in the field such as degree of sulphide liberation and grain size (Brough et al., 2013), sulphide mineralogy, crystallinity and development of relict Fe oxyhydroxide rims.

Geochemical modelling using programs such as PHREEQC (Parkhurst and Appelo, 1999) is frequently used to predict mine drainage quality. These programs are based on mineral–water reactions and their validity is significantly enhanced by the verification of the mineral species actually present in the samples (Alpers and Nordstrom, 1999; Nordstrom and Campbell, 2014). For example, many authors have developed geochemical models to predict the evolution of water quality in mining pit lakes over time in an effort to minimize contamination of surface and groundwaters following mine closure (Bowell, 2002). Pit lakes are complex environmental systems, thus it is essential to have accurate mineralogical information on the compositions, surface areas, and reaction rates of both primary minerals and potential secondary phases as input for geochemical modelling (e.g. Castendyk and

Webster-Brown, 2007). As another example, the oxidation of Fe(II) and neutralization of acid drainage through treatment or dilution lead to precipitation of Fe(III) oxyhydroxides which tend to adsorb many metals and metalloids of potential environmental concern under suitable geochemical conditions. Mineralogical analyses can help to determine if the Fe oxyhydroxide actually forming in a given environmental system is goethite, akaganeite, lepidocrocite or schwertmannite, all of which have are likely to have different abilities to adsorb or sequester potentially hazardous metals. All geochemical modelling efforts benefit from a good understanding of the starting material for mineral–water reaction. For example, is the Cd present in a given ore found in greenockite, or is all Cd in solid solution in sphalerite? These types of questions are all pertinent to effective modelling but cannot be answered without mineralogical analysis. Misidentification of the minerals participating in a reaction, or the assumption of end-members of a solid solution instead of intermediate compositions can result in errors in water quality prediction of several orders of magnitude (Alpers et al., 1994).

2.2. Mineralogy and remediation design

Another valuable outcome from mineralogical studies of mine waste is an understanding of the stability of the reactive and metal-bearing minerals under various redox conditions. A standard practice in many mines is to place tailings and waste rock under water to limit sulphide oxidation. However, if some sulphide oxidation has already taken place, as a result of rapid weathering or the presence of supergene minerals, these secondary phases may dissolve under a water cover and release metal(loid)s. Moreover, in some cases, the solid phases hosting the potentially hazardous elements may become unstable under reducing conditions. For example, roaster and autoclave waste from gold ore processing often includes As hosted in oxide phases. The primary arsenopyrite is destroyed during processing and some of the As is incorporated in Fe oxides, Fe arsenates or Fe sulphate-arsenates (Swash and Monhemius, 1994; Walker et al., 2005; Dutrizac and Jambor, 2007; Gomez et al., 2011). These oxidized phases may destabilize in reducing environments and release As to solution (McCreadie et al., 2000; Andrade et al., 2010).

Water covers are impractical in arid environments and may be unsuitable for permanent mine waste storage because they are typically dependent on the long-term stability of engineered structures. In such cases, planning for soil or other types of dry covers, and designing such covers benefits from a thorough understanding of the reactive phases. For very large waste rock piles, it may be impossible to isolate all reactive mine waste from exposure to weathering, and the mitigation of environmental impact depends on treatment of poor-quality drainage. In this case, designing the optimal treatment to capture all metals and other unwanted constituents would also benefit from mineralogical characterization of the waste.

2.3. Mine waste mineralogy and human health

Much of the focus of the prediction, regulation and remediation of the environmental impact of mine waste is directed towards protection of ecosystem health, particularly aquatic life, but also human health where drinking water sources are potentially affected. The other potentially serious impact of unremediated solid mine waste is damage to the health of humans and other organisms through the direct ingestion or inhalation of contaminated dust or soil. Exposure of this nature may occur near abandoned or active mines where windblown dust was not adequately controlled, or has accumulated in soils after years of airborne transport. This is of particular concern for young children who have lower body weight and ingest soil at a much higher rate than adults. Not all of the ingested metal is absorbed by the body, however, and the fraction that is depends, in part, on particle size, the mineral hosting the contaminant element, and whether the metal-bearing particle is coated with an inert mineral (Ruby et al., 1999). One of the ways of evaluating this risk is by determining the bioaccessibility of metals in the dust or soil, meaning the degree to which the metal-bearing solid phases dissolve in simulated gastric and intestinal fluids (pertinent to ingestion) or pulmonary fluids (pertinent to inhalation) (Plumlee and Morman, 2011).

2.4. Research frontiers in mine waste mineralogy

Research on the environmental impact of mining has been an active and productive field of endeavour over the last few decades. It draws expertise from a range of geological and other disciplines and addresses an important societal problem. Many studies that push the research frontiers in this area include detailed mineralogical analysis. For example, the environmental consequences of mining some strategically important deposits such as rare earth elements and zinc oxide–zinc silicate deposits are poorly understood, but clearly are influenced by mineralogy (e.g. Sangster, 2003; Weng et al., 2013). Recent work aimed at understanding the role of microbes in mine waste usually includes detailed mineral characterization (e.g. Majzlan et al., 2011). The recognition that geological processes govern element mobility in mine waste (e.g. Nordstrom, 2011) and the concept that geologically similar ore deposits will tend to have similar environmental consequences (Plumlee and Nash, 1995; Seal and Hammarstrom, 2003) are rooted in the mineralogy of the starting materials, particularly the primary ore and accessory minerals.

3. Types of minerals in mine waste

Various approaches have been taken to categorizing the types of minerals in mine waste. With respect to tailings, Jambor (1994) distinguished primary minerals as those that have been ground during milling but otherwise unaltered, secondary minerals as those formed within tailings impoundments as a result of weathering reactions, tertiary minerals as those formed after tailings have been removed from the impoundment, and quaternary as those minerals formed during sample storage. Lottermoser (2010) referred to secondary minerals as those that form from weathering of sulphides either pre- or post-mining. Jamieson et al. (2011) separated primary sulphide from non-sulphide minerals and introduced a category for solid phases formed as a result of ore processing.

The most useful approach should fit all the situations in modern mining where mineral–water reactions influence drainage chemistry and environmental risk. For example, not all tailings are in engineered impoundments. Furthermore, some of the most problematic issues are related to the weathering of large volumes of waste rock rather than milled tailings.

For this paper, we consider primary minerals to exist pre-mining (essentially deposit minerals unaltered by processing), and secondary minerals to form post-mining (post-depositional minerals). A third category includes those compounds that form as a result of mineral processing and water treatment, found in waste materials such as slags (Piatak et al., 2015), calcines (Walker et al., 2005) and sludges (Beauchemin et al., 2010). It is recognized that in some cases there is uncertainty as to the origin of a given mineral, particularly for the products of sulphide oxidation, typically Fe oxides, oxyhydroxides, and sulphates that form via oxidizing hydrothermal processes (hypogene), more recent pre-mining weathering (supergene) processes (e.g. Koski, 2010), or by post-mining weathering processes. At developing and operating mine sites such distinctions may be clear; however, at historical operations it may be more difficult to distinguish the different origins of such phases without careful examination of fresh ore material which may or may not be available.

From an environmental risk point of view, the focus is usually on "chemicals of concern" or inorganic contaminants, typically metals or metalloids. Mineralogy determines whether or not these elements become mobile, if they are present in concentrations that are higher than environmental guidelines or if they are potentially bioaccessible (i.e. soluble in body fluids) and may produce a toxic response in a bioreceptor should exposure occur. Less commonly considered in mine waste studies, but equally relevant, is the risk associated with bioavailable forms of metals and metalloids hosted in dust particles that may be ingested or inhaled by organisms. Given that the mechanism of release and attenuation of these metals and metalloids is governed by mineral–water (and mineral–water–microbe) reactions, it is important to distinguish the minerals from an operational stance i.e. primary, secondary, and process-related.

3.1. Primary minerals hosting potential inorganic contaminants

The first sub-group of primary minerals (Table 1) includes both the ore minerals that are the target of the mining activity, and associated (non-economic) metal-bearing sulphides and related minerals. Many of the metals whose properties make them so valuable to our society and an integral part of our built environment are hosted in sulphides in the ore deposits where they are concentrated. Minerals formed as oxidation products (oxides, carbonates, silicates) can also be of sufficient economic value as to constitute ore.

The objective of mining and milling is to extract as much of each valuable metal as economically and technically possible. Inevitably some metals remain in waste rock, which is too low in grade to be economically worth processing, and tailings, which represent the fraction remaining after mill processing. Although the economic metal concentrations may be reduced by several orders of magnitude by mineral extraction, the non-economic metal-bearing minerals (e.g. pyrite) may largely remain in the wastes. In addition, residual concentrations as low as several hundred mg/kg of metal in mine waste, when exposed to weathering and leaching, may still mobilize sufficient metal to have an impact on the environment. For the most part, metallurgical processing aims to selectively concentrate the metal-bearing sulphides (or other minerals) of economic interest for subsequent refining. In an effort to reduce loss of a valuable commodity, modern mill professionals characterize ore, intermediate and waste products carefully and their expertise is an important resource for researchers interested in the mineralogy of mine waste.

Although pyrite and pyrrhotite are rarely sought as a source of Fe or S in modern mining, their presence in mine waste is a dominant factor influencing the nature of mine drainage. The oxidation of these Fe sulphides is fundamental to the ML/ARD process. More specifically, the rate and duration of sulphide oxidation in relation to neutralization rates and duration determines whether ARD will occur and the timing of acid onset. Further, the presence of trace elements contained in these accessory sulphides (e.g. As or Se in pyrite; Co and Ni in pyrrhotite) may contribute to the deleterious nature of mine drainage. Pyrrhotite tends to oxidize more readily than pyrite, and aside from the (bio)geochemical controls on sulphide oxidation the rate and degree of oxidation of both minerals is influenced by the grain size, texture, degree of encapsulation or liberation, and the presence of relict secondary Fe oxyhydroxide rims.

In addition to primary ore sulphide minerals and the Fe sulphides pyrite and pyrrhotite, accessory sulphide minerals, which may or may not provide additional commodities, have an important influence on the environmental risk associated with mine waste because they may host many of the trace elements of environmental concern in waste for a given site. For example, base metal sulphides such sphalerite, galena and chalcopyrite (Table 1) may occur in precious metal deposits and, although not of economic value in the abundances typically found in these deposits, they can carry the majority of the potentially hazardous metals in waste. It has also been determined that mixtures of sulphides can undergo galvanic interaction that results in preferential dissolution of certain sulphides over others (Kwong, 1993; Kwong et al., 2003). Many hydrothermal Au deposits are accompanied by As in arsenopyrite or arsenical pyrite, rarely considered a commodity, but often an environmental concern due to relatively high toxicity and mobility. Thallium, Hg and Cd, all considered toxic at low concentrations, are also present in some sulphide and sulfosalt minerals that can accompany sulphide deposits.

3.2. Other primary minerals

The second subgroup of primary minerals in mine waste includes those that provide acid neutralization capacity and/or control the major element composition of drainage waters. Some of these minerals are reactive in the mine waste weathering environment such as carbonate minerals that dissolve to limit acid generation, and primary clay minerals that release Al and adsorb metals and metalloids released from oxidizing sulphides. Others include those minerals in the "gangue" or "substrate" that, in many cases, remain inert to the chemical processes of mine waste weathering, mainly due to kinetic barriers preventing their participation in metal release and attenuation reactions on a time scale relevant to mine waste management.

