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► **To cite this version:**

Guillaume Losfeld, Laurent L'huillier, Bruno Fogliani, Tanguy Jaffré, Claude Grison. Mining in New Caledonia: environmental stakes and restoration opportunities. *Environmental Science and Pollution Research*, 2015, Combining Phytoextraction and Ecological Catalysis: an Environmental, Ecological, Ethic and Economic Opportunity, 22 (8), pp.5592 - 5607. 10.1007/s11356-014-3358-x . hal-01898232

HAL Id: hal-01898232

<https://hal.umontpellier.fr/hal-01898232>

Submitted on 24 Feb 2021

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Mining in New Caledonia: environmental stakes and restoration opportunities

Guillaume Losfeld · Laurent L'Huillier · Bruno Fogliani · Tanguy Jaffré · Claude Grison

Abstract New Caledonia is a widely recognised marine and terrestrial biodiversity hot spot. However, this unique environment is under increasing anthropogenic pressure. Major threats are related to land cover change and include fire, urban sprawling and mining. Resulting habitat loss and fragmentation end up in serious erosion of the local biodiversity. Mining is of particular concern due to its economic significance for the island. Open cast mines were exploited there since 1873, and scraping out soil to access ores wipes out flora. Resulting perturbations on water flows and dramatic soil erosion lead to metal-rich sediment transport downstream into rivers and the lagoon. Conflicting environmental and economic aspects of mining are discussed in this paper. However, mining practices are also improving, and where impacts are inescapable ecological restoration is now considered. Past and ongoing experiences in the restoration of New Caledonian terrestrial ecosystems are presented and discussed here. Economic use of the local floristic diversity could also promote conservation and restoration, while providing alternative incomes. In this regard, Ecocatalysis, an innovative approach to make use of metal hyperaccumulating plants, is of particular interest.

Keywords Ecological restoration · Conservation · Ecocatalysis · Phytoextraction · Nickel · Manganese

Introduction

In 1864, Jules Garnier discovered an unknown green rock on the Dumbea River, north of Noumea, New Caledonia. This rock was found to be a Ni-Mg silicate and contained about 15 % Ni (weight ratio): It was later named Garnierite for Mr. Garnier. Garnier's discovery was the starting point of nickel exploitation in New Caledonia: First mining operations are reported in 1873 on the Mont-Dore, and the first ore treatment plant was built in 1877 at Pointe Chaleix in Noumea (L'Huillier et al. 2010). Société Le Nickel (SLN) was founded in 1880 and remained the world largest nickel producer until 1905, when exploitation of the Sudbury deposit started in Canada. To date, SLN is still a world class operator of the nickel industry: The Doniambo smelter built in 1910 was still the second largest Ni laterite producer by 2008 (Mudd 2010). According to the latest estimates by the US Geological Survey (USGS), New Caledonia is currently the fifth producer of nickel in the world and may account for 16 % of acknowledged nickel reserves (USGS 1996–2013). Thus, the nickel industry should remain a major component of the island's economy in the upcoming decades.

In spite of its industrial reputation, New Caledonia is also a widely recognised biodiversity hot spot (Myers 1988; Myers et al. 2000) and is sometimes referred to as a living museum (Mittermeier et al. 1996). The marine environment there is highly regarded, and lagoons of New Caledonia are now listed as World Heritage Sites (UNESCO 2013). As regard to terrestrial ecosystems, New Caledonia is of particular interest to study plant

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evolution and diversification. The island has a unique and original flora: Latest studies reported 3,371 vascular plant species, 74.7 % of them being endemic to the archipelago (Morat et al. 2012). The main island, known as Grande Terre, probably separated from Gondwana during Late Cretaceous (80–100 Ma), was submerged during Palaeocene and Early Eocene and re-emerged during Late Eocene (37 Ma), creating a large ultramafic ophiolitic nappe covering the total surface area of Grande Terre, Belep and Isle of Pines (Pelletier 2006). Subsequent biological colonisation by long-distance dispersal occurred (Grandcolas et al. 2008; Pillon et al. 2010), with a high endemism driven by insularity, the high geological diversity and variations in climatic conditions, including rainfall patterns and altitude (Grandcolas et al. 2008; Jaffre 1993; Wulff et al. 2013). According to molecular clocks, numerous clades colonised the island much later than 37 Ma (Barrabe et al. 2014; Pillon 2012), which highlights the complex evolutionary pathways of the biota of New Caledonia and the interest of considering speciation, as well as possible extinctions. Most recent studies of the local flora focussed on *Amborella trichopoda*, whose genome could improve our general understanding of flowering plants (Amborella Genome Project 2013).

As regards to conservation, sclerophyll forests *mainly* on non-ultramafic substrates were the first strongly endangered terrestrial ecosystem from New Caledonia, because they were suitable for agriculture (Bouchet et al. 1995). However, emphasis is now shifting to the flora on ultramafic substrates (Pascal et al. 2008), an aspect discussed in details herein. Apart from hosting major nickel reserves, ultramafic outcrops from New Caledonia also host a unique biodiversity: So far, 2,153 plant species have been identified on such soils, with an endemism of 88 %. A total of 1,160 plant species, 95 % endemic, are strictly restricted to ultramafic areas (L'Huillier et al. 2010), which highlights the major interest of this flora. Species of particular interest such as nickel hyperaccumulators were discovered for the first time in New Caledonia on ultramafic substrates (Jaffre et al. 1976): They are particularly abundant there (Jaffre et al. 2013) and provide material for the fundamental understanding of metal hyperaccumulation (Merlot et al. 2014). Potential applications of nickel hyperaccumulators in phytomining (Chaney et al. 2007; van der Ent et al. 2013b) or Ecocatalysis, an innovative and promising Green Chemistry process (Escande et al. 2013; Escande et al. 2014a, b; Grison et al. 2014; Grison and Escande 2013a, b, c; Grison and Escarre 2011a, b; Losfeld et al. 2012a, b, c; Thillier et al. 2013) have raised awareness about their conservation: They may serve as flagship species for the metallophyte biodiversity, which is particularly threatened by mining operations (Whiting et al. 2004).

Significance of mining for New Caledonia

Geological characteristics

New Caledonia is an archipelago located in the Southwest Pacific (20–23 S, 164–167 E), northeast of mainland Australia, and southwest of Vanuatu. The main islands are located along two northwest-southeast ridges: Belep, Grande Terre (the main island) and Isle of Pines are on the New Caledonia ridge, while the Loyalty Islands, Lifou, Maré, Ouvéa and Tiga are on the Loyalty ridge. Two major tectonic events resulted in terranes found on the New Caledonia ridge: a Late Jurassic to Early Cretaceous tectonic collage and a Late Eocene subduction-collision, overthrusting a large ultramafic ophiolitic nappe (Pelletier 2006). Lateritisation, i.e. the tropical weathering of this nappe mainly composed of peridotite (harzburgite, dunite), produced Ni-rich laterites, as well as other ultramafic substrates. In the lateritisation process, most soluble elements such as K, Na, Mg, Ca or Si are washed, while less soluble elements such as Fe, Al, Ni or Co remain. Lateritisation is quick under tropical conditions and occurs in a two-step process: (i) dissolution of Si and Mg contained in pyroxene and olivine, with accumulation of Fe as oxyhydroxydes and (ii) recombination of Si and Mg as smectite clays. The first step produces ferritic ferralsols, which may be referred to as Ni-rich laterites, or 'terrains miniers' according to the local French denomination. The second step occurs in drier conditions and results in magnesian cambisols usually found at the base of the massifs (Fritsch 2012; Latham et al. 1978). Typical composition of ferritic ferralsols compared to magnesian cambisols can be found in Table 1: They mainly differ by their cation exchange capacity (CEC), higher for magnesian cambisols, due to higher exchangeable Mg.

