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Ultramafic soils and nickel phytomining opportunities: A review

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ABSTRACT: Ultramafic soils are originated from ultramafic rocks such as peridotite and serpentinite and are highly enriched in metals (e.g., Ni, Cr, and Co) and depleted in plant nutrients (e.g., P, K, and Ca). Such characteristics make these soils unfavorable for agriculture and have raised environmental concerns on metal release to the environment. From another perspective, ultramafic soils host a diverse flora with higher endemism than surrounding non-ultramafic areas, which has provided scientists with an opportunity to investigate the evolutionary genetics of plant adaptation. Some plant species adapted to these stressful edaphic conditions developing the ability to accumulate uncommonly high metal concentrations in the harvestable biomass. Such species, called metal hyperaccumulators, can extract metals from ultramafic soils, especially Ni, in a circular economy approach in which the metal-rich biomass is incinerated to generate valuable bio-ores. Phytomining promises to turn ultramafic soils and low-grade ore bodies into economically viable alternatives to metal extraction. Here, we review the current knowledge on ultramafic soils and the most promising hyperaccumulators used to exploit them in temperate and tropical climates. In the tropics, including Brazil, the search for new hyperaccumulator candidates for phytomining and the knowledge to crop these species is incipient and holds untapped opportunities. Despite the feasibility of the phytomining chain has been proven, large-scale demonstrations of profitability are needed to establish the technology.

Keywords: phytoextraction, serpentine soils, soil fractionation, trace elements.

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INTRODUCTION

Ultramafic soils result from the weathering of ultramafic rocks, such as peridotite and serpentinite, which contains predominantly ferromagnesian silicate minerals and less than 45 % silica (SiO_2) (Alexander, 2009; Alfaro et al., 2015; Galey et al., 2017). Peridotite is an ultramafic igneous rock containing olivines and pyroxenes with minor amounts of chromite. Serpentinite, in turn, is produced from peridotite by the addition of water in a metamorphic process called serpentinization. The complete transformation of peridotite into serpentinite requires about 13-14 % water (Alexander and DuShey, 2011). In the process, olivines and pyroxenes are transformed into or replaced by serpentine minerals such as lizardite, chrysotile, and antigorite, with the formula $X_3Si_2O_5(OH)_4$, in which X can represent Mg, Fe, Ni, Mn, Al, and Zn (Alexander and DuShey, 2011; Russell and Ponce, 2020). Because most ultramafic rocks (85-95 %) are serpentinized (Kodolányi et al., 2012), ultramafic soils are commonly called serpentine, although the term is more accurately used to designate a group of minerals.

Phytomining is part of the so-called phytotechnologies, an umbrella term that includes plant-based techniques to extract, volatilize, or immobilize metals in contaminated soils (Nascimento et al., 2021). Although the capacity of certain plants to hyper accumulate metals has been long known (Sachs, 1865; Jaffré et al., 1976), the plan of using such plants to remediate metal-polluted sites or to mine Ni, Co and other metals from metal-enriched soils and substrates was first proposed by Ruffus Chaney, a Research Agronomist at USDA (Chaney, 1983, 1998). These seminal publications boosted a large number of scientific papers with the words ‘phytoremediation’ (17,411) and ‘phytoextraction’ (4,615) on Web of Science search in the last 25 years (Figure 1). The keywords ‘phytomining’ and ‘agromining’ appeared 247 and 50 times in the same period, with an average of 19 and 11 references in the last five years, respectively. The concept of agromining is derived from phytomining to cover the agronomical chain that goes from the cultivation of hyperaccumulators to the production of bio-based metals (Morel, 2015).