For a given waste material this substrate will contain a continuum of minerals that vary in their degree of reactivity with mine waters. Some minerals will remain relatively inert in contact with the mine waste fluids, others will react slowly, and others will react more quickly. As porewater chemistry evolves, the rates of reaction and types of reactions may change for certain minerals. As with the metal-bearing source minerals, surface areas as well as the reaction rate are critical factors in determining the degree to which an individual mineral influences porewater chemistry. Congruent dissolution reactions result in the stoichiometric release of solutes to porewater, whereas incongruent dissolution reactions produce secondary weathering products as well as releasing solutes to porewaters. These substrate minerals can provide surfaces for other secondary mineral precipitates and biofilms that can influence mine water chemistry (e.g. Denef et al., 2010). Dissolution of substrate minerals also releases ligands such as carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) to solution, which can strongly affect the mobility, bioavailability, and toxicity of metals and metalloids in mining environments (Smith and Huyck, 1999).

In the context of ML/ARD, carbonates traditionally have received the most attention as a result of their recognized importance in providing neutralization capacity. In fact, it is often noted that silicate minerals provide the greatest overall source of acid neutralization in the natural environment. However, significant kinetic limitations exist in the ability of such reactions to effectively neutralize acid generation from sulphide oxidation in mine wastes, which occurs at rates generally orders of magnitude greater than the silicate neutralization reactions (Jambor, 2003).

The carbonate minerals play an important role in limiting acid rock drainage because their reaction rates (and especially that of calcite) can rival that of sulphide oxidation. As mentioned above, Fe(II)-bearing carbonate minerals such as siderite, ankerite and ferroan dolomite will provide limited NP (in proportion to the non-Fe carbonate fraction present) due to acid generated by the ultimate oxidation and hydrolysis of Fe(II). Characterization using static test methods does not necessarily capture this effect, and the result can be an overestimation of NP, which may result in inadequate design for mine waste management and costly consequences (Jambor, 2003). Identification of specific carbonate minerals present and adjustment of predictive test results accordingly is recommended.

Manganese (II)-bearing carbonates such as rhodochrosite and mangian calcite and dolomite will release oxidizable Mn(II) on dissolution. In the presence of Mn oxidation and hydrolysis similar acid generation (and no net neutralization) can result. However, Mn tends to oxidize much more slowly than Fe and can persist in reduced form even at ambient surface conditions (Morgan, 2005). Thus, unlike Fe carbonates which generally provide no net NP, Mn carbonate fractions have the potential to provide NP where Mn(II) oxidation is inhibited. Under such conditions, elevated dissolved Mn would be expected to be present.

Should they dissolve in mine waters, silicate minerals normally provide limited neutralization, although they may affect drainage in other ways. Jambor (2003) tested the NP of silicate minerals from the feldspar, pyroxene and amphibole groups and showed that they contribute very little NP, using the standard Sobek NP determination, and emphasized the low potential for most silicates and aluminosilicates to provide effective neutralization except in particularly low sulphide oxidation regimes, or for specific rare mineral cases where reactivity was sufficient to provide some effective NP. Careful examination of the mineral specimens tested indicated that where NP was apparently high, trace amounts of carbonate minerals were present. Wollastonite and olivine were the only silicates of 80 specimens tested that provided non-negligible NP, although there was some indication that serpentine could be important. In some cases, compositional variation within a solid solution is a factor: fayalite-rich olivine would contribute oxidizable Fe(II), and anorthite-rich plagioclase is known to dissolve more rapidly than the more sodic members of the solid solution (Stillings and Brantley, 1995; Jambor, 2003).

Beyond the scope of their contribution to acid neutralization, silicate minerals may also have important influences on mine water composition. Dissolution of aluminosilicates under acidic conditions is the main source of Al in mine drainage, which may pose a risk to aquatic ecosystems (Soucek et al., 2001). Rollo and Jamieson (2006) showed that dissolution of serpentine and gypsum resulted in Mg–Ca–SO_4-bearing mine waters with pH values from 7 to 8 in the kimberlite fines containment facility at Ekati Diamond Mine, NWT, Canada. Lee (2005) reproduced this reaction in a laboratory-scale ball mill using Ekati kimberlite mixed with the water used at the mine for crushing in the processing plant. In less than an hour, the pH, alkalinity, Mg and Ca increased so that the solution resembled process plant discharge waters, demonstrating that the reaction probably takes place during processing. Under the conditions present in the Ekati processing plant, serpentine dissolves rapidly. In another example, Sidenko et al. (2005) described how hydrothermal illite was partially transformed to smectite during cyanide leaching of a gold ore pile at pH > 10. After the mine closed, oxidation of pyrite decreased the pH, and the smectite became unstable, forming kaolinite. Over time, further increases in acidity resulted in the dissolution of kaolinite, thereby generating elevated concentrations of Al in the drainage water (up to 100 mg/L), interfering with the operation of the water treatment plant.

3.3. Compounds produced by ore processing

Often overlooked is the third type of solid phase present in mine waste, compounds created during ore processing (Table 2). These phases should not be considered minerals because their origin is clearly anthropogenic and deliberate rather than accidental (Jambor and Blowes, 1998), yet these compounds can influence the environmental impact of mine waste and thus need to be included in mine waste "mineralogy." In some cases such phases have mineral counterparts in nature and for others equivalent minerals in nature may not exist.

Ore processing may introduce new solid compounds, chemical reagents, and fluids to mine waste environments. The introduction of the fluids can lead to formation of additional secondary minerals. Also, some modern mining practices designed to reduce environmental impact, such as mill water re-circulation, can increase metal concentration and secondary mineral precipitation.

An example of this group of materials is found in the metallurgical pre-treatment of refractory Au ore, where the precious metal is hosted mainly in arsenopyrite and arsenical pyrite. In these instances, ore roasting or pressure oxidation are used to decompose the sulphides to facilitate gold extraction via cyanidation. In the case of roasting, transformation of the sulphides (e.g. pyrite and arsenopyrite) takes place leaving porous Fe oxides, typically maghemite and hematite, and allowing effective extraction of the gold with cyanide (Walker et al., 2005). In roasting such As-bearing materials, as was the case at Giant Mine, near Yellowknife, NWT, some of the As is volatilized and condenses as As trioxide, a relatively soluble and toxic form of As. Although a significant amount of As trioxide was released through the roaster stack during the early years of operation, contaminating the local environment, improved emission controls resulted in the capture and underground storage of almost 300,000 tonnes of As trioxide (Bromstad and Jamieson, 2012). Some of the remaining As is incorporated into the roaster-generated Fe oxides so that they contain as much as several weight percent As. Antimony is also volatilized from stibnite and sulfosalts in the roaster and associated with roaster-generated Fe oxides in mine waste. Volumetrically small quantities of mineralogically complex As- and Sb-rich fines from electrostatic precipitator dust are also present in the tailings. As a result, much of the potentially toxic elements As and Sb in the tailings are hosted in oxide form rather than the primary sulphide phases of the ore. The optimal remediation of this site in the future needs to ensure that these materials are not placed in a reducing environment where they may destabilize and undergo reductive dissolution, possibly releasing As and Sb to solution (Fawcett and Jamieson, 2011).

Other examples of ore processing compounds co-deposited with tailings are S and natrojarosite (Al et al., 1994; Steel et al., 2010). Sludge from on-site water treatment plants may also be co-deposited. Treatment of acid mine drainage tends to produce sludges dominated by gypsum and Fe oxyhydroxide (Beauchemin et al., 2010), whereas treatment of effluents containing high levels of As generates a range of As-bearing precipitates including scorodite, ferric arsenate and arsenical ferrihydrite (Paktunc et al., 2008).

The pyrometallurgical processing of metallic ores produces two main types of slag: (1) ferrous slags from Fe and steel manufacturing, and (2) non-ferrous slags from the recovery of base metals (Cu, Ni, Pb, Zn) and some precious metals (Ag). The smelting process produces a wide range of different mineral and glass phases that influence the environmental impacts of slag, and its reuse as a valuable by-product. The most common phases in ferrous slags are Ca-rich olivine-group silicates, melilite-group silicates that contain Al or Mg, Ca-rich glass, and oxides. In non-ferrous slag, silicates in the olivine, pyroxene, and melilite groups, as well as glass, spinels, and SiO_2 (i.e., quartz and other polymorphs) are the most common phases (Piatak et al., 2015). In general, base metal slags contain higher concentrations of potentially toxic trace elements as compared to ferrous slags, and may also host sulphides and small prills of metallic Cu, Pb, Cd and other elements. Detailed characterization of slag mineralogy, surface area, dissolution kinetics, and field weathering conditions are required to predict the long-term (i.e. tens to hundreds of years) reactivity of these metallurgical wastes (Parsons et al., 2001).

Another example of compounds synthesized as a result of processing can be found in Jambor et al. (2009), who discovered cyanide-bearing compounds formed in Au mine tailings mixed with organic-rich lake sediments; these compounds included $Fe(III)_4[Fe(II)(CN)_6]_3$, commonly known as Prussian Blue. These authigenic cyanide precipitates contained significant amounts of Ni, Cu, and Zn. These cyanide compounds are also observed on spent heap leach pads (Sidenko et al., 2005). This latter example further emphasizes the challenges in categorizing minerals because on one level these may be considered secondary minerals formed subsequent to deposition in the tailings impoundment. For our purposes they are grouped with processing related phases because process-added cyanide is required for their formation.

In cases where metallurgical ore processing largely involves physical separation (e.g. gravity) mineralogical alteration and production of new metal-bearing phases such as those described above may be minor or non-existent. However, failure to consider the potential effects of mineral processing on tailings and identification of special mine waste streams with unique mineralogy can lead to incorrect direction of resources for effective assessment of drainage quality and proper waste management.

3.4. Secondary minerals formed from weathering in the mine waste environment

This group of minerals has probably received more attention in the literature of mine waste than any other. Typically, these form as in-situ relic reaction rims around sulphides and other minerals via incongruent dissolution processes, or as precipitates due to evapoconcentration or mixing of chemically distinct mine waters and porewaters. Given the high concentrations of Fe and SO_4 produced from pyrite and pyrrhotite oxidation, it is not surprising that the list (Table 3) includes many Fe oxyhydroxides and sulphates; however, secondary carbonates, sulphides, silicates and oxides may also form (Alpers et al., 1994; Nordstrom and Alpers, 1999; Lottermoser, 2010).

As Fe oxyhydroxides and other secondary minerals form in waste impoundments they can lead to reductions in sulphide oxidation rates by limiting oxygen diffusion to sulphides and, with prolonged weathering, can lead to the development of near-surface hardpans. More specifically, at circum-neutral pH, sulphide oxidation rates may decline over time due to development of relict Fe oxyhydroxide rims which limit oxygen diffusion to the reacting sulphide surface (Nicholson et al., 1990; Huminicki and Rimstidt, 2009; DeSisto et al., 2011). Thus it can be inferred that at mine sites with long lag times to acid development, relatively short duration kinetic testing programs may predict more rapid sulphide oxidation rates than may actually exist at a later time. It is also unclear whether the high flushing rates used in humidity cell experiments may be aggressive enough to disperse Fe colloids and prevent or limit the formation of such diffusion-limiting rims. For PAG materials or those of uncertain ARD character, this may have important implications for at least the timing of acid onset and perhaps ultimately on whether drainage becomes acidic or not. Sorption of metals on the developing Fe oxyhydroxides may also decrease the net release of metals from pyrite or pyrrhotite in the field more rapidly than predicted from the relatively short-term operation of humidity cells (months or years).