The exceptional biodiversity of New Caledonia is often thought to result from the sole action of soil nickel as a major speciation driver. Yet, soils produced by lateritisation are not only ferritic ferralsols, as discussed in studies by Latham et al. (1978). Magnesian cambisols provide a meaningful example: They also host a unique biodiversity, although they are not subject to mining (Jaffré 1980; Latham et al. 1978). Thus, magnesian cambisols are geologically and ecologically different from Ni-rich laterites, as observed later in other areas (Alexander 2009). Grande Terre is also covered by non-ultramafic soils, after total erosion of 70 % of the initial surface area of the ophiolitic nappe (Pelletier 2006). The fact that New Caledonia has a unique biodiversity is due to insularity, climate (rainfall and altitude) and mountain reliefs (altitude and vicariance) (Grandcolas et al. 2008; Jaffre 1993; Wulff et al. 2013), and also but not only to the high edaphic diversity on ultramafic and non-ultramafic substrates (Jaffré 1980; Latham et al. 1978; Wulff et al. 2013).

Mining in New Caledonia targets ferritic ferralsols, which present a typical profile (Fig. 1): The top surface is made of an

Table 1 Typical composition of the upper horizon (0–20 cm) of ferritic ferralsols found at the ‘Camp des Sapins’ mine, New Caledonia; mine tailings produced at ‘Camp des Sapins’; and magnesian cambisols found in New Caledonia

		Ferritic ferralsol (n=12)		Mine tailings (n=12)		Magnesian cambisol (n=80)	
		Mean	SD	Mean	SD	Mean	SD
	pH	6.4	0.1	7.7	0.2	6.81	0.5
	%N	0.04	0.01	0.01	0.00	na	na
	%C	1.33	0.28	0.37	0.14	na	na
	CEC (meq%)	4.68	0.48	6.88	0.93	40.9	18.2
Exchangeable cations (meq%)	Ca	0.32	0.12	0.13	0.04	2.35	2.31
	Mg	3.71	1.11	9.76	2.30	33.5	15
	Na	0.02	0.01	0.03	0.02	0.35	0.19
	K	0.04	0.01	0.05	0.05	0.22	0.17
Phosphorus (mg/kg)	Available	53.5	6.9	40.5	21.9	108	89
	Total	0.6	0.9	1.1	1.2	na	na
DTPA extraction (mg/kg)	Ni	23	10	134	17	na	na
	Mn	186	100	198	48	na	na
Total extraction (mg/kg)	Ni	8008	523	9251	1935	6000	270
	Mn	6150	612	3645	915	4300	380

‘iron cap’, red and yellow limonites are next, while saprolite boulders are found at the parent bedrock interface, and sometimes include garnierites (Freyssinet et al. 2005). In comparison to weathered horizons, the parent peridotite contains an average 0.3 % Ni, 30–45 % MgO and more than 40 % SiO₂ (weight ratios). Such soils are common under tropical humid climates, e.g. in Indonesia (van der Ent et al. 2013b), South-America (Brazil, Colombia) and the Caribbean (Cuba, Dominican Republic), but they also occur at higher latitudes, e.g. in Mediterranean regions (Greece, the Balkans) or in the USA (Oregon, CA) (Freyssinet et al. 2005). By 2008, world nickel production was mainly from Ni sulphides, (788.6 kt Ni), while Ni-rich laterites only account for a third of the production at 369.1 kt Ni: This is mainly due to technical difficulty in treating lateritic Ni ores. However, Ni laterites now represent about 50 % of the reserve at 31.2 Mt Ni versus 31.6 Mt for sulphide ores, and they probably represent the future of nickel supply (Mudd 2010).

Ultramafic outcrops in New Caledonia cover about 5,600 km², i.e. 30 % of the total area of the main Island. They include Ni-rich laterites, and they are currently largely exploited (Fig. 2). From 1873 until 1988, Ni production from New Caledonia solely relied on saprolitic ores (Fig. 1). These ores were treated using blast furnaces from 1910 to 1957, while rotary kiln electric furnaces (RKEF) were introduced in 1958 and are still in use (Mudd 2010). Since 1988, limonitic ores are also treated using RKEF (Fig. 3) and represent a half of extracted ores but only 23 % of Ni production. This is due to ore grades: an average 2.5 % Ni for saprolites versus 1.7 % for limonites (DIMENC 2008). Low grades and physical properties of limonites, e.g. their water-holding capacity, as well as energy costs could make hydrometallurgy more

economic. Hydrometallurgical processes, aiming to extract nickel and cobalt from limonites, are currently experienced by Vale NC on the Goro deposit South of Noumea, New Caledonia. Several technical difficulties, serious delays and

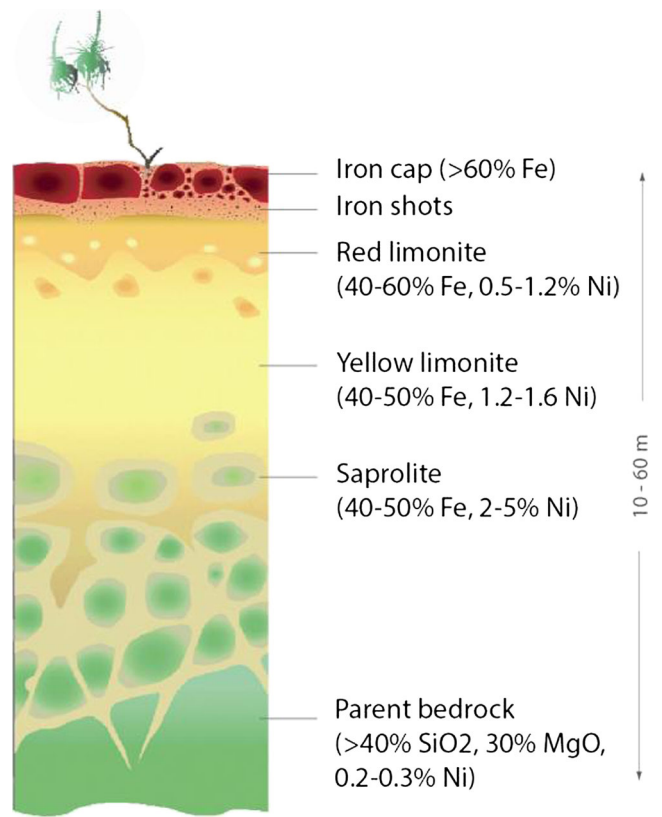
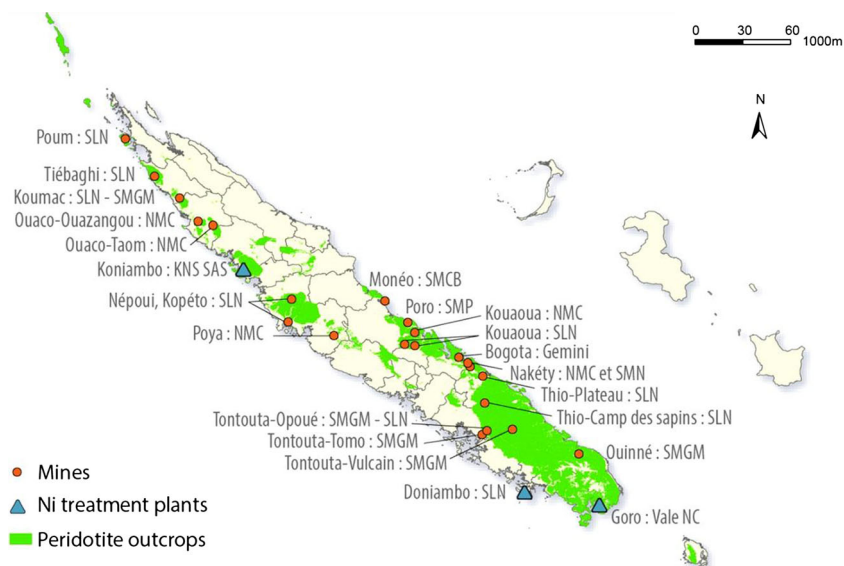