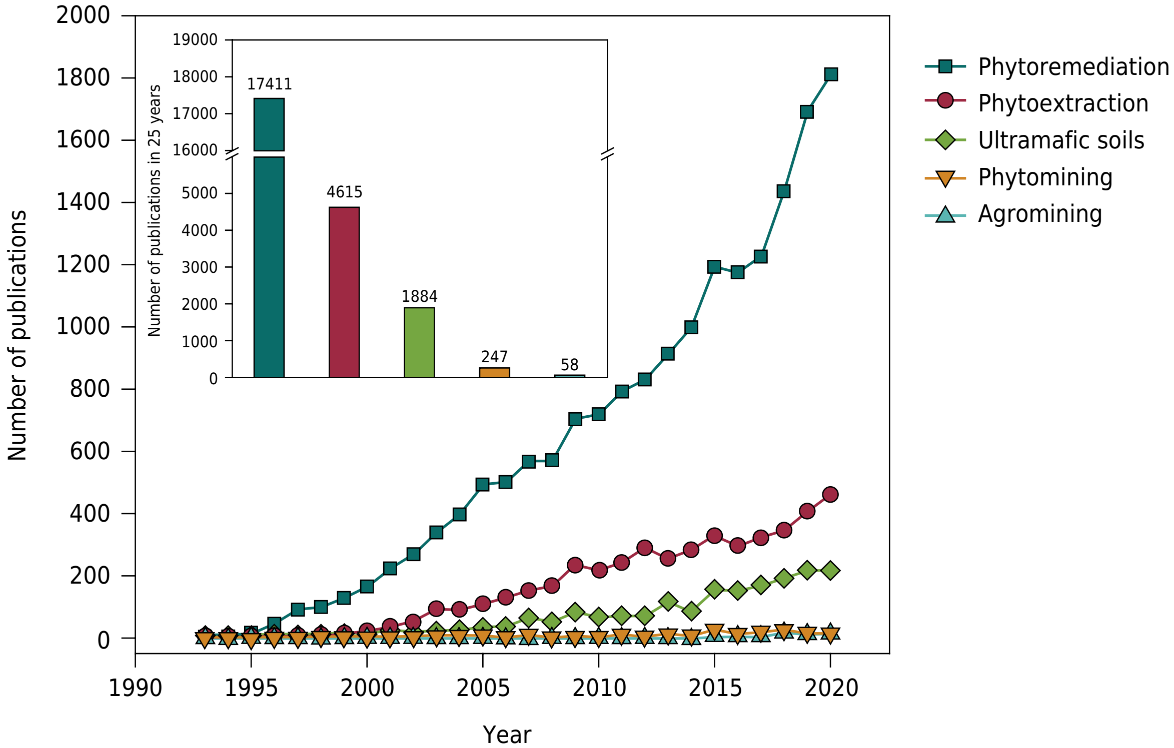

Figure 1. Number of publications per year (1993-2020) and in the last 25 years (small square) on Web of Science search with the words ‘phytoremediation’, ‘phytoextraction’, ‘ultramafic soils’, ‘phytomining’, and ‘agromining’ in the article title, abstract or keywords.

The research in 'ultramafic soils' also significantly increased from an annual mean publication of 30 articles in the 1993-2010 span to 134 papers published yearly in the last decade (Figure 1). The genesis, chemistry, and flora of these types of soils have been extensively studied because of their unique biogeochemistry and promising opportunity to economically extract Ni, Co, Mn, and other metals (Garnier et al., 2009; Kierczak et al., 2016; Nkrumah et al., 2016; Vithanage et al., 2019). Here, we discuss the chemistry, likely impacts on the environment, and ecological importance of ultramafic soils. In addition, the metal hyperaccumulation phenomenon, the search for new plant species able to mine ultramafic soils, and the process of recovering metals from ash biomass are reviewed. The recent advances in phytomining research have paved the way for the sustainable use of plants to produce metals, especially nickel, in a circular economy based on metal-rich soils and hyperaccumulating plants. However, some limitations remain and must be overcome to make phytomining a large-scale and economically feasible technology.

GEOCHEMISTRY OF ULTRAMAFIC SOILS

Ultramafic bedrocks and the soils developed from them have high concentrations of magnesium (Mg), iron (Fe), chromium (Cr), manganese (Mn), nickel (Ni), and cobalt (Co). Ultramafic outcrops occur in all continents and are estimated to cover roughly 3 % of the Earth's surface (Guillot and Hatori, 2013), with significant massifs in temperate (Southern Europe, Turkey and California) and tropical settings (Cuba, New Caledonia, Brazil, The Philippines, Malaysia, Indonesia and Oman), and small and occasional patches worldwide (Galey et al., 2017; Echevarria, 2018; Kierczak et al., 2021). Besides the high concentration of geogenic metals, especially the triad Cr-Ni-Co that can be toxic to plants, ultramafic soils pose a hostile environment for plant growth due to their scarcity of macronutrients such as nitrogen (N), phosphorus (P), potassium (K), or calcium (Ca) and micronutrients such as boron (B) or molybdenum (Mo), and low Ca-to-Mg molar ratios (Nkrumah et al., 2016; Nascimento et al., 2020). Therefore, the vegetation covering ultramafic soils is generally less massive and stunted than the vegetative cover of non-ultramafic soils (Figure 2).

Figure 2. Ultramafic soil landscape in Niquelândia, Brazil, shows the characteristically sparse and stunted vegetation compared to the vegetation of the non-ultramafic soil in the background. Photo by Clístenes Williams Araújo do Nascimento.

Ultramafic rocks in tropical countries commonly originate very deep, clayey, and highly weathered soils, with different serpentinization degrees and nickeliferous deposits formation as is the case in Brazil (Vidal-Torrado et al., 2006; Garnier et al., 2009; Vilela et al., 2019; Ratié et al., 2021). These soils likely develop into Ultisols, Nitosols, or Oxisols, with a predominance of 1:1 minerals and Fe oxides. However, less developed ultramafic soils (e.g., Cambisols and Entisols) can also occur, such as the ones derived from the Limoeiro deposit (Figure 3), which have easily weatherable minerals (e.g., olivine, orthopyroxene, and chromite). The Limoeiro deposit - located in a high-grade mobile belt of the Brasiliano orogenic cycle (650–500 Ma) – is originated by the orthopyroxenite-harzburgite intrusion of the Borborema Province, Northeast Brazil (Silva et al., 2013).