Secondary minerals can form spectacular stalactites from dripping mine drainage such as the colourful collection of Fe sulphates found underground at the Richmond Mine, Iron Mountain, CA (Jambor et al., 2000). In other places, the precipitates may be very fine-grained but widespread and intense in colour such as the red Fe oxyhydroxide precipitates typical of neutralized acid mine drainage, white precipitates of Al oxyhydroxide and sulphate minerals, and yellow jarosite.

The precipitation of secondary minerals can limit the aqueous concentrations of metals, although not necessarily to levels that are low enough to meet environmental guidelines. For example, waters co-existing with Fe sulphate secondary minerals at Iron Mountain and Rio Tinto have very high metal concentrations, with up to 4760 mg/L Cu, 111,000 mg/L Fe, and 23,500 mg/L Zn present in pH -2.5 waters in contact with rhomboclase and römerite at Iron Mountain (Hudson-Edwards et al., 1999; Nordstrom and Alpers, 1999). Moreover, these soluble Fe sulphate minerals are amongst those secondary phases responsible for the "first flush" phenomenon, where precipitation or sudden runoff after a dry period results in dissolution of secondary minerals and release of metals and metalloids to surface and ground water (Nordstrom, 2009).

In other cases, however, secondary minerals play an important role in attenuating potentially toxic elements. The precipitation of Fe oxyhydroxide phases with high surface area provides increased capacity for adsorption both in situ and in environments downstream of mining activities. Arsenic adsorbs effectively to Fe oxyhydroxides, and if concentrations are sufficiently high, As may form Fe arsenate secondary minerals at acidic pH or Ca–Fe arsenates at circum-neutral pH (e.g. Drahota and Filippi, 2009; Walker et al., 2009). Although these reactions can attenuate a large fraction of the As in As-rich systems, dissolved concentrations may still be elevated depending on the solubility of specific secondary minerals present. In particular, where conditions favour precipitation of amorphous hydrous ferric arsenates, the relatively high solubility of these phases in comparison to more crystalline counterparts may lead to elevated As concentrations unless Fe oxyhydroxides are also present in sufficient abundance to limit As mobility by sorption to these high surface area phases (Krause and Ettel, 1989). In addition, the colloidal nature of the secondary crystalline and amorphous Fe oxyhydroxide and Fe arsenate particles provides a further vector for metal mobility in surface and ground water if water chemistry and flow conditions promote dispersion of the colloids (Zänker et al., 2002).

Identification of these secondary minerals provides information on the aqueous conditions under which they form (i.e., pH, redox, metal and sulphate concentrations). Changing conditions may result in their dissolution or transformation into other solid phases (e.g. dehydration, oxidation) which, in turn, affect the composition of co-existing water. For example, dissolution of Fe(II)-bearing sulphate minerals may result in Fe oxidation and hydrolysis which releases hydrogen ions and affects pH. Dissolved Fe(III) is also a powerful oxidizing agent with the potential to trigger additional sulphide oxidation. Sulphate released from sulphide oxidation has an important influence on ionic strength, and can form aqueous complexes with metals that influence their mobility and bioavailability. As another example, the precipitation of Fe(III) oxyhydroxides provides sorption surfaces that attenuate potentially toxic elements from solution. The extent of sorption depends on the identity and surface characteristics (particularly surface area) of the Fe oxyhydroxide mineral, and solution chemistry (especially pH). Upon development of increasingly acid conditions the mobility of many metals increases due to pH-driven desorption from mineral surfaces and eventually through dissolution of the sorbent itself (i.e. Al, Fe, and Mn oxyhydroxides).

For modern mining, one of the most important reasons to understand the mineralogical nature of mine waste weathering products is to assess the long-term stability of these secondary minerals. If tailings or waste rock have partially oxidized and remediation plans call for relocation or a change in disposal conditions, it can be very useful to predict whether metals will be released or pH will change as a consequence. One relatively common possibility is where secondary minerals formed as a result of sulphide oxidation are reburied or flooded and may subsequently undergo destabilization or perhaps even reductive dissolution, releasing metals or metalloids to pore water and potentially affecting the downstream environment.

In addition to their influence on the composition of mine waters, the identity and character of secondary minerals has a profound effect on risk associated with the direct ingestion or inhalation of dust and fine particles from mine waste and soil contaminated by mining activities (Plumlee and Morman, 2011). In general, primary metal sulphides tend to be lower in bioaccessibility in comparison to their weathering products. Whether a metal is hosted as a sulphide or a non-sulphide has environmental consequences. For example, in ore deposits Pb is most commonly hosted in galena (PbS). Although dissolved Pb is relatively toxic, it is not very mobile due to the low solubility of galena and anglesite ($PbSO_4$, the secondary mineral likely to form in acid drainage), and the tendency for Pb to be attenuated through adsorption on Fe oxyhydroxide and other mineral surfaces. However, in circumneutral, oxidizing environments, Pb may be hosted in the Pb carbonate minerals cerussite ($PbCO_3$) or hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], either through weathering of galena in mine waste or through oxidation of the sulphide ore at some point in its geologic history. Lead carbonate is more soluble and represents a different type of environmental risk than Pb sulphide. The Pb in cerussite is highly bioaccessible if orally ingested (close to 100%) as it dissolves readily in acidic gastric fluids, like most carbonate minerals, whereas the oral bioaccessibility of Pb in galena is less than 10% (Casteel et al., 2006).

4. Analytical methods for mine waste mineralogy

4.1. What do we need to know?

Mineral identity is important but not the only useful information derived from the mineralogical examination of mine waste. In fact, it can be difficult to differentiate within certain groups of minerals and pinpoint the exact minerals present. Identifying which member or members of these mineral groups are present at a particular site may be required to predict their long-term stability, to determine how incorporation of potentially toxic elements varies from one mineral to another (e.g. Jamieson et al., 1999), or to guide modelling.

An understanding of the local environmental conditions may provide guidance in identification. Fine-grained yellowish masses of copiapite resemble jarosite but are unlikely to form except under very low pH conditions (Jamieson et al., 2005a). Schwertmannite is most likely to form at pH values between 2 and 4 in the presence of elevated dissolved SO_4, whereas ferrihydrite and goethite are more likely to form at higher pH values (Bigham and Nordstrom, 2000). However, relating mineral precipitates to measured Eh and pH under field conditions can be misleading because many of these mineral precipitates age over time and may not be in equilibrium with co-existing water. Sulphates that precipitated from mine drainage hydrate and dehydrate rapidly, and can transform over the course of a day due to changes in temperature and relative humidity. The mineral analyzed in the lab may not be the one collected in the field (Chou et al., 2013).

Mineral chemistry, meaning the chemical composition of the solid phase, can be an important focus of mine waste mineralogy. Differentiating carbonate minerals or measuring the amount of Fe(II) in dolomite or ankerite provides insight into the neutralization capacity of these minerals, as explained earlier. Analysis of the trace elements in sulphides is important because these may be released through oxidation and dissolution and often cause the most serious impact. Locating and quantifying the minerals that sequester potentially toxic elements aids in prediction and risk assessment.

Particle size is a very important aspect of mine waste mineralogy in terms of both element mobility in the environment and health risk assessment. This is equally important for both sulphides and for the minerals providing neutralization including carbonates, and perhaps to a greater extent silicates and aluminosilicates, where high surface areas may substantially increase reaction rates. Particles with high surface area, including partially altered grains, may provide a large influence on mineral–water interactions that is not obvious without detailed analysis at a fine scale. Iron oxyhydroxides in mine waste systems and primary and secondary clay minerals have high surface areas and are likely to provide an important control on mineral–water reactions. From a human health risk perspective, not only are tiny particles more likely to be ingested or inhaled, but their reactivity and mobility are enhanced by a smaller grain size. Many mine waste precipitates are either colloidal or nanocrystalline, characteristics which have significant effects on their behaviour (Hochella et al., 1999). Additional aspects of mineral texture such as porosity, surface area (normally a function of particle size) and the presence of rims or coatings, may be important to characterize.

A comprehensive understanding of mine waste mineralogy provides the key to interpreting predicted or observed drainage quality and improving human health and environmental risk assessments. Comprehensive mine waste characterization includes a description of the assemblage of minerals present along with textural and chemical information. With regard to ML/ARD, the characterization of acid-generating and acid-neutralizing minerals, the potential of galvanic interaction between multiple oxidizing sulphide minerals, and the presence of highly soluble phases are of prime importance. The bioaccessibility of contaminant-hosting minerals is essential knowledge for assessing risks to ecosystems and human health.

4.2. Bulk analysis of mine wastes and mineral samples

If a monomineralic sample can be acquired or separated, the chemical composition can be analyzed using the following methods, many of which are normally applied to rock or soil samples. Such bulk analytical methods can be divided into non-destructive and destructive methods. Non-destructive methods are those that do not involve dissolution of solid sample.

X-ray fluorescence (XRF) is a well-established technique for elemental analysis. Primary radiation from an electrically excited X-ray tube is used to generate characteristic "secondary" X-ray emissions from an element in a sample. The intensity of these secondary X-rays is roughly proportional to the concentration of the corresponding element in the target area. Desktop units are practical for field labs and portable handheld units may be used in the field. Although detection limits may be higher than some other analytical methods, the concentrations of potentially hazardous metals in tailings and mining-contaminated soils are still likely to be higher than these detection limits (Peinado et al., 2010). Portable instruments are most useful as rapid (as fast as 30 s per analysis) screening tools for elemental analyses to locate metal-enriched areas and to design a sampling program for detailed mineralogy. However, recent studies have shown that care must be taken in calibrating the instruments, analyzing the samples, and interpreting the results (Hall et al., 2014). Haffert and Craw (2009) described the application of portable XRF in analyzing As in tailings, roaster waste, and contaminated soil in the vicinity of an abandoned gold ore roaster site in New Zealand. The As concentrations were correlated with the presence of arsenolite and scorodite and these results contributed to risk analysis.

X-ray diffraction (XRD) is a well-established technique that has been widely applied to mine waste mineralogy. Matching diffraction patterns obtained from a given sample against a database with patterns from thousands of mineral and industrial compounds is a powerful method of mineral identification. X-ray diffractometers are commonly found at universities and in some government and commercial laboratories. Newly-developed handheld XRD units provide an option of field identification of sensitive samples that may not survive transport to a laboratory (Peterson, 2011). Using the Rietveld approach for interpretation of XRD data, the relative amounts of crystalline phases present in a mine waste sample can be evaluated (Raudsepp and Pani, 2003). In some cases, XRD can also provide information on solid-solution compositions. The main limitation of this technique is that it is very difficult to successfully identify minerals that make up less than a few percent of the entire sample. Moreover, poorly crystalline and amorphous materials, typical of many secondary mine waste phases, do not diffract well. In Rietveld XRD, the quantity of amorphous material present can be estimated by including a known quantity of a crystalline standard, although this does not actually identify the amorphous material. In addition, the optimum selection of a suitable standard may not be straightforward because the standard introduces additional peaks in the XRD pattern that may obscure other phases, particularly those in low abundance. Rietveld XRD is often used in mine waste characterization to distinguish carbonate minerals (Raudsepp and Pani, 2003), but EPMA or SEM–EDS may be required to discern carbonate type(s) when in low abundance (e.g. <1 wt.%), or identify the amount of Fe or Mn in Ca–Mg carbonates. As explained below, a microfocused X-ray beam can overcome some of these challenges.