Fig. 1 Typical soil profile on ultramafic outcrops adapted from Pelletier (2006)

Fig. 2 Ultramafic outcrops from New Caledonia and associated mining operations



major concerns about environmental safety (Ali and Grewal 2006) emerged, but hydrometallurgy will nonetheless take a major part in the future of nickel in New Caledonia, with projects also considered by SLN (Lequesne 2014).

According to the latest estimates by the USGS, New Caledonia is currently the fifth Ni producer in the world and may account for 16 % of acknowledged nickel reserves (USGS 1996–2013) and should continue to play a major role in the worldwide Ni industry.

A major economic driver

Current trends in global nickel production show a fairly stable increase since 1950 at an average +4.4 % per year (Mudd 2010). Reserves (according to the USGS definition) of nickel have increased lately from 40 Mt nickel in 1999 to 70 Mt in 2009. At the same time, reserve base increased from 140 to 150 Mt (USGS 1996–2013): This may allow production for a further 40 years at least. Major uses of nickel include stainless

steel production (58 %), Ni-based alloys (14 %), casting alloys and steel (9 %), electroplating (9 %) and rechargeable batteries (5 %) (Mudd 2010). Although useful, nickel is not strategic, and prices remain low compared to other commodities such as Pt or rare earth elements, yet with a high volatility (Fig. 4). Although recycling is technically feasible, it has not developed so far: In the current economic situation, nickel supply mainly comes from primary production. Thus, demand is likely to maintain, with New Caledonia in a good position to reap the benefits.

New Caledonia’s economy is essentially relying on the nickel industry: The share of nickel in the island gross domestic product (GDP) was on average 8.6 % (± 3.6 %) over 1999–2008 and reached a record high above 30 % in year 1968 (Fig. 4). Over the same time span, nickel exports including ores and refined products accounted for an average 93 % (± 3.2 %) of the total value of exports from New Caledonia (Fig. 5). As appears from Fig. 4, the share of nickel in the GDP correlates with nickel prices: Over 1999–2008, 76 % of the

Fig. 3 Types of ores exploited (kt ore) in New Caledonia and total nickel production (kt)

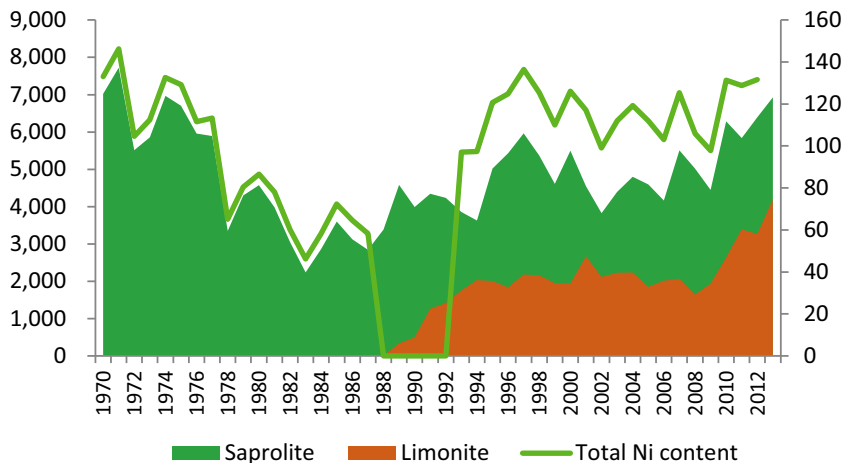
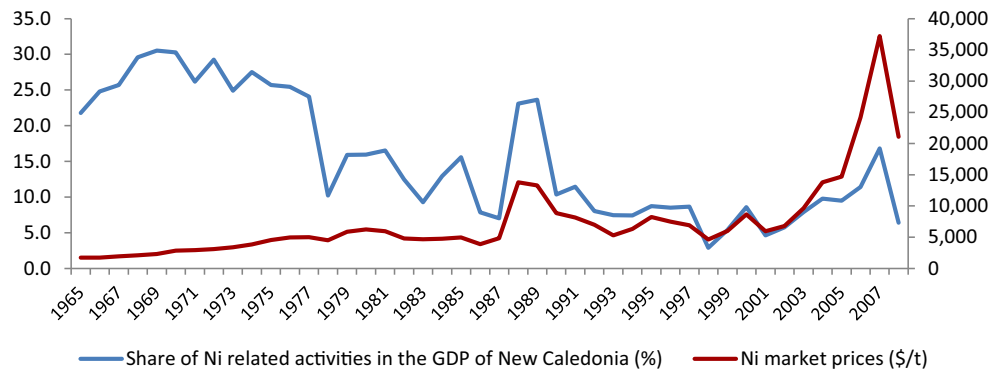


Fig. 4 Share of nickel-related activities in the GDP of New Caledonia along with nickel market prices



variance observed can be explained by nickel prices. The case of the value of nickel exports is similar with 83 % of its variance explained by nickel prices. These data also show a nickel production uncorrelated with nickel prices: A main reason is that mines and smelters cannot react to price volatility. But, it also shows some sort of dependence of the New Caledonian economy on nickel, creating a possible vulnerability to variations in nickel. New Caledonia should probably diversify its sources of incomes, so as to make its economy more resilient to nickel price volatility.

