Geologia Croatica
Journal of the Croatian Geological Survey
and the Croatian Geological Society

2025 | 78/1 | 87–101 | 4 Figs. | 7 Tabs. |

www.geologia-croatica.hr

Croatian Critical Mineral Commodity Letters: Magnesium

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doi: 10.4154/gc.2025.04

Article history:
Manuscript received: February 12, 2024
Revised manuscript accepted: November 19, 2024
Available online: February 27, 2025

Abstract

Magnesium is a critical raw material of high importance to the European Union economy. Magnesium has versatile applications in many industries: the automotive industry (48%), packaging applications (23%), the construction industry (13%), desulphurisation of steel (12%), heavy transportation (air, marine, train; 4%) as well as in medical equipment, sport applications, electrochemical and organic chemistry applications. The Republic of Croatia hosts two major sources of magnesium: (1) primary dolostone deposits and occurrences, mainly used as a high-quality crushed stone aggregate and carbonate mineral raw material for industrial processing, and (2) secondary Mg reject brine from the Nin, Pag and Ston saltpans: (1) Deposits and occurrences of early and late diagenetic dolostone are associated with the South Tethyan Megaplatform (STM; Upper Triassic Hauptdolomite and Lower Jurassic limestone and dolostone) or the Adriatic Carbonate Platform (AdCP; Jurassic limestone and dolostone and Upper Jurassic boundstones, layered and massive dolostone and Lower to Middle Cretaceous dolostone and post-sedimentary, diagenetic breccia). Based on their lithological, mineralogical, and chemical characteristics, STM deposits are considered high-potential magnesium sources, whereas AdCP deposits belong to medium-to-high (Jurassic) and low-potential (Cretaceous) magnesium sources. The overall geological potential of primary magnesium sources at a scale of 1:300,000 has been calculated by excluding areas where exploitation is prohibited. In the resulting areas, exploitation is possible, but additional restrictions arising from the three levels of spatial plans (national, county, and local) must additionally be taken into account. (2) Average annual salt production in Croatia is around 20,000 t. The calculated amount of discharged magnesium from high-saline brines remaining after the precipitation of sodium-chloride is about 2.38 t/annually. The case study on the Đipalo dolostone deposit near Sinj (STM dolostone; exploitation reserves of 5.9 Mt) shows high purity dolostone with MgO > 22 wt%, whereas the sum content of SiO_2, Fe_2O_3 and Al_2O_3 remains below 1 wt%. The Đipalo dolostone can be used in the refractory material industry, as an agent of fusion in ferrous metallurgy, in the production of cement, glass, ceramics, paper or for magnesium metal production. The prices of various Mg-products range from 1.7 €/t construction mineral raw material, 10 €/t for crushed stone aggregate, 100 €/t for refractory (roasted) dolostone and about 2,250 €/t for 99,0% pure magnesium (February 2024). Dolostone consumption for the Đipalo deposit is estimated to be about 10-15 t of dolostone per tonne of Mg metal produced, depending on the process, however, the estimated CO_2 emissions remain a significant negative factor.

Keywords: critical raw materials, magnesium, dolostone, Croatia

1. INTRODUCTION

In general, local societies are rarely aware of the mining activities in their states, and like to perceive their countries as touristic, agricultural, or industrial, but certainly not as “mining”. The average Croatian citizen would hardly ever wonder about the type of mineral raw material that is imbedded in roads, viaducts, tunnels and bridges on their way to the Adriatic seaside or used as a light alloy for manufacturing the car that they are driving, or that is built into the insulating lining of their seaside apartment, as long as these products serve their purposes at reasonable costs. However, when the roads, tunnels or viaducts are damaged and need costly reconstruction, or when expenses for the heating/cooling of apartments and houses doubles or triples, then the wider society will start to wonder about the quality and origin of the mineral raw materials that were initially used, and most importantly on the quantities of the complementary material left for disposal. At this point, the average citizen might ask himself “Are we doing any mining and extraction in Croatia?”

Croatian Critical Mineral Commodity Letters are a serial of review publications focused on selected critical raw materials (CRM) in Croatia. Critical raw materials are non-energy raw materials of high importance to the European Union’s economy across the industrial value chain, irreplaceable in modern and environmental-friendly clean technologies such as solar panels, wind turbines, electric vehicles, and energy-efficient lighting. At the same time, there is a high risk associated with their supply, where the EU mainly relies on their import (GROHOL & VEEH, 2023).

The aims of this series of publications are raising awareness of the Croatian mineral raw materials stakeholders (industry, research, academia, policymakers, investors), as well as the local community on the existence of valuable CRM recourses that exist, but are not being exploited in Croatia, providing a state of the art literature overview and offering evaluation of the economic potential of selected case studies. Selected CRM are commodities in Croatia such as magnesium, bauxite and barite, with high geological potential, high economic value and reasonable exploration/exploitation opportunities. In contrast, graphite and rare earth elements have moderate to modest geological potential, whereas some other commodities such as borates and lithium are currently only at the level of indicative geological potential in Croatia. This estimation is based on the overall geological knowledge on the selected commodity and includes reserve estimation (magnesium, bauxite and barite), resource estimation (graphite and rare earth elements) and potentiality estimation (lithium and boron).

2. MAGNESIUM

Magnesium is the 8th most abundant element in the Earth's crust with at 2.1 mass % and the third most abundant element in sea water at 0.13 mass %. There are over 60 Mg-containing minerals listed (KOEGL et al., 2006), many of which are rock-forming minerals such as olivine, pyroxene, amphibole and the chlorite group of minerals, as well as widespread magnesium carbonates (magnesite, dolomite and magnesium calcite). Commercially important minerals for the extraction of magnesium are the carbonates; magnesite ($MgCO_3$; Mg=28.8 wt%) and dolomite ($CaMg(CO_3)_2$; Mg=13.2 wt%, that serves both the crushed stone aggregate and chemical industries), whereas Mg-rich olivine and serpentine are used for the refractory industries (Table 1; KOEGL et al., 2006).

Magnesium has versatile applications in industries: automotive industry (48%), packaging applications (23%), construction industry (13%), desulphurisation of steel (12%), heavy transportation (air, marine, railway; 4%) as well as medical equipment, sport applications, electrochemical and organic chemistry applications, its importance has been widely acknowledged (GROHOL & VEEH, 2023). This is why the European Commission already listed magnesium as a critical raw material in its first communication in 2011, and it has remained on the list until the present day due to a lack of domestic production and growing demand (EUROPEAN COMMISION COMMUNICATION 2011, 2014, 2017, 2020). During 2019, the world production of magnesium metal was 928 kt. The majority of magnesium is produced in China (89%) and 4% in the US, followed by Russia, Israel, Kazakhstan, Brazil and South Korea. Currently, there is no magnesium production in the EU. However, EU industry annually consumes around 113 kt of magnesium (15% of the total annual world production), 97% of which is imported from China.

Croatia hosts high quantities of high-quality dolostone, currently mined for the crushed stone aggregate industry or carbonate material for industrial processing, as well as several saltpans producing reject brines enriched in magnesium. The aim of this manuscript is to: (1) investigate on the important properties of magnesium-bearing minerals and deposits (including secondary sources) as well as common mining and processing methods and applications; (2) provide a comprehensive overview on the magnesium-bearing deposits, occurrences and potentiality maps within the Republic of Croatia; (3) present a selected magnesium case-study; (4) propose economically justified mining and extraction technology, and potential applications for the selected case study.

2.1. Commercial sources of magnesium

Magnesite, dolomite, brucite, bischofite, carnallite and olivine have been used or are considered to be raw materials for Mg metal production along with brines, Mg-sulphate-bearing brine-residue, fly ash, and serpentine-rich ultramafic rocks (including asbestos tailings). Their magnesium content varies greatly (Table 1).

2.1.1. Primary magnesium sources

Primary minerals for extraction of magnesium are the carbonates magnesite (77% of Chinese and a part of USA domestic production) and dolomite (27% of Chinese domestic production, 100% of Brazil and South Korea and dominant part of USA domestic production), that jointly correspond to >90% of world magnesium production. Evaporite minerals such as carnallite (Russia, Ukraine and Israel), and bischofite (Kazakhstan) are of secondary importance for magnesium production (<10% of the world magnesium production; GROHOL & VEEH, 2023; USGS COUNTRY REPORTS, 2022).

2.1.1.1. Evaporite rocks

Although it has low magnesium content (Mg=8.8 wt%), carnallite is used for magnesium metal production. Carnallite

Table 1. Magnesium content (in wt%) in common raw materials (adopted after SIMANDL, 2007; MAHMUD et al., 2022; INTERNATIONAL MAGNESIUM ASSOCIATION, 2023).