A useful, though not readily available, approach to the identification of mine waste minerals across large areas involves airborne or satellite-based sensors that measure reflected light from mine sites, such as NASA's Airborne Visible/Infrared Imaging Spectrometer (AVIRIS). Swayze et al. (2000) used AVIRIS imaging spectroscopy as a screening tool to rapidly distinguish weathered mine waste zones rich in jarosite (and associated with acidic drainage) from zones rich in goethite at the California Gulch Superfund Site near Leadville, CO. Similar methods have been used to remotely map mine waste mineralogy, surface acidity, and the success of reclamation programs at base metal, gold, and uranium mine sites across Canada (White and Abuelgasim, 2013) and at massive sulphide deposits in Spain (Buzzi et al., 2014).

Destructive methods are those that involve dissolution, combustion or fusion of the mineral sample followed by analysis of the resulting solution or gases. If a complete elemental analysis is desired, total or near-total dissolution by strong acid mixtures is the typical course, followed by analysis of the resulting solution by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectroscopy (ICP-MS).

A useful option which can provide information on the mobility of potentially toxic elements is partial dissolution. Some methods used for mine waste mineralogy originated from geochemical exploration techniques and are designed to elucidate the mineral host and the ease with which an element can be leached from a sample. These are more typically applied to crushed rock, soil, or sediment samples, but are designed to be element-selective and provide insight on mineralogy. Sequential extraction involves subjecting a sample to successive chemical extractions with reagents of variable selectivity under specified conditions (Hall et al., 1996). Corriveau et al. (2011a) described the application of a sequential extraction scheme that was optimized for As in mine waste by testing several pure As minerals (arsenopyrite, scorodite and yukonite). Petrographic and synchrotron-based microanalysis of the samples to which this scheme was applied showed that there was general agreement between the As-hosting phases that were directly observed and those indicated from the sequential extraction. In a similar study, Kim et al. (2003) used both sequential extraction methods and X-ray absorption fine structure (XAFS) spectroscopy to determine Hg speciation in Au mine tailings.

Simulated body fluids can also be used for partial dissolution tests to evaluate the bioaccessibility of elements in the human gastric, intestinal or pulmonary systems. This information is useful for estimating the risk to human health associated with ingesting or inhaling particles of mine waste. In general, the same mineral will behave differently in acid gastric fluids as compared to pH-neutral lung and intestinal fluids (Plumlee and Morman, 2011).

Particle-size analysis provides important information on mine waste materials, including the potential reactivity, movement of gases and liquids, and likelihood of ingestion or inhalation. Several techniques taken from soil science can be used, although an important consideration is that the primary particle size distribution in mine waste is governed by grinding, blasting and disposal techniques and modified later by weathering and other pedogenic processes. The MEND prediction manual (Price, 2009) describes various techniques for grain size analysis, notably dry and wet sieving and differential liquid settling. Techniques that involve immersing or rinsing samples carry the risk that relatively soluble phases such as Fe sulphate minerals may be lost. Clumping and cementation that results from secondary mineral precipitation have an important influence on particle size, particularly in the upper layers of reactive tailings. The degree to which these are disaggregated prior to analysis will depend on the objective of the characterization.

Particle surface area directly influences reactivity, particularly oxidation rates and adsorption capacity. In mine waste samples, it is often difficult to separate the phases of interest (sulphide minerals, Fe oxyhydroxides) to measure this parameter by conventional gas absorption methods (BET, or Brunauer–Emmett–Teller method), which on an unseparated sample provide an aggregate rather than mineral-specific surface area. An alternative approach is to use SEM-based image analysis software, including but not restricted to software such as QEMSCAN (Quantitative Evaluation of Materials by Scanning Electron Microscopy) and MLA (Mineral Liberation Analyzer), both discussed below, which can provide size and shape data on selected phases.

4.3. Microanalysis of individual grains

Mine waste samples are almost always mineral mixtures, and therefore thorough mineralogical characterization usually requires methods to analyze individual grains. Target grains may be any of those discussed previously, but are often primary sulphides (in order to analyze trace elements and characterize the degree and nature of oxidation) or secondary minerals. In many cases, the minerals of interest are present in minor or trace amounts and thus the grains must first be located and then analyzed. For example, a weathered tailings sample with a total Pb concentration of 2000 mg kg^{-1} could have 10 or fewer grains of galena and even fewer alteration products such as anglesite or cerussite in a single thin section, depending on grain size. More highly weathered mine waste samples will tend to have the elements of interest distributed amongst a larger number of secondary phases, including Fe and Mn oxyhydroxides and clays on which the metal is adsorbed. Identifying the presence of high surface area phases may support inferences on sorption-limited mobility or sorption modelling exercises. Surface-sensitive analytical techniques can be used to directly characterize the molecular-scale processes that control the speciation of contaminants at mineral surfaces, which is essential for predicting their environmental behaviour, i.e. their stability,

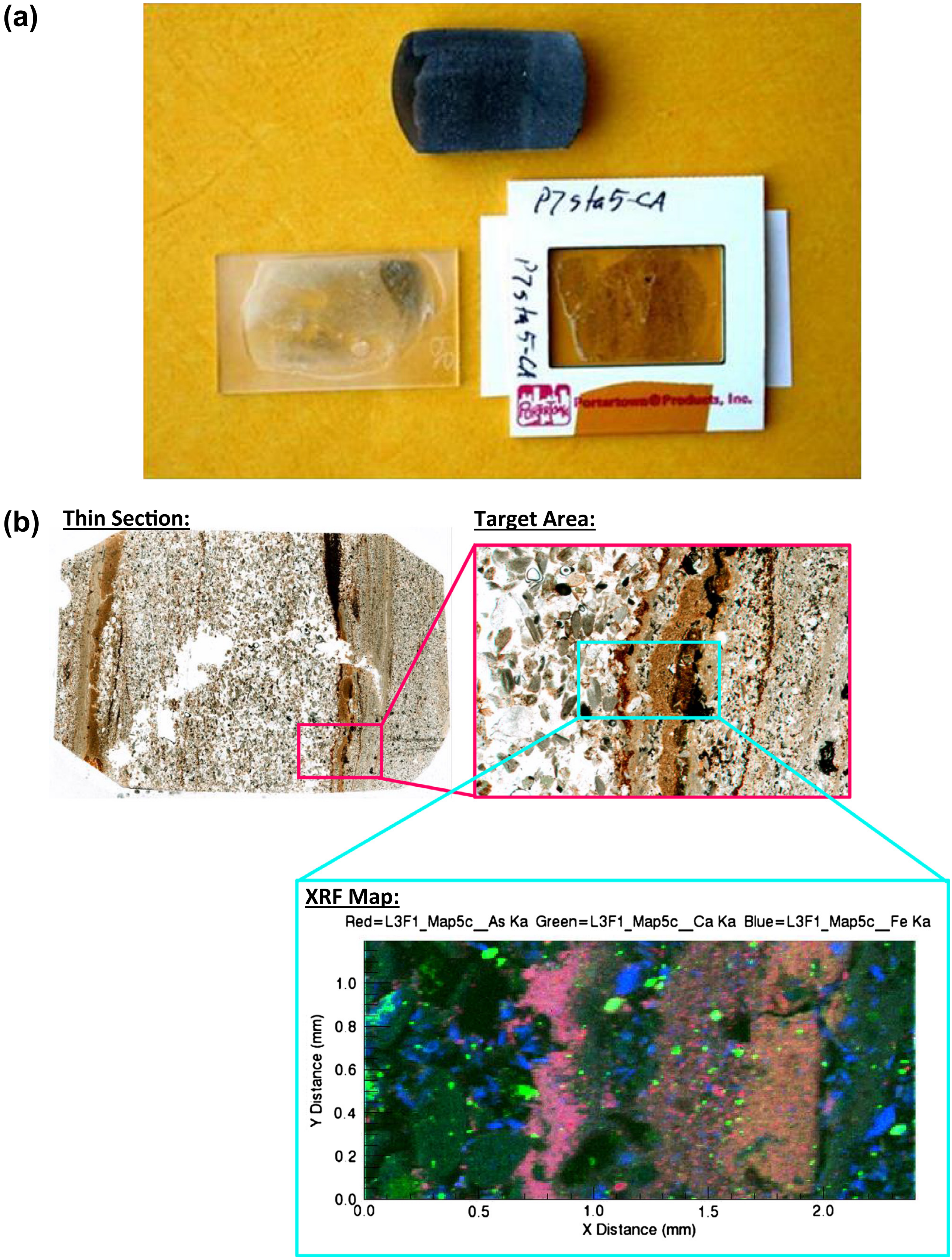

Fig. 1. (a) Geological samples prepared for synchrotron microanalysis. At the top of the photograph is an epoxy-impregnated mine tailings sample, at the lower left, the doubly polished thin section, and at the lower right, the sample removed from the glass slide and mounted on Kapton® tape. (b) Optical scan of a thin section of cemented tailings, and a red–green–blue (RGB) μ-XRF map of the area indicated (from Jamieson and Gault, 2012, used with permission).

mobility, toxicity, and potential bioavailability (Brown and Sturchio, 2002).

Preparation of thin sections, which are useful for many microanalytical techniques, may require special consideration of highly soluble phases such as Fe sulphates and those sensitive to dehydration or other changes during heating. If possible, sections should be prepared using kerosene or a similar non-aqueous grinding fluid, and heating should be avoided. Epoxy which sets at low temperature can be used for impregnating unconsolidated samples before thin sections are made. Fig. 1 shows an example of a polished thin section of cemented tailings used for petrography, SEM, and then “lifted” using acetone and mounted in Kapton® tape for synchrotron-based microanalysis.

Optical petrography using both transmitted and reflected light is a valuable mineralogical tool, particularly in the hands of an experienced observer. Readily discerned are textures associated with weathering sulphides, such as corroded borders and evidence of dissolution along fractures. Secondary precipitates are recognizable as rims and coatings, but may be difficult to identify by petrography alone. The presence and type of carbonate minerals can be distinguished, although chemical microanalysis may be required for verification.