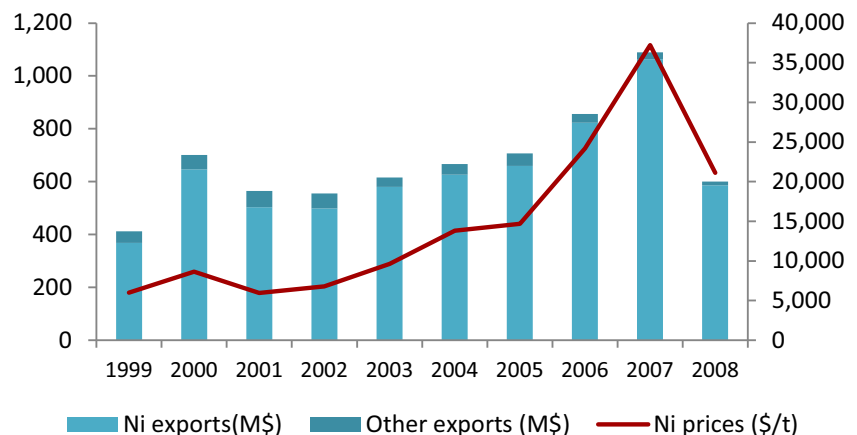
However, major investments in the nickel industry recently took place in New Caledonia: SLN spent 110 M€ to improve existing ore treatment facilities, while Koniambo Nickel SAS (KNS) and Vale NC built two new plants for 2,300 M€ and 2,600 M€, respectively. Although initially planned for 2009 (Ali and Grewal 2006), first casting operations occurred in April 2013 at the KNS plant. In spite of recent financial crisis resulting in drastic decreases in nickel prices, a 3-fold increase in production capacity should result from these investments, raising it from 60,000 t nickel per year to about 200,000 t. Negotiations are also under way to start exploration of major deposits at Creek Pernod and Prony Bay, South of Noumea. Nickel could then represent 30 to 40 % of the GDP of the island (L’Huillier et al. 2010): It is clearly the major driver of the island’s economy, with strong effects on country planning

policy, population growth, livelihoods, ways of life and also the environment.

Environmental impacts

Environmental losses probably occurred in New Caledonia since the Melanesian discovery of the island some 3,500 years ago. Traditional agricultural practices include the use of fire to clean fields between cropping seasons and turned sclerophyll forests into niaouli savannas (*Melaleuca quinquenervia*, a fire-resistant species). French colonisation of the island (1854) dramatically increased losses by clearing large areas of sclerophyll forests for cattle grazing mainly. By now, sclerophyll forests only cover 2 % of their original area and represent a conservation challenge (Bouchet et al. 1995; Gillespie and Jaffre 2003). Introduction of alien animals such as cats, rats, dogs or the Indonesian deer (*Cervus timorensis*) also proved detrimental: Large deer populations exert strong grazing pressures, thus preventing the recovery of forests, while birds such as the flagship species Kagu (*Rhynocetos jubatus*) are threatened by cats, rats and dogs (Mittermeier et al. 1996; Robinet et al. 1998). In the case of alien plants, they may become invasive in savannas and outside ultramafic outcrops in general, but extreme edaphic conditions on ultramafic outcrops make them of lesser concern in this

Fig. 5 Share of nickel exports from New Caledonia along with nickel market prices



environment (Meyer et al. 2006). Although sclerophyll forests are probably the most impacted and endangered terrestrial ecosystem from New Caledonia, mining is also recognised as a potential threat (Dugain 1953; Jaffré et al. 1977) with mining-related environmental issues still high on the agenda (Jaffre et al. 2010; L’Huillier et al. 2010; Pascal et al. 2008; Wulff et al. 2013).

In the beginning, mining operations were mainly carried underground following high-grade lodes (up to 15 % Ni in garnierites). Open cast mining appeared around 1920 as a result of decreasing ore grades (5 % Ni, weight ratio): Before ores can be accessed, vegetation cover, topsoil and low-grade limonites are removed, thus exposing bare ground (Fig. 6). However, it remained limited to small exploitations relying on human forces mainly. Mechanisation occurred after World War II and allowed the exploitation of ores with continuously decreasing Ni content, about 1.7 % Ni in limonites and 2.5 % in saprolites (DIMENC 2008). From 1950 to 1975, mining was conducted recklessly, with high environmental impacts: Low-grade limonites and rocks were usually pushed down the slopes and ended up in thalwegs. Decreasing ore grades also increased the quantity of spoils (non-refined waste from open cast mining) and tailings (waste from ore processing) that have to be treated: Current trends are at 3.5 t spoils moved to access 1 t ore (Table 2).

Resulting perturbations on water flows and dramatic soil erosion (Bird et al. 1984; Dupon 1986; Latham 1971) cause metal-rich sediment transport downstream into rivers and the lagoon (Ambatsian et al. 1997; Fernandez et al. 2006; Migon et al. 2007; Ouillon et al. 2010), with possible bioaccumulation (Bustamante et al. 2000; Hedouin et al. 2007), and potential toxicity to marine organisms (Florence et al. 1994). In some cases, fertile areas along river banks were lost, due to continuing sedimentation of metal-rich sediments (Danloux

and Laganier 1991; Dupon 1986; Jaffré et al. 1977), which may cause phytotoxicity or accumulation in cultivated plants (L’Huillier and Edighoffer 1996). In 1975, new techniques were set up by SLN to limit environmental impacts (Jaffré and Pelletier 1992). These are now generally considered as good practice guidance and include the following:

1. Replacement of crawler dozers by excavators and dump trucks,
2. On site storage of mine spoils using stable and well-drained piles (Fig. 7),
3. Bunds protecting track sides and limiting excavation areas,
4. Effective control of water flows on mines, so as to reduce terrigenous inputs into water streams and the lagoon.

International environmental standards are also being enforced, with SLN expecting to comply with ISO 14 001 by 2014.

However, economic constraints usually prevail, and spoils or tailing storage still happens in thalwegs, where remnant forests may stand (Jaffre et al. 2010). This issue is only to become more acute with the exploitation of lower grade ores, such as limonites. It will result in continuing habitat loss and fragmentation and erosion of the local biodiversity. According to Jaffré et al. (2010), the best practice could be to store mining waste only where severe degradation already occurred, typically old mines. In spite of a general agreement that prevention of further damage is the priority, 20,000 ha of degraded land still needs crucial rehabilitation (DIMENC 2008). The ecological restoration (as defined by the Society for Ecological Restoration (2004)) of ecosystems affected by mining is considered (L’Huillier et al. 2010) but still needs further development. Mine rehabilitation combined with economic uses of

Fig. 6 Impacts of mining as seen at the ‘Camp des Sapins’ mine, Thio, New Caledonia



Table 2 Estimation of the quantity of ore extracted from New Caledonia and the resulting spoil production (DIMENC 2008)

Time span	Extracted ore (t)	Ratio spoil/ore	Spoil (t)
Before 1920	3 048 549	1,0	3 048 549
1921–1950	5 003 762	1,5	7 505 643
1951–1975	78 356 696	2,0	156 713 392
1976–2001	133 118 259	3,5	465 913 907

the local biodiversity provides interesting perspectives, e.g. recycling of metal hyperaccumulating plants through a new chemical concept, termed ‘Ecocatalysis’, which represents an extraordinary environmental opportunity. The concept is based on a novel but very important market in ‘Green Chemistry’, which is ‘Lewis acid’ catalysts used in organic synthesis. This type of catalysis is one of the most powerful tools to obtain chemical transformations with low environmental impacts (Escande et al. 2013; Escande et al. 2014a, b; Grison et al. 2014; Grison and Escande 2013a, b, c; Grison and Escarre 2011a, b; Losfeld et al. 2012a, b, c; Thillier et al. 2013).