Name	Chemical formula	Mg content (wt%)
Primary source		
Earth crust	average	2.1
Carnallite	$KMgCl_3 \times 6(H_2O)$	8.8
Bischofite	$MgCl_2$x6H2O	12.0
Dolomite	$CaMg(CO_3)_2$	13.2
Talc	$Mg_3Si_4O_{10}(OH)_2$	19.2
Huntite	$Mg_3Ca(CO_3)_4$	20.7
Olivine	$(Mg,Fe)_2SiO_4$	25.4
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \times 4H_2O$	26.0
Serpentine	$Mg_3Si_2O_5(OH)_4$	26.3
Magnesite	$MgCO_3$	28.8
Brucite	$Mg(OH)_2$	41.7
Periclase (unstable)	MgO	60.3
Secondary source		
Fly-ash	variable	max. 9.8
Asbestos tailings	variable	23-25
Fluid source		
Seawater	average	0.1
Desalination reject brine	average	0.3
Salt lakes brine	average	max. 9.0

is also major potassium source and is primarily used for manufacturing potassium fertilizers in a two-step process. The process begins with electrochemical production of elemental magnesium (Mg) and solid sludge waste with a high K_2O (≈ 43%) content, used in the second step to manufacture K_2O rich fertilizers (SHARMA et al., 2018). Magnesium from salts such as carnallite and bischofite is recovered using solution mining, starting with the injection of fresh, sometimes heated water in the deep subsurface evaporite structures (>1,100 m) containing potassium/magnesium salt layers which become saturated with KCl and $MgCl_2$ (e.g., at Veendam in the Netherlands; VELAMA et al., 2010).

2.1.1.2. Carbonate rocks

Dolomite (Mg=13.2 wt%), and to a lesser extent magnesite (Mg=28.8 wt%) represent major raw materials for the production of magnesium metal using a thermal reduction process (carbothermic process; SIMANDL et al., 2007). Although huntite and hydro-magnesite have a higher Mg content (20.7 and 26 wt%, respectively), their greatest potential currently appears in flame retardant applications (Table 1; SIMANDL et al., 2000). When exposed to the heat of a fire, those minerals decompose in an endothermic reaction, cooling down the flame and releasing carbon dioxide at the same time (HOLLINGBERY & HULL, 2012).

2.1.1.3. Ultramafic rocks

Extraction of magnesium from silicate minerals associated with ultramafic rocks such as olivine, serpentine or talc is under development. HANSEN & ZANDER (2011) patented a method for the extraction of silica and magnesium from olivine using chemical and thermal treatments (EP 1 373 139 B1). LU & NEELAMEGGHAM (2021), conducted the first successful industrial demonstration, extracting magnesium from serpentinite via an aluminium-silicon thermal reduction line with an annual processing capacity of 21,000 tons.

Brucite has a very high magnesium content, a low level of impurities and low dehydration temperature (Mg=41.7 wt%; the dehydration reaction of brucite to form periclase is ≈550 °C at 1 atm pressure; JOHNSON & WALKER, 1993) making it highly suitable for the extraction of magnesium (SIMANDL et al., 2007). Currently, brucite is only used as a flame retardant. Compared to carbonate flame retardants including huntite and hydro-magnesite, brucite does not contain CO_2; hence no emissions are related to the calcination process upon burning. Periclase is a high-pressure mineral, rarely occurring in nature, and when exposed to weathering is transformed to brucite (DORFMAN et al., 2012).

2.1.2. Secondary magnesium sources

The global annual production of fly-ash is around 600 million tons. Fly-ash is a fine-grained, powdered waste material formed in power plants as a product of the combustion of pulverized coal. Its chemical composition is highly variable (mainly oxides SiO_2, Al_2O_3, CaO, Fe_2O_3) and depends on the type of fuel burned (bituminous or sub-bituminous coal, lignite, wood and peat), however, some types are characterised by an increased magnesium content of up to 9.8 wt% (MYLLYMÄKI et al., 2019). The first production of magnesium metal from fly-ash was expected in 2023 using a combination of patented hydrometallurgical extraction and thermal reduction process (LAROBE MAGNESIUM, 2024).

2.1.2.1. Asbestos tailings

Asbestos tailings (serpentinite, amphibole) raised significant interest as a secondary Mg-source due to their high magnesium content (average Mg=15-18 wt%). Several plants are already in operation in Canada and Europe using electrolytical or pyrometallurgical processes. Leaching with sulfuric acid in the presence of fluorite powder is suggested recently as a more environmentally friendly process compared to conventional methods (LIU et al., 2022).

2.1.2.2. Magnesium from fluid sources

After the desalination of seawater, a large quantity of reject brines is produced with higher salinity concentration than the feed-seawater which represents another important source of magnesium (Mg=0.28 wt%). Currently more than 15,900 desalination plants are in operation worldwide, with a total desalination capacity of about 95 million m^3 per day (JONES et al., 2019).

2.1.2.3. Salt lakes brine

Salt lakes brine currently serve as a dominant source of lithium, accounting for 59% of lithium world reserves (Chile, Bolivia, Argentina, and China; ZHANG et al., 2022). Most brines contain a high Mg/Li ratio, where the Mg content reaches up to 9 wt%. Separation of lithium from magnesium using precipitation methods has been suggested, whereby lithium remains in solution and magnesium precipitates in the form of carbonate, aluminate or phosphate (ZHANG et al., 2022 and references therein).

2.2. Deposit types (primary magnesium sources)

2.2.1. Mg deposits in evaporite rocks

Marine evaporites are layered sedimentary rocks that in most cases chemically precipitate due to the evaporation of seawater in hot, arid areas where generally the amount of water lost by evaporation exceeds the total amount of water from rainfall and influx via rivers and streams (GUILBERT & PARK, 1986). After evaporation of a seawater column of 1000 m, 15-17 metres of beds form, starting with carbonates (0.6%; calcite, dolomite, magnesite, aragonite), sulphates (3.6%; gypsum and anhydrite), and chlorides (78.2% halite, followed by K, Mg salts of 17.6%; sylvite, carnallite, epsomite, kainite) at the uppermost levels of the evaporation sequence. Small amounts of borates, nitrates, and celestine will also form. If tectonically undisturbed, this hypothetical evaporite sequence will occur as well-bedded, with K-Mg salts associated with the uppermost parts of the thick halite layers.

The World's largest K-Mg bearing evaporite basins are (KOGEL et al., 2006; CAPUTO, 2011; STATISTICA, 2024):

(1) Middle Devonian North American Saskatchewan evaporite basin extending through western Canada, toward USA Montana and North Dakota, with estimated reserves of over 1.1 billion tons,

(2) Permian Zechstein basin extending mainly through Germany, Belarus and Russia (for example the Upper

Kama Basin in the Perm region in Russia), with estimated reserves of over 1.3 billion tons, and

(3) Permian-Carboniferous Amazon potash basin, comparable in size with the Saskatchewan basin, with an estimated potential of 30 billion tonnes but mainly halite and sylvite (magnesium sulphates and salts occur subordinately).

2.2.2. Mg deposits in carbonate rocks

2.2.2.1. Dolomite

Dolomite is usually formed from calcite via process of diagenetic replacement called dolomitization. Subordinately, dolomite can precipitate as a primary mineral from seawater or lake, or directly from hydrothermal or metamorphic fluids. Dolomitization includes the replacement of calcium for magnesium in the carbonate structure under the influence of a Mg-bearing fluid. The process usually includes evaporation of seawater in a sabkha environment, the reflux of seawater in shallow lagoons, the mixing of freshwater and hypersaline brine with seawater, basinal brines or with any other source of Mg-rich fluid (WARREN, 2000).

Dolomitic rocks (dolostone) are composed of dolomite or Mg-bearing calcite, or a mixture of both minerals together with calcite and some other terrigenous or evaporite minerals (WARREN, 2000). They are widely distributed throughout the world, and are of different geological ages. Significant production of dolomite for mainly construction purposes exists in North America, China, Russia and the EU (TOP DOLOMITE SUPPLIERS, 2024).

2.2.2.2. Magnesite

The Veitsch-type of sucrose and coarse-grained “sparry” magnesite deposit that forms monomineralic lenses within marine carbonate-platform sediments (limestone and dolomite) is the most common magnesite type (POHL, 1990). It exhibits many diagenetic features, and is commonly interbedded with dolomite, sometimes with limestone, pelitic and psammitic siliciclastics, including in some cases, magnesite pebbles from older formations. Its origin is related to Mg-rich brine circulation and linked to the dolomitization process.