Electron probe microanalysis (EPMA) provides quantitative chemical analysis with high spatial resolution such that grains or grain rims only a few micrometres in thickness can be analyzed. Careful analysis of this type is particularly valuable when similar

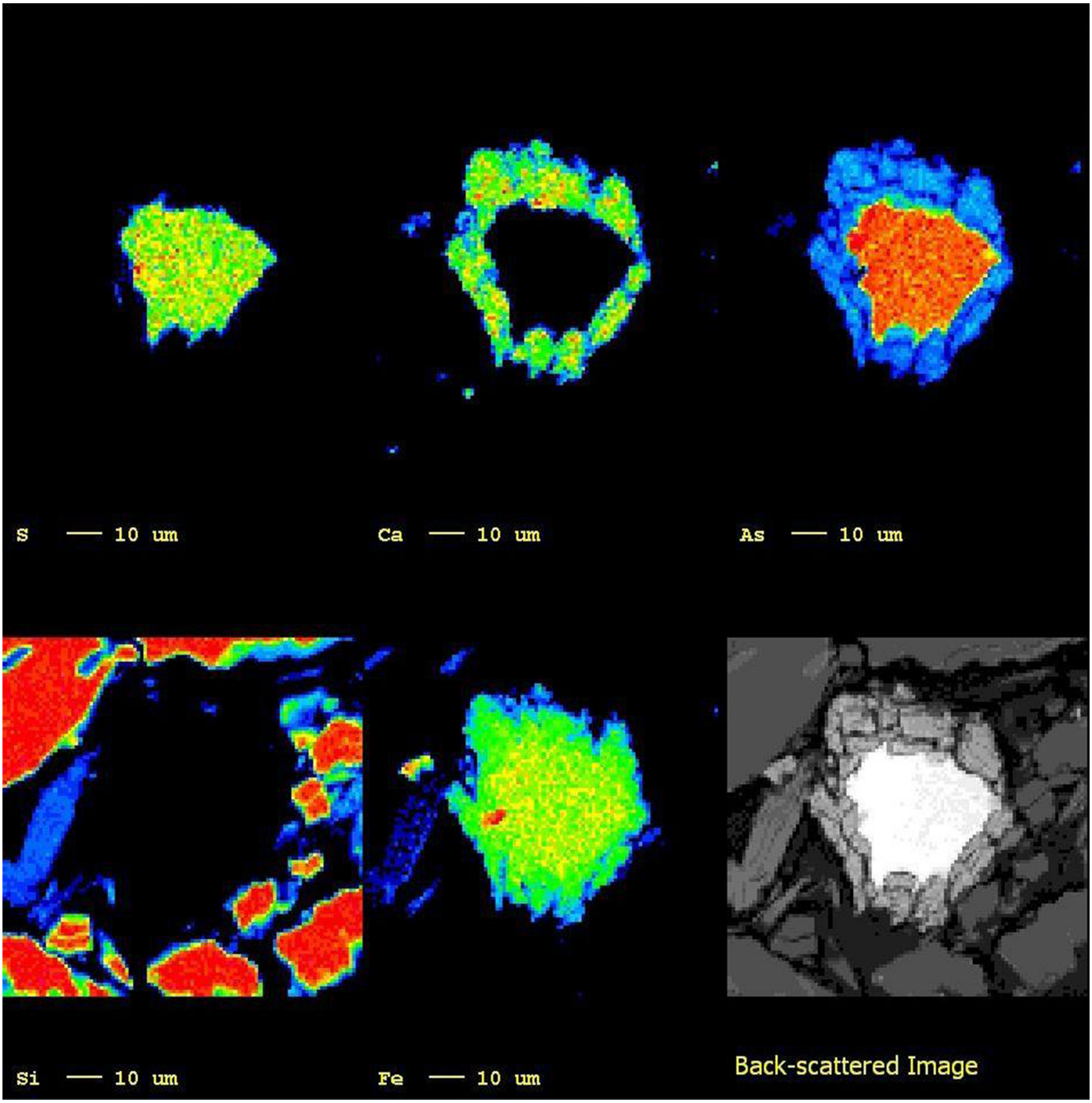

Fig. 2. Element maps and backscattered electron photomicrographs from EPMA analysis of a grain of arsenopyrite with alteration rims of As–Ca-bearing iron hydroxide (from Corriveau et al., 2011a, used with permission).

phases need to be distinguished. For example, scorodite, hydrous ferric arsenate, and As-bearing ferric oxyhydroxide can be differentiated based on relatively small differences in their Fe/As ratios (Paktunc et al., 2008; DeSisto et al., 2011). With EPMA, it is usually possible to accurately analyze trace elements at concentrations as low as a few hundred ppm. Some carbonates and hydrous secondary minerals may dehydrate under the electron beam, necessitating the use of lower beam currents or larger spot sizes. Element mapping (Fig. 2) can be used to document the mobility of elements during weathering and chemical zoning within minerals.

Scanning electron microscopy (SEM) has proved to be a very valuable method of characterizing mine waste minerals. It is closely related to EPMA in that an electron beam is focused on a sample grain and produces secondary electrons and characteristic X-rays. However, the SEM is optimized to provide high-resolution images rather than quantitative analysis and the detection limit for trace elements is higher than EPMA. Backscattered electron (BSE) imaging is particularly useful because the brightest grains in the field of view are those with the highest average atomic number. This means that sulphide grains, including partially oxidized pyrite, pyrrhotite and ore minerals will "stand out" and be relatively easy to find, even in a fine-grained tailings sample (Fig. 3). Semi-quantitative spot or area chemical analyses can be obtained quickly using energy-dispersive spectroscopy (EDS) and may be useful in identifying minerals. Unless the SEM is fitted with a wavelength-dispersive detector, trace elements may be difficult to discern. Perhaps the most powerful aspect of SEM imaging is the ability to examine textures such as intergrowths, rims, and replacement textures and interpret reactions from this information. Instruments that use a field emission gun as an electron beam source generally provide higher resolution images than those that use a tungsten filament. Secondary electron images depict surface morphology including, for example, dissolution and precipitation textures and the presence of biofilms and bacteria. Some SEMs (including the ESEM or "environmental" SEM) allow examination of the sample in a chamber at low vacuum, allowing wet samples to be used. This also makes it possible to obtain SEM images on samples that have not been coated with carbon or another electrically conductive material, which is normally done to prevent charge buildup. This may be useful if one plans to conduct further examination of the sample using other techniques where the coating would interfere. However, low vacuum operation and uncoated samples generally do not produce high quality SEM images.

"Automated mineralogy" software such as QEMSCAN (Quantitative Evaluation of Minerals by SCANning electron microscopy) and MLA (Mineral Liberation Analysis) can enhance SEM characterization of mine waste. Although these packages were originally developed for metallurgical testing, environmental applications are growing due to their ability to characterize a variety of samples including fine-grained materials such as tailings, soil and contaminated sediments (Mermillod-Blondin et al., 2011; Pirrie and Rollinson, 2011; Redwan et al., 2013; Brough et al., 2013). Using the software, mineral grains are differentiated and identified based on their compositions. This allows for particle-by-particle

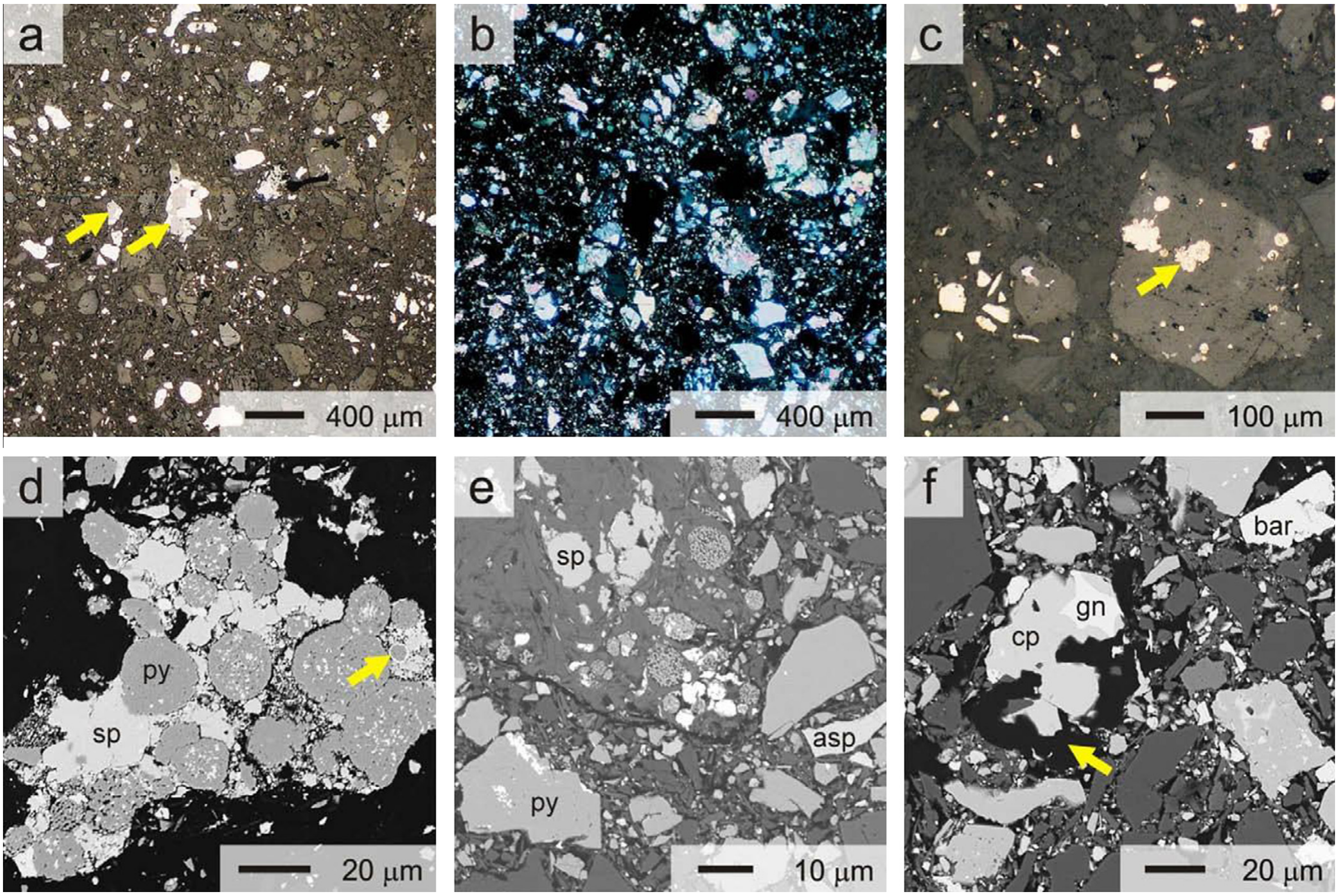

Fig. 3. (a) Photograph of a representative tailings thin section in reflected light and (b) transmitted light with polarizers crossed. (c) Reflected light image of dolomite grain containing framboidal pyrite inclusion at the arrow. (d) Backscattered electron (BSE) image of thin section showing colloform growth of anhedral sphalerite (sp) and framboidal pyrite (py), with galena replacement at the margin of a pyrite framboid indicated by the arrow. (e) BSE image showing euhedral pyrite with galena inclusions, arsenopyrite (asp), and grains of sphalerite, framboidal pyrite and galena contained within aggregated muscovite. (f) BSE image of intergrown chalcopyrite (cp) and galena (gn) with graphite (arrow), and barite (bar) (from Lindsay et al., 2009, used with permission).

quantification and provides information on the chemical composition, size, and shape of each particle. Complex particles with multiple mineralogical phases can be broken down into their components and identified. Bulk mineralogy or specific phases of interest can be targeted, and the relative percentages of solid phases present can be determined.

Transmission electron microscopy (TEM) offers the possibility of high resolution imaging, chemical analysis and electron diffraction at the micrometre to nanometre scale. Samples are typically prepared by embedding grains in epoxy and creating very thin samples using a focused ion beam. An EDS detector can be used to identify elements present and selected area electron diffraction (SAED) can be used to identify nanocrystalline minerals. Hochella et al. (1999, 2005) demonstrated how TEM provides identification and analysis of very fine-grained mine waste reaction products and also addressed the challenge of collecting detailed information from a very small portion of a large mine waste system, a problem of any high resolution approach (Fig. 4). Petrunic et al. (2006a, 2006b) described several examples where TEM was used to understand reaction mechanisms in tungsten and volcanogenic massive-sulphide mine waste.