Opportunities for the restoration of mining-impacted ecosystems

Reclamation, phytoremediation or ecological restoration?

In conjunction with current efforts to make mining less harmful, it is also crucial to address the challenging task of reclaiming the ecosystems affected by mining. A general reflection has been conducted on this aspect but was mainly based on experiences from Western Europe, especially the UK (Bradshaw 1997; Bradshaw 1992; Tordoff et al. 2000). Developing countries are nonetheless catching up, with various experiences reported (Fitamo and Leta 2010; Kamran et al. 2014; Lum et al. 2014; van der Ent et al. 2013b), particularly from China (Shu et al. 2005; Wong 2003; Ye et al. 2000). Past experiences may provide a general framework to plan and assess reclamation schemes and may be

useful for New Caledonia. The main aims identified are the following:

1. prevent soil erosion by water or wind,
2. limit the dispersion of metal-rich particles,
3. and restore the aesthetical value of impacted landscapes.

Such aims can be achieved by the development of a perennial vegetation cover: This approach is deemed cost-effective and boasted better public acceptance (Bradshaw 1997). Limiting factors then fall into three categories:

1. Physical, e.g. poor soil structure resulting in low water-holding capacity,
2. Nutritional, as mine spoils and tailings are often deficient in essential macronutrients,
3. And toxicity, as residual concentrations of metals may hinder the development of a viable vegetation.

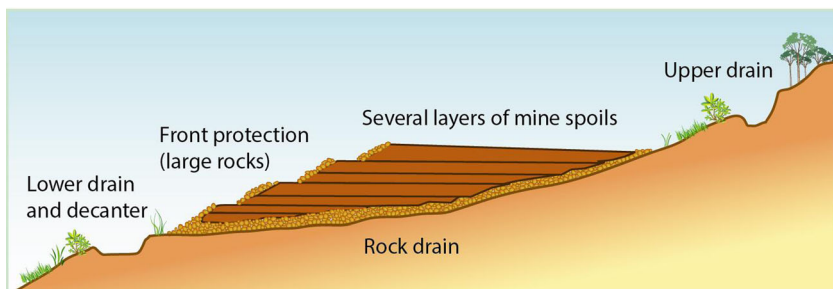
Moreover, although successful reclamation was achieved at specific sites, there is no generally applicable technology, mainly because of large variations in physical, chemical and biological factors, as well as climate (Tordoff et al. 2000). In line with Bradshaw (1997b), it is also necessary to distinguish between simple reclamation and restoration. Both share the aims and issues stated previously, but

1. Reclamation only requires the achievement of an appropriate ecosystem, which may have different structure and functions compared to the original ecosystem (i.e. before mining).
2. Restoration on the other hand requires both structure and functions of the original ecosystem to be achieved.

Taking the unique and original flora of New Caledonia into account, restoration appears as the most desirable possibility.

The concept of phytoremediation emerged in 1993 as a unifying approach to the use of plants to tackle soil contamination issues, including mining-related metal contamination (Cunningham and Berti 1993). Research efforts were mostly focussed on two approaches:

Fig. 7 Typical storage of mine spoils



1. phytostabilisation, where the development of sustainable vegetation should prevent contaminant mobilisation
2. and phytoextraction, where plants are used as bio-pumps to extract contaminants.

Subject to much debate in the literature for its possibly too broad scope and confusing terminology (Conesa et al. 2012; Ernst 2000), phytoremediation is not fully relevant to address mining impacts where lateritic ores are exploited. In the case of New Caledonia, main reasons for that can be the following:

1. Unharmed or less harmed ecosystems can usually be found nearby mines and may provide a reference for restoration. Such ecosystems are recognised for their high endemism and have patrimonial value (Bradshaw 1997b; Jaffré 1980; Whiting et al. 2004)
2. The vegetation naturally occurring on ultramafic outcrops from New Caledonia is already adapted to some of the edaphic constraints found on nickel mines or mining waste, high Mg and low P for instance (Table 1). Additional constraints related to mining impacts, e.g. compaction, heterogeneity, poor soil structure, lack of organic matter and low water-holding capacity, nonetheless exist, but the local and often endemic vegetation can provide suitable candidates for mine site restoration (Jaffré and Pelletier 1992).
3. Ferritic ferralsols found on ultramafic outcrops from New Caledonia are naturally rich in nickel as well as other potentially toxic metals such as Co or Cr (see Table 1), and they are not suitable for agriculture. Therefore, mines cannot be considered as contaminated land. Removal of the metals through phytoextraction is not necessary.

A detailed comparison of the respective cases of nickel mines from New Caledonia (lateritic ores) and Canada (Sudbury, sulphide ores) was made by Bradshaw (1997b): Different impacts can be related to mining practices (open cast in New Caledonia, below ground in Canada), ores chemistry and ore enrichment needs. Such parameters and the local environment need to be thoroughly understood to determine where phytoremediation can be useful, e.g. in Canada and where restoration may be more desirable, e.g. in New Caledonia. A critical look at the literature also shows that phytostabilisation is very similar to reclamation as defined by Bradshaw (1997b) and probably overemphasises the role of the vegetation cover in mine site reclamation. Although useful, vegetation cannot be the sole tool to achieve mine reclamation (Robinson et al. 2009).

Lately, the concept of ecological restoration emerged (SER 2004), along with the idea of natural capital (Clewell and Aronson 2006): It is in line with recommendations by Bradshaw (1997b) and represents the most relevant approach for New Caledonia. Ecosystem services such as the regulation

of water flows or the control of soil erosion are obviously provided by a sustainable plant cover, but ecosystems from New Caledonia also have a patrimonial value: They provide fundamental insights on the evolution of plants (Amborella Genome Project 2013) but also valuable molecules with pharmaceutical properties (Allard et al. 2011; Allard et al. 2012). Nickel hyperaccumulating plant species were also discovered for the first time in New Caledonia (Jaffre et al. 1976), and they are particularly abundant there, along with manganese hyperaccumulators and accumulators (Fernando et al. 2013; Jaffré 1980; Jaffre et al. 2013). Such species provide material for the fundamental understanding of metal hyperaccumulation (Jaffre et al. 2013; Merlot et al. 2014); they may serve as a starting material for innovative applications (Escande et al. 2014a; Grison and Escande 2012; Losfeld et al. 2012b). Thus, ecological restoration of New Caledonian ecosystems affected by mining appears as the most comprehensive objective, since 2009 required by law to plan mine rehabilitation in New Caledonia and good practice guidance issued by local scientists advocates for ecological restoration (L'Huillier et al. 2010).