2.2.3. Mg deposits in ultramafic rocks

2.2.3.1. Magnesite

The Kraubath-type of magnesite deposits consist of veins and stockwork of micro to crypto-crystalline magnesite hosted by ultramafic rocks, and is economically the most significant type (POHL, 1990). It is commonly found associated with serpentinised ultramafic rocks of the Tethyan ophiolites, or within stratified large mafic-ultramafic intrusions (POHL, 1990). Magnesite veins can reach a thickness of 45 metres and strike for up to 4 kilometres, usually following regional fracture patterns. Magnesite appears as snow white, massive or brecciated, sometimes crypto-crystalline with a cauliflower-like nodular infill. When occurring as stockwork, the country rocks are pervasively altered. Genetic models suggest that the Mg-source is the surrounding ultramafic rocks, that are mobilised via near-surface, low-temperature hydrothermal systems (*per ascensum* model) or via deeply circulating meteoric waters (*per descendum* model).

The lacustrine variety of the Kraubath-type is the Bela Stena type, associated with hydrothermal circulation of the Mg-bearing solutions from nearby ultramafic terrains. Upon discharging into lacustrine Neogene basins, magnesite precipitates as cryptocrystalline or nodular aggregates within lake sediments (ILIĆ, 1968; WILSON & EBNER, 2005).

2.2.3.2. Olivine, serpentine, talc

Olivine and serpentine are major minerals constituting ultramafic rocks such as dunite (>90% of olivine), serpentinite (predominantly composed of serpentine) or peridotite (40-90% of olivine) and are widely distributed in the ophiolites of for example the Alpine-Himalayan belt, or associated with large layered mafic-ultramafic intrusions worldwide (Bushweld Great dyke of Zimbabwe, Stillwaters, Mustox, Duluth, Skaegaard, Penikat and Portimo, Kemi, Munni-Munni etc).

Talc is predominantly formed via hydrothermal metamorphism of Mg-silicates (serpentine, pyroxene, amphibole, olivine), in the presence of carbon dioxide and water, and therefore is again associated with ultramafic rocks. Talc can also be formed via skarn reaction including dolomite, silica and water and associated with skarn deposits. In both cases, the appearance of talc will be in the form of irregular lenses, veins and stockwork.

2.3. Mining methods

2.3.1. Solution mining of Mg from evaporite rocks

Solution mining refers to the production of salt by pumping water into subterranean salt deposits, found in many parts of the world, dissolving the salts and pumping the brine to the surface for drying and further use (MACHOVEC, 1980). The mineral carnallite is deliquescent, with the ore absorbing moisture from the atmosphere. This tends to weaken the structural strength of the ore body, and renders it unsuitable for conventional mining but suitable for solution mining. Raw magnesium chloride can be recovered using solution mining at a depth of 1500 to 2000 metres. One example is the NedMag mine near Veendam in the Netherlands where underground caverns are formed in stacked layers of bischofite, carnallite and halite. The salt layers consist largely of NaCl but contain at least 35% magnesium chloride. Recovery is implemented by injection of fresh water in the salt layer, which becomes saturated with magnesium. The carnallite and bischofite layers largely consist of the less soluble NaCl, with interspersed magnesium salts (VELEMA et al., 2010).

2.3.2. Conventional mining methods

Both dolomite and magnesite are mined and concentrated by conventional mining methods including underground and open pit mining (KOGEL et al., 2006). In some cases mines can operate as both an underground and open pit mine at the same time. The mine in Breitenau, Austria owned by RHI Magnesite operates a large underground mine but also an open pit (DRNEK & FRÖMMER, 2008). The main factor for choosing between underground and open pit mining is constrained by the ore to cover-beds ratio. Dolomite and magnesite are more often mined by open pit mining, and the mining process usually includes drilling and blasting, loading, transporting, crushing, grinding, screening, stocking and transfer to the factory. The run-of-mine ore is rarely shipped or used in crude form. It is processed near the mine site to yield magnesia products. Although the open pit mining method is more preferentially used in some mines, various underground mining methods are also in use. In cases where the magnesium ore deposits are located at significant depths, and the value of production covers the higher costs of underground exploitation, underground mining may be the most appropriate method. Underground mining is more complex and expensive than open-pit mining. In the case of high-quality raw magnesite, for example the Koutzi UG mine owned by Grecian Magnesite, a small scale, underground narrow vein mining method can be used.

2.4. Extraction of magnesium

For a long time, roughly half of the magnesium had been recovered from seawater, which remains a significant source of magnesium in some countries. However, after the magnesium seawater plant had been closed in the USA, China has been increasing its share in global production. Today, the predominant magnesium resources are dolomite, magnesite, carnallite and brines. Known Mg extraction methods belong to either the thermal reduction or the electrolytic categories (SIMANDL, 2007).

Thermal reduction methods (silicothermic, aluminothermic and carbothermic) operate at high temperatures. The Silicothermic process relies on the use of ferrosilicon to reduce magnesium oxide to a molten slag at temperatures between 1200-1600 °C. A reduced gas pressure above the slag produces magnesium vapour. This vapour is condensed at a location removed from the main furnace or in the low temperature zone of the converter. The ingots of condensed magnesium are then re-melted, refined and casted. The Pidgeon, Magnetherm and Bolzano processes have all been successfully used in the past (AGHION & GOLUB, 2006).

Although a large number of technically proven electrolytic processes exist, commercial magnesium electrolysis is conducted most commonly in a chloride melt of mixed alkali metals at temperatures below 700 °C. The feed to the electrolysis process is either anhydrous magnesium chloride, $KMgCl_3$ produced from the dehydration of carnallite, or partially dehydrated magnesium chloride. The later feed can be derived from a variety of raw materials including dolomite, magnesite, bischofite, serpentine group minerals, sea water or brines.

A list of the different thermal, reduction and electrolytic, and extraction processes is shown in Table 2 together with the name of the process, sources, feed preparation, reaction and temperature and pressure.

The main differences between the electrolytic and thermal reduction processes in terms of energy type and consumption, capital investment and labour requirements are shown in Table 3.

Table 3 shows that the thermal reduction processes are labour-intensive and energy-intensive, but the required capital investment is quite low. The Pidgeon process is a thermal

Table 2. Different thermal reduction, electrolytic and extraction processes (adopted after WULANDARI et al., 2010).

Process Route	Sources	Feed Preparation	Reaction	Temperature/Pressure
		Thermal Reduction Process		
Silicothermic	Dolomite, FeSi	Calcination; FeSi making; pelleting	MgO+CaO+FeSi= $Mg_{(g)} + Ca_2SiO_{4(s)} + Fe_{(s)}$	T=1160 °C P=1.2 x10^{-4} atm
Carbothermic	Magnesite, Carbon	Calcination; pelleting	MgO+C = $Mg_{(g)} + CO_g$	T=1700 °C P=1 atm
Magnetherm	Dolomite, bauxite FeSi	Calcination; FeSi making	2CaoMgO + (*x*Fe)Si+ nAl_20_3= $2CaOSiO_2$ nAl_2O_3+2Mg+*x*Fe	T=1550 °C P=0.05 atm
Aluminothermic	Dolomite, Al scrap	Calcination	$4MgO_{(s)} + 2Al_{(s)} = 3Mg_{(g)} + MgAl_2O_{4(s)}$	T=1700 °C P=0.85 atm
Mintec	Dolomite, bauxite FeSi, Al scrap	Calcination	2CaoMgO + (*x*Fe)Si+ nAl_20_3= $2CaOSiO_2$ nAl_2O_3+2Mg+*x*Fe $4MgO_{(s)} + 2Al_{(s)} = 3Mg_{(g)} + MgAl_2O_{4(s)}$	T=1700 °C P=0.85 atm
		Electrolytic		
Dow process	Brine/sea water	Neutralization, purification, dehydration	Electrolytic $MgCl2_{(1)} \rightarrow Mg_{(1)} + Cl_{(2)}$	T=700-800 °C P=1 atm
AM process	Magnesite	Mining, leaching with HCl, dehydratation	Anode: $2Cl^- \rightarrow Cl_2 + 2e$	
IG Farben process	Sea water/brine	Neutralisation, prilling, dehydration chlorynation	Cathode: $Mg^{2+} + 2e \rightarrow Mg$	

Table 3. Difference between electrolytic and thermal reduction process (adopted after SIMANDL, 2007).

Method	Electrolytic	Thermal reduction (Pidgeon process)
Energy type	Hydro-electric, gas, oil	Coal, gas
Energy requirements (MWh/t of Mg)	18-28	45-80
Capital investments (USD/t of Mg capacity)	10 000-18 000	≤ 2000
Manpower requirements	X	5x

reduction process based on the silicothermic reduction of magnesium oxide. It is the oldest and simplest extraction process with high energy requirements, which is widely used in China, making China the world's largest supplier of Mg, but also the world's largest polluter.