Micro-XRD (μ-XRD) provides mineral identification by XRD at the grain scale by using a micro-focused X-ray beam. Laboratory based equipment is capable of in-situ XRD of discrete grains or areas in a sample using a micro-focused X-ray beam at between 50 and 500 μm spot size. Flemming (2007) described a range of applications of this technique including mineral identification in mine tailings (see also Flemming et al., 2005). Finer focusing, rapid

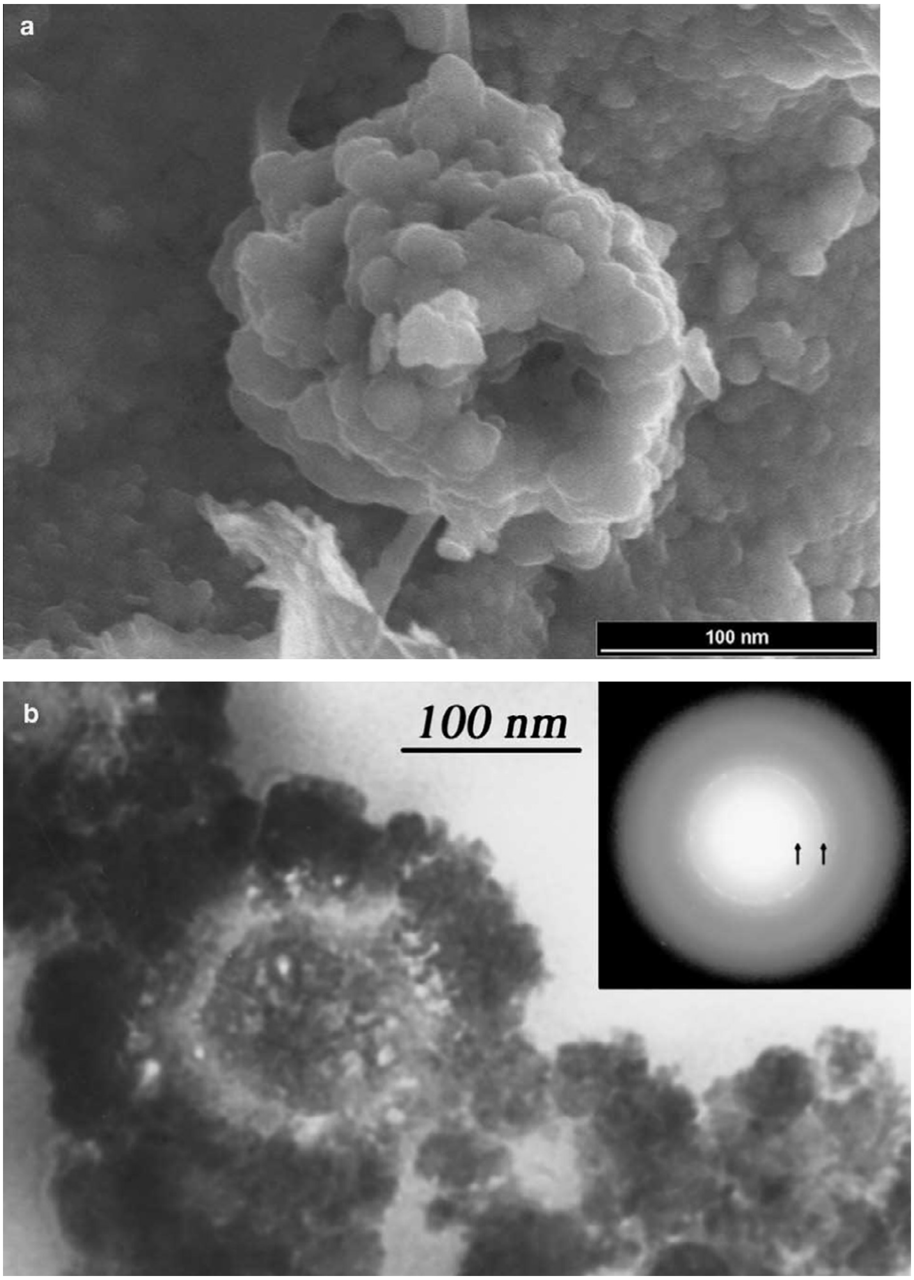

Fig. 4. (a) SEM image of a cluster of chalcopyrite crystals from a mining-impacted riverbed; and (b) TEM image of a similar occurrence of chalcopyrite crystals as (a). Crystals are as small as 10 nm and give a weakly spotted electron diffraction pattern (the inner arrow points to the 3.03 Å line, the outer to the 1.85 Å line of chalcopyrite; the 1.59 Å line is the very faint line just outside of this). Textural evidence suggests that these sulphides are secondary, growing in an anoxic riverbed environment (Hochella et al., 2005, used with permission).

data collection and greater diffraction intensity is obtained using micro-focused synchrotron sources.

Synchrotron methods: The availability of highly energetic, micro-focused, tunable X-ray sources at synchrotron facilities has provided a family of techniques for characterizing mine waste mineralogy both structurally and chemically. X-ray absorption spectroscopy (XAS) is now a well-established technique for obtaining oxidation states and short-range structural information for specific elements of interest in mine waste (Foster et al., 1998). Advantages include the ability to analyze hydrated samples in situ. XAS is a general term that includes XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure). XANES is used to determine oxidation state and coordination chemistry (e.g., octahedral, tetrahedral coordination) of the absorbing atom, while EXAFS is used to determine the distances, coordination number, and species of the neighbours of the absorbing atom. The choice of technique typically depends on the questions to be answered. Typically, XANES data are easier to interpret.

A "bulk" synchrotron beam gathers information from an area several mm in diameter and typically analyses a mixture of minerals. If appropriate standards or model minerals are analyzed with the unknown material, it is possible to identify the host phases and estimate the relative amounts of each phase in a mixture (Kim et al., 2003). Particular advantages of this technique include element selectivity and sensitivity and the ability to handle a wide range of element coordination environments from surface sorbed to crystalline forms (Brown and Sturchio, 2002). Some beamlines use focusing devices to produce micrometre-scale synchrotron beams that provide multiple grain-scale techniques (Lanzirotti et al., 2010; Jamieson and Gault, 2012). Poorly crystalline or nearly amorphous minerals such as Fe, Mn or Al oxyhydroxides that are difficult to differentiate using other techniques may be distinguished using synchrotron-based μ-XRD. Major and trace elements can be mapped using μ-XRF simultaneously with femtogram (10^{-15}) or attogram (10^{-18}) absolute detection sensitivities, allowing metals sorbed or bound on minerals to be characterized, and the nature of this association investigated in more detail with absorption spectroscopy (XAS) (Lanzirotti et al., 2010). Little sample preparation is required and thin sections used for petrographic examination or EPMA or SEM can be also analyzed by synchrotron microanalysis (Fig. 1). Typically the sample does not need to be in a vacuum.

Laser Ablation-Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS) combines the ability to use a finely tuned laser to sample successive layers of a mineral surface (typically the first few micrometres) with high resolution ICP-MS elemental and isotopic analysis. Considered a thin layer rather than a true surface technique, it is assumed that all the elements present in the sample material are removed and analyzed. This is a destructive technique in the sense that the target areas are ablated and cannot be revisited for EPMA or SEM analysis. Intensity signals can be converted to concentration by employing external standards and appropriate correction factors. Müller et al. (2002) used LA-ICP-MS to measure the amount of Cu, Pb, Zn and As absorbed on pyrite surfaces in remediated mine tailings to better understand the attenuation of solutes from the mine-tailings porewater. More recently, Parbhakar-Fox et al. (2013) used LA-ICP-MS in combination with XRD and SEM to investigate the mineralogical changes that influence leachate chemistry during kinetic tests for ARD prediction.

Raman microspectroscopy also requires little sample preparation and provides structural information at high resolution (typically 1 μm diameter). An advantage of Raman analysis is that only a bench-top unit is required. Courtin-Nomade et al. (2003) applied micro-Raman analysis to distinguish jarosite, lepidocrocite, goethite, hematite and other minerals in mine waste following examination by SEM and XRD. Hayes et al. (2009) collected element maps of tailings thin sections using synchrotron-based XRF, and then used micro-Raman to identify the phases associated with high metal concentrations. Levitan et al. (2009) used micro-Raman to distinguish between the serpentine minerals chrysotile and antigorite, which have similar XRD patterns, in asbestos mine waste. Knowledge of the nature and distribution of asbestos minerals at the site has implications for remediation plan design and understanding potential risks to human health.

Particle-Induced X-ray Emission (PIXE) can be used as a quantitative trace element method, particularly if a microfocused beam is employed (μ-PIXE). This method is similar to electron microprobe analysis in providing non-destructive, multi-element spot chemical analysis but the detection limits are lower (hence the ability to analyze trace elements) and the penetration of the proton beam is deeper, producing characteristic X-rays from below the surface. There are a limited number of PIXE facilities because a linear accelerator is required to generate the incident beam. Jamieson et al. (1999, 2005a, 2005b) used μ-PIXE to analyze As, Cd, Cu and Zn and other trace elements in Fe sulphate minerals precipitated from extreme acid mine drainage in the Richmond mine at Iron Mountain, California.

Mössbauer spectroscopy is typically used to evaluate Fe^{2+}/Fe^{3+} ratios in minerals. It can be applied to mixtures as well as amorphous or glassy materials (Wogelius and Vaughan, 2013). Given the importance of Fe in mine wastes, Mössbauer spectroscopy has the potential for application where Fe oxidation state is required for detailed characterization (e.g. Carlson et al., 2002).

X-ray photoelectron spectroscopy (XPS) measures the kinetic energy of electrons excited from their orbitals into the continuum and provides information on binding energy. Conventional or synchrotron-based X-ray sources can be used, with the latter providing the advantage of higher flux and tunable X-ray energy. Importantly, this technique is surface sensitive, typically providing information on the first few 100s of angstroms. The applications to mine waste mineralogy have focused on understanding the mechanisms of sulphide oxidation (e.g. Nesbitt et al., 2000), suggesting, for example, that diffusion of metal ions to the surface of sulphide grains is an important control on sulphide oxidation rates (Wogelius and Vaughan, 2013).

Secondary Ion Mass Spectrometry (SIMS) is a surface-sensitive technique that has been applied relatively rarely but effectively to characterize mine waste minerals. The primary beam can be ions, typically O_2^+ or Cs^+, used to ablate the monolayers of a mineral surface. This technique can provide not only element mapping by rastering the incident beam, but depth profiling, on the scale of nanometres to micrometres, by continuous removal of material. A variant that employs a laser source has been used to characterize trace elements sorbed on mineral surfaces (Martin et al., 1997).

5. How to choose an analytical technique?

The choice of analytical technique depends on the nature of mine waste minerals sampled and, importantly, the questions being asked. Access to instruments and expertise is important. The amount of sample available and requirement for a non-destructive method may influence the decision. A deciding factor is often cost.

Combining multiple techniques is often advantageous because of the inherently challenging nature of environmental mineralogy. Conventional techniques such as optical petrography, SEM–EDS and XRD can be used to identify mine waste minerals in many cases. All three have limitations: it is rarely possible to identify all minor and trace minerals optically, even for an experienced mineralogist; not all phases can be distinguished with SEM imaging or qualitative EDS analysis; and many of the poorly crystalline or nearly amorphous secondary precipitates do not diffract and are missed in bulk XRD analysis. In many cases, these techniques provide a general characterization and can be used to screen samples for further analysis if questions remain unanswered. EPMA can be used for quantitative spot chemical analysis of solid solutions, and can answer questions regarding carbonate mineral composition, trace metals hosted in primary sulphides and secondary minerals, and the identity of silicate minerals contributing to non-carbonate neutralization potential. Prediction of the environmental impact of mining atypical ores such as nonsulphide zinc, rare earth element and other critical metal deposits would benefit from a comprehensive mineralogical analysis involving multiple techniques because the mineralogical controls on drainage quality are not immediately evident.