Past and ongoing experiences from New Caledonia

Selection of metal-tolerant species for mine reclamation or restoration was performed in the UK as early as 1979 (Smith and Bradshaw 1979) but was still not on the go for tropical ecosystems by 2000 (Tordoff et al. 2000). However, there is probably a flaw in reporting experiences, with an extensive literature available in French on mine restoration in New Caledonia (Jaffré et al. 1994; L'Huillier et al. 2010). As appears from the literature, New Caledonia is probably the leader in the restoration of tropical ecosystems impacted by mining. This is due to early realisation of dramatic soil erosion (Dugain 1953) and acute awareness of the value (on various grounds) of the local biodiversity (Myers 1988).

First field experiments to investigate the possibility of mine revegetation started in 1971 in New Caledonia under the direction of the 'Centre Technique Forestier Tropical' (CTFT) at the request of the AMAX company. These experiments conducted in the south of Grande Terre were followed by many others on different mining lands during 10 years, at the request of the mining company SLN, under the supervision of the CTFT or the 'Office de la Recherche Scientifique et Technique d'Outre-Mer' (ORSTOM). The aims of the first experiments were clearly not to achieve the ecological restoration of the areas impacted by mining but merely to control soil erosion and restore some aesthetical value to the impacted landscapes. During this period, the response of many exotic and native species was investigated on various soil types including limonites, mine spoils and tailings, at different altitudes, with different plantation densities, soil preparation and fertilising treatments. A comprehensive report of these

experiments was issued in 1990 after at least 9-year follow-up (Cherrier 1990). The following conclusions could be drawn:

1. any type of soil decompaction before plantation is useful,
2. mulching is a useful way to retain soil humidity,
3. and the use of topsoil and fertilisers always significantly improves plant response.

The above recommendations are still in use now. As regard to species selection, two species gave the best results in terms of their survival and growth: a native legume, *Acacia spirorbis*, and an endemic Casuarinaceae, *Casuarina collina*, which is morphologically and ecologically very similar to the invasive species *Casuarina cunninghamiana*. Because of their gregarious behaviour, these species tend to form monospecific populations and hinder further ecological succession. They are even considered invasive in different conditions of soils and altitude (Meyer et al. 2006). Thus, the widespread use of these sole species has been deprecated (Jaffré et al. 1997; L'Huillier et al. 2010). Introduced legumes and grasses were not successful.

First consideration of restoration rather than mere reclamation appeared in 1989, concretised by several agreements between ORSTOM (now IRD) and SLN, and also by experiments involving CTFT (which became CIRAD Forêt and now IAC), the Southern Province and mining companies. Research has focussed on selecting a set of native pioneer species, herbaceous and shrubby, likely to initiate the phenomenon of secondary succession. These studies led to the selection of around 60 species including Cyperaceae (*Machaerina* (ex. *Baumea*) *deplanchei*, *Schoenus juvenis*, *Schoenus neocaledonicus*, *Costularia comosa* and *Lepidosperma perteres*), nitrogen-fixing species such as *Serianthes calycina* (Fabaceae) or species of the *Gymnostoma* genus (Casuarinaceae), and various species of the 'maquis minier' such as the following: *Grevillea* spp (Proteaceae), *Carpolepis laurifolia*, *Tristaniopsis guillainii* (Myrtaceae), *Oxera neriifolia* (Lamiaceae). Collaboration of SLN, ORSTOM and local research institutes resulted in the publication of a book (Jaffré and Pelletier 1992), with detailed data on about 60 pioneering species usually observed to grow on areas impacted by mining. The publication of such a book made valuable data available and probably spurred the development of commercial tree nurseries to ensure mine reclamation: It was a major step towards the ecological restoration of mining-impacted ecosystems from New Caledonia.

However, seed collection appeared difficult, and the quantity of available seeds was limited. Successful plantation from cuttings was also achieved for various species, but this approach is now less considered as it does not maintain genetic diversity. The perspective of using hydroseeding was also raised as it clearly appeared as a cost-effective option only limited by seed availability. Since 2000, research continues

and now focusses on improving the knowledge on seed ecology, dormancy, germination and seed conservation (Wulff et al. 2012b), on genetic diversity (Wulff et al. 2012a) and structures of plants and associated microorganism communities (Amir et al. 2008; Amir et al. 2007). An improved understanding of the interactions between plants, fauna and microorganisms was achieved: Cyperaceae were particularly investigated for the possibility to produce large quantities of seeds (Lagrange 2009), an improved knowledge of rhizobia associated with *Serianthes calycina* (Chaintreuil et al. 2007; Hery et al. 2005) and frankia associated with Casuarinaceae (Gauthier et al. 1999; Navarro et al. 1999) and mycorrhizal associations (Jourand et al. 2014; Lagrange et al. 2013). This allows improving germination performance, the management of topsoil, taking into account the importance of mycorrhizae in the establishment of plants, recommending a set of plants increasingly diversified and adapted to different environmental conditions. Multiple collaborations resulted in the publication of a collective reference book (L'Huillier et al. 2010), which assesses the knowledge acquired over 40 years on mining environments in New Caledonia, makes recommendations on best available practices in ecological restoration and gives practical information on the use of about a hundred plant species.

Potential for the economical exploitation of Ni and Mn hyperaccumulators from New Caledonia

Phytoremediation by way of phytoextraction and phytomining

Two approaches to the commercial use of metal hyperaccumulators have been widely investigated:

1. Phytoremediation by way of phytoextraction, often referred to as phytoextraction, addresses the issue of metal-contaminated soil and aims to provide a cost-effective way to clean them.
2. Phytomining, initially termed 'biomining' (Cunningham and Berti 1993), refers to the use of plants, usually metal hyperaccumulators, to produce bio-ores subsequently used in metal production (Brooks et al. 1998).

However, the design of both approaches is probably not fully relevant with the aims stated.

A major limitation of metal removal by phytoextraction remains: No relevant uses for the contaminated biomass have been found (Ernst 2000; Sas-Nowosielska et al. 2004). Current reflection in the scientific community suggests finding alternative uses for sites contaminated with metals such as closed mines (Conesa et al. 2012; Ernst 2005). According to Conesa et al. (2012), 'The commercial success of phytotechnologies depends on the generation of valuable

biomass on contaminated land, rather than a pure remediation technique that may not compare favourably with the costs of inaction or alternative technologies'. However, it was previously emphasised that such options are not relevant for New Caledonia, where fast growing high-biomass species usually considered are not available (Grison et al. 2013; Losfeld et al. 2012b) and where introduction of alien species could be undesirable, illegal and probably unproductive (L'Huillier and Edighoffer 1996; L'Huillier et al. 2010).

Phytomining, initially termed biomining (1993), was thought of as a potential outlet for the metal-contaminated biomass produced in phytoremediation by way of phytoextraction: In this case, the biomass should be considered as metal-rich rather than contaminated. However, phytomining now generally refers to the use of plants, usually metal hyperaccumulators, to recover valuable elements from low-grade ores and not from contaminated soil (Brooks et al. 1998). As nickel hyperaccumulating species are most common, phytomining for Ni was considered to have the greatest potential. Au phytomining was also considered (Anderson et al. 1998); although technically more difficult (Wilson-Corral et al. 2012), it is motivated by Au prices 2,500 times higher than Ni.