2.5. Magnesium applications

Due to the fact that magnesium is the lightest structural metal, and due to its low density, it is significantly lighter than widely used aluminium and steel (MORDIKE & EBERT, 2002; INTERNATIONAL MAGNESIUM ASSOCIATION, 2023). In most applications, magnesium is used in the form of MgO, particularly in the manufacturing of refractory products including crucibles, shapes and furnace linings. Pure magnesium is traded at 99.8% Mg or higher (BRITISH GEOLOGICAL SURVEY, 2004).

The principal application of magnesium is in metallurgy for the production of light alloys. It is most frequently alloyed with Al, or Al, Zn and Mn, and it is competitive when weight reduction of the end products in required, as in the airplane and car industries, without compromising strength. In alloy applications for high-speed components, the addition of Mg reduces the internal forces caused by vibrations. When Mg is added to Al alloy, it will be more easily rolled, extruded and welded. Typically, 0.1 to 5 wt% is added to Al alloys (for an overview refer to TAN & RAMAKRISHNA, 2021).

The INTERNATIONAL MAGNESIUM ASSOCIATION (IMA; 2023) summarizes many contemporary applications of magnesium. In the last ten years or so, magnesium has been increasingly used in the automotive industry due to more restrictive fuel consumption regulations as well as requirements for better driving performance, which both impose usage of lighter materials for the production of various car components. Indeed, many car manufactures have already replaced traditionally used metals such as steel and aluminium with magnesium in the production of a number of car parts. Usage of magnesium allows easier casting of larger components, resulting in a smaller number of joints, thus making assembly easier and more cost effective. With further development of alternative power plants, in particular for electric cars, magnesium consumption in the car industry is expected to increase.

Similarly, magnesium has been extensively introduced in the aerospace industry due to the reduction of mass without compromising structural strength, promoting better fuel efficiency and thus lowering operational costs. It is also used in aircraft jet engines as well as in some airplane interior components. Spacecraft and missile production sees magnesium as a favourable material for the same reasons. An additional advantage of magnesium is its high resistance to temperature, and protection from short-wave electromagnetic radiation and high-energy particles.

In metallurgical processing such as steel desulphurization, magnesium is used due to its affinity for sulphur. In the production of ductile cast-iron, magnesium is inevitable, and it plays the role of reducing agent in the production of metals including beryllium, zirconium, uranium and titanium. Magnesium is also used in the fabrication of various anodes, e.g. sacrificial anodes for welding and anodes for the prevention of galvanic corrosion of steel. The latter is widely employed in the protection of pipelines and many household appliances (for instance, water heaters).

Magnesium has a vast application in the production of various electronic products, particularly in small portable devices, again due to its lightness and strength. In this respect, magnesium is incorporated in the housing of many cell phones, notebooks, cameras and similar devices. At the same time, it has favourable thermal properties enabling fast heat dissipation, but also it protects devices from electromagnetic interferences.

In medicine, milk of magnesia [$Mg(OH)_2$] is used as an antacid and laxative. Epsom salts, epsomite ($MgSO_4 \times 7H_2O$) is used for the treatment of minor skin abrasions. Magnesium has also been also used as an orthopaedic biomaterial. It has a high compatibility with the human body, it is not toxic, and the density of magnesium alloys as well as some other physical properties are much more compatible with the bones compared to other materials used for the same purposes, e.g. for various body implants. If uncoated, it is biodegradable, and thus easier to handle in post-surgery treatments, but could be coated if a more permanent application of the implant is required.

For recreational purposes, sports accessories and equipment can also utilize magnesium. Light weight and impact strength are appreciated in the production of golf clubs (sticks), tennis rackets and bicycle frames.

Other various applications include pyrotechnics (appropriate alloying with aluminium in the form of fine powders), in special-purpose batteries, and in the printing industry (wrought magnesium plates).

Magnesium carbonate ($MgCO_3$) is used for some paints and inks but is also added to table salt as an anti-caking additive. In the production of optical lenses MgF_2 films are used to reduce glare and reflection.

3. POTENTIAL MAGNESIUM SOURCES IN THE REPUBLIC OF CROATIA

The Republic of Croatia hosts two major sources (Fig. 1) from which magnesium could be extracted: (1) primary dolomite deposits and occurrences, mainly used as a high-quality crushed stone aggregate and carbonate mineral raw material for industrial processing, and (2) secondary Mg reject brine from the Nin, Pag and Ston saltpans.

Two additional secondary sources of magnesium are not considered here: (1) Mravinačka kava asbestos waste deposits produced by the Salonite factory, located near Solin, and (2) fly-ash deposits produced by the Plomin thermal power plant, Istria. Asbestos waste from Mravinačka kava contains primary olivine and serpentine fibrous minerals with >25 wt% of magnesium. However, the waste deposit was recently recultivated into a sports and recreation area of approx. 0.03 km^2 under the jurisdiction of the Croatian Environmental Protection and Energy Efficiency Fund (EURCO, 2024). The fly-ash deposit from the Plomin thermal power plant in Istria is not considered an important secondary source of magnesium. It seems that the fly-ash has a minor magnesium content (1.8-3.8 wt% for Raša, Istria coals; PECO, 2018), and is currently under reclamation, following the waste management report (CUKON, 2016).

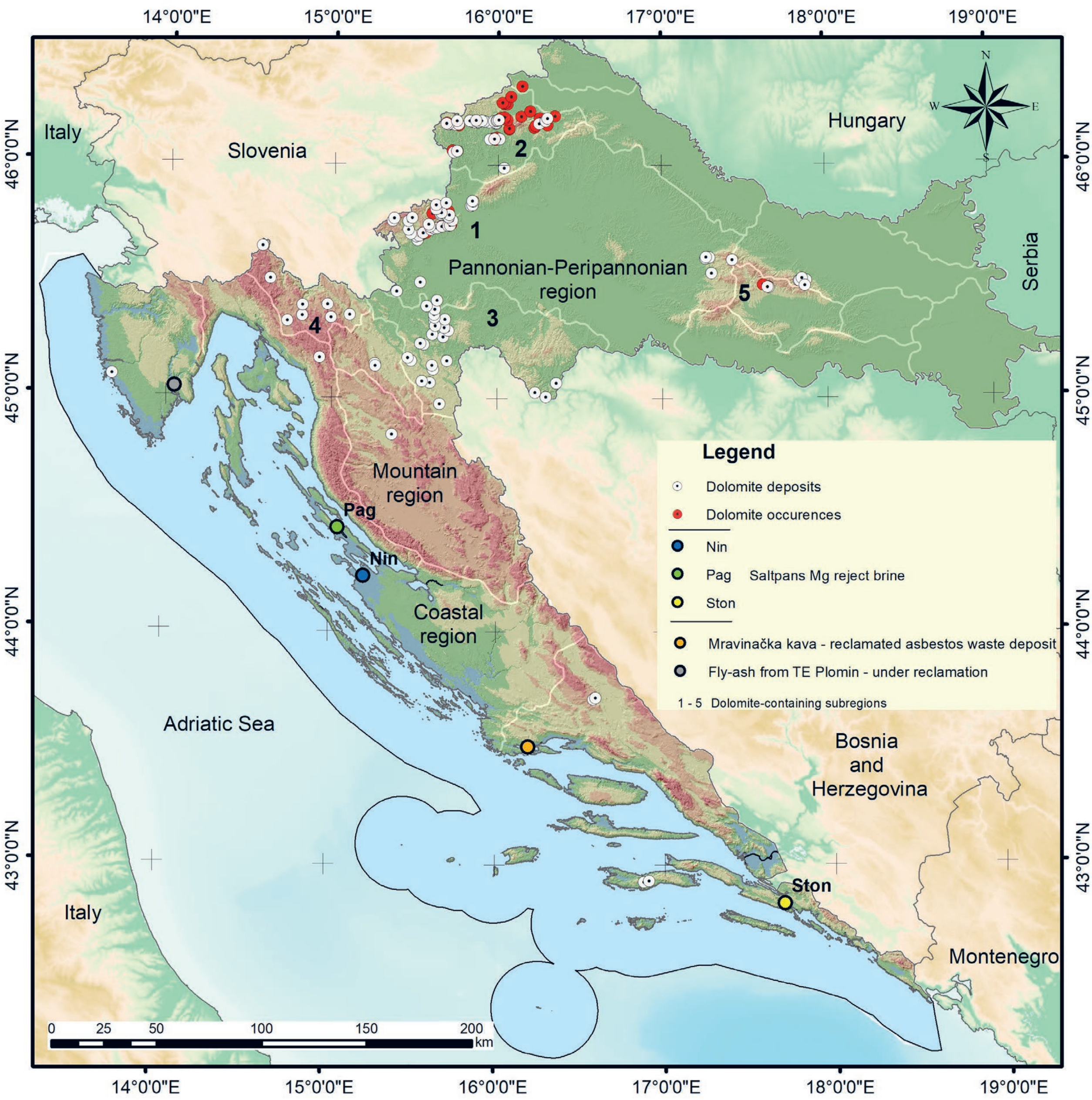

Figure 1. Potential magnesium sources in the Republic of Croatia.