The Ni, Cr, and Co concentrations found in ultramafic soils commonly exceed the soil guideline metal values set by environmental agencies to secure soil quality (Kanellopoulos, 2020; Yan et al., 2021). Therefore, concerns have been raised about the potential of ultramafic rocks and their related soils to threaten the environment by releasing potentially toxic metals to groundwater, with consequences on animal and human health (Becquer et al., 2010; McClain et al., 2017; Vithanage et al., 2019; Garnier et al., 2021). Ultramafic soils are probably the primary source of Ni and Co for the terrestrial ecosystem (Estrade et al., 2015; Echevarria, 2018), but Cr and Mn can also be released in significant amounts from ultramafic soils to groundwaters (Rajapaksha et al., 2013; Papazotos et al., 2019; Vithanage et al., 2014).

Chromite ($FeCr_2O_4$) and other Cr minerals can be sources of the metal in ultramafic soils as Cr oxidation is induced by Fe, Mn, and dissolved organic matter (Rajapaksha et al., 2013; McClain and Maher, 2016). For instance, Fantoni et al. (2002) found Cr concentration in groundwaters of La Sapienza Province, Italy, above the maximum allowable concentration for drinking water; the authors attributed the high water Cr concentration to local

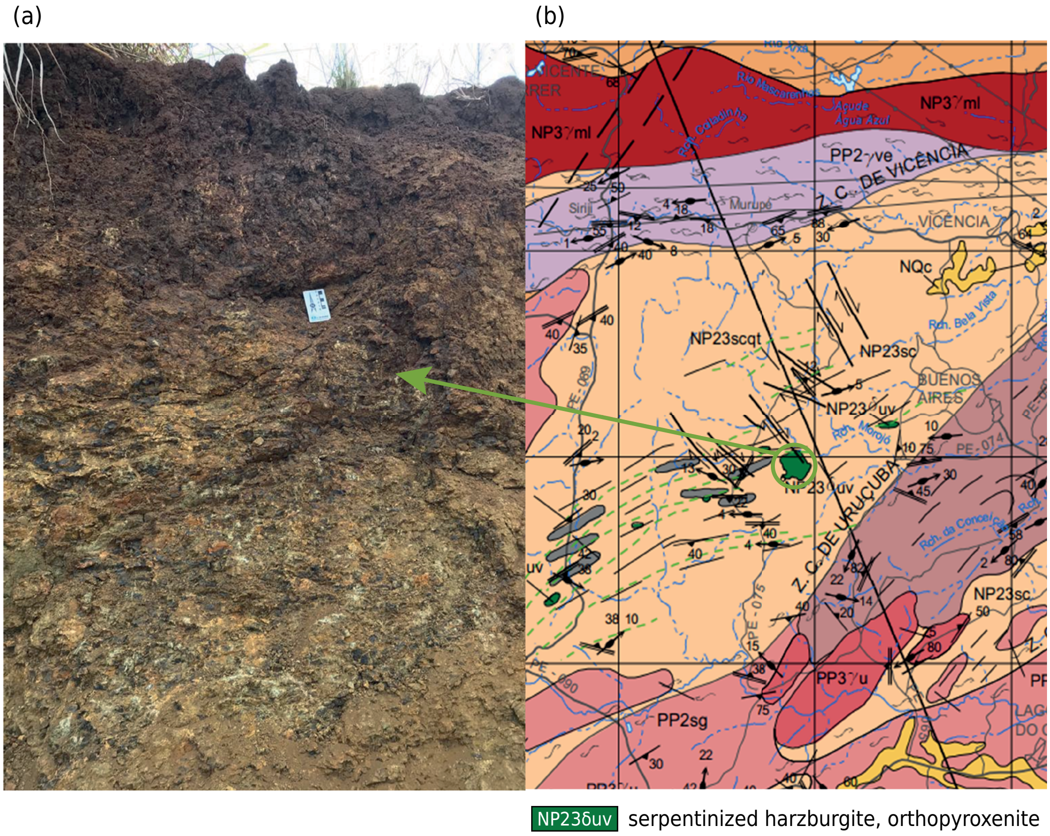

Figure 3. Ultramafic soil profile (a) derived from serpentinized harzburgite-orthopyroxenite intrusion (b) of the Borborema Province (Santos et al., 2020) in Limoeiro, Pernambuco State, Brazil. Photo by Clístenes Williams Araújo do Nascimento.

serpentinites that release Cr through the oxidation of Cr(III) in the rock minerals to Cr(VI) by different electron acceptors (Mn and Fe oxides, H_2O_2, gaseous O_2). The local ultramafic environment had no influence on the Cr, Ni, and Co concentrations in surface waters in Malaysia, but subsurface waters were highly enriched with these elements and exceeded water quality standards (Tashakor et al., 2018). Groundwater contamination by metals released from ultramafic soils has also been reported in Mexico (Robles-Camacho and Armienta, 2000), Greece (Kaprara et al., 2015), and the USA (McClain et al., 2017).