Phytomining was developed for Ni to an industrial level using *Alyssum* species grown in Oregon, USA. Nickel recovery from the biomass was performed by treating plant ashes in pyrometallurgical units (Chaney et al. 2007). Other trials are currently underway, using chemical separation techniques (Barbaroux et al. 2012), with biomass supply originating from Albania (Bani et al. 2007). Although metallophyte biodiversity hotspots are located in tropical areas, e.g. Cuba or New Caledonia (van der Ent et al. 2013a), there are few reports of phytomining experiments in tropical areas, and it was not expected to have the greatest potential (Reeves 2003). First experiments in tropical Ni phytomining were reported by van der Ent et al. (2013b). In spite of the renown of its metallophyte biodiversity, phytomining was never considered in New Caledonia until recently (Losfeld et al. 2012b). Interesting lessons can be drawn from other experiences:

1. Focussing on the local biodiversity may avoid poor results, as reported using *Alyssum* species in Indonesia (Anderson 2013; van der Ent et al. 2013b).
2. It may also avoid the emergence of invasive species as was the case for *Alyssum* species in the USA (Oregon Department of Agriculture 2014).
3. It is a way to promote the conservation of metallophyte species (Whiting et al. 2004).

Considered unrealistic in first instance (Baker et al. 1988), phytomining is not reported to have met the expected commercial success. In the case of nickel, current turmoil in the

industry due to low prices is not likely to make Ni phytomining profitable.

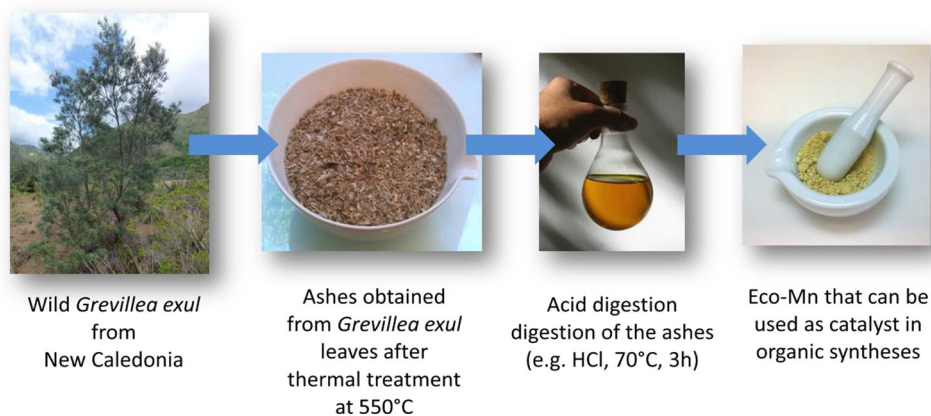
The emergence of Ecocatalysis as a tool for Green Chemistry

New applications for metal-rich biomass emerged in late 2009 in the field of Green Chemistry (Grison and Escarre 2011a; Grison and Escarre 2011b). Plant species able to hyperaccumulate transition metals, e.g. Ni^{2+} and Mn^{2+} , can be directly used as green reagents and catalysts in organic fine chemical reactions (Grison et al. 2014; Grison and Escande 2013a, b, c; Grison and Escarre 2011a, b; Losfeld et al. 2012b, c; Thillier et al. 2013). This original approach brings the first perspective of enhancing the unique metal-rich biomass and establishes a new field of Green Chemistry: Ecocatalysis. The first results show that polymetallic ecocatalysts could present performances and selectivity largely higher than classical homogenous and heterogeneous catalysts. The concept of Ecocatalysis is no longer a simple recovery of phytoremediation technologies. Ecocatalysts are original (unusual oxidation states, new associated chemical species) and effective, and they offer a unique opportunity of cooperative catalysis with the huge potential synergetic activity of plant elemental composition. Their activities, chemo- and stereo-selectivity and recyclability are higher than classical catalysts in various reactions (Escande et al. 2013; Escande et al. 2014a, b; Grison et al. 2014; Grison and Escande 2013a, b, c; Grison and Escarre 2011a, b; Losfeld et al. 2012c). These results encourage a new approach to metal phytomining: It is now recognised as an alternative source of metals for Green Chemistry (Hunt et al. 2014), and various teams are now looking into Ecocatalysis (Parker et al. 2014). The general pathway from zinc, nickel, copper, palladium, manganese-rich plants to ecocatalysts, exemplified for manganese accumulator *Grevillea exul* (Fig. 8), starts with the collection of metal-rich leaves. The leaves are thermally treated (550 °C max), which releases water and destroys organic matter. Metal-rich ashes obtained are treated with diluted acids, e.g. hydrochloric acid to produce polymetallic Lewis acids. Under optimised conditions, the ecocatalyst was dispersed on montmorillonite K10. Composition of the solid finally obtained is original and results in higher catalytic activities compared to pure Lewis acids that are commercially available, e.g. ZnCl_2 or NiCl_2 (Escande et al. 2014a, Grison et al. 2013).

Example application using Grevillea exul leaves to catalyse the Biginelli reaction

The original composition of Eco-Mn derived from *G. exul* prompted us to investigate how this mixture could initiate Lewis acid-catalysed reactions. We wish to give an illustrative example, which culminated in a three-component reaction, the Biginelli reaction leading to dihydropyrimidinones, described

Fig. 8 Key steps to produce solid catalysts from Mn-rich biomass (*Grevillea exul*)



in full details by Grison et al. (2013) and Escande et al. (2014a) with Eco-Zn and Eco-Ni. The chemical reaction can be catalysed by Ni hyperaccumulators, e.g. *Psychotria douarrei* and *Geissois pruinosa*, as well as Zn hyperaccumulators, e.g. *Noccaea caerulescens*. We describe here the first utilisation of Eco-Mn, the ecocatalyst derived from *G. exul* as an example species (useful for the phytoextraction in New Caledonia) in this multi-component reaction. The Biginelli reaction provides access to molecules with interesting pharmacological properties (Kappe 2000) including monastrol, a famous mitosis inhibitor (Mayer et al. 1999). Using ecological catalysts derived from New Caledonian species allows the synthesis of known dihydropyrimidinones with improved yields but also allows access to unknown dihydropyrimidinones with potentially new interesting pharmacological properties (Escande et al. 2014a; Grison et al. 2013). The supported catalyst, the two substrates and the reagent were mixed thoroughly and stirred at 80 °C under solvent-free conditions for 12 h. According to our proposal, Eco-Mn promoted the reaction between benzaldehyde, ethyl 3-ketopentanoate and urea in a one-pot protocol. After recrystallisation, the pure expected heterocycle (ethyl 6-methyl-4-phenyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (monastrol)) was obtained with a high yield (88 %) (Fig. 9).

Typical yield for manganese accumulator *G. exul* in natural conditions is 2-kg dry biomass per individual at 4,000 mg manganese per kg dry leaves. Plantation densities up to 2,500 individual par hectare are possible, which would lead to

potential yields of 20 kg manganese per hectare per harvest. This allows the production of 213-kg manganese-rich catalyst at 9.4 % manganese per cultivated hectare. The use of 213-kg catalyst in one Biginelli reaction (Table 3) could produce 415 kg of the dihydropyrimidinone of interest. The process allows Eco-Mn recycling without significant loss of activity: A second cycle resulted in 830-kg product. The ecocatalyst led to higher yield in greener conditions than commercial Lewis acids. It must be noticed that the added value is generated from selling the chemical product finally obtained, which decorrelates incomes from metal prices. Thus, mine reclamation combined with economic profits has some potential in New Caledonia, an interesting option to support reclamation as well as ecological restoration.