3.1. Primary magnesium resources – carbonate deposits (dolomite)

Regarding the geographical setting, in the Republic of Croatia, dolomite (dolostone) deposits and occurrences are most commonly found in the Pannonian-Peripannonian and Mountain regions. Within these two major regions, dolomite is present in four assembled and labelled subregions (Fig. 1): Središnja zavala (1), Hrvatsko zagorje (2), Banovina, Kordun i karlovački krš (3), and the Gorski kotar (4) subregions. The fifth subregion is Požeština, distinguished from the others, and located in the central part of the Pannonian-Peripannonian region. Dolostone in this subregion is related to the Slavonian Mountains. Additional secondary sources of magnesium are situated along the Coastal region (Fig. 1).

Deposits and occurrences of early and late diagenetic dolostone are associated with two, geodynamically different stratigraphic megaunits (VLAHOVIĆ et al., 2005): (1) The South Tethyan Megaplatform (STM) represented by the Upper Norian, Rhaetian dolostone and Lower Jurassic limestone and dolostone, and (2) the Adriatic carbonate platform (AdCP) represented by thick layered Middle Jurassic limestone and dolostone, Upper Jurassic limestone and dolostone, Kimmeridgian–Tithonian boundstones, Upper Jurassic to Lower Cretaceous layered and massive dolostone and Lower to Middle Cretaceous dolostone and post-sedimentary, diagenetic breccia (Fig. 2).

3.1.1. South Tethyan Megaplatform dolomite (STM)

3.1.1.1. Upper Norian, Rhaetian dolostone, Hauptdolomit

The Hauptdolomit (Dolomia Principale; Upper Norian, Rhaetian, VELIĆ & VLAHOVIĆ, 2009) is a widespread, thick dolomite-bearing unit associated with the Southern Tethyan megaplatform, relics of which can be found throughout the

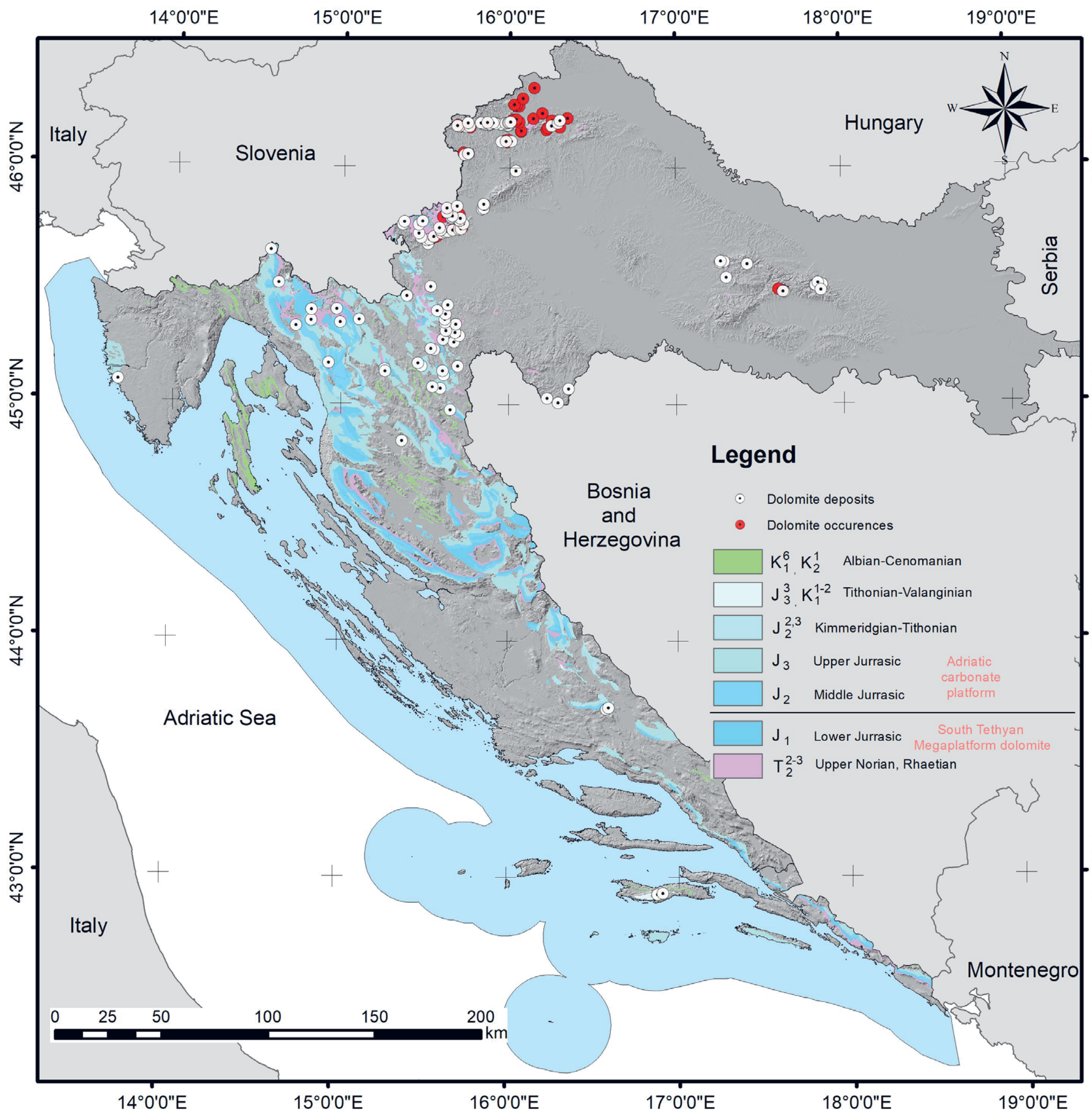

Figure 2. Stratigraphic units hosting significant amounts of dolomite based on CROATIAN GEOLOGICAL SURVEY (2009, 2024). Legend: T_2^{2-3}: Upper Norian, Rhaetian dolostone, Hauptdolomit; J_1: Lower Jurassic limestone and dolostone; J_2: thick layered Middle Jurassic limestone and dolostone; J_3; Upper Jurassic limestone and dolostone; $J_2^{2,3}$: Kimmeridgian–Tithonian boundstones; J_3^3, K_1^{1-2}: Tithonian–Valanginian layered and massive dolostone; K_1^6, K_2^1: Albian–Cenomanian dolostone and post-sedimentary, diagenetic breccia. White and red dots are dolomite deposits and occurrences.

region (Croatia, Slovenia, Bosnia, Austria, Hungary, southern Italy etc.; (VLAHOVIĆ et al., 2005). In Croatia, this unit is extensive through the Pannonian–Peripannonian and Mountain region and covers an area of 74.35 km^2. The carbonate Upper Triassic's development is characterized by the continuity of sedimentation with the Middle Triassic, resulting in a much greater thickness, exceeding 1000 m (VELIĆ & VLAHOVIĆ, 2009). Nevertheless, the thickness of these sediments is not suitable for volumetric calculations of Hauptdolomite at a given locality. The sediment thickness in OGK SFRJ (OGK = *Osnovna Geološka Karta* – basic geological map) data is determined through surface mapping and author interpretation, rather than through specific research methods such as drilling. Consequently, this sediment thickness should not be used in the calculation of mineral resource volumes. Therefore, in the assessment of potentials based on the OGK SFRJ, it is more advisable to utilize the surface representations rather than volumes. The same principle applies to the other mentioned stratigraphic units.

3.1.1.2. Lower Jurassic limestone and dolostone

Lower Jurassic limestone and dolostone have been discovered in almost all parts of the Croatian karst. Based on the prevalence and bilateral relationship between limestone and dolostone, it is possible to distinguish an alternation of limestone and dolomite in the lower part, a predominant representation of limestone in the middle part, and bioturbated limestone in the upper part. Regarding dolomite, it is mostly of late diagenetic origin, but there are also instances of early diagenetic dolostone, although these are less common. In general, dolostone is much less represented in this unit when compared to limestone. The sediments of this unit are rich in fossils in the lower and middle parts, while in the upper part, fossil remains are absent due to changes in palaeoenvironmental conditions (VELIĆ & VLAHOVIĆ, 2009). They are mostly found in the Mountain region of the Republic of Croatia and cover an area of 92.67 km^2. The thickness of this unit is approx. 400-500 m.

3.1.2. Adriatic carbonate platform

3.1.2.1. Middle Jurassic limestone and dolostone

Middle Jurassic limestone and dolostone are primarily associated with the areas where lower Jurassic sediments are observed. The basic lithological characteristic of these sediments is the prevailing occurrence of thick-bedded limestone with thin layers and lenses of late-diagenetic dolostone. These strata are abundant in microfossil communities of foraminifera and calcareous algae (VELIĆ, 2005). The thickness of this unit is very similar to the thickness of the previous stratigraphic unit, but it covers a smaller area, approx. 76.12 km^2.