Less conventional analytical techniques can identify trace quantities of mine waste minerals that have important influences on environmental impact, including all three types of minerals that are described in this article – primary, process-related and secondary. Two techniques stand out in terms of their versatility. Synchrotron-based microanalytical techniques can characterize trace minerals missed by conventional tools by employing μ-XRD to identify poorly crystalline precipitates such as Fe and Mn oxyhydroxides, μ-XRF to map complex intergrowths and reveal trace metals hosted in these phases, and μ-XANES to identify the oxidation state of elements such as As, Cr, Fe, Mn, S, Sb, or U. TEM provides high-resolution imaging, chemical and structural analysis of mine waste minerals and is particularly powerful in revealing reaction products at grain boundaries.

6. The mineralogical fate of As in mine waste: an example from historical gold mines

Arsenic is a relatively common element accompanying many types of ore deposits and can be elevated in mine drainage, especially at neutral to alkaline pH values. Hydrothermally-deposited Au ores, known as orogenic or lode gold deposits, tend to be enriched in As, as both Au and As are complexed by chloride and sulphide in hydrothermal solutions and are concentrated in the vapour phase of fluids at high temperatures and pressures (Groves et al., 1998; Zhu et al., 2011). The primary forms of As in these ores are simple: arsenopyrite and As-bearing pyrite. However, if the mine wastes are exposed to oxidizing conditions, the secondary As mineralogy may become very complex (Drahota and Filippi, 2009). Moreover, if oxidized or partially oxidized As-bearing mine waste is subjected to oxygen-deficient conditions, the secondary As-bearing minerals may be reduced or reductively dissolved, releasing As back to the environment (e.g. Paktunc, 2012).

Recent studies of weathered mine tailings at orogenic lode gold deposits in Nova Scotia have identified several areas where exposure to high-As mine wastes may represent a potential risk to both ecosystem and human health (Parsons et al., 2012). Arsenopyrite is the primary host for As in these deposits, and was concentrated in the tailings during milling. However, in a study of 14 tailings and one soil sample taken from near-surface material at several historical gold mines in Nova Scotia, Walker et al. (2009) found more than a dozen secondary As minerals. These tailings are located close to residential areas and are occasionally used as community walking trails and for racing off-road vehicles. The samples were selected from materials that had distinct colour and texture in the field suggesting different secondary mineralogy. Samples were air dried, sieved to <150 μm, and characterized using ICP-MS, petrography, XRD, EPMA, and synchrotron micro-analysis (μ-XRD, μ-XRF and μ-XANES). The total As concentration of sieved samples ranged from 318 to 313,400 mg/kg As, with the most As-rich samples representing sulphide concentrates or their weathered equivalents. Scorodite and amorphous hydrous ferric arsenate (HFA) were the most common As-bearing secondary minerals, forming discrete grains or coatings on gangue minerals. Other major As phases identified in the tailings include As-bearing amorphous hydrous ferric oxyhydroxides (HFO), kaňkite ($FeAsO_4 \cdot 3.5H_2O$), pharmacosiderite [$KFe_4(AsO_4)_3(OH)_4 \cdot 6–7H_2O$], yukonite [$Ca_7Fe_{12}(AsO_4)_{10}(OH)_{20} \cdot 15H_2O$], amorphous Ca–Fe arsenates, and primary arsenopyrite (Fig. 5). Minor or trace constituents include As-bearing ferric oxyhydroxides with up to 10 wt.% As (goethite, lepidocrocite and akaganeite), As-bearing sulphates (jarosite [$(K,Na,H_3O)Fe_3(SO_4,HAsO_4)$], tooeleite [$Fe_6(AsO_3)_4(SO_4)(OH)_4 \cdot 4H_2O$]) and the sulphide realgar (As_4S_4) that was inferred to be authigenic (Fig. 5). Similar As-bearing phases have also been identified in windblown and vehicle-raised dust originating from these mine tailings (Corriveau et al., 2011b) using a combination of PIXE, SEM–EDS, and synchrotron-based methods.

Further research has shown that the identity of the secondary As minerals in these tailings has a significant influence on (1) the risk associated with human health and (2) the choice of remediation design. The samples that were characterized mineralogically were part of a larger suite tested for As bioaccessibility using an in vitro, two-step physiologically based extraction test (PBET) method (Meunier et al., 2010). The highest As bioaccessibility (up to 49%) is associated with the presence of Ca–Fe arsenate. Samples containing As predominantly as arsenopyrite or scorodite have the lowest bioaccessibility (<1%). These results are consistent with the known geochemical behaviour of these minerals. The coarse-grained primary arsenopyrite probably does not release much As (0.62% of total As present in the sample which is mostly arsenopyrite) during the 1-h gastric (pH = 1.8) and 4-h intestinal (pH = 7) bioaccessibility tests because of kinetic limitations on its dissolution. The scorodite-rich sample released only 0.13% of its total As in the gastric step and 0.32% in the intestinal step, reflecting the pH dependence of scorodite solubility (Langmuir et al., 2006). The significantly higher As bioaccessibility (49%, 29%) associated with samples where Ca–Fe arsenate is the major As host is probably related to the fact that these tailings contain residual carbonate and that the As-hosting Ca-bearing minerals dissolve more readily in the gastric stage. The rather surprising result is that in terms of the risk to human health through ingestion, the most hazardous tailings on the basis of mineralogy are those with Ca–Fe arsenates, which are also the tailings that contain carbonate and are pH-neutral, attributes usually associated with non-acid generating tailings considered to be the least problematic in terms of drainage quality (Jamieson et al., 2011). The results of this study demonstrate that As bioaccessibility in tailings and soils is strongly controlled by mineralogy, and suggest that even the most insoluble forms of As may present a health risk if As is present at very high concentrations.

Column studies testing several tailings types from Montague and Goldenville, two of the publicly-accessible gold mines sites in Nova Scotia, have shown that secondary As mineralogy is more important than input solution composition in determining the nature of the effluent composition (Kavalench, 2010). The experiments were designed to test different cover scenarios, including crushed limestone (carbonate-saturated rainwater leachant, pH = 10), soil and vegetation cover (organic acid leachant, pH = 5.7), and no cover (rainwater leachant, pH = 4.6). No matter what the input solution pH was, the final effluent pH was governed by tailings mineralogy. For example, Kavalench and Jamieson (2012) have shown that hardpan material rich in arsenopyrite and scorodite consistently produced acid effluent (pH = 2) over the 29-week test. After an initial spike, the As concentration of the effluent was between 10 and 15 mg L^{-1}, which is similar to As concentrations in tailings pore waters collected in the field

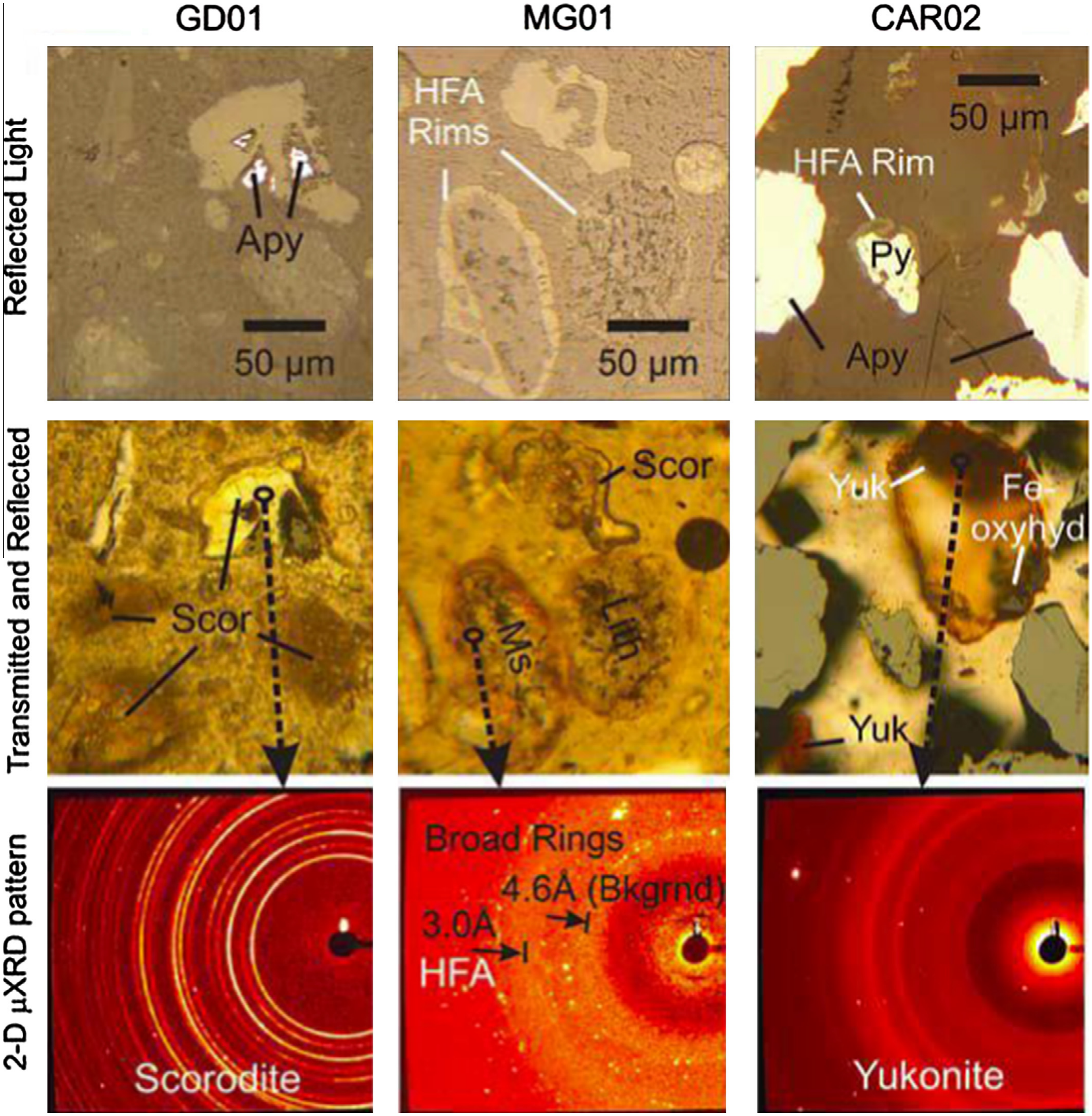

Fig. 5. A variety of As phases occur in weathered gold mine tailings in Nova Scotia, with mixtures of different forms varying from sample to sample. A combination of optical microscopy and µ-XRD allows definitive identification of a range of mineral forms and textures at the micrometre scale. These As-bearing minerals range from finely crystalline transparent to translucent aggregates of scorodite (e.g., GD01 and MG01), to amorphous forms that in some cases coat or cement other grains (e.g., MG01 and CAR02). The broad diffraction-ring at ca. 3 Å (MG01) is indicative of amorphous hydrous ferric arsenate (HFA). Yukonite, a Ca–Fe arsenate, occurs most commonly in carbonate-rich samples. In CAR02, it is present in an arsenopyrite-rich mill concentrate along with other trace oxidized forms of As (from Walker et al., 2009, used with permission).