Bioavailability and mobility of metals in soils are governed by the geochemical pools in which they are bound (Silva et al., 2017), which indicates that measuring the total concentrations of metals in soils does not suffice to assess environmental risks. Therefore, it is paramount to perform single and sequential extractions of metals in ultramafic soils to understand environmental risks better. For instance, ultramafic soils from Sri Lanka showed Ni (72 %; 4,697 mg kg^{-1}) and Cr (83 %; 8,567 mg kg^{-1}) predominantly associated with the residual fractions, with a remarkable association of Cr with soil organic matter (4.6 %; 508 mg kg^{-1}), which can increase the metal mobility; Mn, in its turn, was evenly distributed between Fe-Mn oxides (37 %; 420 mg kg^{-1}) and residual (31 %; 351 mg kg^{-1}) fractions (Vithanage et al., 2014). The DTPA-available contents of metals were 353 mg kg^{-1} (Ni), 76 mg kg^{-1} (Mn), and 0.35 mg kg^{-1} (Cr). Therefore, the ultramafic soils in the study area offer a highly labile source of metals.

We found that ultramafic soils from Brazil and the USA had different total and available Ni, Cr, and Co concentrations and that these metals were differently distributed into soil fractions (Table 1). The varied composition of the ultramafic soils may be partially due to complexes they form with other co-existing rocks such as gabbros, basalts, carbonates, and gneiss (Kierczak et al., 2021). However, despite the diverse composition, all the ultramafic soils have in common the high Ni, Cr, and Co concentrations inherited and redistributed from the parent material during the soil-forming processes.

Regardless of the soil origin, Cr residual percentage was very high (~ 99 %), which is in agreement with other studies on ultramafic soils in temperate (Kierczak et al., 2016) and tropical (Tashakor et al., 2017) countries. Nickel total concentrations and allocation in soil fractions were similar in Limoeiro (Brazil) and Buck Creek (USA) soils, but Ni availability measured by DTPA was considerably higher in the Limoeiro soil, which also had the highest Co availability. The soil from Niquelândia had the highest DTPA-available concentrations of Ni and Cr and the highest proportion of Ni in residual fractions. However, despite the apparently low mobility, Garnier et al. (2021) suggested that the ultramafic soils from Niquelândia are a source of labile Ni and Cr(VI), which can be transferred to surrounding sites either as dissolved metals or associated with Fe-oxides.

Table 1. Total and available Co, Cr, and Ni contents and percentage of these metals in exchangeable (Exc), organic matter (OM), iron and manganese oxides (Fe-Mn Ox), and residual fractions in ultramafic soils from Brazil and the USA

Soils	Metal	Total	DTPA	Exc	OM	Fe-Mn Ox	Residual
		mg kg^{-1}		%			
Limoeiro (PE, Brazil)	Co	87.7	2.4	0.5	0.1	99.3	0.1
	Cr	2485.5	0.0	0.0	0.1	0.4	99.5
	Ni	1428.5	66.1	9.4	0.5	20.6	69.5
Niquelândia (GO, Brazil)	Co	373.5	1.0	0.0	0.0	55.1	44.9
	Cr	1844.5	0.5	0.0	0.4	1.0	98.6
	Ni	9597.5	224.9	1.1	0.3	14.2	84.4
Buck Creek (NC, USA)	Co	169.0	1.0	5.7	0.6	62.8	30.9
	Cr	635.0	0.1	0.0	0.1	1.0	98.9
	Ni	1450.0	5.5	6.0	0.6	22.5	70.9

DTPA extraction followed Lindsay and Norvell (1978). Soil sequential extraction was based on Shuman (1985).

ULTRAMAFIC ECOSYSTEM

The unique chemistry of ultramafic soils often drives the evolution of endemic plant communities with morphological and physiological traits that differentiate them from the flora of bordering areas (Kazakou et al., 2008; Anacker, 2014; Mesjasz-Przybyłowicz and Przybyłowicz, 2020). For example, the diversity and spatial variability of ultramafic soils are considered the primary driver for the plant richness and distinctiveness of New Caledonia, which has >30 % of its territory covered by ultramafic outcrops (Jaffré et al., 2013; Mouly and Jeanson, 2015; Isnard et al., 2016). In addition, the high endemism in ultramafic environments contributes greatly to investigating species genetic adaptation and evolutionary theory (von Wettberg and Wright, 2011; Strauss and Cacho, 2013; Palm and Van Volkenburgh, 2014).