3.1.2.2. Upper Jurassic limestone and dolostone

The Upper Jurassic limestone and dolostone, among all the distinguished Jurassic units on the AdCP, exhibits the greatest areal extent. This unit is characterized by its facies diversity. The main lithological feature of this unit is the lateral alternation of different types of limestone with predominantly late-diagenetic dolostone. The dolostone occurs in the form of irregularly shaped lenses of various dimensions within the limestone or in bodies of greater thickness with a massive habit. Consequently, lenses of non-dolomitized limestone are found within the dolostone. Typically, such larger bodies and occurrences of dolostone are associated with more strongly tectonized areas and fault zones. Stratigraphically, the highest (youngest) occurrence of dolostone has been identified in the youngest Jurassic sediments (VELIĆ & VLAHOVIĆ, 2009). The thickness of this unit is approx. 700 m, and it covers an area of 139.57 km^2.

3.1.2.3. Kimmeridgian–Tithonian boundstones

Kimmeridgian–Tithonian boundstones denote the sediments formed in three types of reef environments. These sediments represent barrier reef, fore-reef, and patch-reefs environments. The predominant role in the lithology of this unit is played by the biogenic component, namely the abundance of fossil remains. Sediments formed in these conditions are partially affected by late-diagenetic dolomitization, resulting in the appearance of light-gray, coarse-crystalline dolostone within the limestone, often as irregular lenses of various dimensions (VELIĆ & VLAHOVIĆ, 2009). The thickness of this unit is variable, between 400-600 m, and it covers an area of 36.05 km^2.

3.1.2.4. Tithonian–Valanginian layered and massive dolostone

Upper Jurassic to Lower Cretaceous (Tithonian–Valanginian) layered and massive dolostones are located only on the island of Korčula, where they form the core of the island. These are gray to dark gray late-diagenetic dolostones, appearing as layered or massive, with micro- and macrocrystalline mosaic structures. Within the dolostone, lenses of dolomitized limestone, dolomite breccias, and nodules of chert are noticeable. Late-diagenetic dolomitization has obliterated almost all the primary components, structures, and textures in these sediments. Due to this, the stratigraphic position of these dolostones can only be determined indirectly based on their superpositional settings. The thickness of this unit is approx. 500 m (KOROLIJA et al., 1976, 1977). Because it occurs only on the island of Korčula it covers a relatively small area, approx. 1.67 km^2.

3.1.2.5. Albian–Cenomanian dolostone and post-sedimentary, diagenetic breccia

Middle to Upper Cretaceous dolomite and post-sedimentary, diagenetic breccia. The transition between the Lower and Upper Cretaceous in a significant part of the Dinarides is characterized by late-diagenetic dolostone and/or alternation of limestone-dolomite breccias without recognizable fossil content. Within the sediments of this unit, in the tectonically less disturbed areas, a gradual transition is clearly visible from thin-bedded, unevenly dolomitized Albian limestone to late-diagenetic dolostone and completely recrystallized limestone, occasionally with relics of early-diagenetic dolostone. A considerably greater challenge is posed in areas with a high prevalence of breccias, where boundaries with older or younger formations are unclear, often as a result of tectonic activity (VLAHOVIĆ et al., 2002). This unit is mostly found in the Mountain and Coastal region of the Republic of Croatia and covers an area of 33.72 km^2. The thickness of this unit varies, between 600-800 m.

3.2. Case study: STM Đipalo-Sinj

The Đipalo dolomite deposit near Sinj is of particular importance to the Republic of Croatia due to its high MgO content and low level of impurities. The deposit is located within the STM dolostone and limestone of middle Triassic age, overlying the lower Triassic red, marly micaceous-shales and sandstones and marly limestone, and underlying the lower Jurassic dark gray fossiliferous and oolitic limestone and dolostone. In 1975 exploration work was carried out with the aim of determining the reserves and quality of the dolomite in the Đipalo deposit. Petrographic characteristics of dolomite were examined in 54 samples, and they all showed similar to identical microstructural characteristics, i.e. the examined dolostones are actually aggregates of anhedral, rarely euhedral grains, of uniform size. The share of non-carbonate admixtures is visible only in traces (clay substance and limonite; GABRIĆ & LUKŠIĆ, 1997).

Chemical analyses showed that the composition of the dolostones is very uniform throughout the entire deposit, both at depth and laterally. The mean values of the analysed elements for the Đipalo deposit are given in Table 4.

The content of MgO in dolomite exceeds 22 wt%, whereas the sum content of SiO_2, Fe_2O_3 and Al_2O_3 remains below 1 wt%. The presence of other harmful components in the

Table 4. Average content of oxides and selected microelements for the Đipalo deposit (in wt%; LoI = Loss of Ignition).

LoI	SiO_2	CaO	MgO	AL_2O_3	TiO_2	S	P	B	Na_2O	K_2O
47.09	0.025	30.32	22.12	0.031	0.001	0.013	0.003	0.00	0.116	0.008

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Table 5. Dolomite reserves of the Điplao deposit (GABRIĆ & LUKŠIĆ, 1997).

Category	Economic reserves (m^3/t)	Exploitation reserves = (economic – exploitation losses) (m^3/t)
A	1,171,126 / 3,197,174	1,1120,570 / 3,3037,316
B	907,313 / 2,476,964	861,947 / 2,353,115
C_1	224,031 /, 611,605	212,829 / 581,023
Sum	2,302,470 /6,285,743	2,187,346 /5,971,454

dolomite is very low: potassium, sodium, titanium, phosphorus and sulphur are present in traces that are not an obstacle to any form of industrial processing. The total rock mass in the deposits represents a usable mineral raw material, therefore correction with accompanying coefficients is unnecessary. Exploitation losses are about 5%. This is quite low when compared to data obtained from similar deposits (GABRIĆ & LUKŠIĆ, 1997). The quantities of dolomite reserves are shown in Table 5.

Reserve classification is based on Eastern European classification system, also known as "Russian code" where reserves of A, B and C1 categories depend on the degree of geological knowledge (having 90, 80 and 70% reliability, respectively).

3.3. Secondary magnesium resources – Mg-rich, reject brine from saltpans

Annually, the Croatian saltpans of Nin, Pag and Ston produce around 20,000 t of sea salt. The majority of the salt is produced in the Pag saltpan (around 18,000 tons), followed by the Ston (0.8 tons) and Nin saltpans (0.5 tons). Halite generally precipitates when around 90% of the seawater evaporates and the concentrations of salt within seawater increase 10 times, i.e. from 3.5% to 35%. The halite will precipitate between 90 and 96% of the seawater evaporation, leaving the remaining 4% of the reject brine enriched in potassium and magnesium