(DeSisto et al., 2011). Other tailings types also exhibited behaviour consistent with mineralogical control. For example, the high Ca/As tailings maintained an effluent pH near 9 even with acidic input solutions, but also released relatively high concentrations of dissolved As (Kavalench, 2010).

These results suggest that As mineralogy is a dominant factor controlling the potential hazards associated with these mine sites, both for human health (should fine particles of tailings be ingested or inhaled) and downstream drainage quality. Knowing the nature of the As minerals present is advantageous, but the tools used for detailed mineralogical characterization by Walker et al. (2009) may not always be available to those involved in managing these or similar sites. Fig. 6 and Table 4 show how bulk compositional analysis, particularly the relative proportions of As, Ca, Fe, and S, can provide clues to As mineralogy, and might be used to select subsamples for detailed mineralogical study. Samples from three Nova Scotia mine sites, Caribou, Goldenville and Montague, are used as examples and plotted on S–Fe–Ca ternary diagrams

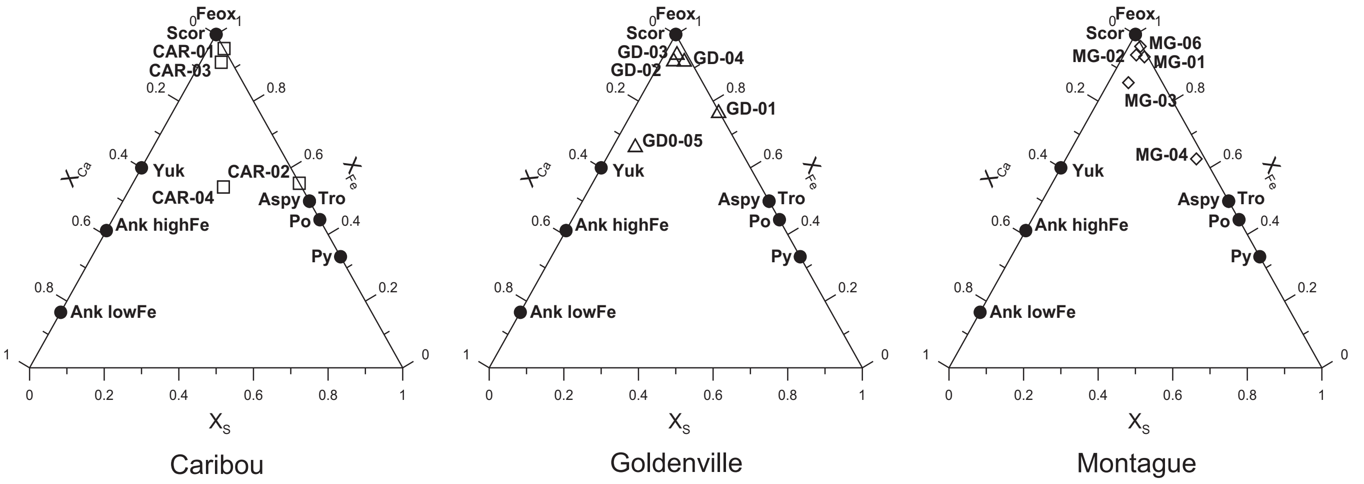

Fig. 6. Sulphur–Fe–Ca ternary diagrams (molar basis) for tailings samples from the historic Caribou (CAR), Goldenville (GD) and Montague (MG) gold mines in Nova Scotia. Pure end member minerals are also plotted for reference (Ank = ankerite, Yuk = yukonite, FeOx = iron (oxyhydr)oxide, Scor = scorodite, Aspy = arsenopyrite, Po = pyrrhotite, Tro = troilite, Py = pyrite). Ratios of major elements are generally predictive of As mineralogy for Nova Scotia mine tailings with Fe arsenate- and Fe oxyhydroxide-rich materials plotting towards the Fe apex, sulphide rich materials plotting towards sulphides projected along the Fe–S join, and Ca–Fe arsenate-rich materials plotting towards Ca–Fe arsenates and carbonates projected along the Fe–Ca join (see Table 4 and text).

Table 4
Summary of Nova Scotia tailings samples (from Walker et al., 2009).

ID	Material type	Arsenic (mg/kg)	Iron (mg/kg)	Sulphur (mg/kg)	Calcium (mg/kg)	Major As-bearing Phases	Classification
CAR-01	Tailings	76,500	75,200	1900	<100	Scor, kank	Fe arsenates
CAR-02	Concentrate	313,400	364,300	168,200	200	Aspy, py	Sulphides
CAR-03	Tailings	21,300	31,900	1100	700	HFA-FeOx	Fe arsenates–Fe oxyhydroxides
CAR-04	Tailings	15,200	40,800	10,700	11,300	Aspy, py	Sulphides
GD-01	Concentrate	210,300	200,400	34,200	<100	Scor	Fe arsenates
GD-02	Tailings	19,200	36,000	700	1200	Scor, HFA	Fe arsenates
GD-03	Tailings	38,900	48,800	900	900	Scor, HFA	Fe arsenates
GD-04	Tailings	48,700	77,600	2900	900	HFA	Fe arsenates
GD-05	Tailings	7209	28,500	1400	8400	Ca-FA, yuk, aspy	Ca–Fe arsenates-sulphides
MG-01	Tailings	62,100	81,800	2900	600	Scor, HFA	Fe arsenates
MG-02	Tailings	24,000	54,800	1100	1200	HFA	Fe arsenates
MG-03	Tailings	23,700	58,800	2100	4500	Phar-yuk	Fe arsenates–Ca–Fe arsenates
MG-04	Tailings	21,400	52,500	16,800	1400	Aspy	Sulphides
MG-06	Soil	318	59,200	1100	200	FeOx	Fe oxyhydroxides

Fe arsenates – scorodite (scor), kankite (kank), hydrous ferric arsenate (HFA), pharmacosiderite (pha).
Sulphides – arsenopyrite (aspy), pyrite (py).
Ca–Fe arsenates – amorphous calcium ferric arsenates (Ca-FA), yukonite (yuk).
Fe oxyhydroxides (FeOx).

(Fig. 6). The composition of pure As-bearing minerals is also shown. The plotting position of each tailings sample on the S–Fe–Ca ternary diagram is shown to be predictive of the overall major As mineral classification (Table 4) even though the underlying mineralogy can be more complex.

For example, sample CAR-02, an unweathered arsenopyrite-rich concentrate that was deposited with the tailings, and MG-04, a sulphide-rich tailings sample, both plot along the Fe–S axis (towards the projected sulphide minerals) on the S–Fe–Ca ternary (Fig. 6). Weathering of the tailings involves a loss of S (presumably to dissolved sulphate) and the transformation of some of the arsenopyrite to scorodite. Sample GD-01 is an example of weathered concentrate and consists of a mixture of scorodite and minor sulphides and plots much closer to the Fe apex on the ternary than the CAR-02 sample. The compositions of most weathered Nova Scotia gold tailings, other than those with carbonate and high Ca/As, fall close to the Fe apex, and their As mineralogy is dominated by scorodite, HFA and kaňkite (Fig. 6, Table 4). HFO minerals such as goethite also plot at this apex (e.g. soil sample MG-06), but for the As-rich tailings samples these secondary Fe oxides are only present in trace amounts. Both weathered concentrates and the Fe-rich weathered tailings are likely to generate acid, As-rich drainage. However, arsenopyrite and scorodite were shown to have low As bioaccessibility (the bioaccessibility of HFA and kankite are not known; Meunier et al., 2010). Calcium-bearing tailings such as CAR-04, which shows only minor evidence of weathering, plot in the centre of the ternary. Ankerite or calcite is present is minor amounts, and the As is contained in arsenopyrite, which has partially oxidized to Ca–Fe arsenate. Sample GD-05 represents more weathered carbonate-bearing tailings where most of the As resides in Ca–Fe arsenates such as yukonite with minor remnant sulphides. The carbonate-bearing tailings tend to produce pH-neutral drainage but contain more bioaccessible As minerals. Detailed mineralogy of sample MG-03 determined the presence of pharmacosiderite and yukonite as the dominant As-bearing minerals (Fig. 6, Table 4). The location of this sample on the Ca–S–Fe ternary plots in the vicinity of the rest of the Fe arsenate phases, but slightly towards the more Ca-rich phases. Samples such as this may represent a transition from formerly carbonate-rich tailings to carbonate-depleted tailings (Walker et al., 2009), and their dominant As mineralogy may be difficult to ascertain from bulk compositional analyses alone.

7. Summary

Decades of experience with prediction tests and water quality management has confirmed the importance of understanding mine waste mineralogy. Overall the relationship between metal-hosting minerals and the risk associated with mine waste in terms of both drainage chemistry and direct exposure is well-established. Research in this field has pushed the frontiers of our understanding of mineral–water interaction in terms of reaction mechanisms, rates and products. Novel insights include the behaviour of mineral nanoparticles, the nature of surface adsorption, and microbe–mineral interaction.

Most modern mining companies include some mineralogical characterization of waste rock and mine tailings in their environmental prediction and management program. The use of more advanced techniques to answer questions not covered in a regular characterization program typically depends on the complexity of the mineralogical issues, awareness of the techniques available, and the relationship between the mining company, environmental consultants, and researchers at universities and government laboratories. Collaboration with the mining industry allows researchers to study different ore deposits and processing techniques and keep the mining industry apprised of the latest research developments and useful outcomes. The most beneficial collaborations are those where information can be openly shared and published.

Despite the multiplicity of techniques, increasing spatial resolution, and decreasing detection limits, there are still unresolved issues in mine waste mineralogy. Leach tests, including sequential extractions, frequently indicate that a fraction of the metal or element of interest is very loosely bound and easily extracted, yet it is not always clear how (or if) that fraction is associated with minerals. This highly mobile and bioavailable metal fraction may be associated with organic matter or in a particular type of surface association with minerals. High resolution techniques with high surface and chemical sensitivity are best suited to clarify this issue. Yet another concern rests with the application of high resolution techniques that scrutinize minerals at the nm to μm scale, and the challenge of extrapolating those results to the broader system. As described by Hochella et al. (1999), "……we are actually looking at only an infinitesimally small portion of an otherwise highly complex, dynamic, and extensive system." The representative nature of samples examined mineralogically can be enhanced by careful selection at the field and hand sample scale, and bulk chemical analyses can be very useful in guiding subsampling. Determining the relative proportion of solid phases in a sample is very useful for risk assessment and drainage prediction but this is difficult to do quantitatively. Automated mineralogy holds the promise of tackling the problem of representativeness and providing a tool for rigorous modal analysis, because thousands of particles can be characterized relatively quickly by grain size, mineralogy and degree of liberation from other minerals (e.g. Mermillod-Blondin et al., 2011; Brough et al., 2013).

Acknowledgements

The authors are particularly grateful to Gwendy Hall of the Geological Survey of Canada and Antonio Lanzirotti of the University of Chicago for their support of our early efforts in applying synchrotron microanalysis to mine waste mineralogical characterization. Stephanie DeSisto provided the original image for Fig. 1. The manuscript was improved by comments from reviewers including J. Hammarstrom and R.R. Seal. This is contribution number 20140331 of the Earth Sciences Sector, Natural Resources Canada.

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