Plant adaptation to ultramafic soils comprises a set of physiological traits, known as the 'serpentine syndrome', a term coined by the American soil scientist Hans Jenny to explain plant survival in these harsh environments. This syndrome includes tolerance to low nutrient contents, high Ni, Cr, and Co levels, Ca-to-Mg ratio imbalance, and water deficit (Isnard et al., 2016; Nkrumah et al., 2016). Some species of the ultramafic flora developed the ability to hyper accumulate metals, but most of them deal with the toxicity by avoiding uptake or translocation of metals to shoots. For example, in some genera, Ni hyperaccumulation is found in one species while other related species growing on the same soils do not show such character (Burge and Barker, 2010; Jaffré et al., 2013). Indeed, only 64 out of the 2145 species adapted to the ultramafic soils of New Caledonia are Ni hyperaccumulators (Jaffré et al., 2013).

It has been long suggested that Ni-hyperaccumulators drive a 'nickel cycle' resulting in the evolution of Ni-resistant microbial strains in the rhizosphere (Schlegel et al., 1991; Mengoni et al., 2001; Pal et al., 2004). Studies on the microbial ecology of ultramafic soils showed a lower microbial density and activity than non-ultramafic soils but a higher number of metal-resistant microbial strains (Pal et al., 2004, 2005). Also, the multiple metal-resistance of the isolates was associated with the resistance to the antibiotics penicillin, ampicillin, cycloserine (Pal et al., 2004). In addition, inoculation with arbuscular mycorrhizal fungi (AMF) isolated from ultramafic soils could improve the nutrition and adaptation of plants to ultramafic soils, with potential benefits to agriculture and ecological restoration of mined ultramafic sites (Amir et al., 2013; Doubková et al., 2013; Bourles et al., 2020).

The interaction between Ni-hyperaccumulators and insect species via herbivory may transfer Ni to these insects, which can contain relatively high Ni contents (Boyd and Martens, 1998; Wall and Boyd, 2002; Boyd, 2009). Fifteen species of 'high-Ni' insects (Ni >500 μg g^{-1}) have been identified in ultramafic areas in New Caledonia, South Africa, and the USA. The highest average Ni concentration found was 3500 μg g^{-1} for nymphs of a Stenoscepa species from South Africa (Boyd, 2009). Mesjasz-Przybyłowicz and Przybyłowicz (2020) found some highly specialized phytophagous insects (leaf beetle *Chrysolina pardalina*, ladybird *Epilachna cf nylanderi*, and grasshopper *Stenoscepa* sp.) fed solely on Ni hyperaccumulators during their complete life cycle in lab conditions for generations with no adverse effect on their development. The investigation of such high-Ni insects in ultramafic ecosystems can aid in the understanding of Ni effects in organisms and how Ni moves through the food chain.

Despite their ecological relevance, endemic ultramafic communities worldwide face a high risk from climate change and anthropogenic activities, as their strict adaptation to ultramafic niches can limit the migration to other edaphic conditions (Harrison et al., 2009). Consequently, some hyperaccumulators are at high risk of extinction (Reeves et al., 2017; Jaffré et al., 2018). For example, in Albania, climate change can decrease the area potentially explored by the Ni hyperaccumulator Alyssium murale by as much as 48 % by 2070 (Lekaj et al., 2019). Likewise, in Brazil, the environmental degradation caused by mining activities can provoke a soaring extinction rate of plants endemic to metal-rich regions (Jacobi et al., 2011; Salles et al., 2019).

In this scenario, ultramafic environments must be protected and their genetic material conserved for current and potential scientific and economic uses. To illustrate, plant species adapted to the high metal stress imposed in ultramafic soils could be helpful in metal tolerance studies, revegetation or reclamation of mined land, remediation of metal-polluted soils, micronutrient biofortification of crops, and phytomining of Ni-enriched soils or substrates (Jaffré et al., 2013; Nkrumah et al., 2016; Clemens, 2017).

DEVELOPMENT AND CURRENT STATE OF PHYTOMINING

Hyperaccumulator species

Phytomining relies on the remarkable ability of certain plant species to naturally accumulate metal contents in shoots hundreds to thousands of times higher than other species growing on the same soil (van der Ent et al., 2013). To date, the countries with the largest quantities of known hyperaccumulators are Cuba (Reeves et al., 1999; Berazaín et al., 2007), New Caledonia (Jaffré et al., 2013), Turkey (Reeves and Adiguzel, 2008), Brazil (Reeves et al., 2007), and Malaysia (van der Ent et al., 2016).