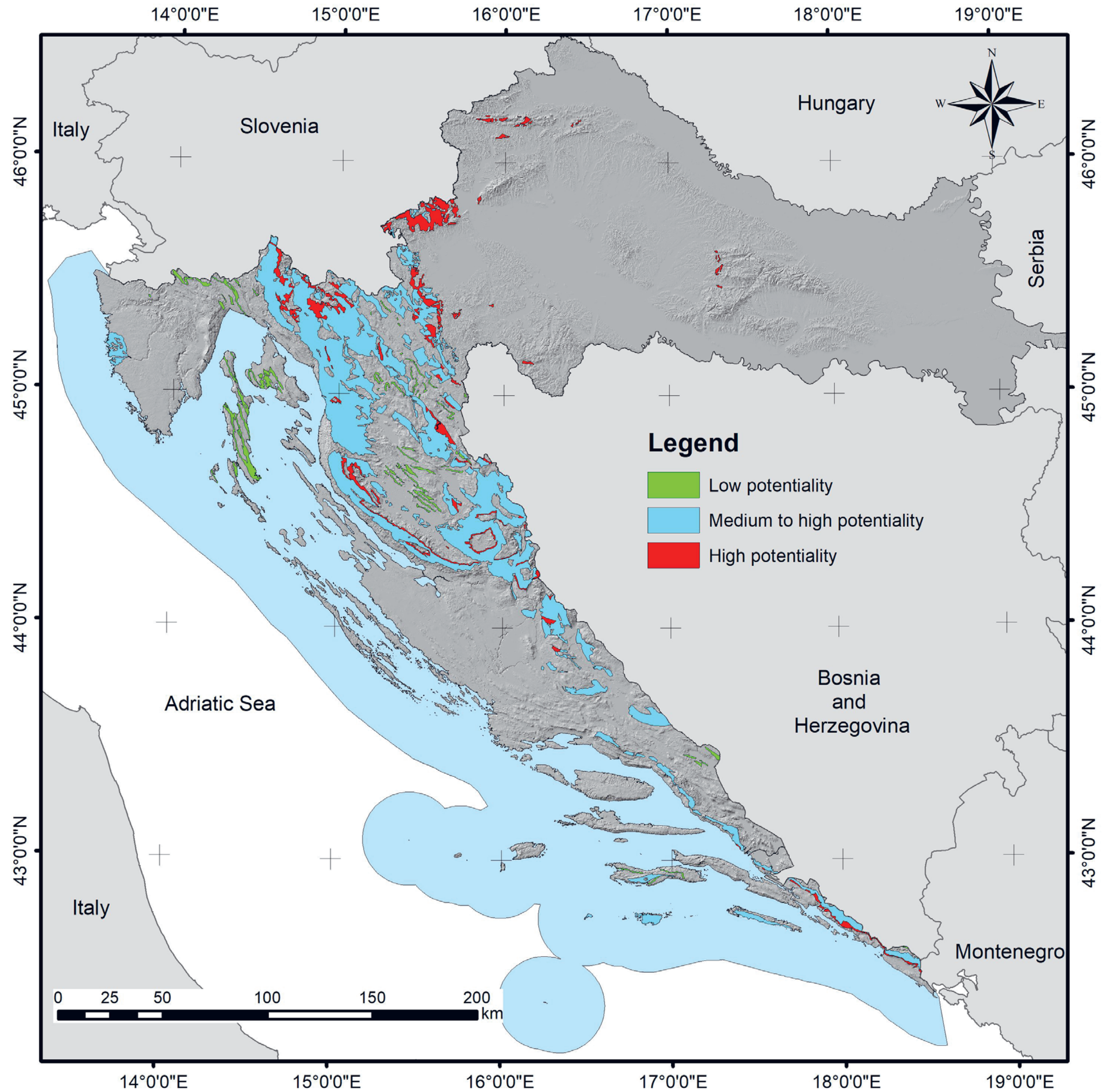

Figure 3. Geological potentiality map of primary magnesium sources based on the Geological map of the Republic Croatia at a scale of 1:300 000 (CROATIAN GEOLOGICAL SURVEY, 2009).

salts, close to the saturation point of kainite, carnallite and bischofite. Considering that the average magnesium composition in the initial seawater is 1.262 ppm, in seawater reaching the halite saturation magnesium composition should be around 1.2%. The amount of secondary Mg reject brine from the saltpans will depend on the salt production. Using an average annual salt production rate of 20,000 t in Croatia, the amount of discharged magnesium will be 2.38 t/annually.

4. DISCUSSION

4.1. Geological potential of the primary magnesium sources

Croatian primary magnesium sources are categorized into three (3) groups according to their lithological, mineralogical, and chemical characteristics as outlined in section 3.1, as well as their prospectivity. These source groups include: 1) High-potential magnesium sources, 2) Medium-to-high magnesium potential sources, and 3) Low-potential magnesium sources (Fig. 3). Only the T_2^{2-3}, Upper Norian, Rhaetian dolomite (Hauptdolomit) can be included in the first (1) group. The medium to high potentiality group (group 2) comprises the following stratigraphic units; J_1; Lower Jurassic limestone and dolostone, J_2; thick-bedded Middle Jurassic limestone and dolostone, J_3; Upper Jurassic limestone and dolostone, $J_2^{2,3}$; Kimmeridgian–Tithonian boundstones, and J_3^3, K_1^{1-2}; Tithonian–Valanginian layer and massive dolostone. Group three encompasses, specifically the Cretaceous sediments, K_1^6, K_2^1; Albian–Cenomanian dolostones and the post-sedimentary, diagenetic breccias.

The Republic of Croatia has eight national parks (NP), where the exploitation of mineral raw materials is banned. Therefore, NP areas must be excluded from the calculation of mineral raw materials potentiality (Fig. 4). Primary magnesium sources potentiality in suitability zones are grouped into the

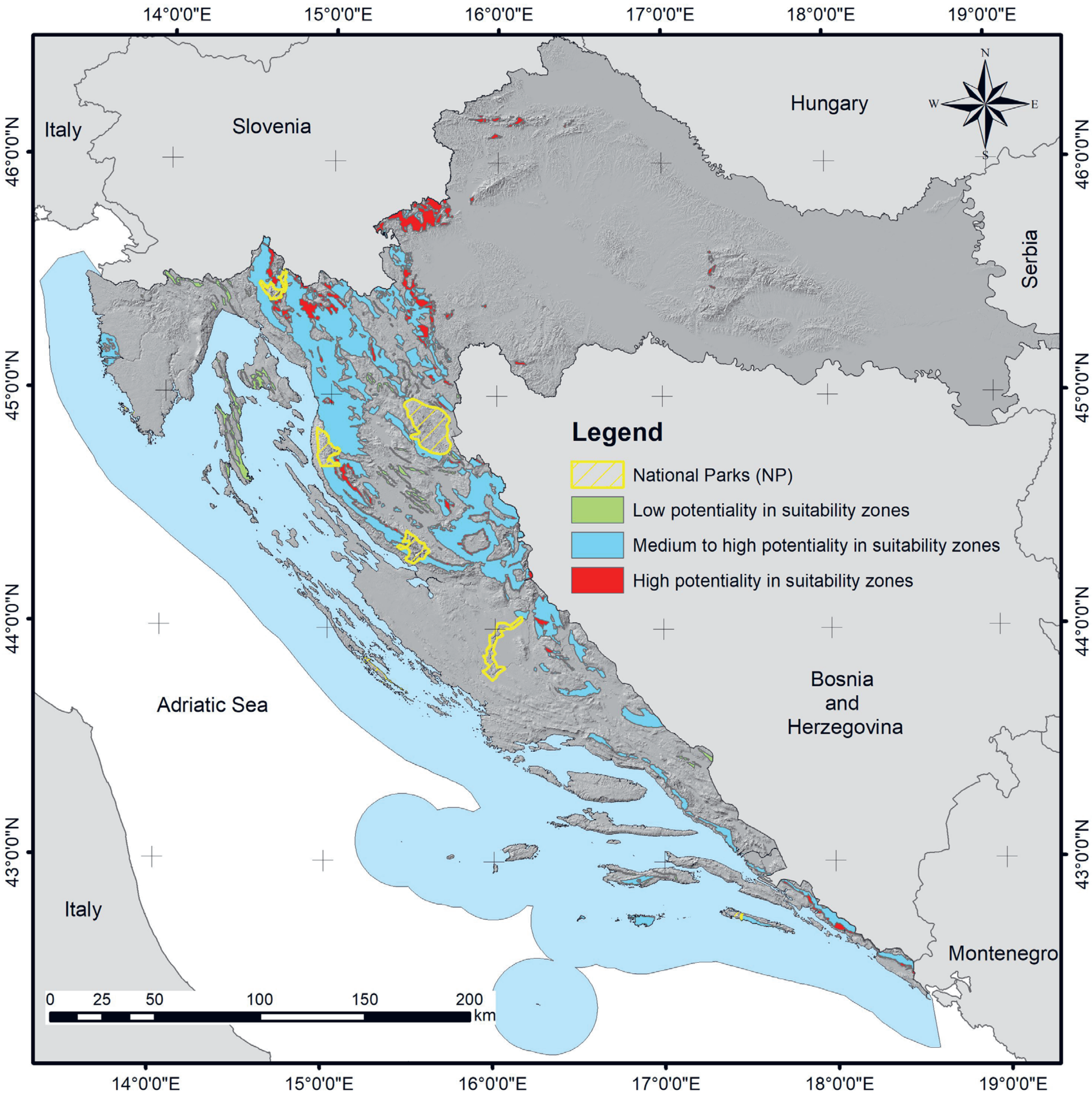

Figure 4. Calculated primary magnesium sources potentiality in suitability zones.

low potentiality (436 km^2), and the medium to high potentiality categories in the suitability zones (5,285 km^2) and into the high potentiality category in suitability zones (807 km^2, Fig. 4). Total primary magnesium sources potentiality in the Republic of Croatia amounts to 6,528 km^2. Since this potential is based on geological data at a scale of 1:300,000, it is necessary to consider certain calculation deviations. The detailed primary magnesium sources potentiality will be determined for the area of a higher potential shown on a larger scale.

The future Croatian national exploration programme will include magnesium as one of the commodities with high potential in the Republic of Croatia. This exploration programme will be primarily focused on the high potentiality of the Upper Norian, Rhaetian dolomite (Hauptdolomit).