Conclusion

At present, the economy of New Caledonia is largely supported by nickel production and ore exports: The archipelago is currently the fifth world producer of this metal and may account for some 16 % of acknowledged reserves. Thus, future economic development is also likely to rely on further exploitation of nickel. Yet, New Caledonia is also recognised for its remarkable biodiversity, the flora on ultramafic substrates being a major component of this biodiversity. Nickel-rich laterites, locally known as terrains miniers, host a particularly original flora, including various species with the ability to accumulate nickel or manganese.

Fig. 9 Synthesis of a pyrimidinone (Biginelli reaction)

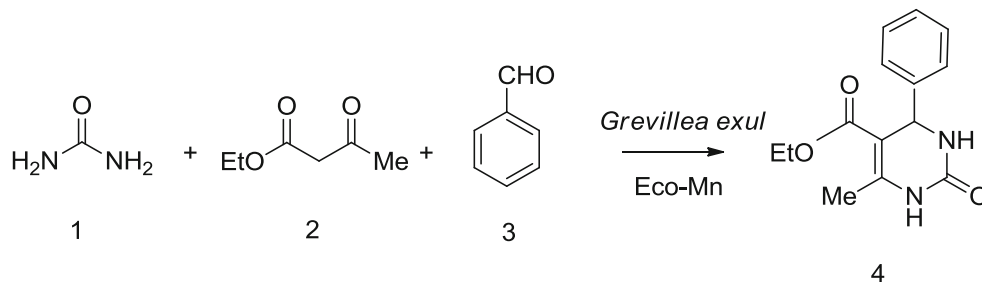
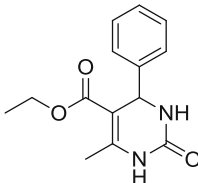


Table 3 Stoichiometry and yields of an example of the Biginelli reaction

Reagents	1	2	3	Catalyst	4
-	Urea	Ethyl acetoacetate	Benzaldehyde	Mn from <i>Grevillea exul</i> Eco-Mn@ 9 wt% Mn	
Stoichiometry	1	2	2	0.2	1 (with 88 % yield)

Mining for nickel started some 140 years ago in New Caledonia, with significant production increases in the last decade. As a result, fires and mining are now the major threats to the terrestrial biodiversity of the archipelago. In an attempt to reduce the impacts of nickel exploitation, mining companies have progressively developed new practices for prospection, mine layouts and the management of mining effluents. However, mining is still open cut, and with decreasing ore grades, large surface areas will be stripped, and large volumes of soil disturbed. Because of the value of the local and often endemic flora, as impacts cannot be fully circumvented, restoration of the mining environment has to be considered.

Research on these aspects is led by various institutes and was often funded by mining companies themselves. It increased the understanding of the mining environment and allowed the selection of species suitable for restoration, with the ability to withstand poor edaphic conditions. First experiments focussed on exotic species, or local species with gregarious or even invasive behaviours. The results obtained remained far from the expectations of ecological restoration.

Further experiments aimed at using native pioneer species along with species with the ability to improve soil properties. Long-term studies allowed the selection of species that were able to withstand different types of land degraded by mining. Understanding phenology at the specific level and organising seed collection were also decisive: It allowed the creation of nurseries and made hydraulic seeding potentially available. By now, there are still various studies currently in progress, with the following priorities:

1. improve the performance of species presenting nitrogen-fixing or mycorrhizal (endo or ecto) symbioses,
2. develop efficient seed collection, their germination and conservation, and also investigate seed production,
3. improve the understanding of topsoil recycling, so as to develop good practice guidance for mining operators.

Field experiments using local species adapted to the ultramafic substrates confirmed the interest of the 'ecological restoration' approach. Yet, the results remain heterogeneous,

and in addition to understanding plant responses, site-specific approaches are necessary due to high variability in soil chemical and physical properties, as well as climatic condition. Such constraints plus the lack of organisation in seed collection (and production) entail high restoration costs, without a guarantee for long-term success. Thus, it is still difficult to provide turnkey restoration solutions for mining companies.

The approach to the restoration of mining areas is currently at a crossroads, with a possible diversification of the stated aims. While the current option is to focus on single exploitation areas without proper conservation plans, massifs appear as the right ecological unit to plan conservation *and* restoration. Most representative and significant scrublands in each massif should be totally preserved, along with all residual forests in thalwegs. Avoiding destruction of these areas, and even promoting their extension, could be a way to maintain their ecological diversity and functions without excessive costs. This seems more feasible in the short run than ambitious and costly ecological restoration of severely harmed ecosystems. In such an approach, it would be possible to focus restoration efforts on the first step of the ecological succession, where a restricted number of species known to improve soil and growing conditions could be used.

Metallophyte species, including metal hyperaccumulators, also have some interest: Various species proved useful for mine restoration (*Geissois* spp., *Grevillea* spp., *Phyllanthus* spp.) and the development of new outlets, e.g. ecological catalysts could provide revenues. Developing reclamation schemes for highly degraded quarries or spoil storage areas using metal hyperaccumulators along with Cyperaceae and other soil-improving species could provide an efficient way to control soil erosion and water flows on degraded land. Generating alternative incomes through the valuation of metal-rich biomass used in organic chemistry could cover the cost of the operation but also generate alternative economic activities for the country.

Such prospects, built with the idea of managing biodiversity at a larger scale, taking the specificities of each massif into account, could lead to an improved conservation of the unique and original metallophyte and ultramafic flora of New Caledonia. Economic use of nickel and manganese

hyperaccumulators opens new perspectives for the restoration of mining-impacted ecosystems, for the economy of New Caledonia, but also for scientific research as it raises new questions on metal hyperaccumulation. The new concept of Ecocatalysis can be the starting point of a novel plant-inspired metallo-catalytic platform for the synthesis of biologically interesting molecules and should spur the development of phytoextraction. The approach can be extended to access to numerous molecules with high added value (e.g. aromatic heterocycle scaffolds, building blocks for chemical industries and numerous molecules of biological and medicinal interest). The development of this new concept can create a paradigm shift in sustainable and green chemistry: Phytoextraction can become new efficient catalytic systems.

Ecological restoration or rehabilitation of sites with large reserves of transition metals, but also high nature conservation value, e.g. in New Caledonia, can be accelerated by these new phytotechnologies, and partly financed by the ecocatalysts produced in the recycling process of biomass. This activity should enable to develop a new green circular economy.

Acknowledgments The authors warmly thank Marion Anquez (IAC) for providing the picture used as Fig. 6. Financial support from the 'Agence Nationale pour la Recherche' (ANR 11ECOT01101), Société Le Nickel (SLN), and Ecole Polytechnique, Paris Tech (PhD studentship) is also gratefully acknowledged.

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