The threshold concentration that identifies the phenomenon of hyperaccumulation varies with the considered metal. For example, plants with more than 1,000 mg kg^{-1} of Ni in the dry leaf matter are considered hyperaccumulators of the element (the term 'hypernickelophore' is reserved to a subset of plants accumulating >10,000 mg kg^{-1} of Ni). The hyperaccumulation threshold for cadmium (Cd), thallium (Tl), and selenium (Se) is 100 mg kg^{-1}. For cobalt (Co), chromium (Cr), and copper (Cu) above 300 mg kg^{-1}; and zinc (Zn) and manganese (Mn) thresholds are 3,000 and 10,000 mg kg^{-1}, respectively (van der Ent et al., 2015; Reeves et al., 2017). Plants that reach such metal concentrations growing in hydroponics and spiked or chelator-treated soils are not considered hyperaccumulators. Currently, 746 plant species from 52 families and c. 130 genera are known to be hyperaccumulators of metals; Brassicaceae (83 species) and Phyllanthaceae (69 species) are the families most strongly represented (Reeves et al., 2017). The vast majority of these species (532) are Ni-accumulators, followed by Cu (53), Co (42), Mn (42), Se (41), Zn (20) and Cd (7) (Corzo-Remigio et al., 2020). Most field surveys for hyperaccumulators were carried out in ultramafic soils, mainly enriched in nickel. This fact and the market value for Ni are the likely reasons for the higher number of Ni hyperaccumulators discovered so far. Therefore, these species are the most studied and promising for commercial phytomining.

There is still a lack of systematic search for hyperaccumulators in several ultramafic regions, including Brazil, and new hyperaccumulators are certainly to be discovered in the coming years. For example, a recent systematic assessment of metal hyperaccumulators from New Caledonia using a portable XRF spectrometer (pXRF) revealed the existence of 34 new Ni-hyperaccumulators (Gei et al., 2020). The pXRF screening of 7,300 herbarium specimens from Malaysia discovered 28 new Ni hyperaccumulators, 12 Co hyperaccumulators, and 51 Mn hyperaccumulators (van der Ent et al., 2019). The tree species *Blepharidium guatemalense* was found to concentrate >4.0 % Ni in leaves when growing in soils of southeastern Mexico that are neither ultramafic nor Ni-contaminated through anthropogenic activities (Gutiérrez et al., 2021). Such a surprisingly finding brought a new perspective for the search for hyperaccumulators beyond the ultramafic domains.

The potential of Brazil (and South America) for phytomining remains largely unexplored. The country is home to 33,951 native Angiosperms (18,793 endemics) and 26 native Gymnosperms (3 endemics), a plant species number greater than any other country

(Jardim Botânico do Rio de Janeiro, 2021). In addition, Brazil is one of the leaders in Ni production and third on the list of countries with the largest Ni reserves. Unfortunately, published systematic surveys of hyperaccumulators in Brazil are scarce and restricted to the ultramafic massifs of Macedo-Niquelândia and Barro Alto, Goiás State (Reeves et al., 2007; Pessoa-Filho et al., 2015; Andrade et al., 2018).

Reeves et al. (2007) collected 800 specimens from the ultramafic soils of Goiás, with more than 30 species showing Ni hyperaccumulation; some of them are shown in figure 4. Notable Ni-hyperaccumulators of this area include *Pfaffia sarcophylla*, *Justicia lanstyakii*, *Heliotropium salicoides*, and *Lippia lupulina*. However, the distribution of Ni concentrations in these species seems to be highly variable in the field. For example, we found Ni values measured by a pXRF in four specimens of *P. sarcophylla* growing in a hill nearby Niquelândia varying between 370 and 1,044 mg kg^{-1}. Such a high variation among specimens is uncommon in other ultramafic plant surveys, in which the distinction between Ni hyperaccumulators and non-accumulators is clear (Reeves et al., 2007) and hence deserves studies. Nevertheless, field experiments are needed to assess Brazilian hyperaccumulators' agronomical performance and profitability for phytomining programs.

Agronomy of Ni phytomining

Although ultramafic soils can have high contents of other metals such as Cr, Mn, and Co, Ni phytomining has been the most promising approach so far because of the combination of good market value for Ni and a large number of Ni hyperaccumulators identified. Cobalt, for example, has higher value compared to Ni (Ni USD 18.7 kg^{-1} and Co USD 54.3 kg^{-1}, London Metal Exchange, price for July 2021), but the foliar accumulation of Co and consequently the annual yield of the metal per hectare is much lower than Ni (van der Ent et al., 2018a; Nascimento et al., 2020). Despite that, the growing increase in the market price for metals, along with the discovery of new metal hyperaccumulators having enough high metal concentration in shoots and biomass yield, suggests that phytomining might be economically viable for other metals than Ni in the future. Case studies for other metals such as Co, Cu, Mn, Cd, and Zn can be found in van der Ent et al. (2018b).