4.2. Economic assessment of the Đipalo dolomite deposit

4.2.1. Potential uses

Considering the high MgO content >22 wt%; (GABRIĆ & LUKŠIĆ, 1997), the Đipalo dolomite can be used in the refractory material industry, as an agent of fusion or "flux" in ferrous metallurgy; in the production of cement; in the glass and ceramics industry; in the production of paper etc. Research performed by JAKIĆ et al. (2016) showed that chemical, mineralogical and granulometric characteristics of the dolomitic lime extracted by calcination of the Đipalo dolomite can be used as a reagent for the precipitation of magnesium hydroxide from seawater.

4.2.2. Suggested mining and extraction methods

The average chemical content of dolomite from the Đipalo deposit (30.32% CaO and 22.12% MgO) is close to the stoichiometric value (GABRIĆ & LUKŠIĆ, 1997). The need to refine/process the mineral raw material is therefore completely redundant. Taking into consideration the final use of the dolomite as a material for industrial processing, the technological process will necessarily involve the steps of blasting, crushing, and pulverizing the dolomite. Although production of magnesium from dolomite is associated with high environmental impacts and is mainly conducted in China, it is important to note that dolomite is suitable for magnesium production using the Pidgeon process. Dolomite consumption in the Pidegon process depends on the content of Mg, the purity of the raw material and ranges between 10 and 15 kg of dolomite per kg of Mg metal produced (RAMAKRISHNAN & KOLTUN, 2004).

4.2.3. Economic assessment

Currently, only the quantities of mineral reserves are known, and a mining project has not been developed. As part of the mining project, a detailed description of the exploitation-method should be included together with a techno-economic analysis, including the costs of exploitation. In the absence of such data, the approximate extraction price for similar dolomite deposits in the Republic of Croatia was taken into consideration in our calculations (GALIĆ & PAVELIĆ, 2020; Table 6).

The mining costs for 1 m^3 of dolomite after blasting are about 3 €/m^3. After blasting, the volume of dolomite increases by about 40% compared to the *in situ* volume of the deposit, which means that the total volume of dolomite extracted is about 3 000 000 m^3.

Table 6. The average costs of exploitation of 1 m^3 of technical-building stone after GALIĆ & PAVELIĆ (2020).

No	Costs	€/m^3
1	Costs of exploration works and preparation of the topographic base	0.05
2	Costs of assessing the quality of mineral raw materials	0.02
3	Costs of managing property-legal relations for land parcels	0.05
4	Costs of technical documentation and acts	0.05
5	Exploitation fee costs	0.18
6	Transport infrastructure costs	0.27
7	Costs of purchasing machines and equipment for excavation	0.48
8	Maintenance costs of digging machines and equipment	0.27
9	Material and energy costs	0.72
10	Excavation labour costs	0.68
11	Costs of occupational safety, environmental and nature protection, utility fees	0.13
12	Costs of remediation of the exploitation field	0.07
	Sum	2.95

The mining costs for 1 t of dolomite are about 1.51 €/t (using an average density of dolostone as 2.73 kg/m^3). The minimum market value of the dolomite after blasting is about 3.33 €/m^3 or 1.67 €/t, which means that the value of the deposit is about 10 M€. The value of the deposit increases with the refining and processing of the mineral raw material, which varies depending on the end use of the dolomite. Table 7 shows the number of different products that can be achieved with various forms of dolomite processing. It is difficult to estimate the profit because the costs of the individual processes are currently unknown.

Although the quantities of dolomite products from construction raw material to pure magnesium are significantly reduced, the market price rises considerably. The prices of products are approx. 1.7 €/t for construction raw material; 10 €/t for crushed stone aggregate; 100 €/t for high-quality dolomite and 2,250 €/t for 99.0%-purity magnesium metal. Considering the high atmospheric emissions and the high-energy consumption in magnesium production, it is unlikely that the production of magnesium from dolomite will take place on EU territory. The categories for the global impact of different Mg production processes range between 1.04 and 4.20 (10^4 kg CO_2 eq.) or between 20.74 and 298.49 (kg SO_2 eq.) per ton of Mg ingot (CHERUBINI et al., 2008). However, there are examples of existing Mg production plants in Serbia or planned production plants in Bosnia and Herzegovina (MFE MAGNESIUM FOR EUROPE, 2024).

Table 7. Quantity of different dolomite products from Đipalo deposits.

Type of product	Quantity (t)	Processing efficiency (%)
Construction raw material	5 971 454	100
Stone aggregate	5 374 308	90
Refractory industry (roasted)	3 164 870	53
Magnesium (99.0%)	590 000	below 10

5. CONCLUSION

The important properties of magnesium bearing minerals and deposits (including secondary sources) as well as the common mining and processing methods and applications are:

- Primary sources of magnesium are evaporite rocks (carnallite, bischofite) carbonate rocks (dolomite, magnesite) and ultramafic rocks (olivine serpentinite, talc), and to some extent also brucite and periclase.
    - Mg deposits in evaporite rocks are located in the uppermost levels of the evaporite sequence, associated with potassium and linked to the last stage of seawater evaporation, following the precipitation of sodium-chloride (<90-96% of evaporation),
    - Mg deposits in carbonate rocks are: (1) dolomitic rocks, usually created from calcite via process of dolomitization under the influence of Mg-rich fluids, related to a sabkha environment, shallow lagoons or basinal brines, and (2) magnesite that forms monomineralic lenses within marine carbonate-platform sediments,
    - Mg deposits in ultramafic rocks are: (1) the Kraubath-type of veins and stockworks of micro to crypto-crystalline magnesite; (2) the Bela Stena type, a lacustrine variety associated with hydrothermal circulation of the Mg-bearing solutions from nearby ultramafic terrains; (3) Olivine and serpentine, major minerals constituting ultramafic rocks (dunite, serpentinite) within ophiolite belts or within layered mafic-ultramafic intrusions, (4) Talc related to hydrothermal metamorphism of Mg-silicates.
- Secondary sources of magnesium are fly-ash and asbestos tailings.
- Significant quantities of magnesium can be found in the reject brines after desalinization or evaporation of the seawater and salt lake brines.
- Commercially important minerals for the extraction of magnesium are carbonates (magnesite and dolomite) for the crushed stone aggregate and chemical industry, whereas Mg-rich olivine and serpentine are used for refractory industries.
- Solution-mining is recommended for the extraction of Mg from evaporite rocks (pumping water into subterranean salt deposits, dissolving the salts and pumping the brine to the surface), where dolomite and magnesite are mined and concentrated also by conventional mining methods including underground and open pit mining.
- Magnesium is extracted via thermal reduction methods (silicothermic, aluminothermic and carbothermic) operating at high temperatures or recovered from seawater.
- Metallic magnesium has applications in the automotive industry, packaging applications, the construction industry, steel production, heavy transportation, medical equipment, sport applications, electrochemical and organic chemistry.

The magnesium sources within the Republic of Croatia:

- Primary dolostone deposits and occurrences are mainly used as high-quality crushed stone aggregates and carbonate mineral raw materials for industrial processing, and not for production of metallic magnesium.
- Secondary Mg reject brine from the Nin, Pag and Ston saltpans remains unrecognised as a potential source of Mg, although discharged magnesium is about 2.38 t/*annum*.
- Geologically, primary dolostone deposits are grouped to STM (Upper Triassic to Lower Jurassic) and AdCP (Jurassic to Middle Cretaceous) groups.
- STM deposits are considered as high-potential magnesium sources, whereas AdCP deposits belong to medium-to-high (Jurassic) and low-potential (Cretaceous) magnesium sources.
- At a scale of 1:300,000, the overall geological potential of primary magnesium sources has been calculated. According to this calculation, in the Republic of Croatia, there are 807 km² of high potentiality geological strata (STM Hauptdolomite), 5285 km² of medium to high potentiality, and 436 km² of low potentiality within areas where exploitation is not prohibited. However, additional restrictions arising from the three levels of spatial planning must also be considered.
- Based on the presented analysis, a Croatian national exploration programme will develop new magnesium case-studies.

Magnesium case-study (an example):

- The Đipalo dolostone deposit near Sinj (STM dolostone; exploitation reserves of 5.9 Mt) shows high-purity dolostone with MgO > 22 wt%. The sum content of SiO_2, Fe_2O_3 and Al_2O_3 is below 1 wt%.
- Extraction processes include conventional mining methods of open-cast operation, blasting, crushing, and pulverizing.
- The material can be used in the refractory industry, ferrous metallurgy, production of cement, glass, ceramics, paper or for magnesium metal production.
- The value of the products increases in order from: construction raw material < crushed stone aggregate < refractory (roasted) dolostone < 99.0% pure metallic magnesium (more than 2,000 times).
- In the case of production of magnesium metal, dolomite consumption is estimated as 10 to 15 t of dolostone per 1 t of Mg produced, depending on the technological process.
- CO_2 emissions and energy consumption of all analysed metallurgical processes remain high.

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