Alyssum murale (syn *Odontarrhena chalcidica*), probably the most studied plant for phytomining to date (Tappero et al., 2007; Chaney et al., 2007; Bani et al., 2010, 2014; Nascimento et al., 2020), is regarded as the most promising Ni hyperaccumulator for temperate phytomining. This species has the ability to concentrate >1 % Ni in aerial tissues, high biomass and seeding rate, and ease of cropping (Bani et al., 2015a; Nkrumah et al., 2016; Cerdeira-Pérez et al., 2019). Because of these characteristics, technologies to potentially agromine ultramafic soils and clean up Ni-polluted soils using *A. murale* are economically feasible (Li et al., 2003; Chaney et al., 2007; Chaney and Baklanov, 2017). In addition, a process for recovering Ni metal from *A. murale* biomass was developed (Barbaroux et al., 2011, 2012).

Figure 4. Nickel hyperaccumulators growing on ultramafic soil in Niquelândia - GO, Brazil. From left to right: *Lippia lupulina*, *Manihot sparsifolia*, and *Justicia lanstyakii*. Photos by Clístenes Williams Araújo do Nascimento.

Pioneering greenhouse and field studies to develop commercial phytomining were conducted in the USA using *Streptanthus polygaloides*, a Ni hyperaccumulator endemic to California (Nicks and Chamber, 1995) and *Alyssum* species (Li et al., 2003; Chaney et al., 2007). Nicks and Chamber (1995) found that *S. polygaloides* naturally growing on ultramafic soil containing 3,340 mg kg^{-1} of Ni produced biomass of 4.8 t ha^{-1} and averaged 5,300 mg kg^{-1} of Ni in shoots, with a Ni crop value of USD 476 ha^{-1}. Phytomining would not be economically viable with this figure, so the Ni accumulation and biomass yield must be doubled. More promising results were reported by Li et al. (2003), who found that *A. murale* and *Alyssum corsicum* could accumulate over 20,000 mg kg^{-1} in shoots and yield biomass as high as 22 t ha^{-1}, with up to two harvests per year. Under the price of Ni at the time this review was written, phytomining would have a crop value of approximately USD 7,480 ha^{-1} or BRL 38,715 (Brazilian reais) per harvest, making Ni phytomining a profitable phytotechnology. These values are far more than those attainable with commercial crops, especially on the Ni-toxic, unfertile ultramafic soils. By comparison, a corn crop yielding 5,500 kg ha^{-1} (2020 average yield in Brazil) makes approximately USD 1,453 ha^{-1} (BRL 8,250) per harvest.

Commercial returns from phytomining decrease over time due to the gradual exhaustion of the Ni plant-available pool in the soil. However, the time frame for economic phytomining may be considerable (van der Ent et al., 2015). Considering that only 10 % of the 96 t ha^{-1} of the total Ni over 1 m depth of soil in Niquelândia (Table 2) will replenish the plant-available pool and a crop produces 100-200 kg ha^{-1} Ni, phytomining could be economically feasible for at least 48 years.

Although the high Ni accumulation and biomass yield of *A. murale* reported by Li et al. (2003) have rarely been found in the literature, they are achievable with appropriated crop management. Liming, mineral and organic fertilization, weed control, bacteria inoculation, plant density, and improved cultivars can increase the Ni phytomining efficiency (Chaney et al., 2007; Bani et al., 2015a,b; Hipfinger et al., 2021) and should be considered in any commercial phytomining program and developed for the hyperaccumulator of interest. Also, combining *A. murale* cultivation with citric acid application to ultramafic soils increased Ni and other metals accumulation (Nascimento et al., 2020), but field studies are needed to confirm the potential observed in controlled conditions.

The first large-scale experiments assessing phytomining feasibility in Europe started in 2005 in Albania (Bani et al., 2007, 2018), a country with 11 % of its territory covered by ultramafic substrates (Lekaj et al., 2019). These trials assessed the performance of *A. murale* growing on an ultramafic Vertisol during a five-year study in Pojske, Albania (Bani et al., 2015a). The crop value estimated for *A. murale* in Albania for a shoot Ni concentration of 11.5 mg kg^{-1} and a biomass yield of 9 t ha^{-1} (USD 1,055) was lower than obtained in the more intensive USA trials (Li et al., 2003). However, Bani et al. (2015a) stated that such profit makes extensive commercial Ni phytomining feasible for the Balkans context owing to the low economic input and possibility of *A. murale* rotates with traditional crops.

Field studies on tropical Ni phytomining are scarce compared to those developed in the USA and Europe. However, the technology is potentially attractive as some of the top nickel-producing countries in 2020 (Indonesia, The Philippines, Brazil, New Caledonia, Cuba, and the Dominican Republic) are tropical. Nkrumah et al. (2019) carried out pot and field trials to establish the first 'metal farm' in the tropics, which took place in Sabah (Malaysia) using the hyperaccumulator *Phyllanthus rufuschaneyi*. The results of this large-scale demonstration of Ni phytomining were promising. The notably high Ni concentrations in leaves of *P. rufuschaneyi* grown in field conditions (up to 28,000 mg kg^{-1}) and the high purity of the bio-ore generated show that phytomining can be economically attractive in Malaysia and other similar settings in the Asia-Pacific region. Countries in

South America, the Caribbean, and Africa also hold untapped opportunities to develop commercial phytomining.

Transforming Ni hyperaccumulator biomass into valuable products

Nickel recovering from the dried biomass of hyperaccumulators is the final step in the phytomining chain. The extraction of Ni from the biomass is carried out by pyrometallurgical or hydrometallurgical processes. Pyrometallurgy includes three primary operations (calcination, prereduction, and smelting) followed by further raw material refining to remove impurities (Keskinkilic, 2019). Hydrometallurgy, in turn, is the aqueous chemical processing of metals performed at relatively low temperatures through leaching, solution-phase upgrading, and purification of the recovered product (Simonnot et al., 2018). The raw material for these processes in the context of this review is the biomass of Ni hyperaccumulators, which can yield a bio-ore containing 10-25 % Ni, a figure much higher than the 1-2 % Ni in mined ores (Boominathan et al., 2004; van der Ent et al., 2015).

After drying and crushing of the plants, Ni can be thermally (with combustion) or chemically (without combustion) extracted from the biomass (Simonnot et al., 2018). The thermal approach can be performed by either feeding the plant ash into an existing smelter plant together with Ni sulfide and lateritic ores to produce ferronickel (Li et al., 2003) or ashing the biomass in an electrical furnace followed by metal leaching (Barbaroux et al., 2011), which seems more promising as the natural Ni purification made by plants is lost in the smelting process. In the chemical approach, dried and crushed biomass is directly acid leached to obtain a Ni-rich solution from where Ni is recovered (Barbaroux et al., 2011, 2012). However, leaching Ni from ashes is more efficient as Ni in the ash is 10 to 20 fold more concentrated than in plants (Zhang et al., 2016).

Once in an aqueous solution at enough concentration and purity, Ni can be recovered as a pure metal or a compound by chemical or evaporative precipitation. For instance, Barbaroux et al. (2012) produced an ammonium nickel sulfate hexahydrate (ANSH) salt ($Ni(NH_4)_2(SO_4)_2.6H_2O$) containing 13.2 % of Ni. Briefly, the method consisted of the following steps: 1) washing the ashes of *A. murale* aboveground tissues with water; 2) leaching of Ni from the washed ash with H_2SO_4 1.9 mol L^{-1} heated to 100 °C for 2 h (150 g L^{-1} of ash) followed by filtration; 3) adjustment of the ash leachate to pH 5.0 with a NaOH 5 mol L^{-1} followed by evaporation; 4) selective recovery of Ni by crystallization of the ANSH salt; and, 5) purification of the ANSH salt through resolubilization, precipitation of MgF_2 and recrystallization of the Ni salt. The same research group later improved this process by eliminating the number of steps to save water, chemicals, and energy (Zhang et al., 2016). The method was then up-scaled from the lab to the pilot scale (Houzelot et al., 2017) using an industrial furnace to increase the production of nickel salts and develop a valuable method for the recovery of nickel. Further efforts are in place to improve the efficiency of these processes, and they will undoubtedly bring new options to recover metals in large-scale phytomining programs.

CONCLUSIONS AND PERSPECTIVES

The interest in the study of ultramafic soils has sharply increased in the last two decades in parallel with the research on metal phytoextraction, which seems to derive from the potential to use these soils as low-grade ores to be commercially exploited using metal hyperaccumulating plants. However, the ultramafic environment also has ecological value as a unique ecosystem that deserves protection from degradation by anthropic impacts. Thus, phytomining operations must consider the economic issues and the environmental and social consequences related to the use of ultramafic lands.

Despite the impressive outcomes of the phytomining research in the last years, anchored in discovering new Ni hyperaccumulators worldwide, the technology has not been tested on a large scale by the mining industry. These demonstrations are crucial to building a case with the mineral sector. Phytomining can also offer opportunities to farmers in developing countries to add an extra income to these low-productivity agricultural soils. Although this review focused on ultramafic soils, phytomining can also provide opportunities for sustainable reclamation of metal-polluted sites and mine site rehabilitation.

From the hyperaccumulators agronomy to the Ni recovery, the feasibility of the phytomining chain has been proven in temperate and tropical settings. However, especially for the tropics, there are untapped opportunities in places with large ultramafic outcrops and Ni production, such as Indonesia, The Philippines, Brazil, New Caledonia, and Cuba. It is likely that the progress made in the recent and future studies, along with a partnership with the mining industry, will enable phytomining to be converted into a sustainable technology to recover metals from low-grade ores that otherwise would not be economically viable.

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